Some Basic Concepts of Chemistry

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Chapter

① CLASSIFICATION OF MATTER

- Matter can exist in three physical states viz solid, liquid and gas
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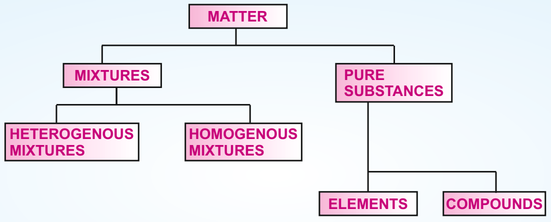


- A **mixture** contains particles of two or more pure substances in any ratio.
- **Movement of air follow pressure gradient.**
- In **Homogeneous mixture**, components completely mix with each other.
- In **Heterogeneous mixture**, composition is not uniform.
- Constituent particles of **pure substance** have fixed composition.
- **Compound** is formed when two ore more atoms of different elements combine together in definite ratio.

② PROPERTIES OF MATTER AND THEIR MEASUREMENT

- Properties are of two types viz. physical and chemical properties.
- **Physical properties** can be measured or observed without changing the identity or the composition of the substance.
- **Chemical properties** requires a chemical change to occur.
- Colour, odour, melting point, density etc are some physical properties.
- Composition, combustibility, reactivity with acids and bases are examples of chemical properties.
- Quantitative measurement of physical properties represented by a number followed by **units**.
- SI system has seven base units.
- Base physical quantities and their units.

Length (m)
Time (s)
Thermodynamic Temperature (K)
Mass (kg)
Electric current (A)
Amount of substance (mol)
Luminous intensity (cd)

SOME PREFIX USED IN SI SYSTEMS ARE

10^{-12} (pico), 10^{-9} (nano), 10^{-6}(micro) 10^{-3}(milli), 10^{-2}(centi),
10^{3}(kilo), 10^{6}(mega) 10^{9}(giga)

SOME COMMON UNITS

- 1 L = 1000 mL = 1000 cm^3 = 1 dm^3, °F = 9/5 (°C) + 32, K = °C + 273.15

③ UNCERTAINTY IN MEASUREMENT

- **Scientific notation** is exponential notation in which any number represented in N × 10^n, where n is exponent having positive or negative values and N is number between 1.000 … and 9.999 .....
- **Significant figures** are meaningful digits which are known with certainity plus one which is estimated or uncertain.
- **Rules for determining the number of significant figures.**
- All non zero digits are significant.
- Zeros preceding to first non-zero digit are non significant.
- Zeroes between two non-zero digits are significant.
- Zeroes at the end or right of a number are significant provided they are on the right side of decimal point.
- Counting numbers have infinite significant figures.
- In a number written in scientific notation, all digits are significant.
- **Precision** refers to the closeness of various measurements for the same quantity.
- **Accuracy** is the agreement of a particular value to the true value of the result.
- In **addition** and **subtraction** of significant figures the result cannot have more digits to the right of the decimal point than either of the original numbers.
- In multiplication and division of significant figures the result must be reported with no more significant figures as are there in the measurement with the fewer significant figures.

- **Important points for rounding off the numbers.**
  - If the rightmost digit to be removed is more than 5, the preceding number is increased by one.
  - If the rightmost digit is less than 5, the preceding number is not changed.
  - If the rightmost digit is 5 then preceding number increased by 1 only if it is an odd number.
- Method used to interconversion of unit is known as **dimensional analysis, unit factor method.**

④ LAWS OF CHEMICAL COMBINATION

- **Law of conservation of mass** conclude that in all physical and chemical changes, there is no net change in mass during the **change**.
- **Law of definite proportions/composition** stated that a given compound always contains exactly the same proportion of elements by weight.
- **Law of multiple proportions** stated that, if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of other element are in the ratio of small whole number.
- **Gay Lussac's law of gaseous volume** : When gases combine or are produced in a chemical reaction they do so in a simple ratio by volume, provided all gases are at same temperature and pressure.
- **Avogadro's law** proposed that equal volumes of all gases at same temperature and pressure should contain equal number of molecules.
- **Dalton's Atomic Theory** proposed to following points
  - Matter consists of indivisible atoms.
  - All atoms of a given element have indentical properties, including identical mass, atoms of different elements differ in mass
  - Compounds are formed when atoms of different elements combine in a fixed ratio
  - Chemical reactions involve **reorganisation** of atoms. These are neither created nor destroyed in a chemical reaction.

⑤ ATOMIC AND MOLECULAR MASS

- One **atomic mass unit (amu)** is defined as a mass exactly equal to one-twelfth of the mass of one C-12 atom, **1 amu = 1.66056×10^{-24} g.**
- At present amu has been replaced by **unified mass (u)**
- **Average atomic mass** can be computed when we take into account the existence of isotopes and their relative abundance.
- **Molecular mass** is the sum of atomic masses of the elements present in a molecule.
- **Formula mass** is used instead of molecular mass for ionic solids as in solid state they do not exist as a single entity.

⑥ MOLE CONCEPT AND MOLAR MASSES

- Mole (Symbol, mol) is seventh base quantity for amount of a substance.
- One mole contains exactly **$6.02214076 \times 10^{23}$** elementary entities. This number is the fixed numerical value of the **Avogadro's constant (N_A)**.
- The mass of one mole of a substance in grams is called its **molar mass**.
- **Mass% of an element** = Mass of that element in the compound × 100 / Molar mass of the compound.

- **Empirical formula** represents the simplest whole number ratio of various atoms present in a compound, whereas, the **molecular** formula shows exact number of different types of atoms present in a molecule of a compound.

⑦ STOICHIOMETRY AND STOICHIOMETRIC CALCULATIONS

- Stoichiometry deals with calculation of masses (sometime volume) of the reactants and products involved in a chemical reaction.
- Reactant, which gets consumed first, limits the amount of product formed is called limiting reagent.
- A majority of reactions are carried out in solutions. The **concentration** of a solution can be expressed in following ways.
- **Mass percent** = Mass of solute × 100 / (Mass of solution)
- **Mole fraction** of solute = No. of moles of solute/No. of moles of solution
- **Molarity** (M) = No. of moles of solute / Volume of solution in litres
  - For dilution of solutions, $M_1V_1 = M_2V_2$
- **Molality** (m) = No. of moles of solute/Mass of solvent in kg.

Structure of Atom

2 Chapter

① SUBATOMIC PARTICLES

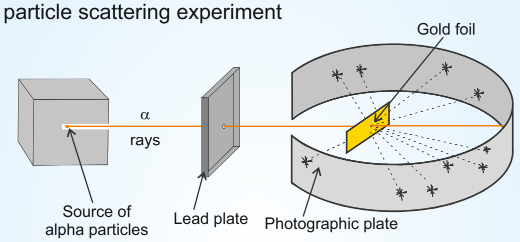
Name	**Discovery**	**Charge**	**Mass/kg**
Electron (e)	Cathode rays	-1.6×10^{-19} C	9.1×10^{-31}
Proton (p)	Anode rays	$+1.6 \times 10^{-19}$ C	1.67×10^{-27}
Neutron (n)	α particles bombarded on Be thin sheet	0	1.67×10^{-27}

② ATOMIC MODELS

- **Thomson model (Plum pudding model)**

  The atom is of spherical shape in which positive charge is uniformly distributed and electrons are embedded in it.
- **Rutherford's Nuclear Model**

  α particle scattering experiment



Observation of experiment

(i) Most of α ray passed through gold foil undeflected

(ii) A small fraction of the α-particles was deflected by small angles

(iii) A very few α-particles bounced back

- On the basis of Rutherford experiment most of the space in an atom is empty, a centre of atom is occupied by the nucleus in which positive charge is concentrated in a very small volume. The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular path called **orbits** while electrostatic forces of attraction held nucleus and electrons together.
- **Draw back of Rutherford model**

  It cannot explain the stability of atom.

Atomic no. (Z) = Number of protons

Mass no. (A) = Number of protons and neutrons

Isotopes = Same atomic number but different mass number *e.g.* ${}^{12}_{6}$C, ${}^{14}_{6}$C

Isobars = Atoms with same mass number but different atomic number *e.g.* ${}^{14}_{6}$C, ${}^{14}_{7}$N

③ ELECTROMAGNETIC WAVES

- Unlike sound wave, electromagnetic waves do not require medium and can move in vacuum.
- Electromagnetic waves are characterised by the properties, frequency (ν) and wave length (λ) and travel with speed of light *i.e.*, $c = 3 \times 10^8$ m/s

  $c = \nu\lambda$
- **Wave number ($\bar{\nu}$) = $\frac{1}{\lambda}$**

$\bar{\nu} \xrightarrow{\text{dec}}$, $\lambda \xrightarrow{\text{inc.}}$

γ rays	X rays	UV	Visible	IR	Micro wave	Radio wave

- Experiment supporting wave nature of electromagnetic radiation are interference & diffraction
- Experiment supporting particle nature of electromagnetic radiations are photoelectric effect and black body radiations.

Planck's Quantum Law: Atoms and molecules could emit or absorb energy only in discrete quantities and not in continous manner known as quantum

$E = h\nu$

E = energy of quantum

- **Photoelectric effect:** Ejection of electrons when certain metals were exposed to beam of light.

Observation of photoelectric effect

- No time lag between ejection of electrons from metal surface and striking of light beam.
- Number of ejected electrons proportional to the intensity or brightness of light.
- Minimum frequency required to eject electron is known as **threshold frequency (ν_0).**
- **Einstein photoelectric equation**

  $$h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

④ ATOMIC SPECTRA

- The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum.**
- An absorption spectrum is like photographic negative of an emission spectrum.

Line Spectrum of Hydrogen

- $\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_1^2}\right) \text{cm}^{-1}$

  where $\bar{\nu}$ is the wave number of spectral line in hydrogen spectrum.

Series	**n_1**	**n_2**	**Spectral Region**
Lyman	1	2, 3...	Ultraviolet
Balmer	2	3, 4...	Visible
Paschen	3	4, 5...	Infrared
Brackett	4	5, 6...	Infrared
Pfund	5	6, 7...	Infrared

⑤ BOHR'S MODEL FOR HYDROGEN ATOM

Key points of Bohr's theory

- Electron in the hydrogen atom can move in circular path of fixed radius and energy known as **orbits**.
- The energy of orbit does not change with time.
- Electron moves from a lower stationary state to higher state when required amount of energy is absorbed by the electron.
- Electron move from higher energy state to lower energy state leaving the extra energy in the form of electromagnetic waves.
- Angular momentum of electron is quantized.

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

- Frequency of radiation absorbed or emitted

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

- $r_n = \frac{52.9\ (n^2)}{Z}$ pm; radius of nth orbit
- $E_n = -2.18 \times 10^{-18}\left(\frac{Z^2}{n^2}\right)$ J; energy of electron in nth orbit

⑥ DUAL BEHAVIOUR OF MATTER

- **de-Broglie relationship** between wavelength (λ) and momentum (P) of the material particle.

$$\lambda = \frac{h}{P} = \frac{h}{mv}$$

- **Heisenberg's Uncertainty Principle**

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.

$$\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}$$

- Heisenberg uncertainty principle is not valid for macroscopic objects.
- **Failure of Bohr model:** It ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

⑦ QUANTUM MECHANICAL MODEL OF ATOM

- Orbitals and quantum number

(1) **Principal quantum number 'n'** determines the size and energy of orbital.

- Number of allowed orbital in a shell = n^2

(2) **Azimuthal quantum number 'l'** defines the three-dimeinsional shape of orbital

- For a given n, possible value of l = 0, 1, 2 ... (n – 1)
-

Value of l	0	1	2	3	4	5
Notation of subshell	s	p	d	f	g	h

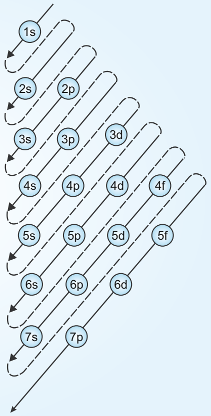
(3) **Magnetic orbital quantum number 'm_l'** gives information about the spatial orientation of the orbital with respect to standard set of coordinate axis.

- For any subshell, 2l + 1 values of m_l are possible.
-

Subshell	s	p	d	f	g	h
Number of orbitals	1	3	5	7	9	11

(4) Two orientations of electrons are distinguished by the **spin quantum numbers (m_s)** which can take value of $+\frac{1}{2}$ and $-\frac{1}{2}$.

⑧ FILLING OF ORBITALS IN ATOM



- **Aufbau Principle:** In the ground state of the atoms, the orbitals are filled in order of their increasing energies.
- The maximum number of electrons in a shell = $2n^2$
- **Hund's Rule of Maximum Multiplicity**

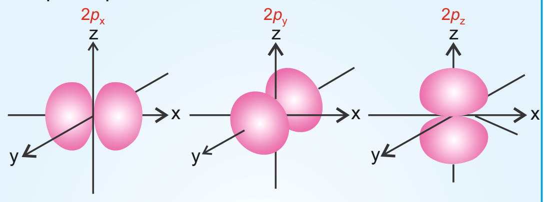
Pairing of electrons in degenerate orbitals take place only after each degenerate orbitals is singly filled.

- **Pauli Exclusion Principle**

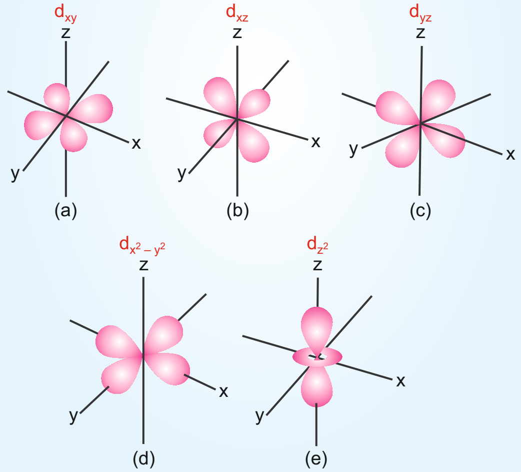
No two electrons in an atom can have the same set of four quantum numbers.

⑨ SHAPES OF ATOMIC ORBITALS

- Shapes of p-orbital



- Shapes of d-orbitals



- **Total nodes** = n – 1, angular nodes = l, radial nodes = n – 1 – l

Energies of Orbitals

- 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < (for hydrogen)
- **(n + l) rule** – the lower the value of (n + l) for an orbital, the lower is its energy. It two orbitals have the same value of (n + l), the orbital with lower value of n will have the lower energy for multielectron atom.
- Energies of the orbital in the same subshell decreases with increase in the atomic number (Z_{eff})

e.g. $E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K)$

Classification of Elements and Periodicity in Properties

3

Chapter

① GENESIS OF PERIODIC CLASSIFICATION

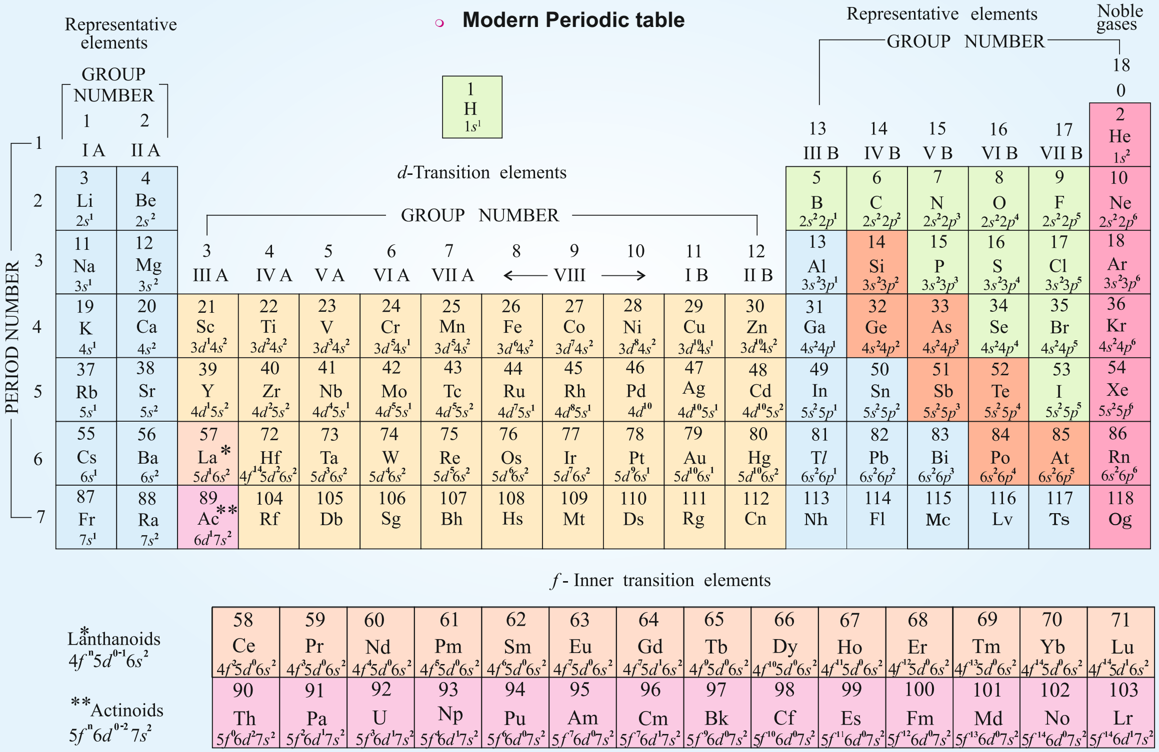
- **Dobereiner's Triad:** Middle element of each of the triads had an atomic weight about half way between the atomic weights of other two and also the properties of middle element were in between other two.
  e.g. (Li, Na, K), (Ca, Sr, Ba), (Cl, Br, I)
- **Law of Octaves:** On arranging the elements increasing order of their atomic weights, every eighth element had properties similar to the first element e.g Li, Be, B, C etc resemble with Na, Mg ,Al and Si respectively.
- **Lother Meyer:** Plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern.
- **Mendeleev Periodic law:** The properties of elements are a periodic function of their atomic weights.
  Mendeleev predicted elements **Eka-Aluminium** as Gallium and **Eka-Silicon** as Germanium.

③ Nomenclature of elements having Z > 100

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Un unnillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

② MODERN PERIODIC LAW AND TABLE

- **Modern Periodic Law:** States that the physical and chemical properties of the elements are periodic functions of their atomic numbers.
- **Modern Periodic table**



Representative elements

d-Transition elements

Representative elements

Noble gases

f - Inner transition elements

1
H
$1s^1$

PERIOD NUMBER	GROUP NUMBER 1 I A	2 II A	3 III A	4 IV A	5 V A	6 VI A	7 VII A	8 ← VIII	9 VIII	10 →	11 I B	12 II B	13 III B	14 IV B	15 V B	16 VI B	17 VII B	18 0
1																		2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

*Lanthanoids $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^06s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^06s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinoids $5f^n6d^{0-2}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

④ ELECTRONIC CONFIGURATION

- **3d series** from Z = 21 to Z = 30
- **4d series** from Z = 39 to Z = 48
- **4f-inner transition series** from Z = 58 to Z = 71, also known as **lanthanide series**
- **5f-inner transition series** from Z = 90 to Z = 103 also known as **actinoid series**
- General outer electronic configuration
  s-block = ns^{1-2}
  p-block = ns^2np^{1-6}
  d-block = $(n-1)d^{1-10}\ ns^{0-2}$
  f-block = $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

⑤ IMPORTANT TERMINOLOGIES

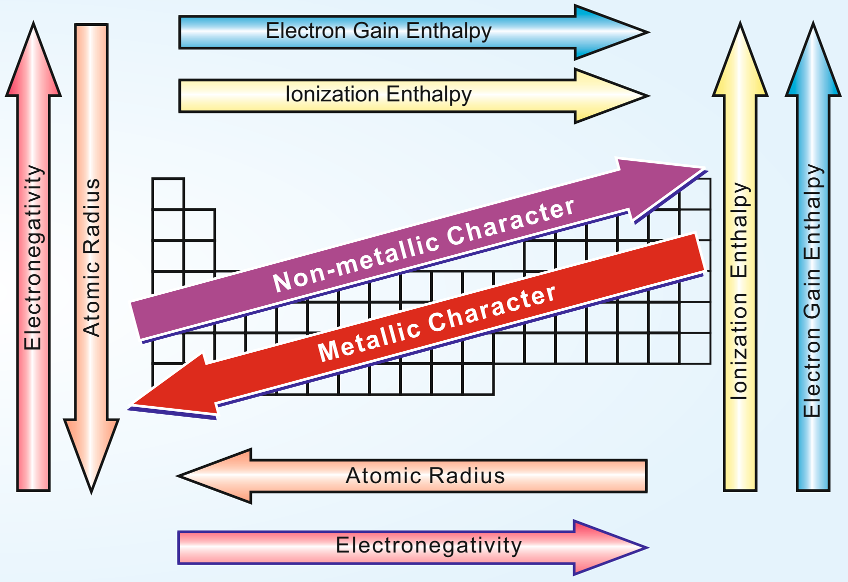
- **The elements of group 1 (alkali metals)** and **group 2 (alkaline earth metals)** are known as **s-block elements**.
- **The elements of group 13** to **18** are known as **p-block elements**.
- s-block and p-block elements together known as **Representative elements** or **Main Group elements**.
- All the orbitals in the valence shell of the **noble gases** are completely filled.
- **Group 17** elements are known as **halogens**.
- **Group 16** elements are known as **chalcogen**s.
- Elements of **group 3** to **12** are known as **d-block elements**.
- **Transition metals** form a bridge between the **s-block elements** and **group 13 elements**
- Two rows of elements at the bottom of the periodic table called the **Lanthanoid** and **Actinoids** and combinely known as **Inner-transition elements** or **(f-block elements)**
- The elements after uranium are called **Transuranium elements**

⑥ PERIODIC TRENDS IN CHEMICAL PROPERTIES

- The **valence** of representative elements is usually equal to valence electrons or 8-valence electrons.
- Second period elements show **anomalous behaviour** due to their small size, large charge/radius ratio, high electronegativity of the elements and only four valence orbitals.
- Li and Be is more similar to Mg and Al respectively and this sort of similarity is known as **diagonal relationship**.
- The normal oxide formed by the element on extreme left is most **basic** (e.g. Na_2O), whereas that formed by the element on extreme right is most **acidic** (e.g. Cl_2O_7)
- Oxides of elements in centre are **amphoteric** (e.g. Al_2O_3, As_2O_3) or neutral (e.g. CO, NO, N_2O)
- **Amphoteric oxides** behaves as acidic with bases and as basic with acids, whereas neutral oxide have no acidic or basic properties.

⑦ TRENDS IN PHYSICAL PROPERTIES

- **Covalent radius** is half of the bond distance between two similar atoms.
- **Metallic radius** is half the inter nuclear distance separating the metal cores in the metallic crystal.
- **Atomic radius** refer to both covalent or metallic radius depending upon the element is a non metal or a metal
- Atoms or ions which contains same number of electrons are called **isoelectronic species** *e.g.* O^{2-}, F^-, Na^+ etc.
- **Ionic radii** can be estimated by measuring the distance between cations and anions
- A cation is always smaller than its parent atom while an anion is always bigger than its parent atom.
- **Ionization enthalpy** is the energy required to remove an electron from an isolated gaseous atom.
- Third ionization enthalpy is higher than second and so on.
- The effective nuclear charge experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of the **"shielding"** or **"screening"** of valence electron from the nucleus by intervening core electrons
- 2p electron of boron is more shielded from the nucleus than the 2s electron therefore ionization energy of boron is slightly less than that of beryllium.
- In nitrogen atom, three 2p-electrons reside in different orbitals whereas in oxygen atom, two of four 2p-electrons must occupy the same 2p-orbital resulting in increased repulsion therefore ionization enthalpy of N is greater than that of O.
- **Electron Gain enthalpy** is the enthalpy change when an electron is added to a gaseous neutral atom to convert it into a negative ion.
- $\Delta_{eg}H$ of O and F is less negative than that of succeeding element due to interelectronic repulsion.
- **Electronegativity** is a qualitative measure of the ability of an atom in a chemical bond to attract shared electrons.
- F is the most electronegative element while the electron gain enthalpy of Cl is most negative.



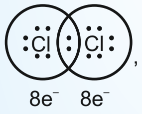
Chemical Bonding and Molecular Structure

4

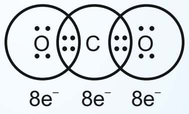
Chapter

① CHEMICAL BOND

- The attractive force which holds various constituents (atoms, ions etc) together in different chemical species is called a **chemical bond.**
- Lewis postulated that atoms achieve the stable octet when they are linked with chemical bonds.
- Simple notation to represent valence electrons in an atom is called **Lewis symbols** e.g. $\dot{\mathrm{Li}}$, $\underset{\bullet}{\dot{\mathrm{Be}}}$, $\cdot\dot{\mathrm{B}}\cdot$
- The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the **electrovalent bond** or **ionic bond**.
- **Octet rule** – According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells.
- **Covalent bond** – When two atoms share electron pair(s) they are said to be joined by covalent bonds.
- It two atoms share one electron pair, the covalent bond between them is called single bond, if two electrons pairs then double bond e.g.



Cl – Cl



O = C = O

- **Formal charge** $= \begin{bmatrix}\text{Total number of}\\ \text{valence electrons}\\ \text{in free atom}\end{bmatrix} - \begin{bmatrix}\text{Total number of}\\ \text{non-bonding}\\ \text{electrons}\end{bmatrix}$

$$-\frac{1}{2}\begin{bmatrix}\text{Total number of}\\ \text{bonding}\\ \text{electrons}\end{bmatrix}$$

② LIMITATION OF OCTET RULE

- In some compounds, the number of electrons surrounding the central atom is less than eight eg. LiCl, BeH_2.
- Molecules with an odd number of electron e.g. NO and NO_2.
- In number of compounds there are more than eight valence electrons around the central atom. eg. PF_5, SF_6, H_2SO_4 etc.
- Some noble gases also combine with oxygen and fluorine eg. XeF_2.
- Does not account for the shape of molecules.

③ IONIC BOND OR ELECTROVALENT BOND

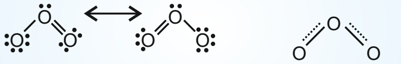
- Ionic bonds will be formed more easily between elements with comparatively low ionisation enthalpies and elements with comparatively high negative value of electron gain enthalpy.
- **Lattice enthalpy** of an ionic solid is defined as the energy required to completely seperate one mole of a solid ionic compound into gaseous constituent ions.

④ BOND PARAMETERS

- Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.
- The **Covalent Radius** is measured approximately as the radius of on atom's core which is in contact with the core an adjacent atom in a bonded situation.
- The **vander Walls Radius** represents the overall size of atoms which included the valence shell in a non-bonded situation.
- **Bond Angle** is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/ ion.
- **Bond Enthalpy** is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. For polyatomic molecules the term mean or average bond enthalpy is used.
- **Bond Order** is given by the number of bonds between the two atoms in a molecule.
- Isoelectronic molecules and ions have identical bond orders for example F_2 and O_2^{2-} have bond order 1, N_2 CO and NO^+ have bond order 3.
- With increase in bond order, bond enthalpy increases and bond length decreases.

⑤ RESONANCE STRUCTURES

- According to the concept of resonance, whenever a single lewis structure cannot describe a molecule accurately, a number of structures with similar energy, position of nuclie, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.



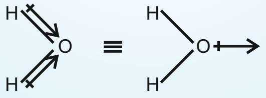
(Canonical structures) (Resonance hybrid)

- **Misconceptions** with resonance
- The cannonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms.
- There is no such equilibrium between the cannonical forms.

⑥ POLARITY OF BONDS

- In non-polar covalent bonds electron pair is situated exactly between the two identical nuclei.
- In polar covalent bond electron pair between the two atoms gets displaced more towards more electronegative atom.
- Dipole moment is the product of the magnitude of the charge and the distance between the centres of positive or negative charge and denoted by μ
- Dipole moment is a vector quantity and represented by crossed arrow ($+\!\!\!\longrightarrow$)

  eg $\mathrm{H}\overset{+\!\!\!\longrightarrow}{—}\mathrm{F}$
- Unit of μ is Debye ($1\,\mathrm{D} = 3.33564 \times 10^{-30}$ C m)
- In polyatomic molecules, the dipole moment depend upon individual dipole moments of individual bonds and spatial arrangement of bonds eg.



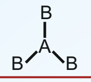
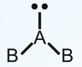
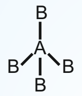
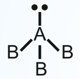
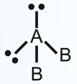
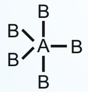
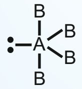
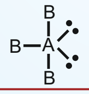
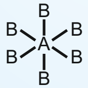
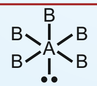
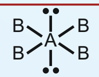
Bond dipole Resultant dipole

7 FAJAN'S RULE

- The smaller the size of cation and larger the size of the anion, the greater is the covalent character of an ionic bond.
- Greater the charge on the cation greater is the covalent character.
- For cations of the same size and charge, the one having *d*-electrons is more polarising, thus its salts have greater covalent character.

8 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

- The model used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other therefore try to remain as far apart as possible
- The order of electron pair repulsion is lp – lp > lp – bp > bp – bp.
- Shape (geometry)

Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs	Shape	Example
2	0	B–A–B	Linear	BeF_2
3	0		Trigonal planar	BF_3
2	1		Bent	SO_2
4	0		Tetrahedral	CH_4
3	1		Pyramidal	NH_3
2	2		Bent	H_2O
5	0		Trigonal bipyramidal	PCl_5
4	1		See saw	SF_4
3	2		T-shape	ClF_3
6	0		Octahedral	SF_6
5	1		Square pyramid	BrF_5
4	2		Square Planar	XeF_4

9 VALENCE BOND THEORY

- Discusses bond formation in terms of overlap of orbitals
- In case of the formation of H_2 molecule from two H-atoms involves overlap of *s* orbitals of two H-atoms which are singly occupied. The potential energy of the systems gets lowered as the two H-atoms come near to each other.
- Types of overlapping.

Sigma (σ) bond is formed by the end to end overlap of bonding orbitals along the internuclear axis.

Pi (π) bond is formed in such a way that atomic orbital axes remain parallel to each other and perpendicular to the internuclear axis.

Hybridisation – Atomic orbitals combine to form new set of equivalent orbitals known as *hybrid orbitals* and this phenomenon is known as hybridisation.

- Number of hybridised orbitals formed is equal to number of atomic orbitals intermixed.
- Hybridised orbitals only form sigma bond.
- Various types of hybridisations are sp, sp^2, sp^3, sp^3d, dsp^2 etc.

10 MOLECULAR ORBITAL THEORY

- LCAO method is used for the formation of molecular orbitals.
- For two atomic orbitals having wave function ψ_A and ψ_B the molecular orbital (MO) are given as $\psi_A \pm \psi_B$
- MO formed by the addition of atomic orbitals is called Bonding Molecular Orbital (BMO) or σ and π while formed by the subtraction of atomic orbitals is called anti bonding molecular orbital (ABMO) or σ^* and π^*.
- Increasing order of energies for diatomic molecules upto 14 electrons is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

- Increasing order of energies for diatomic molecules with more than 14 electrons is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

- Bond order $= \frac{1}{2}(N_B - N_A)$
- Bond order $\propto$ Bond strength $\propto \frac{1}{\text{Bond length}}$
- If all the molecular orbitals in a molecule are doubly occupied then the substance is diamagnetic else paramagnetic.

11 HYDROGEN BONDING

- Hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule or within the same molecule.

Types of H-bond

- Intermolecular hydrogen bond is formed between the atoms of two different molecules e.g. H_2O, NH_3, HF, C_2H_5OH etc.
- Intramolecular hydrogen bond is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule eg. orthonitrophenol.

States of Matter

5

Chapter

① INTERMOLECULAR FORCES

- Forces of attraction and repulsions between interacting particles
- Types of intermolecular forces
  - (i) Dispersion forces or London forces
    - (a) Force of attraction between instantaneous dipole and induced dipole.
    - (b) Interaction energy proportional to $\frac{1}{r^6}$, where r is the distance between two particles.
  - (ii) Dipole-Diple forces act between the molecules possessing permanent dipole. Dipole-dipole intereaction energy between stationary molecules is proportional to $\frac{1}{r^3}$.
  - (iii) Dipole-Induced dipole forces operate between the polar molecules having permanent dipole and the molecule lacking permanent dipole. Interaction energy is proportional to $\frac{1}{r^6}$.
  - (iv) Hydrogen bond is a special case of dipole-dipole interaction and is found in the molecules in which highly polar N – H, O – H, or H – F bonds are present.

② THERMAL ENERGY

- Energy of a body arising from motion of its atoms or molecules and it is directly proportional to the temperature

- Gas → Liquid → Solid

  Predominance of intermolecular force intereactions
- Gas ← Liquid ← Solid

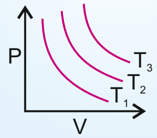
  Predominance of thermal energy

③ GASEOUS STATE

- Gaseous state is characterised by following physical properties
  - (i) Highly compressible
  - (ii) Exert pressure equally in all direction
  - (iii) Much lower density than solid /liquid
  - (iv) Indefinite shape and volume
  - (v) Mix evenly and completely in all proportions without any mechanical aid

④ GAS LAWS

- Boyle's law
  - (i) At constant temperature, pressure of a fixed amount of gas varies inversely with its volume.
  - (ii) $P = k_1 \frac{1}{V} \Rightarrow pV = k_1$

    $P_1V_1 = P_2V_2$
  - (iii) 

    $T_3 > T_2 > T_1$

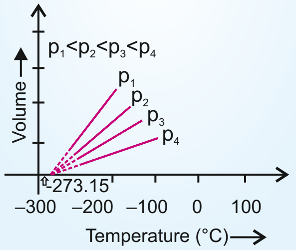
⑤ CHARLE'S LAW

(i) Pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.

(ii) $\frac{V}{T} = k_2$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

(iii) $V_t = V_0\left(1 + \frac{t}{273.15}\right)$

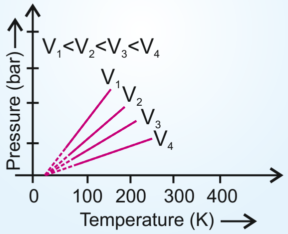
V_t and V_0 are volumes of gas at t°C and 0°C respectively.

(iv) 

⑥ GAY LUSSAC'S LAW

(i) At constant volume, pressure of a fixed amount of gas varies directly with temperature

(ii) $P \propto T$ or $\frac{P}{T} = k_3$



⑦ AVOGADRO LAW

(i) Equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

(ii) $V \propto n$

(iii) At standard temperature and pressure (STP), molar volume of ideal gases is 22.7 L mol^{-1}.

⑧ IDEAL GAS EQUATION

- Boyle's law, Charles' law and Avogadro law can be combined together in single equation known as ideal gas equation.
- Ideal gas equation : PV = nRT
- R is universal gas constant and equal to
  - (i) $8.314 JK^{-1} mol^{-1}$
  - (ii) 8.20578×10^{-2} L atm $K^{-1} mol^{-1}$
- Density of gas = $\frac{PM}{RT}$

⑨ DALTON'S LAW OF PARTIAL PRESSURE

(i) Total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.

$P_{total} = P_1 + P_2 + P_3 + ...$ (at constant T, V)

(ii) $P_{Dry\ gas} = P_{Total}$ – Aqueous tension

(iii) $P_1 = P_{Total}\ x_1$, $P_2 = P_{Total}\ x_2$ where x_1, x_2 are the mole fractions of gas 1 and 2 in the mixture.

⑩ KINETIC ENERGY AND MOLECULAR SPEEDS

- Average speed (u_{av}) = $\frac{u_1 + u_2 + \ldots u_n}{n}$

  where n number of molecules in the sample and u_1, u_2 .... are their individual speeds.
- KE = $\frac{1}{2} mu^2_{rms}$
- Most probable speed(u_{mp}) is the speed possessed by the maximum number of molecules
- Root mean square speed(U_{rns}) is the square root of the mean of the square of speeds.

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 \ldots . u_{n^2}}{n}}$$

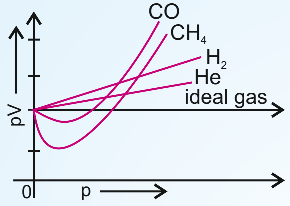
- $u_{mp} : u_{av} : u_{rms} :: 1 : 1.128 : 1.224$

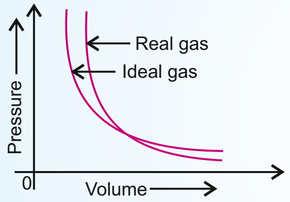
⑪ KINETIC MOLECULAR THEORY OF GASES

- Postulates of kinetic molecular theory
  - (i) Gases consist of large number of identical particles and their actual volume is negligible in comparison to the empty space between them
  - (ii) No force of attraction between particles at ordinary temperature and pressure
  - (iii) Particles of gas are always in constant random motion.
  - (iv) Particles of gas move in all possible direction in straight lines and during motion they collide with each other and with wall of container elastically.
  - (v) Individual speed of particles are changing but distribution of speeds remains constant at a particular temperature.

⑫ BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

- It is found that real gases do not follow, Boyle's law, Charles law and Avogadro law perfectly under all conditions.





- Two assumption of kinetic theory do not hold good for real gases i.e (i) No interparticle attraction and (ii) Negligible volume of molecule of gas in comparison to space occupied by the gas.
- Real gases show deviations from ideal gas because molecules of gases intereact with each other. This affects the pressure exerted by the molecules on the walls of container.

$$P_{ideal} = \underset{\text{(observed pressure)}}{P_{real}} + \underset{\text{(correction term)}}{\frac{an^2}{V}}$$

- Volume occupied by the molecules also become significant because instead of moving in volume V, these are now restricted to volume V-nb where nb is approximately the total volume of molecules occupied by themselves.
- van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V\text{-}nb) = nRT$$

a and b are called van der waals constant and depends on nature of gas.

- Compressibility factor Z
  - (i) $Z = \frac{PV}{nRT}$, $Z = \frac{V_{real}}{V_{ideal}}$
  - (ii) For ideal gas Z = 1
  - (iii) At very low pressure $Z \approx 1$ for all gases.
  - (iv) At high pressure Z > 1 and at intermediate pressure most gases have Z < 1.
- Boyle temperature or Boyle point

  The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure.

⑬ LIQUIFACTION OF GASES

- Critical temperature (T_c) is the highest temperature at which liquid is observed.
- Critical volume (V_c) is the volume of one mole of the gas at critical temperature and pressure.
- For CO_2, T_C is 30.98°C

⑭ LIQUID STATE

- Vapour pressure is the pressure at equilibrium between liquid and vapour phase.
- The temperature at which vapour pressure of liquid is equal to external pressure is called boiling temperature at the pressure.
- At 1 atm pressure boiling temperature is called normal **boiling point** and at 1 bar then the boiling point is called **standard boiling** point of the liquid.
- Surface Tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. Denoted by γ and SI unit is Nm^{-1}.
- Viscosity
  - (i) It is a measure of resistance to flow which arises due to internal friction between layers of fluid as they slip past one another while liquid flows.
  - (ii) In laminar flow there is a regular gradation of velocity in passing from one layer to next.
  - (iii) $F = \eta A \frac{du}{dz}$ where F is force of viscosity; A, area of contact; $\frac{du}{dz}$ velocity gradient; η, coefficient of viscosity
  - (iv) SI unit of η is Nsm^{-2}, in cgs system unit is poise

    1 poise = 1 $gcm^{-1}s^{-1}$

    = 10^{-1} $kgm^{-1}s^{-1}$.

Thermodynamics

6

Chapter

① THERMODYNAMIC TERMS

- (i) **System** - Part of universe under observation.
  (ii) **Surroundings** - Include everything other than system.
- There are three **types of system.**
  (i) **Open system** - Exchange of energy and matter between system and surroundings.
  (ii) **Closed system** - No exchange of matter but exchange of energy is possible.
  (iii) **Isolated system** - There is no exchange of energy or matter between the system and surroundings.
- The state of a thermodynamic **system** is described by its measurable properties. P, V, T, n etc are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached.

② FIRST LAW OF THERMODYNAMICS

- Commonly known as the law of conservation of energy i.e. energy can neither be created nor be destroyed.
- $\Delta U = q + w$ is mathematical statement of the first law of thermodynamics

Internal Energy (U)

- Sum of chemical, electrical, mechanical or any other type of energy of the system.

Work (W)

- Work is done on an ideal gas when it is compressed and work is done by an ideal gas when it is expanded

$$W = -\int_{V_i}^{V_f} P_{ex} dV$$

- A process or a change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. Process other than **reversible** are known as **irreversible processes**.
- For isothermal irreversible change $q = -W = P_{ex}(V_f - V_i)$
- For isothermal reversible change $q = -W = nRT \ln \frac{V_f}{V_i}$
- For adiabatic change, $q = 0 \quad \Delta U = W_{ad}$
- $W = 0$ in free expansion

③ ENTHALPY (H)

- Thermodynamic function is equal to $U + pV$
- It is a state function.
- $\Delta H = q_P$, heat absorbed by system at constant pressure.
- $\Delta U = q_V$ at constant volume
- $\Delta H > 0$ for endothermic and $\Delta H < 0$ for exothermic reaction.
- $\Delta H = \Delta U + \Delta n_g RT$ where Δn_g is change in gaseous moles.

④ EXTENSIVE AND INTENSIVE PROPERTIES

- An extensive property is a property whose value depends on the quantity or size of matter present in the system e.g. mass, volume, enthalpy etc.
- Properties which do not depend on the quantity or size of matter present are known as **intensive properties** e.g. temperature, density, molar heat capacity etc.

Heat Capacity

- Molar heat capacity is the quantity of heat required to raise the temperature of one unit mole of a substance by 1°C or 1 K, $q = nc\Delta T$
- Molar heat capacity at constant pressure is C_P and molar heat capacity at constant volume is C_V and $C_P - C_V = R$.
- Bomb calorimeter is used to find ΔU.

⑤ REACTION ENTHALPY ($\Delta_R H$)

- The **standard enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states.

Enthalpy Change During Phase Transformation

- The enthalpy change that accompanies melting of one mole of solid substance in standard state is called **standard enthalpy of fusion** ($\Delta_{fus}H°$).
- Amount of heat required to vaporise one mole of liquid at constant temperature and under standard pressure (1 bar) is called **standard enthalpy of vaporisation** $\Delta_{vap}H°$.
- **Standard enthalpy of sublimation,** ($\Delta_{sub}H°$) is the change in enthalpy when one mole of a solid substance sublimes at constant temperature and under standard pressure (1 bar).

  Standard Enthalpy of Formation ($\Delta_f H°$) is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation.

Standard Molar Enthalpies of Formation ($\Delta_f H^\ominus$) at 298 K of a few Selected Substances

Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})	Substance	$\Delta_f H^\ominus$ / (kJ mol^{-1})
$Br_2(l)$	0	$H_2O(l)$	–285.83
$Br_2(g)$	+30.91	$NO(g)$	+90.25
C(diamond)	+1.89	$NO_2(g)$	+33.18
C(graphite)	0	$SiO_2(s)$ (quartz)	–910.94
$Cl_2(g)$	0	C(g)	+716.68
$H_2(g)$	0	H(g)	+217.97
$H_2O(g)$	–241.82	Cl(g)	+121.68

Hess's Law of Constant Heat Summation

- Enthalpy change for a reaction is the same whether it occurs in one step or in series of steps.

  Standard Enthalpy of Combustion ($\Delta_c H°$) is defined as the enthalpy change per mole of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

  Bond Enthalpy ($\Delta_{bond} H°$) is energy required to break a bond or energy released when a bond is formed.

  Enthalpy of Atomization ($\Delta_a H°$) is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.
- In case of diatomic molecules, the enthalpy of atomization is also the bond **dissociation** enthalpy.
- $\Delta_r H° = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$

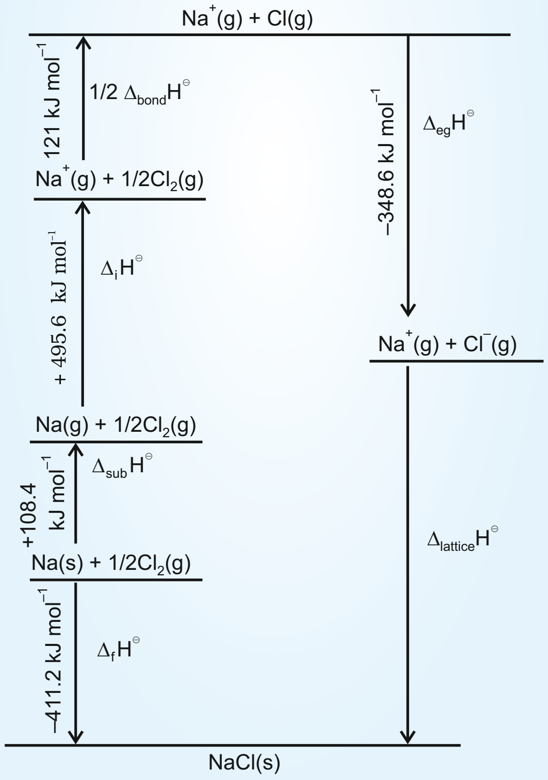
Some Mean Multiple Bond Enthalpies in kJ mol^{-1} at 298 K

N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

Lattice Enthalpy of an ionic compound is the enthalpy change which occurs when one mole of a ionic compound dissociates into its ions in gaseous state.

- It is impossible to determine lattice enthalpies directly by experiment therefore we use indirect method **Born-Haber cycle**.

Enthalpy diagram for lattice enthalpy of NaCl



Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for

$M(g) \rightarrow M^+(g) + e^-$ (for ionization)

$M(g) + e^- \rightarrow M^-(g)$ (for electron gain)

at temperature, T is

$$\Delta_rH^\ominus(T) = \Delta_rH^\ominus(0) + \int_0^T \Delta_rC_P^\ominus dT$$

The value of C_P for each species in the above reaction is 5/2 R ($C_V = 3/2R$)

So, $\Delta_rC_P^\ominus = +5/2\,R$ (for ionization)

$\Delta_rC_P^\ominus = -5/2\,R$ (for electron gain)

Therefore,

$\Delta_rH^\ominus$ (ionization enthalpy)

$= E_0$ (ionization energy) $+ 5/2\,RT$

$\Delta_rH^\ominus$ (electron gain enthalpy)

$= -A$ (electron affinity) $- 5/2\,RT$

Enthalpy of Solution ($\Delta_{sol}H°$) is the enthalpy change when one mole of it dissolves in a specified amount of solvent.

$$\begin{tikzcd} AB(S) \arrow[r, "\Delta_{sol}H^\ominus"] \arrow[d, "\Delta_{lattice}H^\ominus"'] & A^+(aq) + B^-(aq) \\ A^+(g) + B^-(g) \arrow[ur, "\Delta_{hyd}H^\ominus"'] & \end{tikzcd}$$

- $\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$

⑥ SECOND LAW OF THERMODYNAMICS

- It explain the criterion of spontaneity.

Spontaneity

- A spontaneous process is an irreversible process and may only be reversed by some external agency.

  Entropy S is measure of the degree of randomness or disorder in the system.

  $$\Delta S = \frac{q_{rev}}{T}$$

- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$ of a spontaneous process.
- $\Delta S = 0$ and S in maximum at equilibrium.

Gibbs Energy (G) and spontaneity

- $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$.
- Gibbs function, G is an extensive property and a state function.
- If $\Delta G < 0$, process is spontaneous.
- If $\Delta G > 0$, process is non spontaneous.
- $\Delta G° = -RT \ln K = -2.303\,RT \log K$.
- $\Delta_rG° = \Delta_rH° - T\Delta_rS° = -RT \ln K$.

$\Delta_rH^\ominus$	$\Delta_rS^\ominus$	$\Delta_rG^\ominus$	Description
–	+	–	Reaction spontaneous at all temperatures
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction non-spontaneous at high temperature
+	+	+ (at low T)	Reaction non-spontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction non-spontaneous a all temperatures

⑦ ABSOLUTE ENTROPY AND THIRD LAW OF THERMODYNAMICS

- The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics

Equilibrium

7

Chapter

① EQUILIBRIUM IN PHYSICAL PROCESSES

- **Solid-Liquid Equilibrium**
  (i) During equilibrium, the mass of solid and liquid do not change with time and temperature remains constant. However equilibrium is not static. The rate of transfer of molecules from solid into liquid and liquid into solid are equal.
  (ii) For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called **normal melting point** or **normal freezing point.**
- **Liquid-Vapour Equilibrium**
  (i) At equilibrium, **rate of evaproation = rate of condensation**.
  (ii) At equilibrium, the pressure exerted by the vapour is called **equilibrium vapour pressure**,
  (iii) Vapour pressure increases with increase in temperature and different liquids have different vapour pressures at same temperature.
  (iv) Liquid having higher vapour pressure is more volatile and has a lower boiling point.
  (v) The temperature at which the liquid and vapour is at equilibrium at one atmospheric pressure is called **normal boiling point** of liquid
- **Solid-Vapour Equilibrium -** at equilibrium rate of Sublimation = rate of condensation
- **Equilibrium involving dissolution of solid or gases in Liquids**
  (i) **Solids in liquids** - In a saturated solution, a dynamic equilibrium exists between the solute molecules in solid state and in the solution i.e. rate of dissolution = rate of crystallisation
  (ii) **Gases in Liquids**
    (a) There is equilibrium between the molecules in the gaseous state and the molecules dissolved in liquid under pressure.
    (b) **Henry's Law** states that the mass of a gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent

② EQUILIBRIUM IN CHEMICAL PROCESSES

- When the rates of the forward and reverse reactions become equal, the concentrations of the reactant and the products remain constant. This is the stage of **chemical equilibrium**
- Chemical reaction reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition

Law of chemical Equilibrium and Equilibrium Constant

- For a general reversible reaction

$A + B \rightleftharpoons C + D,$

$K_c = \frac{[C][D]}{[A][B]} (K_C = \text{Equilibrium constant})$

- At a given Temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficient has a constant value. This is known as the E**quilibrium Law or Law of chemical equilibrium**
- Equilibrium constants and its multiples

$aA + bB \rightleftharpoons cC + dD$	K_C
$cC + dD \rightleftharpoons aA + bB$	$K_C' = 1/K_C$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_C'' = (K_C)^n$

Homogenous Equilibrium

- When all the reactants and products are in same phase e.g $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- Equilibrium constant in terms of partial pressure is K_P
- For the general reaction $aA_{(g)} + bB_{(g)} \rightleftharpoons cD_{(g)} + dD_{(g)}$

$K_P = K_C (RT)^{\Delta n}$ where $\Delta n = (c + d) - (a + b)$

Hetrogeneous Equilibrium

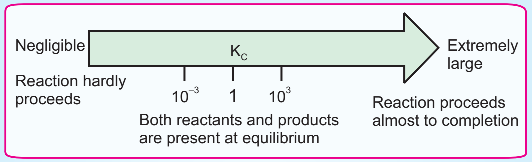
- Equilibrium in a system having more than one phase e.g $H_2O(l) \rightleftharpoons H_2O(g)$
- **Unit of equilibrium constant**

$K_C = (\text{mol L}^{-1})^{\Delta n}$, $K_P = (\text{atm})^{\Delta n}$ or $(\text{bar})^{\Delta n}$

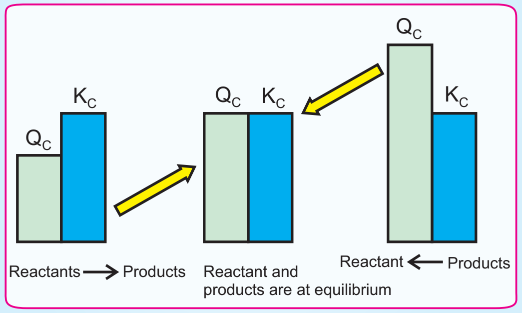
Where Δn = change in gaseous moles

③ APPLICATION OF EQUILIBRIUM CONSTANTS

- **Predicting the Extent of reaction**



- **Predicting the direction of reaction**



Relationship between K, Q and G

- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G^\circ = -RT \ln K$

④ FACTORS AFFECTING EQUILIBRIA

- **Le Chatelier's Principle** states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.
- **Factors** which can **influence** the equilibrium are
  (a) Effect of concentration change
  (b) Effect of pressure change
  (c) Effect of inert gas addition
  (d) Effect of temperature change
  (e) Effect of a catalyst
  (f) Effect of inert gas addition

5 IONIC EQUILIBRIUM IN SOLUTION

- Substances which conduct electricity in their aqueous solution are called **electrolytes while** the other are called **non-electrolytes**.
- **Strong electrolytes** on dissolution in water are ionized almost completely, while the **weak electrolytes** are only partially dissociated.
- **Acids and Bases**

(i) **Arrhenius concept of Acids and Bases**

Acid gives $H^+(aq)$ and base gives $OH^-(aq)$ in aqueous solution eg. HCl(Acid), NaOH(Base).

(ii) **The Bronsted-Lowry Acids and Bases**

(a) According to this theory, acid is a substance that is capable of donating a hydrogen ion, H^+ and bases are substances capable of accepting a hydrogen ion, H^+,

(b) The acid-base pair that differ only by one proton is called the **conjugate acid-base pair** eg. OH^- is conjugate base of HOH.

(c) Strong Bronsted acid has weak conjugate base and vice-versa.

e.g. HI → I^- + H^+

Strong acid — weak conjugate base

(iii) **Lewis Acids and Bases**

According to this theory an acid is a species which accepts electron pair and base which donates an electron pair.

e.g. $AlCl_3$ [Lewis acid], NH_3 (Lewis base)

Ionization Constant of Water and its Ionic Product

- Ionic product of water $K_w = [H^+][OH^-]$
- Concentration of H^+ and OH^- in pure water at 298 K = 10^{-7} M and $K_w = 10^{-14}\ M^2$
- In **acidic solution $[H_3O^+] > [OH^-]$**, in **neutral solution $[H_3O^+] = [OH^-]$** and in basic solution **$[H_3O^+] < [OH^-]$**

6 THE pH SCALE

- Negative logarithm to base 10 of the activity (a_{H+}) of hydrogen ion

$pH = -\log a_{H^+} = -\log [H^+]$

$pOH = -\log a_{OH^-} = -\log [OH^-]$

- $pK_w = pH + pOH = 14$ at 298 K

7 IONIZATION CONSTANTS OF WEAK ACIDS (K_a)

- For a weak acid HX,

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{C\alpha^2}{1-\alpha}$$

where C is the initial concentration of acid and α is degree of dissociation of acid

Ionization Constants of Weak Bases (K_b)

- For a weak base MOH,

$$K_b = \frac{[M^+][OH^-]}{[MOH]} = \frac{C\alpha^2}{1-\alpha}$$

- For conjugate acid-base pair

$K_a.K_b = K_w$

$pK_a + pK_b = pK_w$

Di-and Polybasic Acids and Di-and Polyacidic Bases

- Acids having more than one ionizable proton per molecule are known as polybasic acids
- Higher order ionization constant (K_{a2}, K_{a3}) are smaller than the lower order ionization constant (K_{a1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

Common ion effect defined as a shift in equilibrium on adding a substance that provides more of ionic species already present in the dissociation equilibrium

8 SALT HYDROLYSIS

- The cations/anions formed on ionization of salts interact with water to reform corresponding acid/bases depending upon the nature of salt is known as hydrolysis.
- Salts of strong acid and strong base do not undergo salt hydrolysis.
- The pH of CH_3COONa solution in water is more than 7
- The pH of NH_4Cl solution in water is less than 7
- pH of salt solution of weak acid and weak base

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

9 BUFFER SOLUTIONS

- The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali called **Buffer solution**
- **Acidic Buffer**

(i) Aqueous solution containing weak acid and its salt with strong base can act as acidic buffer (eg $CH_3COONa + CH_3COOH$)

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

- **Basic Buffer**

(i) Aqueous solution of weak base and its salt with strong acid can act as basic buffer (eg NH_4Cl + NH_4OH)

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

Sparingly Soluble Salts

- Salts having solubility < 0.01 M are considered saparigly soluble salts
- The equilibrium constant between the undissolved solid and the ions in a saturated solution is known as Solubility product (K_{sp}).
- For sparingly soluble salt M_xX_y with molar solubility S

$K_{sp} = x^x.\ y^y\ (S)^{(x+y)}$

Redox Reactions

8

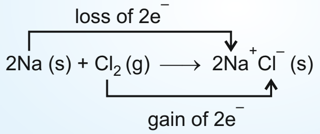
Chapter

① CLASSICAL IDEA OF REDOX REACTIONS

- **Oxidation**- addition of oxygen/electronegative elements to a substance or removal of hydrogen/electropositive element from a substance.
- **Reduction** is the removal of oxygen/electronegative element from a substance or addition of hydrogen/ electropositive element to a substance.

② REDOX REACTION IN TERMS OF ELECTRON TRANSFER REACTIONS

- Half reactions that involve loss of electrons are called **oxidation reactions**.
- Half reactions that involve gain of electrons are called **reduction reactions**.



$$2Na\,(s) + Cl_2\,(g) \longrightarrow 2\overset{+}{Na}\overset{-}{Cl}\,(s)$$

- **Oxidising agent :** Acceptor of electron(s).
- **Reducing agent :** Donor of electron (s)

③ OXIDATION NUMBER

- Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron pair in a covalent bond belongs entirely to more electronegative element
- Rules of the calculation of oxidation numbers:
  (1) In elements in the free state, oxidation number of each atom is zero.
  (2) For ion containing single atom, oxidation number is equal to charge on the ion.
  (3) Oxidation number of oxygen in oxide = –2, in peroxide = – 1, in super oxide = –½, in OF_2 = + 2, in O_2F_2 = + 1
  (4) Oxidation number of hydrogen is + 1 in binary compound except with metal eg: LiH, CaH_2
  (5) Oxidation number of F is –1, other halide ions is – 1, positive oxidation number of halogens (except F) in oxoacids and oxoanions.
  (6) Algebraic sum of oxidation number of all atoms in a compound is 0. In polyatomic ions, the algebraic sum of oxidation number of all atoms is equal to charge present on the ions.
- **Stock notation** is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of metal in the molecular formula eg. Au (III) Cl_3
- **Oxidation :** An increase in the oxidation number of the element in the given substance.
- **Reduction :** A decrease in the oxidation number of the element in the given substance.
- **Oxidising agent :** A reagent which can increase the oxidation number of an element in a given substance
- **Reducing agent :** A reagent which can decrease the oxidation number of an element in a given substance.

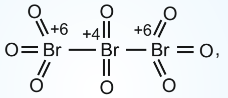
④ TYPES OF REDOX REACTIONS

- **Combination reactions**
  $A + B \longrightarrow C$
  (Either A and B or both A and B must be in the elemental form)
  eg : $C(s) + O_2(g) \longrightarrow CO_2(g)$
- **Decomposition reactions** are the opposite of combination reaction.
  e.g : $2NaH\ (s) \xrightarrow{\Delta} 2Na\ (s) + H_2\ (g)$
  All decomposition reactions are not redox reactions
  e.g : $CaCO_3 \xrightarrow{\Delta} CaO(s) + CO_2\ (g)$
- **Displacement reaction** are those in which an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element.
  $X + YZ \rightarrow XZ + Y$
  Types of displacement to reactions.
  (1) **Metal displacement reaction** in which a metal in a compound can be displaced by another metal in uncombined state.
  e.g. $CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$
  (2) **Non-metal displacement** redox reaction generally include hydrogen displacement
  e.g. $2Na(s) + 2H_4O(\ell) \rightarrow 2NaOH(aq) + H_2(g)$
- **Disproportionation reactions**
  In this type of reaction an element in one oxidation state is simultaneously oxidised and reduced.
  eg: $2H_2O_2(aq) \longrightarrow 2H_2O\ (l) + O_2(g)$

⑤ PARADOX OF FRACTIONAL OXIDATION NUMBER

In certain compound, the oxidation number of a particular element in the compound is in fraction. Actually this fractional oxidation state is the average oxidation state of same element in the compound.

eg: Br_3O_8 →

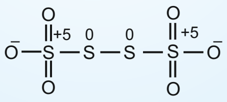


Oxidation no. of Br = 16/3

eg: C_3O_2 → $O=\overset{\div 2}{C}=\overset{0}{C}=\overset{+2}{C}=O$

Oxidation no. of C = 4/3

eg: $S_4O_6^{2-}$ →



Oxidation of S = 2.5

⑥ BALANCING OF REDOX REACTIONS

1. **Oxidation Number Method**

$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$ (in basic medium)

Step 1: The Skeletal ionic equation

$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

Step 2: Assign oxidation number for Mn and Br

$\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br}^-(aq) \rightarrow \overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$

This indicates that permanganate ion is the oxidant and bromide ion in the reductant.

Step 3 : Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.

$2\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br}^-(aq) \rightarrow 2\overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$

Step 4 : As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add $2OH^-$. ions on the right to make ionic charges equal

$2MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

Step 5 : Finally, count the hydrogen atoms and add appropriate number of water molecule (i.e. one H_2O molecule, on the left side to achieve balanced redox change.)

$2MnO_4^-(aq) + Br^-(aq) + H_2O(\ell) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

2. **Half Reaction Method:**

Suppose we have to balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium, wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr^{3+} ions.
The following steps are involved in this task.

Step 1: Produce unbalanced equation for the reaction in ionic form :

$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$

Step 2: Separate the equation into half reactions:

Oxidation half : $\overset{+2}{Fe}{}^{2+}(aq) \rightarrow \overset{+3}{Fe}{}^{3+}(aq)$

Reduction half : $\overset{+6}{Cr_2}O_7^{2-}(aq) \rightarrow \overset{+3}{Cr}{}^{3+}(aq)$

Step 3: Balance the atoms other than O and H in each half reaction individually. Here the oxidation half reaction is already balanced with respect to Fe atoms. For the reduction half reaction, we multiply the Cr^{3+} by 2 to balance Cr atoms.

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms. Thus, we get :

$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2\,Cr^{3+}(aq) + 7H_2O(l)$

Step 5: Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate number.
The oxidation half reaction is thus rewritten to balance the charge:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O\ (l)$

To equalise the number of electrons in both the half reactions, we multiply the oxidation half reaction by 6 and write as :

$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$

Step 6: We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation as :

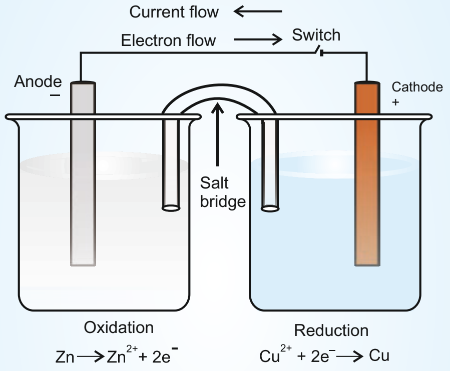
$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6\,Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to number of atoms and the charges.

For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each H^+ ion, add an equal number of OH^- ions to both sides of the equation. Where H^+ and OH^- appear on the same side of the equation, combine these to give H_2O.

⑦ REDOX REACTIONS AND ELECTRODE PROCESSES

- A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.
- **Daniell cell**



- The potential associated with each electrode is known as **electrode potential**.
- If the concentration of each species taking part in the electrode reaction is unity at 298 K then the potential of each electrode is said **standard electrode potential**.
- By convention the **standard electrode potential** (E°) of **hydrogen electrode** is 0 volts.
- A negative E° means redox couple is a stronger reducing agent than H^+/H_2 couple.
- A positive E° means redox couple is weak reducing agent than H^+/H_2 couple.

Hydrogen

9
Chapter

① POSITION OF HYDROGEN IN THE PERIODIC TABLE

- Hydrogen has electronic configuration $1s^1$ therefore has a resemblance to alkali metals which loose one electron to form unipositive ions, as well as halogens, which gains one electron to from uninegative ion; Thus, it is unique in behaviour and is therefore, best placed seperately in the periodic table.

② DIHYDROGEN

- Occurrence
  - (i) Dihydrogen is most abundant element in the universe(70% of the total mass of the universe)
  - (ii) 0.15% by mass in the earth atmosphere and 15.4% of the earth crust and oceans
  - (iii) Occurs in plant and animal tissues, carbohydrate, proteins etc.

③ ISOTOPES

(i) Hydrogen has three isotopes: Protium ^1_1H, deuterium, ^2_1H or D and tritium ^3_1H or T

(ii) The relative abundance of H, D and T are 99.985, 0.0156 and 10^{-15}% respectively

(iii) Only tritium is radioactive and emits low energy β^- particles ($t_{1/2}$, 12.33 years)

④ PREPARATION OF DIHYDROGEN

- **Lab method**

(i) Reaction of granulated zinc with dilute hydrochloric acid

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

(ii) Reaction of zinc with aqueous alkali

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

- **Commercial Production**

(i) Electrolysis of acidified water using Pt electrodes

$$2H_2O(l) \xrightarrow[\text{Traces of Acid/Base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) High purity (> 99.95%) dihydrogen is obtained by electrolysis of warm aqueous $Ba(OH)_2$ solution with Ni electrodes.

(iii) Byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution

At anode : $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

At cathode : $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Overall reaction : $2Na^+(aq) + Cl^-(aq) + 2H_2O(l)$

$$\downarrow$$

$Cl_2(g) + H_2(g) + 2Na^+(aq) + 2OH^-(aq)$

(iv) Reaction of steam on hydrocarbon or coke at high temperature with catalyst

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{\text{1270 K}} nCO + (2n + 1)H_2$$

- Mixture of CO and H_2 is called water gas or syngas
- The production of H_2 can be increased by reacting CO of syngas with steam in the presence of iron chromate as catalyst

$$CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{\text{673K}} CO_2(g) + H$$

(Water gas shift reaction)

- Presently 77% of industrial H_2 is produced from petrochemicals 18% from coal, 4% from electrolysis

⑤ PROPERTIES OF DIHYDROGEN

- **Physical Properties :** H_2 is a colourless, odourless, tasteless and combustible gas, lighter than air and insoluble in water
- **Chemical Properties :**

(i) Reaction with halogens :

$H_2(g)+X_2(g) \rightarrow 2HX(g)$

(X = F, Cl, Br, I)

(ii) Reaction with dioxygen :

$$2H_2(g) + O_2(g) \xrightarrow[\text{heating}]{\text{Catalyst or}} 2H_2O(l), \Delta H = -285.9 \text{ kJ mol}^{-1}$$

(iii) Reaction with dinitrogen :

$$3H_2(g) + N_2(g) \xrightarrow[\text{200atm, Fe}]{\text{673K}} 2NH_3(g), \Delta H = -92.6 \text{ kJ mol}^{-1}$$

(iv) Reaction with metals :

$H_2(g) + 2M(g) \rightarrow 2MH(s)$, M = alkali metals

(v) Reaction with metal ions and metal oxide

$H_2(g) + Pd^{2+}(aq) \rightarrow Pd(s) + 2H^+(aq)$

$yH_2(g) + MxOy(s) \rightarrow xM(s) + yH_2O(l)$

(vi) Reaction with organic compounds :

- Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine or vanaspati ghee)
- Hydroformylation of olefins

  $H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$

  $H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH$

⑥ USES OF DIHYDROGEN

- For synthesis of NH_3 which is used in manufacture of nitric acid & fertilizers
- It is used in the manufacture of vanaspati ghee, organic chemicals, metal hydride and hydrogen chloride.
- In metallurgical process
- Atomic hydrogen and oxy hydrogen torch, rocket fuel and fuel cell

⑦ HYDRIDES

- Binary compound of hydrogen with other elements called hydrides.
- Types of hydrides

(i) **Ionic or saline hydrides**

- Stoichiometric compounds of H_2 with most of the s-block elements.
- Significant covalent character is found in lighter metal hydrides *e.g.,* LiH, BeH_2 and MgH_2.
- Their melts conduct electricity and on electrolysis liberate H_2 gas at anode which confirms the existence of H^- ion.
- Reacts violently with H_2O

  $NaH(s) + H_2O(aq) \rightarrow NaOH(aq) + H_2(q)$

(ii) **Covalent of Molecular Hydride**

- H_2 forms molecular compounds with most of p-block elements *e.g.,* CH_4, NH_3, H_2O and HF
- Hydrogen compounds of non metal considered as hydride. They are volatile in nature.
- Molecular hydrides are classified further as :

(1) **Electron deficient hydride** has too few electrons for writing its conventional lewis structure *e.g.,* B_2H_6.(In fact all group 13 hydrides).

(2) **Electron precise hydrides** have the required number of electrons to write conventional Lewis structure *e.g.,* All elements of group 14 form such compounds.

(3) **Electron-rich hydrides** have excess electrons which are present as lone pairs *e.g.,* elements of group 15 – 17 form such compounds.

(iii) **Metallic of Non-stoichiometric (or interstials) Hydrides**

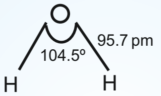
- These are formed by many d-block and f-block elements
- Metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH.
- They are almost always non-stoichiometric and law of costant composition does not hold good.
- E.g., $LaH_{2.87}$, $YbH_{2.55}$, $NiH_{0.6\text{-}0.7}$ etc.

⑧ WATER

- **Physical properties**

(i) It is colourless and tasteless liquid. The unusual properties of water in the condensed phase are due to the presence of extensive hydrogen bonding between water molecule.

(ii) Structure of water



(iii) Structure of ice - At atmospheric pressure ice crystallizes in the hexagonal form but at very low temperature it condenses to cubic form. Density of ice is less than water due to open type structure with wide holes.

- **Chemical properties**

(i) Amphoteric nature -H_2O has, the ability to act as an acid as well as base

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

acid-1 base-2 acid-2 base-1

(Self ionization of water)

(ii) Hydrolysis reaction - Due to high dielectric constant, it has a very strong hydrating tendency.

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

(iii) Redox reaction

$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$

(iv) Hydrate formation- from aqueous solution many salt can be crystallised as hydrated salt viz., coordinated water (*e.g.,* $[Cr(H_2O)_6]^{3+}3Cl^-$), interstitial water(*e.g.,* $BaCl_2.2H_2O$), hydrogen-bonded water (*e.g.,* $CuSO_4.5H_2O$).

⑨ HARD & SOFT WATER

- Presence of calcium and magnesium salts in the form of hydrogen carbonate, chlorides and sulphate makes water **'hard'**, Hard water does not give lather with soap
- Water free from soluble salts of calcium and magnesium is called soft water
- **Temporary Hardness** is due to presence of Mg and Ca hydrogen carbonates. It can be removed by

(i) **Boiling** During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$.

(ii) **Clark's method :** Calculated amount of lime is added.

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$

- **Permanent Hardness** is due to the presence of soluble sulphates and chlorides of Mg and Ca. It can be removed by

(i) **Treatment with washing soda**

$MCl_2 + Na_2CO_3 \rightarrow MCO_3\downarrow + 2NaCl$

(M = Mg,Ca)

$MSO_4 + Na_2CO_3 \rightarrow MCO_3\downarrow + Na_2SO_4$

(ii) Calgon's method - Sodium hexametaphosphate ($Na_6P_6O_{18}$) , commercially called 'calgon' when added to hard water following reactions takes place

$Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$

(M = Mg, Ca)

$M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$

(iii) **Ion-exchange method :** This method is also called **zeolite/permutit process**.

$2NaZ(s) + M^{2+}(aq) \rightarrow MZ_2(s) + 2Na^+(aq)$

(NaZ is $NaAlSiO_4$), (M = Mg,Ca)

Exhausted zeolite regenerated for further use by treating with an aqueous sodium chloride solution

$MZ_2(s) + 2NaCl(aq) \rightarrow 2NaZ + MCl_2(aq)$

(iv) **Synthetic resins method**

Cation exchange resins contain large organic molecule with-SO_3H group and are water insoluble. RSO_3H is changed to RNa by treating it NaCl. The resin exchanges Na^+ ions with Ca^{2+} and Mg^{2+} ions present in hard water to make the water soft

⑩ HYDROGEN PEROXIDE(H_2O_2)

- Preparation

(i) $BaO_28H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq) + 8H_2O(l)$

(ii) $2HSO^-_4(aq) \xrightarrow{\text{Electrolysis}} HO_3SOOSO_3H(aq) \xrightarrow{\text{Hydrolysis}}$ $2HSO^-_4(aq) + 2H^+(aq) + H_2O_2(aq)$

This method is now used for lab preparation of D_2O_2

$K_2S_2O_8(s) + 2D_2O(l) \rightarrow 2KDSO_4(aq) + D_2O_2(l)$

(iii) **Industrial method**

2-ethylanthraquinol $\underset{H_2/Pd}{\overset{O_2(air)}{\rightleftharpoons}}$ H_2O_2 + (Oxidised product)

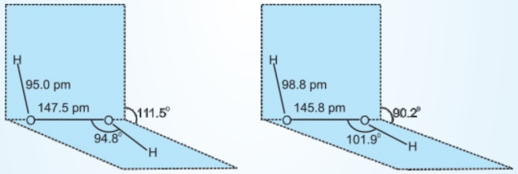
- **Physical properties**

(i) H_2O_2 is an almost colorless liquid

(ii) H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.H_2O$. A 30% solution of H_2O_2 is marketed as 100 volume hydrogen peroxide.

(iii) 100 volume means 1mL of 30% H_2O_2 solution will give 100 mL of O_2 at STP.

- Structure



(a) Gas phase (b) Solid phase

- **Chemical properties**

(i) Oxidising action in acidic medium

$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$

(ii) Reducing action in acidic medium

$2MnO^-_4 + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

(iii) Oxidising action in basic medium

$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2\bar{O}H$

(iv) Reducing action in basic medium

$I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$

⑪ HEAVY WATER, D_2O

- Extensively used as a moderator in nuclear reactors
- It is used to prepare other deuterium compounds

The s-Block Elements

10

Chapter

① GROUP-1 ELEMENTS : ALKALI METALS

- **Hydration Enthalpy**
  - (i) Hydration enthalpies decrease with increase in ionic sizes.
  - (ii) Li^+ has maximum degree of hydration.
- **Physical Properties**
  - (i) Alkali metals are silvery white, soft and light metals.
  - (ii) Alkali metals have low density which increases down, from Li to Cs. However potassium is lighter than sodium.
  - (iii) The melting and boiling point are low due to weak metallic bond.
  - (iv) **Flame colour:** Li(Crimson red), Na (Yellow), K(Violet), Rb(Red Violet), Cs(Blue)
- **Chemical Properties**
  - (i) **Reactivity towards air** - Burns vigorously in oxygen. Li forms Li_2O, Na forms Na_2O_2 and K, Rb and Cs form superoxides, Li also forms Li_3N.
  - (ii) **Reactivity towards water**
    - (a) $2M + 2H_2O \rightarrow 2M^+ + 2O\bar{H} + H_2$: (M = An alkali metal)
    - (b) Li has most negative E° but reacts less vigorous than Na which has least negative E°.
  - (iii) **Reactivity towards dihydrogen :** $2M + H_2 \rightarrow 2M^+H^-$
  - (iv) **Reactivity towards halogen**
    - (a) Alkali metals react vigorously with halogens to form ionic halide M^+X^-.
    - (b) Due to high polarisation capability of Li^+, lithium halides are somewhat covalent. LiI is most covalent in nature due to bigger size of I^- ion.
  - (v) **Reducing nature**
    - (a) Alkali metals are strong reducing agents.
    - (b) Li is most and Na is least powerful reducing agent.
    - (c) Dispite of high ionisation enthalpy, E° of Li is most negative due to its high hydration enthalpy.
  - (vi) **Solution in Liquid ammonia**
    - (a) Alkali metals give deep blue solution when dissolved in liquid ammonia.

      $M + (x+y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$ (Blue colour)
    - (b) The solutions are paramagnetic and on standing slowly liberate H_2 and form amide.
    - (c) In concentrated solution, the blue colour of solution changes to bronze and becomes diamagnetic.

② GENERAL CHARACTERISTICS OF THE COMPOUNDS OF ALKALI METALS

- **Oxides and Hydroxides**
  - (a) On combustion in excess of air, Li forms mainly Li_2O (plus some Li_2O_2), Na forms Na_2O_2 (plus some NaO_2) whilst K, Rb and Cs form superoxides.
  - (b) These oxide are easily hydrolysed to form hydroxides.

    $M_2O + H_2O \rightarrow 2M^+ + 2\bar{O}H$

    $M_2O_2 + 2H_2O \rightarrow 2M^+ + 2\bar{O}H + H_2O_2$

    $2MO_2 + 2H_2O \rightarrow 2M^+ + 2\bar{O}H + H_2O_2 + O_2$
  - (c) The oxides and peroxides are colourless while superoxides are yellow or orange in colour and paramagnetic.
- **Halides**
  - (a) Alkali metal halides are high melting, colourless crystalline solids.
  - (b) $\Delta_f H^\circ$ values of fluorides become less negative down the group while reverse is true for chlorides, bromides and iodides.
  - (c) For given metal $\Delta_f H^\circ$ always become less negative from fluoride to iodides.
  - (d) MP/BP trend: fluoride > chloride > bromide > iodide.
- **Salts of Oxo-Acids**
  - (a) Alkali metals form salt with all oxoacids
  - (b) Their carbonates and hydrogen carbonates are highly stable to heat except that of Li.

③ ANOMALOUS PROPERTIES OF LITHIUM

- The anomalous behaviour of Li is due to the (i) Exceptionally small size, and (ii) High polarising power.
- Li shows diagonal relationship to Mg.

④ SOME IMPORTANT COMPOUNDS OF SODIUM

- **Sodium carbonate**, Na_2CO_3 (washing soda)
  - (i) (a) Prepared by Solvay process

    $2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$

    $(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$

    $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

    $NaHCO_3$ crystal separates out. These are heated to give sodium carbonate.

    $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$
  - (b) NH_3 is recovered using $Ca(OH)_2$

    $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$
  - (c) K_2CO_3 cannot be prepared by Solvay process because $KHCO_3$ is too soluble to be precipitated out.
  - (d) It is white crystalline solid exist as $Na_2CO_3.10H_2O$. On heating it forms $Na_2CO_3{\cdot}H_2O$ and above 373 K forms Na_2CO_3, a white powder known as soda ash.
- **NaCl, Sodium Chloride**

  Most abundant source is sea water and impurities like $CaCl_2$ and $MgCl_2$ make table salt deliquescent.
- **Sodium hydroxide (caustic soda), NaOH**

  In Castner Kellner Cell a brine solution is electrolysed using Hg cathode and carbon anode. **(Commercial method)**

  Cathode : $Na^+ + e^- \xrightarrow{Hg} Na - \text{amalgam}$

  Anode : $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

  $2Na\text{-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$

  NaOH is white crystalline deliquescent solid and readily soluble in water to give strong alkaline solutions.
- **Sodium Hydrogencarbonate (Baking Soda) $NaHCO_3$**

  $NaHCO_3$ is known as baking soda because it decomposes on heating to generate bubbles of CO_2 to make cakes or pastries fluffy. It is made by saturating a solution of Na_2CO_3 with CO_2.
- **Biological importance of sodium and potassium**
  - (i) Sodium ions are found primarily on outside of cells, in blood plasma and in the interstitial fluids which surrounds the cell.
  - (ii) These ions participate in the transmission of nerve signal, in regulating flow of water across cell membrane etc.
  - (iii) Potassium ions are most abundant within cell fluids.

⑤ GROUP 2 ELEMENTS : ALKALINE EARTH METALS

- Except beryllium, group 2 elements are known as alkaline earth metals.
- **Atomic and Ionic Radii**
  - (i) The atomic and ionic radii of group-2 elements are smaller than corresponding alkali metals.
  - (ii) Within group, atomic and ionic radii increases with increase in atomic number.
- **Ionization Enthalpies**
  - (i) Alkaline earth metals have low ionization enthalpies due to fairly large size of atoms.
  - (ii) The 1st ionization enthalpies of alkaline earth metal are greater than corresponding group 1 metals. The 2nd ionization enthalpies of alkaline earth metals are smaller than corresponding alkali metals.
- **Hydration enthalpies** decrease down the group and are larger than those of alkali metals.

⑥ PHYSICAL PROPERTIES

(i) BP and MP are higher than alkali metals.

(ii) Ca, Sr and Ba give brick red, crimson and apple green flame colour respectively.

⑦ CHEMICAL PROPERTIES

- **Reactivity towards air and water**
  - (i) Be and Mg are kinetically inert to oxygen and water because of formation of oxide film on their surface.
  - (ii) Powdered Be readily burns to give BeO and Be_3N_2
  - (iii) Other elements give oxide and nitride.
- **Reactivity towards halogens**
  - (i) $M + X_2 \xrightarrow{\Delta} MX_2 : (X = F, Cl, Br, I)$
  - (ii) $(NH_4)_2BeF_4 \xrightarrow{\Delta} 2NH_4F + BeF_2$
  - (iii) $BeO + C + Cl_2 \xrightleftharpoons{600-800\,K} BeCl_2 + CO$
- **Reactivity towards hydrogen**

  All elements except Be combine with hydrogen to form hydrides, MH_2 ; $2\,BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$
- **Reactivity towards Acids :** $M + 2HCl \rightarrow MCl_2 + H_2$
- **Reducing nature**
  - (i) Be has least negative E° within group.
- **Solutions in liquid ammonia**
  - (i) Alkaline earth metals give deep blue black colour solution with ammonia.

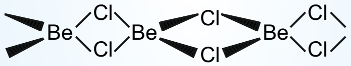
    $M + (x + 2y)NH_3 \rightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^{-}$

⑧ GENERAL CHARACTERISTICS OF COMPOUNDS OF THE ALKALINE EARTH METALS

- **Oxides and Hydroxides**
  - (i) All oxides except BeO (amphoteric) are basic in nature and react with water to form sparingly soluble hydroxides $M(OH)_2$.
  - (ii) The solubility, thermal stability and basic character of hydroxides increase down the group however these are less basic and less stable than alkali metal hydroxides.
  - (iii) $Be(OH)_2$ is amphoteric.

    $Be(OH)_2 + 2\overline{O}H \rightarrow [Be(OH)_4]^{2-}$ (Beryllate ion)

    $Be(OH)_2 + 2HCl + 2H_2O \rightarrow [Be(OH)_4]Cl_2$
- **Halides**
  - (i) Except Be all other halides of alkaline earth metals are ionic.
  - (ii) $BeCl_2$ has chain structure in solid state



  - (iii) In vapour phase, $BeCl_2$ is a dimer
- **Salts of oxo-acids**
  - (i) **Carbonates**
    - (a) All are insoluble and solubility decreases down the group.
    - (b) Thermal stability increases down the group.
  - (ii) **Sulphates**

    Solubility decreases down the group.
  - (iii) **Nitrates**

    All of them decompose on heating

    $2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$

    (M = Be, Mg, Ca, Sr, Ba)

⑨ SOME IMPORTANT COMPOUNDS OF CALCIUM

- **Calcium oxide or quicklime, CaO**
  - (i) Commercial method of preparation - heating limestone in rotary kiln at 1070-1270 K.
  - (ii) It absorbs moisture and CO_2

    $CaO + H_2O \rightarrow Ca(OH)_2$

    $CaO + CO_2 \rightarrow CaCO_3$
  - (iii) Addition of limited amount of water breaks the lump of lime. The process is called slaking of lime.
- **Calcium Hydroxide (Slaked lime), $Ca(OH)_2$**
  - (i) It is white amorphous powder, sparingly soluble in water. The aqueous solution is known as lime water and suspension of slaked lime in water is known as milk of lime.
  - (ii) CO_2 turns lime water milky due to the formation of $CaCO_3$ and on passing excess CO_2, the precipitate dissolves to form $Ca(HCO_3)_2$.
  - (iii) Milk of lime reacts with Cl_2 to form hypochlorite.

    $2Ca(OH)_2 + 2Cl_2 \rightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$

    (Bleaching powder)
- **Calcium Sulphate (Plaster of Paris) $CaSO_4 \cdot \frac{1}{2}H_2O$**
  - (i) It is a hemihydrate of $CaSO_4$
  - (ii) Obtained on heating gypsum, $CaSO_4 \cdot 2H_2O$ at 393 K

    $2(CaSO_4 \cdot 2H_2O) \xrightarrow{\Delta} 2(CaSO_4) \cdot H_2O + 3H_2O$
  - (iii) Heating above 393 K form $CaSO_4$ known as dead burnt plaster.
- **Cement is an important building material**
  - (i) Portland cement composition is

    CaO, 50-60%; SiO_2, 20-25%; Al_2O_3, 5-10%; MgO, 2-3%; Fe_2O_3 1-2% and SO_3, 1-2%
  - (ii) The ingredients of portland cement are dicalcium silicate (Ca_2SiO_4)26%, tricalcium silicate (Ca_3SiO_5)51% and tricalcium aluminate ($Ca_3Al_2O_6$)11%
  - (iii) When cement is mixed with water the setting of cement takes place to give hard mass. The purpose of adding gypsum is only to slow down the process of setting of the cement.

⑩ BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM

(i) All enzymes that utilize ATP in phosphate transfer require Mg as the cofactor.

(ii) Chlorophyll contains Mg.

(iii) Calcium plays important roles in neuro muscular functions, blood coagulation etc.

The *p*-Block Elements

11

Chapter

① THE *p*-BLOCK ELEMENTS

- General valence shell electronic configuration of *p*-block elements is ns^2np^{1-6}.
- Maximum oxidation states = total number of valence electrons.
- The occurence of oxidation states two unit less than the group oxidation states are sometime attributed to the inert pair effect
- The second period elements of *p*-groups are restricted to a maximum covalence of four (using 2*s* and there 2*p* orbitals)
- Third period elements of *p*-groups can expand their covalence above four due to vacant 3*d* orbitals
- Only first member of group can form $p\pi$ - $p\pi$ multiple bonds to itself. The heavier elements do form π bonds but this involves *d*-orbitals ($d\pi$ - $p\pi$ or $d\pi - d\pi$).

② GROUP 13 ELEMENTS : THE BORON FAMILY

- B (non-metal), Al (metal but shows many chemical similarities to B) Ga, In, Tl, Nh (metal)
- Boron mainly occurs as orthoboric acid (H_3BO_3), borax ($Na_2B_4O_7.10H_2O$) and kernite ($Na_2B_4O_7.4H_2O$)
- Boron has two isotopes ^{10}B(19%) and ^{11}B(81%)
- Aluminium is the most abundant metal, Bauxite ($Al_2O_3.2H_2O$) and cryolite (Na_3AlF_6) are important minerals of aluminium.
- **Outer electronic configuration** of boron family is ns^2np^1
- **Atomic Radii**
  - (i) B < Al > Ga < In < Tl
  - (ii) Atomic radius of Ga is less than Al due to poor screening effect of 10d - electrons of Ga.
- **Ionization Enthalpy**
  - (i) The decrease from B to Al is associated with increase in size.
  - (ii) The observed discontinuity between Al and Ga, and between In and Tl are due to inablity of *d*-and *f*-electrons to cause screening effect.
- **Electronegativity –** First decreases from B to Al and then increases marginally.
- **Physical Properties**
  - (i) Boron is hard and black coloured solid, exists in many allotropic forms, high melting point due to strong crystalline lattice.
  - (ii) Rest members are soft metals
  - (iii) Gallium has low melting point (303 K) and high boiling poin (2676 K)
  - (iv) Density increases down the group
- **Chemical Properties**
  - (i) B forms only covalent compounds.
  - (ii) In Ga, In and Tl, both +1 and +3 oxidation states are observed. Relative stability of +1 oxidation state :

    Al < Ga < In < Tl
  - (iii) For Tl, + 1 is predominant and +3 oxidation state is oxidising
  - (iv) Reactivity towards air

    $4E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$

    $2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$

    B_2O_3(Acidic), Al_2O_3 and Ga_2O_3 (Amphoteric)

    In_2O_3 and Tl_2O_3(Basic).
  - (v) Al dissolves in mineral acids and aqueous alkalies thus shows amphoteric character

    $2Al(s) + 6\,HCl\,(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$

    $2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq) + 3H_2(g)$
  - (vi) Reactivity towards halogen

    $2E(s) + 3X_2(g) \rightarrow 2EX_3(s)\ (X = F, Cl, Br, I)$
- **Important Trends and Anomalous Properties of Boron**
  - (i) Tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water.
  - (ii) Monomeric trihalides are electron deficient and strong Lewis acids.
  - (iii) Halides other than boron are dimerised through halogen bridging.
- **Some Important Compounds of Boron**

(i) Borax ($Na_2B_4O_7.10H_2O$)

(1) Contains tetranuclear units $[B_4O_5(OH)_4]^{2-}$ therefore the correct formula is $Na_2[B_4O_5(OH)_4].8H_2O$.

(2) Borax give alkaline solution in water

$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$

(3) On heating, borax first loses water molecules and swells up. On further heating turns into a transparent liquid with solidifies into glass like borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

Metaborates of many transition metals have characteristic colour therefore borax bead test is used to detect metals.

(ii) Orthoboric acid

(1) White crystalline solid with soapy touch, sparingly soluble in water but highly soluble in hot water.

(2) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$

(3) Layer structure in which planar BO_3 units are linked by H-bonds.

(4) H_3BO_3 monobasic Lewis acid not protonic acid.

$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$

(5) $H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$

(iii) Diborane (B_2H_6)

(1) Preparation : $4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$

(2) Lab method : $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

(3) Industrial method : $2BF_3 + 6NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$

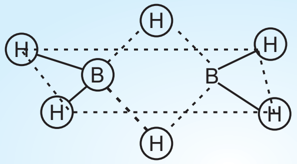
(4) Colourless, highly toxic gas, catches fire spontaneously in air

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$

(5) Readily hydrolyse to give boric acid

(6) $3B_2H_6 + 6NH_3 \rightarrow 3\,[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$ ($B_3N_3H_6$ inorganic benzene)

(7)



Four terminal B – H are regular two centre-two electron bonds while the two bridge (B – H – B) bonds are three centre-two electron bonds.

(8) Lithium and sodium tetrahydridoborate also known as **borohydrides**

$2\,MH + B_2H_6 \rightarrow 2M^+[BH_4]^-$ (M = Li or Na)

③ GROUP 14 ELEMENTS : THE CARBON FAMILY

- C, Si, Ge, Sn, Pb and Fl are 14th group elements.
- C has two stable isotopes : ^{12}C and ^{13}C and radioactive isotope ^{14}C
- Ge exists only in traces, Sn as cassiterite (SnO_2), Pb as galena (PbS)
- General valence shell electronic configuration ns^2np^2
- **Physical Properties**
  C and Si (Non-metals), Ge (metalloid), Sn and Pb (Metals)
- **Covalent Radius :** Considerable increase in covalent radius from C to Si, small increase thereatfer due to completely filled *d* and *f* orbitals of heavier members.
- **Electronegativity** values from Si to Pb are almost same
- **Ionization Enthalpy:** In general decreases down the group, small decrease from Si to Ge to Sn and slight increase from Sn to Pb.
- **Anomalous Behaviour of Carbon**
  (i) Maximum covalence = 4
  (ii) Order of catenation C > > Si > Ge ≈ Sn, Pb does not show catenation.
- **Allotropes of Carbon**
  (i) Diamond – sp^3 hybridised, crystalline lattice
  (ii) Graphite – Layered structure (held by van der Waals forces), sp^2 hybridised, conducts electricity
  (iii) Fullerenes

- **Chemical properties**
  (i) Common oxidation states are + 4 and + 2, C also exhibits negative oxidation states.
  (ii) +4 oxidation state are generally covalent in nature Heavier elements show + 2 oxidation state.
  (iii) Halides of group 14 elements except carbon undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species.
  (iv) **Reactivity towards oxygen :** (1) All members form mainly two types of oxides MO and MO_2.
    (2) CO_2, SiO_2, GeO_2 are acidic and SnO_2, PbO_2 are amphoteric
  (v) **Reactivity towards water**
    (1) C, Si and Ge are not affected by water, Tin decomposes steam to form SnO_2 and H_2
    $Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$
    (2) Pb is unaffected by H_2O due to protective oxide film formation
  (vi) **Reactivity towards halogen**
    (1) Form halides of formula MX_2 and MX_4.
    (2) Except C all other members react directly with halogen
    (3) Most MX_4 are covalent except SnF_4 and PbF_4
    (4) PbI_4 does not exist as energy released due to bond formation is not sufficient to unpair $6s^2$ electrons.
    (5) GeX_4 is more stable than GeX_2 whereas PbX_2 is more stable than PbX_4
- **Some Important compound of Carbon and Silicon**
  (i) **Carbon Monoxide (CO)**
    (1) Preparation
    $C(s) + H_2O(g) \xrightarrow{473\text{-}1273\,K} \underset{\text{(Water gas)}}{CO(g) + H_2(g)}$
    $2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\,K} \underset{\text{(Producer gas)}}{2CO(g) + 4N_2(g)}$
    (2) In CO molecule, there is one sigma and two π bonds
    (3) CO is highly poisonous due to its ability to form a complex with haemoglobin
  (ii) **Carbon Dioxide (CO_2)**
    (1) Lab preparation
    $CaCO_3(s) + 2HCl\,(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
    (2) Colourless, odourless gas, low solubility in H_2O, with water forms carbonic acid H_2CO_3(weak dibasic acid)
    (3) H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood.
    (4) CO_2 is removed from atmosphere by photosynthesis
  (iii) Silicon Dioxide (SiO_2): It resists the attack of halogens, dihydrogen and most of the acids and metals even at elevated temperature. However it is attacked by HF and NaOH.
    $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
    $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$
  (iv) Silicones
    (1) $-\!(R_2SiO)\!-$ as a repeating unit.
    (2) Preparation

$$\begin{tikzcd} & 2CH_3Cl + Si \arrow[r, "\text{Cu Powder}", "570\,K"'] & (CH_3)_2SiCl_2 \arrow[d] \\ \text{Silicone} & (CH_3)_2Si(OH)_2 \arrow[l, "\text{Polymerisation}"', "-H_2O"] & \arrow[l, "+2H_2O"', "-2HCl"] \end{tikzcd}$$

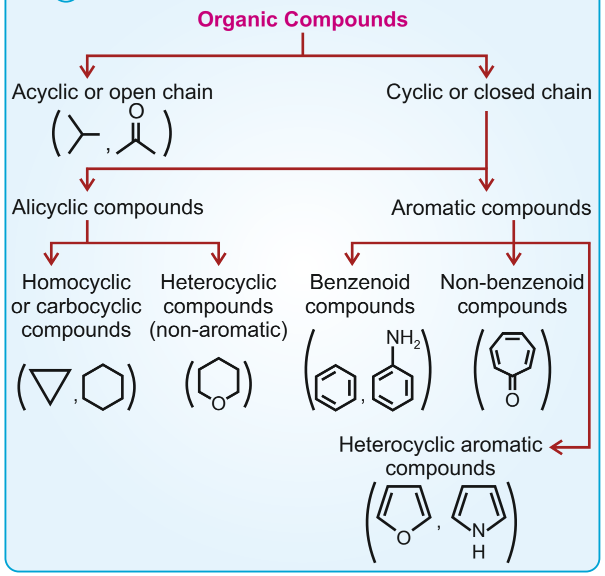
    The chain length of polymer can be controlled by adding $(CH_3)_3\,SiCl$
  (v) Silicates :
    (1) Silicates mineral like feldspar, Zeolites, mica etc. exist in nature
    (2) The basic structural unit of silicates is SiO_4^{4-}
  (vi) Zeolites
    (1) If aluminium atoms replace few silicon atoms in three-dimensional network of silicondioxide, overall structure known as aluminosilicate
    (2) A type of zeolite ZSM-5 used to convert alcohols directly into gasoline

Organic Chemistry - Some Basic Principles and Techniques

12

Chapter

① CLASSIFICATION OF ORGANIC COMPOUNDS



Organic Compounds

Acyclic or open chain

Cyclic or closed chain

Alicyclic compounds

Aromatic compounds

Homocyclic or carbocyclic compounds

Heterocyclic compounds (non-aromatic)

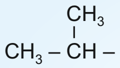
Benzenoid compounds

Non-benzenoid compounds

Heterocyclic aromatic compounds

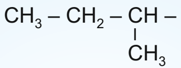
② NOMENCLATURE

Abbreviation for alkyl groups



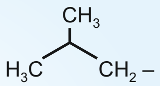
$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-$

Isopropyl –

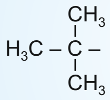


$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-$

sec-Butyl –

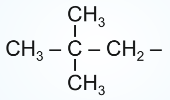


Isobutyl –



$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$

tert-Butyl –



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-$

Neopentyl –

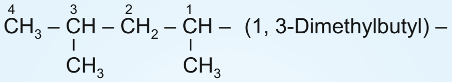
Nomenclature of Branched Chain Alkanes: (Rules)

(a) Longest carbon chain is identified

(b) Numbering is done so that branched carbon atoms get the lowest possible numbers

(c) For two substituents present at equivalent positions, the lower number is given to the one coming first in alphabetical listing

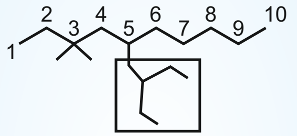
(d) For branched alkyl groups, the carbon atom of the branch that attaches to the root alkane is numbered (1) such as



$\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{1}{C}H}-$ (1, 3-Dimethylbutyl) –

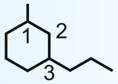
(e) While writing the names of the substituents in alphabetical order, the prefixes iso and neo are considered to be the part of fundamental name of alkyl group but sec- and tert- are not considered to be the part of fundamental name.

(f) If two chains are of equal size then that chain is to be selected which contains more number of side chains



5-(2-Ethylbutyl)-3, 3-dimethyldecane

Nomenclature of Cyclic Compounds



(Alphabetic order of numbering)
1-Methyl-3-propylcyclohexane

Nomenclature of organic compounds having functional groups(s)

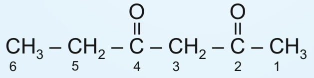
(a) The functional group present in the molecule is identified which determines the choice of appropriate suffix.

(b) The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.

(c) The order of decreasing priority for some functional groups:

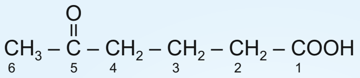
$-COOH$, $-SO_3H$, $-COOR$, $-COCl$, $-CONH_2$, $-CN$,

$-HC=O$, $>C=O$, $-OH$, $-NH_2$, $>C=C<$, $-C\equiv C-$



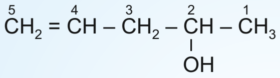
$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$

Hexane-2, 4-dione



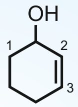
$\underset{6}{CH_3}-\underset{5}{\overset{\overset{O}{\|}}{C}}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$

5-Oxohexanoic acid



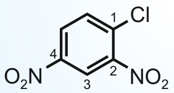
$\overset{5}{C}H_2=\overset{4}{C}H-\overset{3}{C}H_2-\underset{\underset{OH}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$

Pent-4-en-2-ol

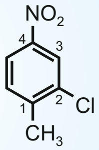


Cyclohex-2-en-1-ol

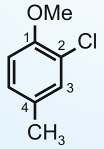
Nomenclature of substituted benzene compounds



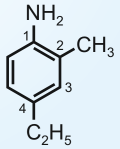
1-Chloro-2, 4-dinitrobenzene



2-Chloro-1-methyl -4-nitrobenzene



2-Chloro-4-methylanisole



4-Ethyl-2-methylaniline

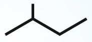
③ ISOMERISM

(a)**Structural Isomerism**

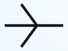
Compounds having the same molecular formula but different structures are classified as structural isomers.

(i) **Chain isomerism:** Example, C_5H_{12} represents three chain isomers

Pentane

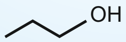


2-Methylbutane

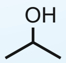


(2, 2-Dimethylpropane)

(ii) **Position isomerism:** Example, C_3H_8O represents two alcohols

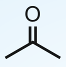


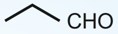
Propan-1-ol



Propan-2-ol

(iii) **Functional group isomerism:** Example, C_3H_6O represents an aldehyde and a ketone


propanone



propanal

(iv) **Metamerism:**

It arises due to different alkyl chains on either side of the functional group.

Example : $CH_3OC_3H_7$ and $C_2H_5OC_2H_5$ are metamers.

(b) **Stereoisomerism**

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. They are classified as

(i) Geometrical isomerism

(ii) Optical isomerism

4 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

$$\begin{tikzcd} \text{Organic molecule (Substrate)} \arrow[r, "\text{Attacking reagent}"] & \text{[Intermediate]} \arrow[r] \arrow[d] & \text{Byproduct(s)} \\ & \text{Product(s)} & \end{tikzcd}$$

(a) **Fission of Covalent bond**

(i) **Heterolytic cleavage** and (ii) **Homolytic cleavage**

(i) **Heterolytic cleavage**

In heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

- **Carbocations:**
  - A species having a carbon atom possessing sextet of electrons and a positive charge is called carbocation.
  - Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects.
    - Stability order:

      $(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$
- **Carbanions:**
  - A carbon species carrying a negative charge on carbon atom is called carbanion.
  - Carbon in carbanion is generally sp^3 hybridised and its structure is distorted tetrahedral.
    - Stability order:

      $\bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(ii) **Homolytic cleavage:** One of the electrons of the shared pair in a covalent bond goes with each of bonded atoms resulting in formation of free radicals.

- Free radicals : Stability order

  $\dot{C}H_3 < CH_3\dot{C}H_2 < (CH_3)_2\dot{C}H < (CH_3)_3\dot{C}$

(b) **Nucleophiles and Electrophiles**

- **Nucleophiles:** A reagent that brings an electron pair to the reactive site is called a nucleophile (Nu:)

  Examples: H_2O, NH_3, $CH_3\bar{O}$, $\bar{S}H$
- **Electrophile :** A reagent that takes away an electron pair from reactive site is called electrophile (E^+)

  Example: $AlCl_3$, BF_3, $\overset{+}{N}O_2$, Cl^+

(c) **Electron Displacement Effects in Covalent Bonds**

(i) **Inductive effect**

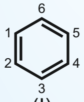
- When covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom.
- It operates through σ-bonds
- The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom.
- It is a permanent effect
- It is of two types

  +I effect : e.g. $-CH_3$, $-CH_2CH_3$ etc.

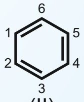
  –I effect : e.g. $-NO_2$, –CN, –CHO, –COOH etc.

(ii) **Resonance structures**

- Benzene can be represented by energetically identical structures (I) and (II) called resonance structures.



(I)



(II)

- Actual structure is resonance hybrid of (I) and (II)
- The resonance structures (canonical structures) are hypothetical and individually do not represent any real molecule.
- The energy of actual structure of the molecule is lower than that of any of the canonical structures.
- The difference in energy between the actual structure and the lowest energy resonance structure is called the resonance energy.

(iii) **Resonance effect**

- It is a permanent effect
- It operates through π-bond(s)
- It is of two types

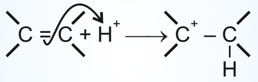
  +R effect : Halogens, –OH, –OR, –OCOR, $-NH_2$ etc.

  –R effect : –COOH, –CHO, –CN, $-NO_2$ etc.

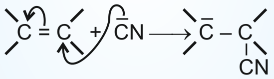
(iv) **Electromeric effect**

- It is a temporary effect
- Organic compounds having multiple bond (a double or triple bond) show this effect in presence of attacking reagent
- It is of two types

  Positive electromeric effect (+E effect)

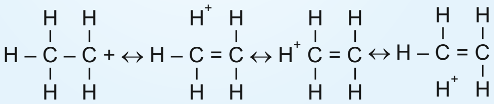


  Negative electromeric effect (–E effect)



(v) **Hyperconjugation**

- It involves delocalisation of σ electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p* orbital



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}+ \leftrightarrow H-\underset{H}{\overset{H^+}{C}}=\underset{H}{\overset{H}{C}} \leftrightarrow H^+\ \underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \leftrightarrow H-\underset{H^+}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$$

- It is a permanent effect.

5 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

The common techniques used for purification:

(i) Sublimation (ii) Crystallisation

(iii) Distillation : It is used to separate

(a) Volatile liquids from non-volatile impurities.

(b) The liquids having sufficient difference in boiling points e.g. mixture of chloroform (b.p. 334 K) and aniline (b.p. 457 K) is separated by this method.

(c) Distillation can be achieved by three different ways

- **Fractional Distillation:** This is applicable if boiling points of two liquids is not much, e.g. this is applicable to separate different fractions of crude oil in petroleum industry.

- **Steam Distillation:** This technique is applied to separate substances which are steam volatile and are immiscible with water.

  Example: Aniline is separated by this technique from aniline water mixture.
- **Distillation under reduced pressure:** This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points.

  Example: Glycerol can be separated from spent-lye in soap industry by using this technique.

(iv) **Differential Extraction:**

- When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- The organic solvent and the aqueous solution should be immiscible with each other.
- They form distinct layer which can be separated by separatory funnel.
- The compound is obtained by evaporating the organic solvent.

(v) **Chromatography:** It is an important technique extensively used to separate mixtures into their components.

Based on the principle involved it is classified into two main categories.

(a) Adsorption chromatography and

(b) Partition chromatography

(a) **Adsorption Chromatography:** It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. It is of two types

- Column chromatography
- Thin layer chromatography

(b) **Partition Chromatography:** It is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

⑥ QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test. The elements present in the compound are converted from covalent form into the ionic form by fusing compound with sodium metal.

$$Na + C + N \xrightarrow{\Delta} NaCN$$

$$2Na + S \xrightarrow{\Delta} Na_2S;\ Na + X \xrightarrow{\Delta} NaX\ (X = Cl, Br\ or\ I)$$

(A) **Test for nitrogen**

$$6\bar{C}N + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \mathbf{Fe_4\,[Fe(CN)_6]_3 \cdot xH_2O}$$

(Prussian blue)

(B) **Test of Sulphur**

(i) $S^{2-} + Pb^{2+} \rightarrow$ **PbS (black)**

(ii) $S^{2-} + \underset{\text{Nitroprusside}}{[Fe(CN)_5NO]^{2-}} \rightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$

In case, nitrogen and sulphur both are present, sodium thiocyanate is formed

$$Na + C + N + S \rightarrow NaSCN$$

$$Fe^{3+} + SC\bar{N} \rightarrow [Fe(SCN)]^{2+}\ \textbf{(Blood red)}$$

(C) **Test of Halogen**

$$X^- + Ag^+ \rightarrow AgX$$

- A white precipitate, soluble in NH_4OH shows presence of chlorine.
- A yellowish precipitate soluble, sparingly soluble in NH_4OH shows presence of Br
- A yellow precipitate insoluble in NH_4OH shows presence of iodine

(D) **Test of Phosphorus**

$$\begin{tikzcd}
\text{Compound} \arrow[r, "Na_2O_2"] & Na_3PO_4 \arrow[r, "HNO_3"] & H_3PO_4 \arrow[dl, "(NH_4)_2\,MoO_4"] \\
 & \mathbf{(NH_4)_3PO_4 \cdot 12\ MoO_3} &
\end{tikzcd}$$

(Yellow ppt)

⑦ QUANTITATIVE ANALYSIS

(A) **Nitrogen is estimated by Dumas and Kjeldahl's method**

(i) **Dumas method**

Let volume of nitrogen at STP = V mL

Mass of organic compound = m g

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

(ii) **Kjeldahl's Method**

$$\begin{tikzcd}
\text{Organic compound} + H_2SO_4 \arrow[r] & (NH_4)_2SO_4 \arrow[d, "NaOH"] \\
(NH_4)_2SO_4 & NH_3 \arrow[l, "H_2SO_4"']
\end{tikzcd}$$

Let mass of organic compound = m g

Volume of H_2SO_4 of molarity M needed for neutralisation of ammonia produced = V mL

$$\%\ \text{of nitrogen} = \frac{V \times 2M \times 1.4}{m}$$

- Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in ring (e.g. pyridine).

(B) **Halogens**

Carius method:

$$\text{Organic compound} \xrightarrow[AgNO_3\ \Delta]{\text{Fuming}\ HNO_3} AgX \downarrow$$

Let mass of compound = m g

Mass of AgX formed = m_1 g

$$\%\ \text{of halogen} = \frac{\text{atomic mass of } X \times m_1 \times 100}{\text{molecular mass of Ag X} \times m}\ \%$$

(C) **Sulphur**

Carius method:

$$\text{Organic compound} \xrightarrow{Na_2O_2} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 \downarrow$$

Let mass of compound = m g

Mass of $BaSO_4$ = m_1 g

$$\%\ \text{of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}\ \%$$

(D) **Phosphorus**

$$\text{Organic compound} \xrightarrow[HNO_3]{\text{Fuming}} H_3PO_4 \xrightarrow{(NH_4)_2MoO_4} (NH_4)_3PO_4 \cdot 12MoO_3 \downarrow$$

Let mass of compound = m g

Mass of $(NH_4)_3\,PO_4 \cdot 12MoO_3$ = m_1 g

Molar mass of $(NH_4)_3PO_4 \cdot 12MoO_3$ = 1877 g

$$\%\ \text{of P} = \frac{31 \times m_1 \times 100}{1877 \times m}\ \%$$

Hydrocarbons

13

Chapter

① AIKANES

- General formula (C_nH_{2n+2})
- Alkanes show structural isomerism
- C_6H_{14} has got five structural isomers whereas C_7H_{16} has nine.
- **Preparation**

(i) Hydrogenation

$$CH_2 = CH_2 + H_2 \xrightarrow{Pt/Pd/Ni} CH_3 - CH_3$$

(ii) From alkyl halides

(a) Reduction of alkyl halides

$$CH_3 - Cl + H_2 \xrightarrow[H^+]{Zn} CH_4$$

(b) Wurtz reaction

$$2CH_3Br + 2Na \xrightarrow{\text{dry ether}} CH_3 - CH_3$$

It is used for the preparation of higher alkanes containing even number of carbon atoms.

(iii) From carboxylic acids

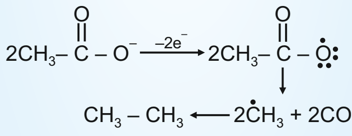
(a) Decarboxylation

$$CH_3COO^-Na^+ \xrightarrow[\Delta]{\text{Soda lime}} CH_4 + Na_2CO_3$$

(b) Kolbe's electrolytic method

$$2CH_3COO^-Na^+(aq) \xrightarrow{\text{Electrolysis}} CH_3 - CH_3$$

- Reaction at anode:



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\dot{\ddot{O}}: \;\downarrow\; \quad CH_3 - CH_3 \longleftarrow 2\dot{C}H_3 + 2CO_2\uparrow$$

- Reaction at cathode:

$$H_2O + e^- \longrightarrow {}^-OH + \dot{H}$$

$$2\dot{H} \longrightarrow H_2\uparrow$$

- Methane cannot the prepared by this method

- **Physical Properties**

Isomeric alkanes having more branching has lower boiling point.

- **Chemical properties**

(i) Substitution reaction

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

- Rate of reaction of alkanes with halogens is

$F_2 > Cl_2 > Br_2 > I_2$

- Rate of replacement of hydrogens of alkanes is : 3° > 2° > 1°

(ii) Combustion

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

(iii) Controlled oxidation

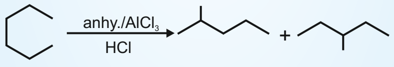
$$\text{(a) } 2CH_4 + O_2 \xrightarrow[100\text{ atm}]{Cu/523\text{ K}} 2CH_3OH$$

$$\text{(b) } CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} CH_3OH + H_2O$$

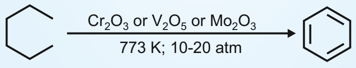
$$\text{(c) } 2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

$$\text{(d) } (CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3COH$$

(iv) Isomerisation



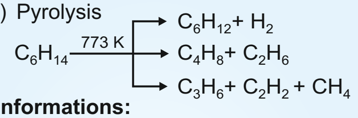
(v) Aromatisation



(vi) Reaction with steam

$$CH_4 + H_2O \xrightarrow[1273\text{ K}]{Ni} CO + 3H_2$$

(vii) Pyrolysis



$$C_6H_{14} \xrightarrow{773\text{ K}} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_2 + CH_4 \end{cases}$$

- **Conformations:**

Alkanes show conformational isomerism due to C – C bond rotation as is seen in ethane.

- Ethane molecule (C_2H_6) contains a carbon-carbon single bond.
- C – C bond results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom.
- These are called conformational isomers
- One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called **eclipsed** conformation.
- The conformation in which hydrogens are as far apart as possible is known as **staggered** conformation.
- Any other intermediate conformation is called **skew** conformation.

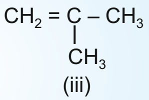
(i) **Eclipsed form** (ii) **Staggered form**

② AIKENES

- General formula (C_nH_{2n})
- Alkenes show structural isomerism

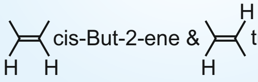
$CH_2 = CH - CH_2 - CH_3$ (i)

$CH_3 - CH = CH - CH_3$ (ii)



$CH_2 = \underset{\underset{\displaystyle CH_3}{|}}{C} - CH_3$ (iii)

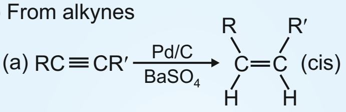
- Alkenes show geometrical isomerism



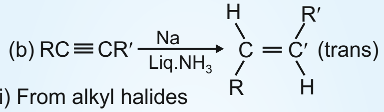
cis-But-2-ene & trans-But-2-ene are geometrical isomers

- **Preparation**

(i) From alkynes



$$\text{(a) } RC{\equiv}CR' \xrightarrow[BaSO_4]{Pd/C} \underset{H}{\overset{R}{\diagdown}}C{=}C\underset{H}{\overset{R'}{\diagup}} \text{ (cis)}$$



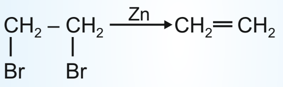
$$\text{(b) } RC{\equiv}CR' \xrightarrow[Liq.NH_3]{Na} \underset{R}{\overset{H}{\diagdown}}C = C'\underset{H}{\overset{R'}{\diagup}} \text{ (trans)}$$

(ii) From alkyl halides

$$CH_3 - CH_2 - Cl \xrightarrow[\Delta]{alc./KOH} CH_2 = CH_2$$

- The reaction is called β-elimination
- It is observed that for halogens, the rate is : iodine > bromine > chlorine
- The rate for alkyl groups is : tert > secondary > primary

(iii) From vicinal dihalides



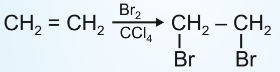
$$\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} \xrightarrow{Zn} CH_2{=}CH_2$$

- **Chemical Properties**

(I) Addition of dihydrogen

$$RCH{=}CH_2 \xrightarrow[H_2]{Pd} R - CH_2 - CH_3$$

(ii) Addition of halogens

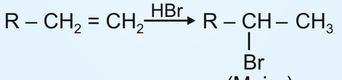


$$CH_2 = CH_2 \xrightarrow[CCl_4]{Br_2} \underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}}$$

- The reddish orange colour of bromine solution in CCl_4 is discharged when Br_2 adds to unsaturation site. this is test for unsaturation.

(iii) Addition of hydrogen halides

(a) Markovnikov's reaction



$$R - CH_2 = CH_2 \xrightarrow{HBr} R - \underset{Br}{\underset{|}{CH}} - CH_3$$

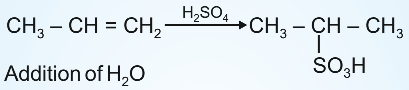
(Major)

(b) Anti Markovnikov addition

$CH_3-CH=CH_2 \xrightarrow[(C_6H_5CO)_2O_2]{HBr} CH_3CH_2CH_2Br$ (Major)

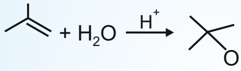
- Peroxide effect is not observed in addition of HCl and HI

(iv) Addition of H_2SO_4



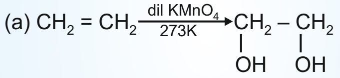
$CH_3-CH=CH_2 \xrightarrow{H_2SO_4} CH_3-\underset{SO_3H}{\underset{|}{CH}}-CH_3$

(v) Addition of H_2O



2-methylpropan-2-ol (Major)

(vi) Oxidation reaction



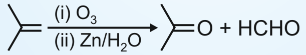
(a) $CH_2=CH_2 \xrightarrow[273K]{\text{dil } KMnO_4} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$

Cold, dilute, aqueous solution of $KMnO_4$ is called Baeyer's reagent

Decolorisation of $KMnO_4$ solution is used as a test of unsaturation.

(b) $CH_3CH=CHCH_3 \xrightarrow[H^+]{KMnO_4} 2CH_3COOH$

(vii) Ozonolysis



(vii) Polymerisation

$nCH_2=CH_2 \xrightarrow[\text{Catalyst}]{\text{High T/P}} \text{+}\!\!(CH_2-CH_2)\!\!\text{+}_n$

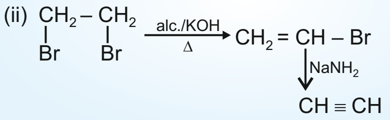
Polythene

3 ALKYNES

- General formula (C_nH_{2n-2})

Preparation

(i) $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$



(ii) $\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow[\Delta]{\text{alc./KOH}} CH_2=CH-Br \xrightarrow{NaNH_2} CH\equiv CH$

- **Chemical Properties**

(i) Acidic character

$CH_3-C\equiv CH + Na \rightarrow CH_3-C\equiv C^-Na^+ + \frac{1}{2}H_2$

Acidity order of some hydrocarbons :

$HC\equiv CH > CH_2=CH_2 > CH_3-CH_3$

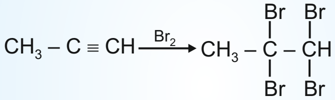
$HC\equiv CH > CH_3-C\equiv CH >> CH_3-C\equiv C-CH_3$

(ii) Addition reactions

(a) Addition of dihydrogen

$R-C\equiv CH + 2H_2 \xrightarrow{Pd} RCH_2CH_3$

(b) Addition of halogens



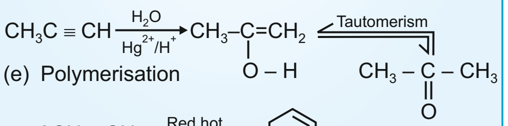
$CH_3-C\equiv CH \xrightarrow{Br_2} CH_3-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{CH}}}}$

Reddish orange colour of the solution of bromine in CCl_4 is decolourised.

(c) Addition of hydrogen halides

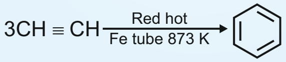
$CH\equiv CH \xrightarrow{HBr} [CH_2=CH-Br] \xrightarrow{HBr} CH_3-CHBr_2$

(d) Addition of water



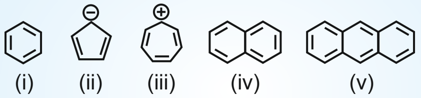
$CH_3C\equiv CH \xrightarrow[Hg^{2+}/H^+]{H_2O} CH_3-\underset{O-H}{\underset{|}{C}}=CH_2 \xrightarrow{\text{Tautomerism}} CH_3-\underset{O}{\underset{||}{C}}-CH_3$

(e) Polymerisation



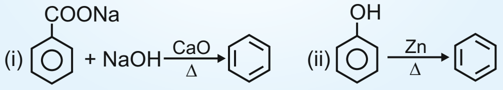
4 AROMATIC HYDROCARBON

- Species which is cyclic, planar having delocalised π electrons and follow's Huckel's (4n + 2)π rule is aromatic. n is an integer (n = 0, 1, 2...)



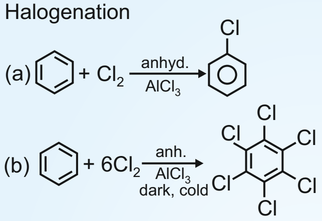
are aromatic species

- Preparation of benzene

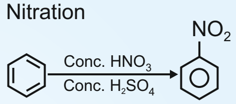


- **Chemical Properties**
- Electrophilic substitution reaction

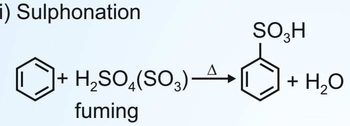
(i) Halogenation



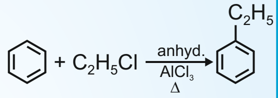
(ii) Nitration



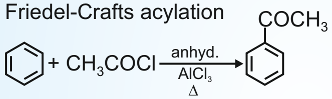
(iii) Sulphonation



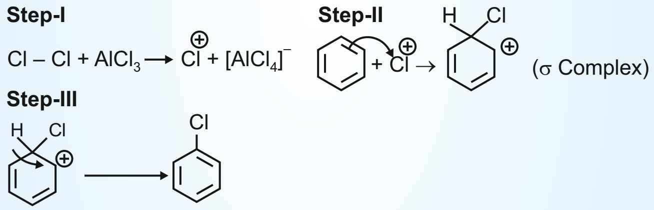
(iv) Friedel-Crafts alkylation



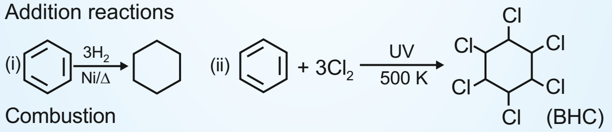
(v) Friedel-Crafts acylation



- Mechanism of electrophilic substitution reaction Halogenation



- Addition reactions



- Combustion

$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O$

$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{4}H_2O$

- **Directive influence of function group towards EAS reaction:**

o/p directing groups : – OH, – NH_2, – NHR, – $NHCOCH_3$, – OCH_3, –CH_3, – C_2H_5 etc.

Meta directing groups : – NO_2, – CN, – CHO, – COR, – COOH, –COOR, – SO_3H etc.

Environmental Chemistry

14

Chapter

① ENVIRONMENTAL POLLUTION

- It is effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings.

② ATMOSPHERIC POLLUTION

- It is studied as tropospheric and stratospheric pollution.
- **Troposphere** extends to the height of ~10 km from sea level.
- **Stratosphere** lies between 10 and 50 km above sea level. It contains N_2, O_2, O_3 and little H_2O vapour. The presence of O_3 in it prevents about 99.5% of sun's harmful UV radiations from reaching earth's surface.
- Tropospheric pollution is due to gaseous air pollutants and particulate pollutants.

(i) Gaseous air pollutants

- SO_2 which causes respiratory diseases, irritation to eyes resulting in tears and redness.
- Due to burning of fossil fuel in automobile engine, NO and NO_2 are produced.
- The irritant red haze in the traffic and congested places is due to oxides of nitrogen.
- NO_2 is lung irritant.
- Hydrocarbons are carcinogenic.
- CO is highly poisonous and produced as a result of incomplete combustion of carbon.
- CO binds to Haemoglobin to form carboxy haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex.
- High level of CO in blood may induce premature birth and deformed babies.
- CO_2 is released in atmosphere by respiration, burning of fossil fuel and also during volcanic eruptions.
- Increased amount of CO_2 in the air is mainly responsible for global warming.

(ii) Particulate pollutants

- These are minute solid particles or liquid droplets in air.
- **Viable particulates:** Bacteria, fungi, moulds, algae etc.
- **Non-viable particulates:** Cigarette smoke, Dust, Sand, Cement, fly ash, Sulphuric acid mist, fume particles etc.
- The effect of particulate pollutants are largely dependent on the particle size.
- Lead used to be a major air pollutant emitted by vehicles.

- **Stratospheric pollution** is due to the depletion of protective ozone layer. CFCs combine with ozone and damage ozone layer.

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + \dot{C}F_2Cl(g)$$

$$\dot{C}l(g) + O_3(g) \longrightarrow Cl\dot{O}(g) + O_2(g)$$

$$Cl\dot{O}(g) + O(g) \longrightarrow \dot{C}l(g) + O_2(g)$$

③ GLOBAL WARMING AND GREEN HOUSE EFFECT

- About 75% of the solar energy reaching the earth is absorbed by the earth surface, which increases its temperature.
- **Green house gases:** CO_2, CH_4, O_3, CFCs, H_2O vapour, N_2O, O_3.
- CO_2 molecules trap heat as they are transparent to sunlight but not to the heat radiation.
- CO_2 is the major contributor to **global warming**.

④ ACID RAIN

- When the pH of rain water drops below 5.6, it is called acid rain.
- Oxide of S, N and C causes acid rain.
- The Taj Mahal is being slowly disfigured and marble is getting discoloured and lustreless due to acid rain. The acid rain reacts with marble, $CaCO_3$ of Taj Mahal.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

⑤ SMOG

- It is mixture of smoke and fog.
- **Classical smog** is mixture of smoke, fog and SO_2, occurs in cool humid climate. It is a reducing mixture.
- **Photochemical smog** results from action of sunlight on unsaturated hydrocarbons and nitrogen oxides. It occurs in warm, dry and sunny climate. Its main components are O_3, NO, acrolein, HCHO and PAN. It is called oxidising smog.

⑥ WATER POLLUTION

(i) **Pathogens:** Bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contain bacteria such as **Escherichia coli** and **streptococcus faecalis** which cause gastrointestinal diseases.

(ii) **Organic waste:** Leaves, Grass, Trash, Excessive phytoplankton growth etc.

- If the concentration of dissolved oxygen (DO) in water is below 6 ppm, the growth of fish gets inhibited.
- The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water is called Biochemical Oxygen Demand (BOD).
- The amount of BOD in the water is a measure of the amount of organic material in the water.
- Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

(iii) **Chemical Pollutants:**

- Water soluble inorganic chemicals such as Cd, Hg, Ni etc. These metals can damage kidneys, central nervous system, liver etc.
- NaCl and $CaCl_2$ are used to melt snow and ice in the colder climates.
- Petroleum products pollute many sources of water e.g. major oil spills in oceans.
- Pesticides that drift down from sprays or runoff from lands.
- Polychlorinated biphenyls (PCBs) which are used as cleansing solvent, detergents and fertilizers. PCBs are suspected to be carcinogenic.
- Fertilizers contain phosphates. The addition of phosphates in water enhances algae growth, which reduces oxygen concentration in water.

- The process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as **Eutrophication**.
- International standards for drinking water.

(1) **Fluoride:** Its deficiency causes tooth decay. It makes enamel on tooth much harder by converting $[3\ Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ into $[3\ Ca_3(PO_4)_2 \cdot CaF_2]$.

F^- ion concentration above 2 ppm causes brown mottling of teeth.

(2) **Lead:** Upper limit of lead in drinking water is 50 ppb.

(3) **Sulphate:** Excessive sulphate (>500 ppm) in drinking water causes laxative effect.

(4) **Nitrate:** Upper limit of nitrate in drinking water is 50 ppm. Excess of it causes diseases such as methemoglobinemia ('blue baby' syndrome)

(5) **Other metals:**

Metal	Fe	Mn	Al	Cu	Zn	Cd
Maximum Concentration (ppm)	0.2	0.05	0.2	3.0	5.0	0.005

⑦ SOIL POLLUTION

- Insecticides, pesticides and herbicides cause soil pollution.
- Prior to World War II, nicotine were used as pest controlling substance for major crops.
- After the World War II, DDT was used in various crop diseases.
- Pesticides are basically synthetic toxic chemicals with ecological repercussions.
- As insect resistance of DDT increased, other organic toxins such as **Aldrin** and **Dieldrin** were introduced.
- These days herbicides such as $NaClO_3$ and Na_3AsO_3 have more attention. Some herbicides cause birth defects.

⑧ INDUSTRIAL WASTE

- **Biodegradable waste:** It is generated by cotton mills, paper mills and textile factories.
- **Non-Biodegradable waste:** It is generated by thermal power plants, iron and steel plants etc.
- Now a days, fly ash and slag from steel industry are utilised by the cement industry.
- Fuel obtained from plastic waste has high octane rating. It contains no lead and is known as **"green fuel"**.

⑨ WASTE MANAGEMENT

- The improper disposal of wastes is one of the major causes of environmental degradation. Therefore the management of wastes is of utmost importance.
- Two programmes are being implemented

  Swatchh Bharat Mission - Urban (SBM - U)

  Swatchh Bharat Mission - Gramin (SBM - G)

⑩ GREEN CHEMISTRY

- It is a way of thinking and it about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment.
- Tetrachloroethene ($Cl_2C = CCl_2$), was earlier used as solvent for dry cleaning and is also a suspected carcinogen. Now, liquefied CO_2 with a suitable detergent is used.
- Chlorine gas was used earlier for bleaching paper. These days, H_2O_2 with suitable catalyst is used.
- Ethanal is prepared commercially by one step oxidation of ethene.

$$CH_2 = CH_2 + O_2 \xrightarrow[\text{Pd(II)/Cu(II) (in water)}]{\text{Catalyst}} CH_3CHO\ (90\%)$$

- Kernel of tamarind seeds has been found to be effective to make waste water clean.
- Green chemistry is a cost effective approach which involves reduction in material, energy consumption and waste generation.

The Solid State

1
Chapter

① CLASSIFICATION BASED ON CRYSTAL LATTICE

Crystalline Solids
- True solids
- Long range order
- Have definite pattern of arrangement of particles
- Anisotropic
- *eg.* NaCl, Solid SO_2
- Are categorised according to intermolecular forces, into Ionic, Metallic, Molecular and Covalent solids

② CRYSTAL LATTICE AND UNIT CELL

Primitive Unit Cells
- Constituent particles are present only at the corner of unit cell
- 7 types of Primitive unit cells with 14 Bravis lattices

Non-Primitive Unit Cells
- Constituent particles are present at corner as well as body-centre or face centre.

Amorphous Solids
- Pseudo solids or super cooled liquids
- Short range order
- Do not have a definite pattern of arrangement of particles
- Isotropic
- *eg.* rubber, glass

③ CUBIC SYSTEM

$$\text{Density} = \frac{ZM}{N_A a^3}$$

Type	Position of atoms	Z	CN	Relation of r, d, a	Packing efficiency
Simple cubic	Corner	$8 \times \frac{1}{8} = 1$	6	$r = \frac{d}{2} = \frac{a}{2}$	52.4%
BCC	Corner and Body centre	$8 \times \frac{1}{8} + 1 = 2$	8	$r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$	68%
FCC	Corner and face centre	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$	12	$r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$	74%

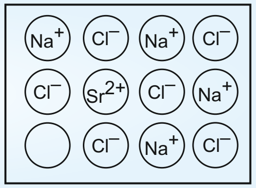
④ TYPE OF DEFECTS

⑤ NON-STOICHIOMETRIC DEFECTS

- **Metal excess defect :**
  - (i) Arises due to anionic vacancies, leaving a hole which is occupied by an electrons thus maintaining electrical neutrality. The anionic sites, occupied by unpaired electrons known as F-centre and impart colour to the crystal. eg : NaCl with Na vapour impart yellow colour.
  - (ii) Arises due to presence of extra cations at interstitial sites. e.g. on heating ZnO loses oxgen and excess Zn^{2+} move to interstitial sties.
- **Metal deficiency defect :** Arises when metal shows variable valency. The defect occurs due to missing a cation from its lattice site and the loss of positive charge is made up by the presence of the cation having higher charge in the adjacent lattice site eg. FeO is found with composition of $Fe_{0.95}O$

⑥ IMPURITY DEFECTS

- When molten NaCl containing a little amount of $SrCl_2$ is crystallised, some sites of Na^+ are occupied by Sr^{2+} . Each Sr^{2+} replaces two Na^+ ions.
- Another similar example is the solid solution of $CaCl_2$ and AgCl.

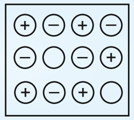


⑦ STOICHIOMETRIC DEFECTS

(Intrinsic or thermodynamic defect)

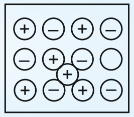
⑧ SCHOTTKY DEFECT

- It is due to equal number of cations and anions are missing from lattice sites.
- It results in decrease of density of crystal
- It is found in crystals having almost similar size of cation and anion eg. NaCl, KCl, AgBr etc.



⑨ FRENKEL DEFECT

- Due to dislocation of ions (usually cations) from the lattice sites and occupy interstitial sites.
- Has no effect on density
- Found in crystals with large difference in size of ions.
- eg: AgCl, ZnS, AgBr etc.



⑩ CLOSE PACKING

- In one dimension : Co-ordination number (CN) = 2
- In two dimension : (a) AAA type : Square close packing have CN = 4
  (b) ABAB type : hexagonal close packing have CN = 6
- In three dimension :(a) AAA type : simple cubic lattice have CN = 6
  (b) ABAB type : hcp lattice have CN = 12
  (c) ABCABC type : fcc lattice have CN = 12
- In fcc unit cell, two tetrahedral voids are present on each body diagonal and octahedral voids are present on body centre and on each edge centres.

Voids in fcc lattice : if N atoms in lattice

- Tetrahedral voids = N
- Octahedral voids = 2N

⑪ CLASSIFICATION OF SOLIDS

⑫ Based on Electrical Properties

- Conductors : Conductivity $10^4 – 10^7$ ohm^{-1} m^{-1}
- Insulators : Conductivity $10^{-20} – 10^{-10}$ ohm^{-1} m^{-1}
- Semiconductors : Conductivity $10^{-6} – 10^4$ ohm^{-1} m^{-1}

Semiconductors : When the energy gap between the valence band and conduction band is small eg.: Si, Ge

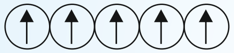
n-type semiconductor : When Si is dopped with P or As.

p-type semiconductors : When Si is dopped B or Al.

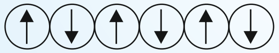
- Diode is a combination of n-type and p-type semicoductors and used as a rectifier.
- VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

⑬ Based on Magnetic Properties

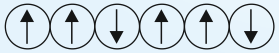
- Paramagnetic substance : Which are weakly attracted by external magnetic field eg.: O_2, Cu^{2+} etc.
- Diamagnetic substances : Which are weakly repelled by external magnetic field : eg.: NaCl, H_2O etc.
- Ferromagnetic substances : substance which show permanent magnetism even in the absence of external magnetic field. eg Ni, Fe, Co, CrO_2 etc.



- Antiferromagnetic substances, which have zero net dipole moment even though they have large number of unpaired electrons eg. MnO



- Ferrimagnetic substances : Which posses very small net magnetic moment even through they have very large number of unpaired electrons eg. Fe_3O_4, $MgFe_2O_4$. These substance lose ferrimagnetism on heating and become paramagnetic.



Solutions

2

Chapter

① EXPRESSING CONCENTRATION OF SOLUTIONS

- Mass percentage (w/w) = $\frac{\text{Mass of a component}}{\text{Mass of solution}} \times 100$
- Volume percentage (v/v) = $\frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 100$
- Mass by volume percentage (w/v) = $\frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$
- Parts per million (ppm) = $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$
- Mole fraction (X) = $\frac{\text{Mole of a component}}{\text{Total moles of all components}}$
- Molarity (M) = $\frac{\text{Moles of solute}}{\text{Volume of solution (l)}}$
- Molality (m) = $\frac{\text{Mass of solute}}{\text{Mass of solvent (kg)}}$

- Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.

② SOLUBILITY OF A SOLID IN A LIQUID

- Significantly affected by temperature change.
- Pressure does not have any significant effect.

③ SOLUBILITY OF A GAS IN A LIQUID

- Henry's law: $p = K_H x$
- Decreases with increase in temperature.
- Increases with increase in pressure.
- The air tanks of scuba divers are diluted with He to avoid bends.
- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

④ RAOULT'S LAW

- For non-volatile solute in volatile solvent
  $p_{solution} = p^o_{solvent}\, x_{solvent}$
- For volatile liquids:
  $p_{total} = p_1 + p_2 = p_1^o x_1 + p_2^o x_2 = p_1^o + (p_2^o - p_1^o)x_2$
- Mole fraction of any component in vapour phase:
  $y_1 = p_1/p_{total}$

⑤ TYPE OF SOLUTIONS

- **Ideal solutions:** A – B interactions are of same magnitude as A – A and B – B interactions. $\Delta V_{mix} = 0$ and $\Delta H_{mix} = 0$
  eg.: n-hexane and n-heptane, bromoethane and chloroethane.
- **Non-ideal solutions:** A – B interactions are of different magnitude than A – A and B – B interactions. $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$.
- **(+)ve deviations:** A – B interactions are weaker than A – A and B – B interactions.
  - $\Delta H_{mix} > 0, \Delta V_{mix} > 0, P_{obs} > P_{cal}$
  - eg: acetone + ethanol,
- **(–)ve deviations:** A – B interactions are stronger than A – A and B – B interactions.
  - $\Delta H_{mix} < 0, \Delta V_{mix} < 0, P_{obs} < P_{cal}$
  - eg: nitric acid + water, chloroform + acetone
- **Azeotropes:** constant boiling mixtures whose composition does not change on distillation.
- **Minimum boiling azeotrope:** 95% C_2H_5OH and 5% H_2O by volume
- **Maximum boiling azeotrope:** 68% HNO_3 and 32% H_2O by mass

⑥ COLLIGATIVE PROPERTIES

- Relative lowering of vapour pressure : $\frac{p_1^o - p_1}{p_1^o} = x_{solute}$
- Elevation in boiling point: $\Delta T_b = T_b - T_b^0 = K_b m$
  Where, $K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap}H}$
- Depression in freezing point: $\Delta T_f = T_f^0 - T_f = K_f m$
  Where, $K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus}H}$
- Osmotic pressure: $\pi = CRT = \left(\frac{n}{V}\right)RT$
- Osmotic pressure method is widely used to determine molar mass of proteins, polymers.
- Isotonic solution have same osmotic pressure.
- Osmotic pressure associated with the fluid inside the blood cell is equivalent to 0.9% (mass/vol) of NaCl solution.

⑦ van't Hoff FACTOR AND ITS SIGNIFICANCE

$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property}}$

$= \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$

- For normal solute (i = 1)
- For association, i < 1
- For dissociation, i > 1

⑧ MODIFIED COLLIGATIVE PROPERTIES

- $\frac{p_1^o - p_1}{p_1^o} = \frac{in_2}{n_1}$
- $\Delta T_b = iK_b m$
- $\Delta T_f = iK_f m$
- $\pi = iCRT$

Electrochemistry

3

Chapter

① TYPE OF CELLS

- **Electrochemical cell :** Device used to convert chemical energy of a redox reaction into electrical energy. It is also known as galvanic cell.
- **Electrolytic cell :** Device which uses electricity to bring about a non-spontaneous redox reaction.

② DANIELL CELL

- Cell reaction : $Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$
- When external opposite potential is applied to the cell in standard state
  - (a) $E_{ext} = 1.1$ V, no flow of electrons.
  - (b) $E_{ext} > 1.1$ V, electrons flow from Cu rod to Zn rod.
  - (c) $E_{ext} < 1.1$ V, electrons flow from Zn rod to Cu rod.

③ CELL POTENTIAL

- **Electrode potential :** It is the potential difference developed between the electrode and the electrolyte. When the concentration of all the species involved is unity it is known as **standard electrode potential**.
- **Cell potential :** The difference between the electrode potentials (reduction potentials) of the cathode and anode.
- **EMF of cell :** The cell potential when no current is drawn through the cell.
- $E_{cell} = E_{right} - E_{left}$
- $E^\circ_{cell} = E^\circ_R - E^\circ_L$
- In a galvanic cell :
  - (a) Anode has negative potential w.r.t solution.
  - (b) Cathode has positive potential w.r.t solution.
- **Standard hydrogen electrode :**

$$\underset{(1\,M)}{H^+(aq.)} + e^- \longrightarrow \frac{1}{2}\underset{(1\,bar)}{H_2(g)}, \quad E^\circ = 0 \text{ Volt (Assumed)}$$

④ NERNST EQUATION

- For the reaction : $M^{n+} + ne^- \longrightarrow M$

$$E = E^\circ - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

- For the reaction : $aA + bB \xrightarrow{ne^-} cC + dD$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- For a reaction at equilibrium, $E_{cell} = 0$.
- $E^\circ_{cell} = \frac{2.303\,RT}{nF}\log K_C = \frac{0.0591}{n}\log K_C$

⑤ GIBBS ENERGY

- It is the reversible work done by the galvanic cell.
- $\Delta_r G = -nF\,E_{cell}$
- $\Delta_r G^\circ = -nF\,E^\circ_{cell}$
- $\Delta_r G^\circ = -RT\ln K = -2.303\,RT\log K$

⑦ CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

- Resistance : $R = \frac{\rho\ell}{A}$, unit = ohm
- Resistivity : $\rho = \frac{RA}{\ell}$, unit = ohm-cm
- Conductance : $G = \frac{1}{R} = \kappa\frac{A}{\ell}$, unit = ohm^{-1} or S
- Cell constant : $G^* = \frac{\ell}{A}$, unit = cm^{-1}
- Conductivity : $\kappa = \frac{G\ell}{A}$, unit = $ohm^{-1}\,cm^{-1}$
- Molar conductivity : $\Lambda_m = \frac{\kappa \times 1000}{M}$, unit = $S\,cm^2\,mol^{-1}$

⑥ ELECTROCHEMICAL SERIES

- A negative E° means that the redox couple is stronger reducing agent than the H^+/H_2 couple.
- A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Increasing Strength of Oxidising Agent ↑

Oxidised form	Reduced form	E°/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

⑧ DILUTION EFFECT ON CONDUCTANCE

- Conductivity always decreases with decrease in concentration (means on dilution) both for weak and strong electrolytes.
- For weak electrolytes, molar conductivity increases steeply on dilution.
- For strong electrolytes, molar conductivity increases slowly with dilution.
- For strong electrolyte : $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$.

⑨ KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

- Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte at infinite dilution.
- If an electrolyte on dissociation given v_+ cations and v_- anions then $\Lambda_m^\circ = v_+\lambda_+^\circ + v_-\lambda_-^\circ$
  - λ_m° : $H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$
  - λ_m° : $OH^- > SO_4^{2-} > Br^- > Cl^- > CH_3COO^-$
  - For a weak electrolyte : $\alpha = \Lambda_m/\Lambda_m^\circ$
  - For acetic acid : $K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{C\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$

⑩ FARADAY'S LAW OF ELECTROLYSIS

- **First law :** $w = ZQ = ZIt = \dfrac{E}{96500} \times It$
- **Second law :** $\dfrac{w_1}{w_2} = \dfrac{E_1}{E_2}$
- 1F = Charge on 1 mol electron = 96487 C ≃ 96500 C

⑪ PRODUCTS OF ELECTROLYSIS

- Molten NaCl : Anode : Cl_2, Cathode : Na
- Aqueous NaCl : Anode : Cl_2, Cathode : H_2
- Dilute H_2SO_4 : Anode : O_2, Cathode : H_2
- Concentrated H_2SO_4 : Anode : $S_2O_8^{2-}$, Cathode : H_2

⑫ BATTERIES

- **Primary Batteries :** Which cannot be reused.
  (1) **Dry cell :** (Leclanche cell)

  Anode : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

  Cathode : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

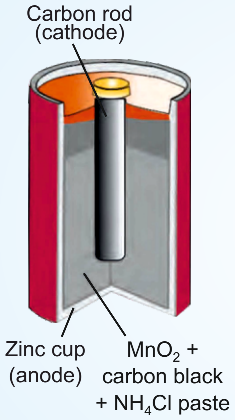


Fig. A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.

  (2) **Mercury cell :** Cell potential (≃ 1.35 V) remains constant during its life

  Anode : $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

  Cathode : $HgO + H_2O + 2e^- \longrightarrow Hg(\ell) + 2OH^-$

- **Secondary batteries :** Which can be recharged
  (1) **Lead storage battery :**

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O(\ell)$$

  (2) **Nickel cadmium cell :** It has longer life than lead storage cell :

$$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(\ell)$$

- **Fuel cells :** Galvanic cell that converts the energy produced during combustion of fuel directly into electrical energy

  e.g: $H_2 — O_2$ fuel cell

  Anode : $H_2(g) + 2OH^-(aq.) \longrightarrow 2H_2O(\ell) + 2e^-$

  Cathode : $O_2(g) + 2H_2O(\ell) + 4e^- \longrightarrow 4OH^-(aq.)$

  The cell was used in Apollo space programme

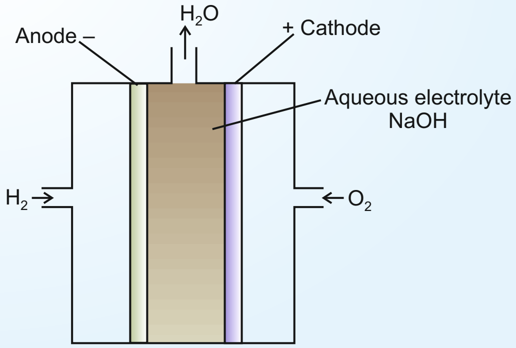
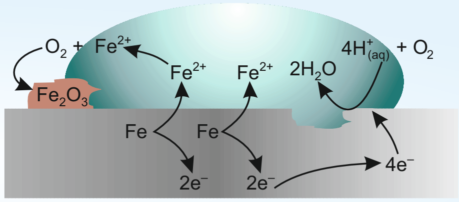


Fig. Fuel cell using H_2 and O_2 produces electricity

⑬ CORROSION

- It slowly coats the surfaces of metallic objects with oxides or other salts of metal.
- Corrosion of iron is called rusting. It is an electrochemical phenomenon.
- Rust is $Fe_2O_3 \cdot xH_2O$.
- Prevention of rusting can be done by
  (i) Covering the surface with paint or by chemicals (e.g. bisphenol)
  (ii) Cover the surface by other metals (Sn, Zn etc.)
  (iii) Provide a sacrificial electrode of other metal (Mg, Zn etc.)



Oxidation : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction : $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Atmospheric oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2(g) \rightarrow Fe_2O_3 + 4H^+$

Fig. Corrosion of iron in atmosphere

Chemical Kinetics

4
Chapter

① RATE OF REACTION

- For a reaction, aA + bB → xX + yY

  $\text{rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{x}\frac{d[X]}{dt} = \frac{1}{y}\frac{d[Y]}{dt}$
- Unit of rate of reaction :

  (i) $\text{mol L}^{-1}\text{s}^{-1}$

  (ii) atm s^{-1}
- Average rate $= \frac{-\Delta[R]}{\Delta t} = \frac{-([R_2]-[R_1])}{t_2 - t_1}$
- Instantaneous rate $= -\frac{d[R]}{dt} = \frac{d[P]}{dt}$

② ORDER

- For a rate law equation : rate = $k[A]^x\,[B]^y$ order of reaction = x + y
- Order of reaction can be 0, 1, 2, 3 and even a fraction.
- Order of reaction is an experimental quantity.
- Order is applicable to elementary as well as complex reaction.
- For complex reaction, order is given by slowest step.

③ MOLECULARITY

- It is the number of atoms, ions are molecules that must collide simultaneously with one another to result into a chemical reaction
- It cannot be zero or a non-integer
- It is applicable only for elementary reactions

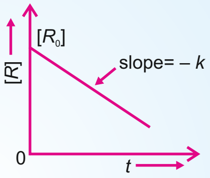
④

Reaction order	Unit of rate constant
Zero	$\text{mol L}^{-1}\,\text{s}^{-1}$
First	s^{-1}
Second	$\text{mol}^{-1}\,\text{L s}^{-1}$

⑤ INTEGRATED RATE EQUATION AND HALF LIFE

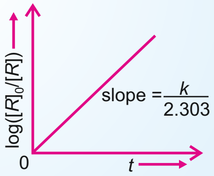
Zero order reaction:

- Rate $= \frac{-d[R]}{dt} = k[R]^{\circ}$
- $[R] = [R]_0 - kt$
- $t_{\frac{1}{2}} = \frac{[R]_0}{2k}$
- $t_{100\%} = \frac{[R]_0}{k}$



First order reaction:

- Rate $= \frac{-d[R]}{dt} = k[R]^1$
- $\ln [R] = \ln [R]_0 - kt$
- $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$
- $k = \frac{2.303}{(t_2 - t_1)}\log\frac{[R]_1}{[R]_2}$
- $t_{\frac{1}{2}} = \frac{0.693}{k}$
- For n^th order reaction, $t_{\frac{1}{2}} \propto [R_0]^{1-n}$



⑥ PSEUDO FIRST ORDER REACTIONS

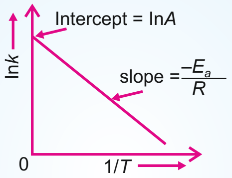
- Hydrolysis of ethyl acetate in acidic medium
- Inversion of cane sugar in acidic medium

⑦ ORDER OF SOME REACTIONS

Reaction	Order
$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130\text{ K}} N_2(g) + 3H_2(g)$	Zero
$2HI(g) \xrightarrow[\Delta]{\text{Gold surface}} H_2(g) + I_2(g)$	Zero
Radioactive decay	First
$N_2O_5(g) \xrightarrow{\Delta} 2NO_2 + \frac{1}{2}O_2$	First

⑧ TEMPERATURE DEPENDENCE OF THE RATE OF REACTION

- For a chemical reaction with rise in temperature by 10°, the rate of reaction is nearly doubled
- Arrhenius equation : $k = Ae^{\frac{-E_a}{RT}}$



- $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$
- The energy required to form the reaction intermediate, called activated complex, is known as activation energy (E_a)
- Threshold energy = Activation energy

  + energy possessed by reacting species.
- For biomolecular reaction. $\text{Rate} = PZ_{AB}e^{\frac{-E_a}{RT}}$

  where, P is steric factor and Z_{AB} is Collision frequency.

⑨ EFFECT OF CATALYST

- Catalyst increases the rate of reaction by reducing the activation energy of reaction.
- A small amount of the catalyst can catalyse a large amount of reactants
- A catalyst does not alter Gibbs energy, ΔG of a reaction.
- Catalyst does not change the equilibrium constant of a reaction
- A catalyst can catalyse the spontaneous reactions only.

Surface Chemistry

5

Chapter

① ADSORPTION

- The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed **adsorption**.
- The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**
- In **adsorbtion** the concentration of the adsorbate increases only at the surface of the adsorbent, while in **absorbtion** the concentration is uniform throughout the bulk of solid.

Mechanism of adsorption

- The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.
- Another important factor featuring adsorption is the heat of adsorption during adsorption, there is decrease in surface energy which appears as heat therefore adsorption is an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption i.e., ΔS is negative for a process to be spontaneous, ΔG must be negative at constant pressure and temperature.
- As the adsorption proceeds ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained

Types of adsorption

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	1. It is caused by chemical bond formation.
2. It is not specific in nature.	2. It is highly specific in nature.
3. It is reversible in nature.	3. It is irreversible.
4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol^{-1})	5. Enthalpy of adsorption is high (80-240 kJ mol^{-1}).
6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the increase of temperature.
7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	8. It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	9. It results into unimolecular layer.

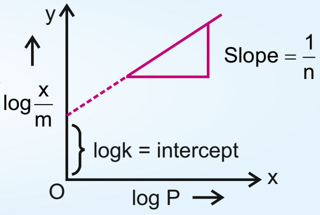
② ADSORPTION ISOTHERMS (FREUNDLICH ADSORPTION ISOTHERM)

- $\frac{x}{m} = kp^{1/n} (n > 1)$

  x = mass of gas adsorbed, m = mass of adsorbent
  p = pressure of gas, K, n = constants depend on nature of adsorbent and gas at a particular temperature

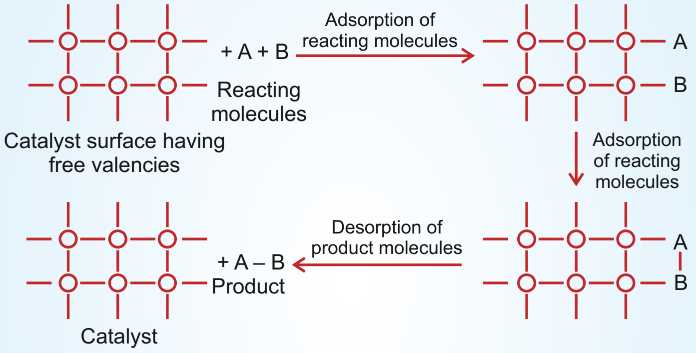
- $\log\frac{x}{m} = \log K + \frac{1}{n}\log P$

  $\frac{1}{n}$ lies between 0 to 1 (probable range 0.1 to 0.5)



③ CATALYSIS

- Substance, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as **catalyst**
- **Promoters** are substance that enhances the activity of catalyst
- **Poisons** decrease the activity of a catalyst
- When the reactants, products and the catalyst are in same phase, the process is said to be **homogeneous catalysis**
- The catalytic process in which the reactants and the catalyst are in different phases is known as **heterogeneous catalysis**



- The **activity** of a catalyst depends upon the strength of chemisorption to a large extent
- The **selectivity** of a catalyst is its ability to direct a reaction to yield a particular product selectively, when under the same reaction conditions many products are possible
- The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product is called **shape-selective catalysis** e.g. zeolites.
- Numerous reactions that occur in bodies of animals and plants are catalysed by **enzymes** termed as **biochemical** catalyst
- Characteristics of enzyme catalysis
  - (i) Most highly efficient
  - (ii) Highly specific nature
  - (iii) Highly active under optimum temperature
  - (iv) Highly active under optimum pH
  - (v) Increasing activity in presence of activators and co-enzymes.
  - (vi) Influence of inhibitors and poisons

SOME ENZYMATIC REACTION

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Amino acids

④ COLLOIDS

- A colloid is a Heterogeneous system in which one substance is dispersed (**dispersed phase**) as very fine particles in another substance called **dispersion medium**
- The range of diameters of colloidal particles is between 1 to 1000 nm
- **Classification of colloids**
  (i) Classification based on physical state of dispersed phase and dispersion medium

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, butter
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

(ii) **Classification based on nature of interaction between dispersed phase and dispersion medium**

(a) **Lyophilic colloids** directly formed by mixing substances like gum, gelatin, starch, rubber etc with a suitable liquid. These sols are **reversible** in nature

(b) **Lyophobic colloids** can be prepared only by special methods. These sols are readily coagulated on addition of small amount of electrolyte by heating or by shaking and hence are not stable. These sols are **irreversible** in nature.

(iii) **Classification based on type of particles of dispersed phase**

(a) **Multimolecular colloids** contains a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range. e.g., Gold sol, sulphur sol

(b) **Macromolecular colloids** - Macromolecules in suitable solvents form solutions in which the size of the macromolecule may be in colloidal range e.g., starch, protein etc.

(c) **Associated colloids (Micelles) :** At low concentrations behave as normal strong electrolyte, but at higher concentrations exhibit colloidal behaviour due to formation of aggregates (micelles) Micelles formation takes place above a particular temperature called **Kraft temperature (T_K)** and above a particular concentration called **critical micelle concentration** (CMC) e.g. soaps and synthetic detergents

⑤ PREPARATION OF COLLOIDS

- Chemical methods

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} As_2S_3(sol) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(Sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3(sol) + 3HCl$$

- **Electrical disintegration or Bredig's Arc method** - In this method, electric arc is struck between electrodes of metal immersed in dispersion medium. The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size. Colloidal sols of metals such as gold, silver, platinum etc. can be prepared by this method.
- **Peptization -** Process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**

⑥ PURIFICATION OF COLLOIDAL SOLUTIONS

The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution.

- **Dialysis :** Process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.
- **Electro-dialysis :** Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte.
- **Ultrafiltration** is the process of separating the colloidal particles from the solvent and soluble. solutes present in the colloidal solution by specially prepared filters which are permeable to all substance except the colloidal particles.

7 PROPERTIES OF COLLOIDAL SOLUTIONS

- **Colligative properties :** Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to the true solution hence colligative properties are of small order as compared to true solutions.
- **Tyndall effect** is due to the fact that colloidal particles scatter light in all directions in space which illuminates the path of beam. The bright cone of light is known as **Tyndall cone**.
- **Colour :** Depends on the wavelength of light scattered. The wavelength depends on size and nature of the particles. The colour of colloidal solution also changes with the manner in which the observer receives the light
- **Brownian movement :** Zig-zag continuous motion of colloidal particles and depends on the size of particles and viscosity of solution.
- **Charge on colloidal particles:**

Positively charged sols	Negatively charged sols
Hydrated metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$. etc. Basic dye stuffs. e.g., methylene blue sol. Haemoglobin (blood) Oxides, e.g., TiO_2 sol.	Metals, e.g., copper, silver, gold sols. Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS sols. Acid dye stuffs, e.g., eosin. congo red sols. Sols of starch, gum, gelatin, clay, charcoal, etc.

- **Zeta potential :** The potential difference between the fixed layer and diffused layer of opposite charges is called electrokinetic potential or zeta potential.
- **Electrophoresis :** Movement of colloidal particles under an applied electric potential.
- When electrophoresis i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed **electroosmosis**.
- **Coagulation** or **precipitation**

  The process of settling of colloidal particles. The coagulation of lyophobic sols can be carried out by

  (a) Electrophoresis
  (b) By mixing two oppositely charged sols
  (c) By boiling
  (d) By persistent dialysis
  (e) By addition of electrolytes

HARDY-SCHULZE RULE

Greater the valence of the flocculating ion added, greater is its power to cause precipitation.

For –ve colloids flocculating power is in the order : $Al^{3+} > Ba^{2+} > Na^{+}$

For +ve colloids flocculating power is in the order : $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

- **Coagulating value :** The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours. The smaller the quantity needed, the higher will be the coagulating power of an ion.

8 EMULSIONS

These are liquid-liquid colloidal systems. These are of two types

- Oil dispersed in water (O/W type) e.g., : milk and vanishing cream.
- Water dispersed in oil (W/O type) e.g., butter and cream

9 COLLOIDS AROUND US

- The styptic action of alum and ferric chloride solution is due to the coagulation of blood forming a clot which stops further bleeding
- When river water meets the sea water, the electrolyte present in sea water coagulate the colloidal solution of day resulting in the deposition with the formation of delta.
- Argyrol is a silver sol used as eye lotion.
- Colloidal antimony is used in curing kalaazar.
- Colloidal gold is used for intramuscular injection.
- Milk of magnesia is used for stomach disorders.
- Animal hides are colloidal in nature when soaked in tannin results in hardening of lather. This process is known as tanning. Chromium salts are also used in place of tannin.

General Principles and Processes of Isolation of Elements

6

Chapter

① OCCURRENCE OF METALS

- The most abundant metal in the earth's crust is aluminium.
- Gem 'ruby' (impure Al_2O_3) has Cr impurity
- Gem 'sapphire' (impure Al_2O_3) has Co impurity
- The second most abundant metal on earth crust is iron.
- **Minerals:** These are naturally occuring chemical substances containing metal in the earth's crust and are obtain through mining.
- **Ores:** Minerals which are viable to be used as source of the metal are called ores.
- **Gangue:** The undesired impurities such as sand, clay associated with the ore are called gangue or matrix.
- Principal ores of some important metals:

Metal	**Ore**	**Composition**
Aluminium	Bauxite	$AlOx(OH)_{3-2x}$ where, $0 < x < 1$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
Copper	Copper pyrite	$CuFeS_2$
	Malachite	$CuCO_3 . Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

② METALLURGY

The entire scientific and technological process used for isolation of the metal from its ore is known as metallurgy. It involves following main operations

(i) Concentration or dressing of ore
(ii) Isolation of crude metal
(iii) Purification or refining of metal

③ CONCENTRATION OF ORES

The removal of impurities from the ores is known as concentration or dressing or benefaction of ore. The concentration is done in number of ways depending upon the nature of impurities.

(i) Hydraulic Washing: The process of removing of lighter particles of sand, clay etc. by washing with water using hydraulic classifer. Separation is based on difference between specific gravity of the ore and gangue particles. It is type of a gravity separation.

(ii) Magnetic Separation: This is used when either the ore or the gangue is attracted towards magnetic field. Wolframite ($FeWO_4$), a magnetic ore is separated from non-magnetic ore, cassiterite (SnO_2) by this method.

(iii) Froth Floatation Method: This method is used for the concentration of sulphides ore. This process is based on the preferential wetting of ore particles by pine oil and gangue particles by water.

- Pine oil, fatty acids and xanthates are used as collectors.
- Cresols, aniline are used as froth stabilizer.
- In case of ore containing ZnS and PbS, the depressant NaCN is used which prevents ZnS from coming to the froth.

(iv) Leaching: It involves the treatment of the ore with a suitable reagent to make it soluble while impurities remain insoluble. The ore or the metal is recovered from the solution by a suitable chemical method. examples

- **Leaching of Alumina from bauxite:** Bauxite is digested with aqueous solution of NaOH, where Al_2O_3 dissolves forming sodium aluminate while impurities such as Fe_2O_3 and TiO_2 remain insoluble

  $$Al_2O_3(s) + 2NaOH(aq.) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq.)$$

  The pure alumina is recovered from filtrate.

  $$2Na[Al(OH)_4](aq.) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq.)$$

  $$Al_2O_3 . xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g)$$

- Ores of Ag and Au are treated with aqueous dilution solution of NaCN in presence of oxygen. The Ag and Au particles get dissolved forming complex cyanides. Ag or Au recovered from solution by adding Zn.

  $$4M(s) + 8CN^-(aq.) + 2H_2O(aq.) + O_2(g)$$
  $$\rightarrow 4[M(CN)_2]^-(aq.) + 4OH^-(aq.)\ (M = Ag\ or\ Au)$$
  $$2[M(CN)_2]^-(aq.) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq.) + 2M(s)$$

④ EXTRACTION OF CRUDE METAL FROM CONCENTRATED ORE

Extraction involves following two steps

(i) Conversion of ore into metallic oxide
(ii) Reduction of metallic oxide

(i) Two methods ore used for conversion into oxide

(a) Calcination: It involves heating of ore below its fusion temperature in the absence of air

$$Fe_2O_3 \cdot xH_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + xH_2O(g)$$

$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

(b) Roasting: It involves heating of ore below its fusion temperature in regular supply of air.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

- The sulphide ores of copper are heated in reverberatory furnace. If the ore contains iron, silica is added before heating. Iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte which contains Cu_2S and FeS

  $$FeO + SiO_2 \rightarrow FeSiO_3\ (slag)$$

(ii) Reduction of the oxide ore into free metal is done by a suitable reducing agent.

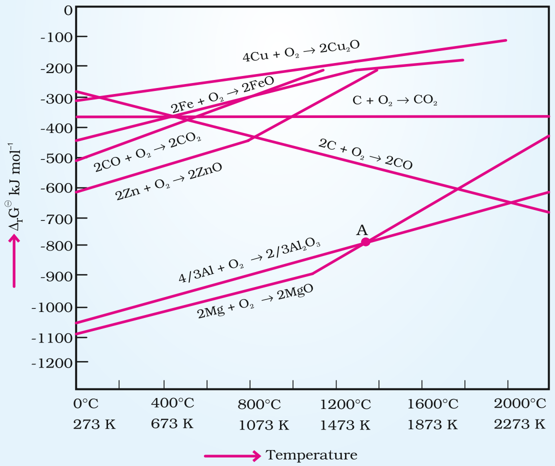
- **Smelting:** When C or CO or other metal are used as reducing agent at high temperature. The process in general known as pyrometallurgy

  $$M_xO_y + yC \rightarrow xM + yCO$$

⑤ THERMODYNAMIC PRINCIPLES OF METALLURY

- For considering the choice of reducing agent in reduction of oxide, Elligham Diagram is used.
- Ellingham diagram consists of plots of $\Delta_f G°$ vs T for the formation of oxides of metals and reducing agents.

  eg: $2x\,M(s) + O_2(g) \rightarrow 2M_xO(s)$
- The difference in the two $\Delta_r G°$ values determines whether reduction of the oxide of the element of the upper line is feasible by the element of which oxide formation is represented by the lower line. If the difference is large, the reduction is easier.



⑥ EXTRACTION OF IRON FROM ITS OXIDE

Reduction of oxides of iron (Fe_2O_3, Fe_3O_4) is done in blast furnace.

- Iron obtained from blast furnace contains 4% carbon, known as pig iron.
- Cast iron is obtained by melting pig iron with scrap iron and coke using hot air blast. It contains about 3% carbon.
- Wrought iron is the purest form of commercial iron and prepared in a reverberatory furnace lined with haematite.

⑦ EXTRACTION OF COPPER FROM CUPROUS OXIDE

- The sulphide ores containing iron are roasted/smelted to give oxide

  $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
- The oxide is reduced to copper using coke

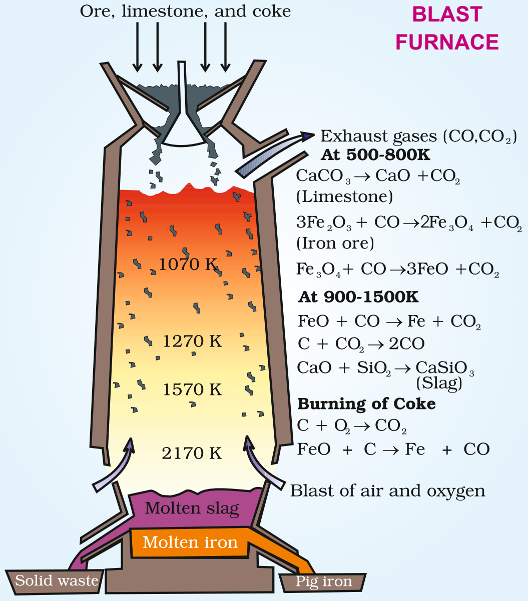
  $Cu_2O + C \rightarrow 2Cu + CO$
- The ore is heated in a reverberatory furnace after mixing with silica, where iron oxide "slags of" as iron silicate

  $FeO + SiO_2 \rightarrow FeSiO_3(\text{slag})$
- Copper is produced as copper matte containing Cu_2S and FeS, which is then charged into silica lined convertor in presence of hot air blast.

$$FeS \xrightarrow[-SO_2]{O_2} FeO \xrightarrow{SiO_2} FeSiO_3$$

$$Cu_2S \xrightarrow[-SO_2]{O_2} Cu_2O \xrightarrow[-SO_2]{Cu_2O} Cu(\text{blister copper})$$

BLAST FURNACE



⑧ HALL-HEROULT PROCESS

Purified Al_2O_3 is mixed with Na_3AlF_6 (Cryolite) and CaF_2 (fluorspar) to lower the melting point of the mixture and to increase conductivity

$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

- Steel vessel with lining of carbon acts as cathode and graphite is acts as anode.

⑨ REFINING

The process of purifying impure metals is called refining.

(i) **Distillation:** It is used for those metals which are volatile. The impure metal is heated and the vapours are separately condensed in receiver. It is used for purification of Zn, Hg etc.

(ii) **Liquation:** When impurities are less fusible than the metal itself then this process is used. The impure metal such as Sn is purified by liquation.

(iii) **Electrolytic refining:** Metal like Cu are purified by this method. The impure metal is made the anode and a strip of a pure metal is made as cathode while the electrolytic solution consists of solution of a suitable salt of metal.

(iv) **Zone refining:** It is based on the concept that impurities are more soluble in melt than in the solid state of the metal. This method is useful for Ge, Si, B for obtaining highly pure metals.

(vi) **Vapour phase refining:**

(a) Mond process: $Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4(\uparrow)$

$Ni(CO)_4 \xrightarrow{450-470\ K} Ni + 4CO$

(b) Van Arkel method: (for Zr/Ti)

$Zr + 2I_2 \rightarrow \underset{(\text{volatile})}{ZrI_4} \xrightarrow{1800\ K} Zr + 2I_2$

(vii) **Chromatographic Methods:** Column chromatography is used for purification of elements which are available in minute quantities and impurities are not very different in the chemical properties from the element to be purified.

⑩ USES OF METALS

- Zn is used for galvanising iron.
- Zn in Alloys (Brass : Cu + Zn, german silver: Cu + Zn + Ni).
- Al is used in extraction of Cr and Mn from their oxides.
- Cu is used for making wires used in electrical industry
- Wrought iron is used making anchors, wires, bolts.
- Chrome steel is used for cutting tools.

The p-Block Elements

7

Chapter

① GROUP 15 ELEMENTS

1. **Pnictogens:** $\underbrace{\textbf{N, P,}}_{\text{non-metals}}\ \underbrace{\textbf{As, Sb,}}_{\text{Metalloids}}\ \underbrace{\textbf{Bi, Uup}}_{\text{metals}}$
2. Physical properties:
   - Covalent radii : $N < P < As < Sb < Bi$
   - Ionisation enthalpy : $N > P > As > Sb > Bi$
   - Electronegativity: $N > P > As > Sb = Bi$
3. Nitrogen is a gas, which all remaining elements are solids.
4. Nitrogen is a diatomic molecule with very large bond enthalpy ($941.4\ kJ\ mol^{-1}$)
5. The boiling points, in general increase from top to bottom in the group but melting points increases upto arsenic and then decreases upto bismuth.
6. Only nitrogen in this group is capable of forming $p\pi{-}p\pi$ multiple bonds within itself and with carbon, oxygen etc, due to small size. Phosphorus and other elements do not form $p\pi{-}p\pi$ multiple bonds. Phosphorous and arsenic can form $d\pi{-}d\pi$ bond.
7. Except nitrogen, all elements show allotropy
8. Single N–N bond is weaker than single P-P bond.
9. Maximum covalency of N and P are 4 and 6 respectively.
10. Common oxidation state: –3, +3 and + 5
11. Due to inert pair effect, stability of +5 oxidation state deceases and stability of + 3 state increases on moving down the group.
12. The only well characterised Bi^{5+} compound is BiF_5
13. All oxidation states +1 to +4 for nitrogen tend to disproportionate in acid solution.
    $3H\overset{+3}{N}O_2 \longrightarrow H\overset{+5}{N}O_3 + H_2O + 2\overset{+2}{N}O$
14. Anomalous behaviour of nitrogen is due to its
    (i) small size
    (ii) High electronegativity
    (iii) High ionization enthalpy
    (iv) Non-availability of d-orbitals
15. All elements of this group form hydrides of type MH_3
    (i) Melting point: $\mathbf{NH_3} > SbH_3 > AsH_3 > PH_3$
    (ii) Boiling Point: $BiH_3 > SbH_3 > \mathbf{NH_3} > AsH_3 > PH_3$
    (iii) Bond angle: $NH_3 > PH_3 > AsH_3 > SbH_3$
    (iv) Bond enthalpy: $NH_3 > PH_3 > AsH_3 > SbH_3$
    (v) Basicity: $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$
16. All elements of this group form two types of oxides: E_2O_3 and E_2O_5
    $\underbrace{N_2O_3,\ P_2O_3,}_{\text{Acidic}}\ \underbrace{As_2O_3,\ Sb_2O_3,}_{\text{Amphoteric}}\ \underbrace{Bi_2O_3}_{\text{Basic}}$
17. Except nitrogen, the rest of the elements form two type of halides : EX_3 and EX_5. Nitrogen does not form pentahalide due to absence of d-orbitals. Among trihalides of nitrogen only NF_3 is stable.
18. Preparation of Dinitrogen
    (i) $NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(\ell) + NaCl(aq)$
    (ii) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$
    (iii) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$(very pure)
19. Nitrogen combines with CaC_2 to form nitrolim ($CaCN_2 + C$) at 100°C, which is used as a fertilizer.
20. Liquid dinitrogen is used as a refrigerant to preserve biological materials and in cryosurgery.
21. Preparation of ammonia
    (i) $NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$
    (ii) $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$
    (iii) Haber's process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),\ \Delta H < 0$
22. NH_3 behave as a lewis base
    $\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$
    $\underset{\text{(white ppt)}}{AgCl(s)} + 2NH_3(aq) \longrightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$
23. Oxides of nitrogen:

N_2O	Neutral	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
NO	Neutral	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$
N_2O_3	Acidic	$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$
NO_2	Acidic	$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$
N_2O_4	Acidic	$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$
N_2O_5	Acidic	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

24. Preparation of nitric acid on large scale is done by Ostwald's process.
    $4NH_3(g) + \underset{\text{(from air)}}{5O_2(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt/Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$
    $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
    $3NO_2(g) + H_2O(\ell) \longrightarrow 2HNO_3(aq) + NO(g)$
25. Concentrated nitric acid attacks most metals except noble metals such as Pt and Au.
    $Cu \xrightarrow{\text{dil. } HNO_3} Cu(NO_3)_2 + NO$
    $Cu \xrightarrow{\text{conc. } HNO_3} Cu(NO_3)_2 + NO_2$

26. **Brown ring test:**

$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(brown ring)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$

27. Phosphorus exists in a number of allotropic forms.
   - (i) **White phosphorus :** It is less stable and therefore more reactive than the other solid phases under normal conditions (bond angle 60°), poisonous, soluble in CS_2 and glows in dark (Chemiluminescence).

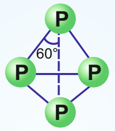


Fig. White phosphorus

   - (ii) **Red phosphorus :** Non-poisonous and insoluble in CS_2. It is polymeric and less reactive than white phosphorous.

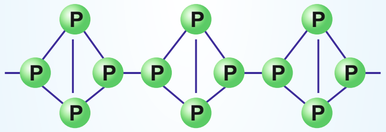


Fig. Red phosphorus

   - (iii) **Black phosphorus :** It has two forms α and β-phosphorus.

28. Preparation of phosphine:
   - (i) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
   - (ii) $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

29. PH_3 becomes inflammable due to presence of P_2H_4 and P_4 vapours. Spontaneous combustion of phosphine is technically used in Holme's Signals.

30. Preparation of PCl_5:
   - (i) $P_4 + 10Cl_2 \longrightarrow 4PCl_5$
   - (ii) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

31. Oxoacids of phosphorus:

Name	Formula	Characteristic bonds and their number
Hypophosphorous (Phosphinic)	H_3PO_2	One P – OH Two P – H One P = O
Orthophosphorous (Phosphonic)	H_3PO_3	Two P – OH One P – H One P = O
Pyrophosphorous	$H_4P_2O_5$	Two P – OH Two P – H Two P = O
Hypophosphoric	$H_4P_2O_6$	Four P – OH Two P = O One P – P
Orthophosphoric	H_3PO_4	Three P – OH One P = O
Pyrophosphoric	$H_4P_2O_7$	Four P – OH Two P = O One P – O – P
Cyclotrimetaphosphoric	$(HPO_3)_3$	Three P – OH Three P = O Three P – O – P

32. (i) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$
   - (ii) $4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4\,Ag + 4HNO_3 + H_3PO_4$

② GROUP 16 ELEMENTS

1. Chalcogens : $\underbrace{O,\ S,}_{\text{non-metals}}\ \underbrace{Se,\ Te,}_{\text{metalloid}}\ \underbrace{Po,}_{\text{Metal}}\ Lv$
2. $(-\Delta_{eg}H)$: S > Se > Te > Po > O.
3. Oxygen (O_2) is a gas whereas sulphur (S_8) exist as solid.
4. Oxygen shows generally negative oxidation state - 2.
5. The stability of +6 oxidation state decreases down the group and stability of +4 oxidation state increases due to inert pair effect.
6. Anomalous behaviour of oxygen is due to its
   - (i) Small size
   - (ii) High electronegativity
   - (iii) Absence of d-orbitals
7. All the elements of group-16 form hydrides of type H_2E
   - (i) Melting point : $\mathbf{H_2O} > H_2Te > H_2Se > H_2S$
   - (ii) Boiling point : $\mathbf{H_2O} > H_2Te > H_2Se > H_2S$
   - (iii) Acidic nature : $H_2Te > H_2Se > H_2S > H_2O$
8. S, Se, Te and Po form oxides of type EO_2 and EO_3, all are acidic in nature.
9. These elements form halides of type EX_6, EX_4 and EX_2.
   - (i) Stability order of halides : $F^- > Cl^- > Br^- > I^-$
   - (ii) SF_6 is exceptionally stable
   - (iii) All elements except oxygen form dichlorides and dibromides
   - (iv) Dimeric halides undergo disproportionation

     $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$
10. Preparation of dioxygen
   - (i) $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$
   - (ii) $2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$
11. Hydrazines with liquid oxygen is used as fuel in rockets.
12. (i) Mixed oxide : Pb_3O_4, Fe_3O_4, Mn_3O_4
   - (ii) Simple oxides:
     - (a) Acidic oxide : SO_2, Cl_2O_7, N_2O_5
     - (b) Basic oxide : CaO, Na_2O
     - (c) Amphoteric oxide : Al_2O_3
     - (d) Neutral oxide : CO, NO, N_2O
13. Ozone is allotropic form of oxygen and prepared by passing silent electric discharge through dry oxygen.

14. Ozone is powerful oxidising agent

$$PbS\ (s) \xrightarrow{O_3} PbSO_4\ (s)$$

$$2I^{\ominus}(aq) \xrightarrow{O_3} I_2\ (s)$$

15. Sulphur exists in several allotropic forms (i) Rhombic sulphur (α-sulphur), (ii) Monoclinic sulphur (β-sulphur).

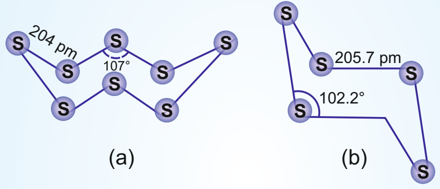


Fig. The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

16. Rhombic sulphur transform into monoclinic sulphur above 369 K. At elevated temperature (~ 1000 K), S_2 is dominant species and is paramagnetic like O_2

17. All oxoacids of sulphur are dibasic acid. H_2SO_3 : sulphurous acid, H_2SO_4 : Sulphuric acid, $H_2S_2O_8$: Peroxodisulphuric acid, $H_2S_2O_7$: Pyrosulphuric acid (Oleum), $H_2S_2O_6$: Dithionic acid

18. H_2SO_4 is manufactured by contact process

$$S \xrightarrow{O_2} SO_2 \xrightarrow[\text{Catalyst}]{V_2O_5} SO_3 \xrightarrow{H_2SO_4} \underset{\text{Oleum}}{H_2S_2O_7}$$

③ GROUP 17 ELEMENTS

1. Halogens : F, Cl, Br, I, At
2. Atomic and physical properties of halogens
   - (i) Bond energy : $Cl_2 > Br_2 > \mathbf{F_2} > I_2$
   - (ii) Electron affinity : Cl > **F** > Br > I
   - (iii) Electronegativity : F > Cl > Br > I
   - (iv) Physical state : $\underset{\text{(gas)}}{F_2, Cl_2}$, $\underset{\text{(liq.)}}{Br_2}$, $\underset{\text{(Solid)}}{I_2}$
   - (v) Colour : $\underset{\text{Yellow}}{F_2}$, $\underset{\text{Greenish yellow}}{Cl_2}$, $\underset{\text{Red}}{Br_2}$, $\underset{\text{Violet}}{I_2}$
3. Chemical properties
   - (i) Oxidising power : $F_2 > Cl_2 > Br_2 > I_2$
   - (ii) Reaction with H_2O :
     - $2F_2(g) + 2H_2O(l) \longrightarrow 4HF + O_2$
     - $Cl_2(g) + H_2O(l) \longrightarrow HCl + HOCl$
4. All the halogens react with hydrogen to form volatile covalent hydrides of type HX.
   - (i) Acidic nature : HI > HBr > HCl > HF
   - (ii) Boiling point : HF > HI > HBr > HCl
   - (iii) Melting point : HI > HF > HBr > HCl
5. Halogen formed many oxide with oxygen.
   - (i) F formed two oxides OF_2 and O_2F_2
   - (ii) Stability order of oxides form by halogen : I > Cl > Br
6. **Preparation of Cl_2**
   - (i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
   - (ii) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
   - (iii) **Deacon's process :**

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

7. **Reactions of Cl_2**
   - (i) $\underset{\text{(Cold and dil.)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
   - (ii) $\underset{\text{(Hot and conc)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
   - (iii) $2Ca(OH)_2 + 2Cl_2 \longrightarrow \underset{\text{(Bleaching powder)}}{Ca(OCl)_2} + CaCl_2 + 2H_2O$
8. Aqua regia (3HCl + HNO_3) is used for dissolving noble metals.

   $Au \longrightarrow AuCl_4^-$, $Pt \longrightarrow PtCl_6^{2-}$
9. Fluorine forms only one oxoacid (HOF), other Halogen-forms several oxoacids.

HOX	HOXO	$HOXO_2$	$HOXO_3$
Hypohalous acid	Halous acid	Halic acid	Perhalic acid

10. **Interhalogen compound :** XX', XX'_3, XX'_5, XX'_7
    - (i) All the solid or liquid at 298 K except ClF
    - (ii) These are more reactive than Halogen except F_2
    - (iii) $ClF + H_2O \longrightarrow HF + HOCl$

④ GROUP 18 ELEMENTS

1. Noble gas : He, Ne, Ar, Kr, Xe, Rn, Og
2. ΔH_{eg} : Ne > Ar ≃ Kr > Xe > Rn > He
3. 1^{st} compound of noble gas element is formed by Neil Bartlett on the concept of similar IP of O_2 and Xe

   $Xe + PtF_6 \longrightarrow Xe^+[PtF_6]^-$
4. **Xenon-fluorine compounds preparation :**
   - (i) $\underset{\text{(excess)}}{Xe} + F_2 \xrightarrow{673\ K,\ 1\ bar} XeF_2(s)$
   - (ii) $\underset{1\ :\ 5}{Xe + F_2} \xrightarrow{873\ K,\ 1\ bar} XeF_4(s)$
   - (iii) $\underset{1\ :\ 20}{Xe + 3F_2} \xrightarrow{573\ K,\ 60\text{-}70\ bar} XeF_6(s)$
   - (iv) $XeF_4 + O_2F_2 \xrightarrow{143\ K} XeF_6 + O_2$
5. **Hydrolysis reactions**
   - (i) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
   - (ii) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
   - (iii) $XeF_6 + 3H_2O \longrightarrow \underset{\text{(explosive)}}{XeO_3} + 6HF$
6. **Xenon fluoride reaction with F^- donors and acceptors:**
   - (i) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$
   - (ii) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$
   - (iii) $XeF_6 + NaF \longrightarrow Na^+ [XeF_7]^-$
7. He is used in filling balloons for meteorological observations
8. Liquid He is used as cryogenic agent
9. Ne is used in discharge tubes and fluorescent bulbs for advertisement display
10. Ar is used to provide an inert atmosphere in arc welding.

The d- and f-Block Elements

8

Chapter

① d-BLOCK ELEMENTS

1. The d-block of the periodic table contains the elements of the group 3-12.
2. **Transition metals :** Metals which have incomplete d-subshell either in neutral atom or in their ions.
3. **General electronic configurations**

   $(n-1)d^{1-10}\ ns^{1-2}$, but this has several exceptions due to very little energy difference between $(n-1)d$ and ns orbitals.
4. There are mainly four series of the transition metals : 3d series (Sc to Zn), 4d series (Y to Cd), 5d series (La and Hf to Hg), and 6d series (Ac and Rf to Cn)
5. Zn, Cd and Hg are not regarded as transition metals.
6. With the exceptions of Zn, Cd, Hg and Mn, these have one or more typical metallic structures at normal temperatures.
7. With the exception of Zn, Cd, and Hg, these metals are very hard and have low volatility.
8. These elements have high melting and boiling point. In any row the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc.
9. These metals have high enthalpy of atomisation due to strong interatomic interactions. Metals of 2nd and 3rd series have more enthalpies of atomisation than the corresponding elements of 1st series due to much more frequent metal-metal bonding.
10. Tungsten (W) has highest melting point among d-block elements.
11. The filling of 4f before 5d orbitals results in a regular decrease in atomic radii called lanthanoid contraction. The net result of it is that the 2nd and 3rd d-series exhibits similar radii (e.g. Zr and Hf).
12. The 1st ionisation enthalpy in any d-series generally increases but the magnitude of increase in 2nd and 3rd ionisation enthalpies for the successive elements, is much higher along a series.
13. The trend of steady increase in 2nd and 3rd ionisation energies for 1st transition series breaks for the formation of Mn^{2+} and Fe^{3+} respectively as both ions have d^5 configuration.
14. The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy.
15. Ionisation energy of Mn^+ is lower than Cr^+ as there is no loss of exchange energy at d^6 configuration.
16. Mn exhibits all the oxidation states from +2 to +7.
17. Sc(II) virtually unknown.
18. The only oxidation state of Zn is +2.
19. In group-6, Mo(VI) and W(VI) are found to be more stable than Cr(VI)
20. Among 3d series elements, $E°(M^{2+}/M)$ is positive only for copper because high energy to transform Cu(s) to Cu^{2+}(aq.) is not balanced by its hydration enthalpy. Only oxidising acids (nitric and hot concentrated sulphuric) reacts with Cu.
21. Among 3d series, the value of $E°(M^{2+}/M)$ for Mn, Ni and Zn are more negative than excepted from the trend.
22. In halides of 3d series, the highest oxidation numbers are achieved in TiX_4, VF_5 and CrF_6.
23. V^{+5} halide is represented only by VF_5, the other Halides undergo hydrolysis to give oxohalides VOX_3.
24. Cu(II) halides are known except the iodide.
25. Many Cu(I) compounds are unstable in aqueous solution and undergo disproportionation.

    $2Cu^+ \longrightarrow Cu^{2+} + Cu$
26. The stability of Cu^{2+}(aq) rather than Cu^+(aq.) is due to the much more negative $\Delta_{Hyd}H°$ of Cu^{2+}(aq.) than Cu^+(aq), which more than compensates for the second ionisation enthalpy of Cu.
27. Ferrates $(FeO_4)^{2-}$ are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2.
28. The highest Mn fluoride is MnF_4 whereas highest oxide is Mn_2O_7
29. Mn_2O_7 is a covalent oxide in which each Mn is tetrahedrally surrounded by O's including Mn–O–Mn bridge.
30. Order of oxidising power : $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$
31. Ti & V, in practise, are passive to dilute non-oxidising acids at room temperature.
32. $E°(M^{3+}/M^{2+})$ values shows that Mn^{3+} and Co^{3+} ions are strongest oxidising agents in aqueous solutions among 3d series.
33. The ions Ti^{2+}, V^{2+} and Cu^{2+} are strong reducing agents among 3d series and will liberate H_2 from dilute acids.
34. Each unpaired electron has a magnetic moment associated with its spin angular momentum and orbital angular momentum.
35. For the compounds of first transition series metals, magnetic moment is determined by 'spin only' formula : $\mu = \sqrt{n(n+2)}$ BM
36. The colour of some aquated transition metal ions :

    Sc^{3+}, Ti^{4+}, Zn^{2+} : Colourless, V^{3+}, Fe^{2+}, Ni^{2+}: Green , Fe^{3+}: Yellow, Mn^{2+} : pink.

37. These metals form a large number of complex compounds due to comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d-orbitals for the bond formation.
38. These metals and their compounds are used as a catalyst due to their ability to adopt multiple oxidation states and to form complexes.
39. When small atoms like H, C or N are trapped inside the crystal lattice of these metals, the combination are called interstitial compounds which are usually non-stoichiometric.
40. Due to similar radii, transition metals form alloy. eg. : Brass (Cu – Zn), Bronze (Cu – Sn).
41. Manganese (VI) becomes unstable relative to manganese (VII) and manganese (IV) in acidic solution

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

42. All 3d metals forms MO oxides except scandium.
43. Mn_2O_7 is acidic, Cr_2O_3 is amphoteric and CrO is basic in nature
44. Preparation of $K_2Cr_2O_7$:

$$\underset{\text{Chromite ore}}{FeCr_2O_4} \xrightarrow[O_2]{Na_2CO_3} Fe_2O_3 + CO_2 + \underset{\text{(Yellow)}}{Na_2CrO_4} \xrightarrow{H_2SO_4} \underset{\text{(Orange)}}{Na_2Cr_2O_7}$$

$$Na_2Cr_2O_7 \xrightarrow{KCl} K_2Cr_2O_7$$

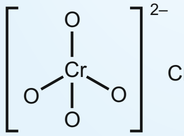
45. $Na_2Cr_2O_7$ is more soluble than $K_2Cr_2O_7$
46. Chromate and dichromate are interconvertible in aqueous solution depending upon pH of the solution.

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

$$CrO_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

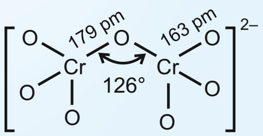
47.

CrO_4^{2-} :



(tetrahedral)
(Chromate ion)

$Cr_2O_7^{2-}$:



(dichromate ion)

48. In acidic solution, $K_2Cr_2O_7$ is used as oxidising agent as

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \ (E° = 1.33 \text{ V})$$

49. Preparation of $KMnO_4$

(i) $MnO_2 \xrightarrow[O_2]{KOH} \underset{\text{(Green)}}{K_2MnO_4} \xrightarrow{H^+} \underset{\text{(Pink)}}{MnO_4^-} + MnO_2$

(ii) Lab method : $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10\,SO_4^{2-} + 16\,H^+$

50. $KMnO_4$ decomposes at 513 K as :

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

51. $KMnO_4$ behaves as oxidising agent as :
    - **Basic medium :** $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$
    - **Neutral/faintly alkaline medium :**

      $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$
    - **Acidic medium :**

      $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
52. $KMnO_4$ oxidises I^- into I_2 and IO_3^- respectively in acidic and faintly alkaline medium.
53. Permangnate titrations in presence of HCl are unsatisfactory since HCl is oxidised to Cl_2.

② f-BLOCK ELEMENTS

1. The f-block consists of elements in which 4f and 5f orbitals are progressively field and known as inner-transition elements.
2. The two series of inner transition elements : 4f (Ce to Lu) and 5f (Th to Lr) are known as lanthanoids and actinoids respectively.
3. **Lanthanoids (Ln) :**
    - Outer electronic configuration : $4f^{1-14}\,5d^{0-1}\,6s^2$
    - The overall decrease in atomic and ionic radii from La to Lu due to poor shielding to 4f is known as lanthanoid contractions
    - Most common oxidation state is +3
    - Pr, Nd, Tb and Dy also exhibit +4 oxidation state but only in oxides, MO_2
    - Eu and Yb also exhibit +2 oxidation states.
    - Their melting point range between 1000 to 1200 K but Sm melts at 1623 K
    - Ln^{3+} ions may be coloured due to presence of f-electrons
    - Lanthanoids form $Ln(OH)_3$ which are basic like alkaline earth metal hydroxides.
    - Mischmetal is an alloy which consists lanthanoids (~95%) and Iron (~5%)
4. **Actinoids**
    - Outer electronic configuration : $5f^{0-14}\,6d^{0-1}\,7s^2$
    - All actinoids are radioactive elements
    - There is gradual decrease in the size of atoms or M^{3+} ions across the series known as actinoid contraction, which is greater than lanthanoid contraction.
    - Their general oxidation state is +3 but these element can show variety of oxidation states.

③ APPLICATION OF d- AND f-BLOCK ELEMENTS

1. TiO is used in pigment industry
2. MnO_2 is used in dry battery cells
3. $TiCl_4$ and $Al(CH_3)_3$, Ziegler catalyst is used to manufacture polyethene
4. $PdCl_2$ is used as catalyst in Wacker process.
5. AgBr is used in photographic industry.

Coordination Compounds

9

Chapter

1 WERNER'S THEORY

- In coordination compounds metals posses two type of valences: primary and secondary
- The primary valences are normally ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and satisfied by neutral molecules or negative ions.

2 SOME IMPORTANT TERMS

- **Double salts :** Which are stable in solid state but broken down into individual constituents when dissolved in water eg. Mohr's salt, $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ and potash alum $[KAl(SO_4)_2 \cdot 12H_2O]$
- **Coordination compounds :** Which retain their identity in solid state as well as in solution eg $K_4[Fe(CN)_6]$
- **Ligands :** Species which are directly linked with the central metal in complex. These are Lewis base.
  - (a) Unidentate ligand : Cl^-, H_2O, NH_3
  - (b) Didentate ligand : $NH_2CH_2CH_2NH_2$, $C_2O_4^{2-}$
  - (c) Hexadentate ligand : $EDTA^{4-}$
  - (d) Ambidentate ligand : NO_2^-, SCN^-
- **Coordination number :** The number of atoms of the ligands that are directly bound to the central metal

  eg. $[Fe(C_2O_4)_3]^{3-}$, here CN = 6, $[Ni(NH_3)_4]^{2+}$, here, CN = 4
- **Homoleptic complex :** Only one kind of ligands are present eg. $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complex :** More than one kind of ligands are present eg. $[Co(NH_3)_4Cl_2]^+$

3 NAMING OF COORDINATION COMPOUNDS

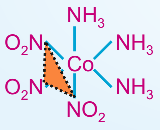
- $[Cr(NH_3)_3(H_2O)_3]Cl_3$: Triamminetriaquachromium(III) chloride
- $K_2[Zn(OH)_4]$: Potassium tetrahydroxidozincate(II)
- $[Ni(CO)_4]$: Tetracarbonyl nickel(0)
- $[CoCl_2(en)_2]^+$: Dichloridobis(ethane-1,2-diamine)cobalt(III) ion.
- $[Pt(NH_3)_2Cl(NO_2)]$: Diamminechloridonitrito-N-Platinum(II)

4 STRUCTURAL ISOMERISM

- **Ionisation isomerism** : Isomers give different ion in solution eg. $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
- **Solvate isomerism** : Different number of solvent molecule bonded to metal eg. $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
- **Coordination Isomerism** : The ligands are interchanged in both the cationic and anionic ions. eg. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
- **Linkage isomerism** : It is due to presence of ambidentate ligand eg. $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$.

5 STEREOISOMERISM

- **Geometrical isomers :** Common in heteroleptic complexes with in CN = 4 (square planar) and CN = 6.
  - (i) Square planar complex : $[MX_2L_2]$ (2 isomers), [MABXL] (3 isomers) show cis-trans isomerism.
  - (ii) Octahedral complex : $[MX_2(L-L)_2]$, $[Ma_3b_3]$ (fac-mer isomers).



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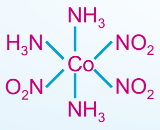
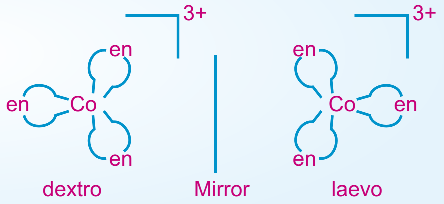


Mer

- **Optical isomers :** These are mirror images that cannot be superimposed on one another.
  - (i) $[Co(en)_3]^{3+}$ have d and ℓ isomer



  - (ii) Cis-$[PtCl_2(en)_2]^{2+}$ show optical activity

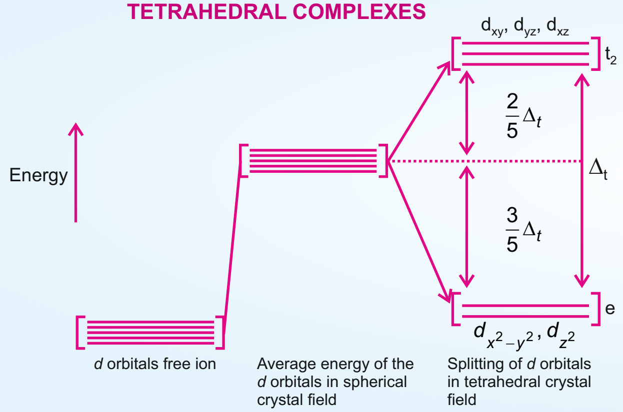
6 IMPORTANT COMPLEXES

Complex	Coordination number	Hybridisation	Shape	Nature	Unpaired electrons
$[Co(NH_3)_6]^{3+}$	6	d^2sp^3	Octahedral	Diamagnetic	Zero
$[CoF_6]^{3-}$	6	sp^3d^2	Octahedral	Paramagnetic	Four
$[NiCl_4]^{2-}$	4	sp^3	Tetrahedral	Paramagnetic	Two
$[Ni(CO)_4]$	4	sp^3	Tetrahedral	Diamagnetic	Zero
$[Ni(CN)_4]^{2-}$	4	dsp^2	Sequare planar	Diamagnetic	Zero
$[Mn(CN)_6]^{3-}$	6	d^2sp^3	Octahedral	Paramagnetic	Two
$[MnCl_6]^{3-}$	6	sp^3d^2	Octahedral	Paramagnetic	Four
$[Fe(CN)_6]^{3-}$	6	d^2sp^3	Octahedral	Paramagnetic	One
$[FeF_6]^{3-}$	6	sp^3d^2	Octahedral	Paramagnetic	Five
$[Co(C_2O_4)_3]^{3-}$	6	d^2sp^3	Octahedral	Diamagnetic	Zero

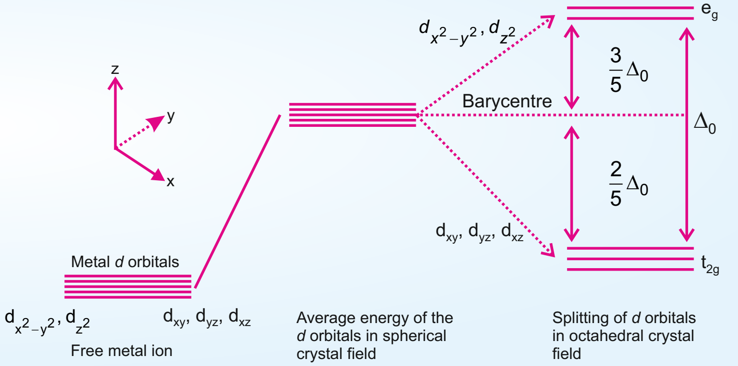
7 CRYSTAL FIELD THEORY (CFT)

According to CFT, under the influence of ligand field, degeneracy of *d*-orbitals is destroyed and they split into two or more energy levels. The extent of spilliting depends upon the strength of ligand.

TETRAHEDRAL COMPLEXES



OCTAHEDRAL COMPLEXES



8 SPECTROCHEMICAL SERIES

Arrangement of ligands in order of increasing field strength.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O$
$< NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

- If $\Delta_0 < P$, complex is high spin and ligand is weak field ligand
- If $\Delta_0 > P$, complex is low spin and ligand is strong field ligand
- $\Delta_t = (4/9)\Delta_0$

11 APPLICATIONS OF COORDINATION COMPOUINDS

- Hardness of water is estimated by titration with Na_2EDTA
- $[(Ph_3P)_3RhCl]$, Wilkinson catalyst is used for the hydrogenation of alkenes.
- Excess of Cu and Fe are removed by the chelating ligands D-penicillamine and desferrioxime B.
- EDTA is used in the treatment of lead poisoning
- Cis-platin effictively inhibit the growth of tumors.
- In photography, hypo ($Na_2S_2O_3$) solution on reaction with AgBr form $(Ag(S_2O_3)_2)^{3-}$ ion.

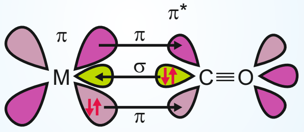
9 COLOUR OF COMPLEXES

- Colour of complex can be explained by *d-d* transition
- Metal atom/ion of d^0 or d^{10} configuration do not show *d-d* transition.
- The colour of the complex is complementry to that which is absorbed.

Complex	Colour
$[Ti(H_2O)_6]^{3+}$	Violet
$[Cu(H_2O)_4]^{2+}$	Blue
$[Co(NH_3)_6]^{3+}$	Yellow orange
$[CoCl(NH_3)_5]^{2+}$	Violet
$CuSO_4 \cdot 5H_2O$	Blue
$[Co(CN)_6]^{3-}$	Pale yellow
$[Ni(H_2O)_6]^{2+}$	Green
$[Ni(H_2O)_4(en)]^{2+}$	Pale blue
$[Ni(H_2O)_2(en)_2]^{2+}$	Blue/Purple
$[Ni(en)_3]^{2+}$	Violet

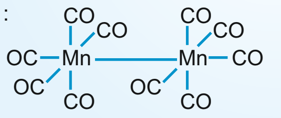
10 METAL CARBONYLS

- The metal-carbon bond in metal carbonyls possess both σ and π character.
- The M – C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.
- The M – C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π* orbital of carbon monoxide.
- Metal to ligand bonding is known as synergic effect.



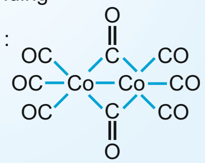
Synergic bonding

eg :



$[Mn_2(CO)_{10}]$
Decacarbonyldimanganese(0)

eg :



$[Co_2(CO)_8]$
Octacarbonyldicobalt(0)

Haloalkanes and Haloarenes

10

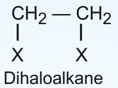
Chapter

① CLASSIFICATION

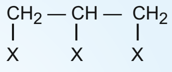
(a) On the basis of number of halogen atoms

C_2H_5X

Monohaloalkanes


$\underset{X}{CH_2}-\underset{X}{CH_2}$

Dihaloalkane


$\underset{X}{CH_2}-\underset{X}{CH}-\underset{X}{CH_2}$

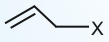
Trihaloalkane

(b) Compounds containing sp^3 C– X bond:

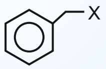
(i) Alkyl halides or haloalkanes (R – X)

Primary (1°) Secondary (2°) Tertiary (3°)

(ii) Allylic halides

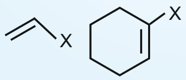


(iii) Benzylic halides

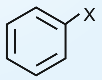


(c) Compounds containing sp^2 C – X bond:

(i) Vinylic halides :



(ii) Aryl halides :



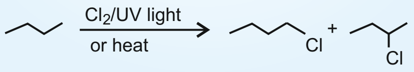
② METHOD OF PREPARATION

(a) From alcohols

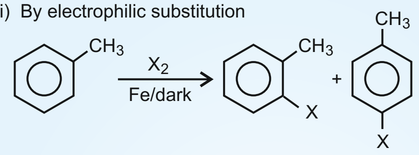
- $R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$
- $R-OH + NaBr \xrightarrow{H_2SO_4} R-Br + NaHSO_4 + H_2O$
- $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$ (X = Cl, Br)
- $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$
- $R-OH \xrightarrow[X_2 = Br_2,\ I_2]{Red\ P/X_2} R-X$
- $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$

(b) From Hydrocarbons

(i) Free radical halogenation

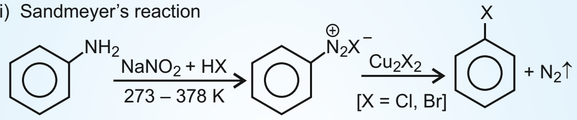


(ii) By electrophilic substitution



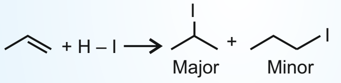
- Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(iii) Sandmeyer's reaction



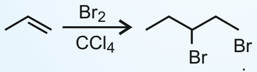
(iv) From alkenes

- Addition of halogen halides :



- Addition of halogen:

  Addition of Br_2 in CCl_4 to an alkene results in discharge of reddish brown colour of Br_2



vic-dibromide

(c) Halogen Exchange

- **Finkelstein reaction :**

  $R-X + NaI \longrightarrow R-I + NaX$ [X, Cl, Br]
- **Swarts reaction :**

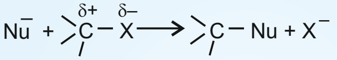
  $CH_3-Br + AgF \longrightarrow CH_3-F + AgBr\downarrow$

③ PHYSICAL PROPERTIES

- Boiling point of alkyl halide decrease in the order:
  RI > RBr > RCl > RCl > RF
- Boiling point of isomeric haloalkanes decrease with increase in branching

④ CHEMICAL REACTIONS REACTION OF HALOALKANE

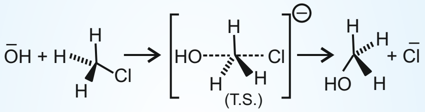
(A) Nucleophilic substitution reaction


$\bar{Nu} + >\overset{\delta+}{C}-\overset{\delta-}{X} \longrightarrow >C-Nu + X^-$

Mechanism : This reaction has been found to process by two different mechanism.

(i) **Substitution nucleophilic bimolecular (S_N2) :**

- The reaction between CH_3Cl and $\bar{O}H$ ion to yield methanol follows a second order kinetics, *i.e.* the rate depends upon the concentration of both reactants.

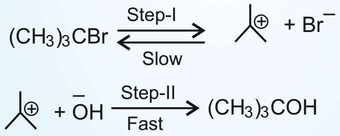


- Transition state (T.S.) is formed
- Reaction is generally carried out in acetone or polar aprotic solvents

(ii) **Substitution nucleophilic unimolecular (S_N1) :**

- It occurs in two steps

$HO^- + (CH_3)_3C-Br \longrightarrow (CH_3)_3C-OH + Br^-$



- Greater the stability of carbocation greater is the rate of reaction
- S_N1 and S_N2 order can be generalised as

For S_N2 reaction

$\longrightarrow$

Tertiary halide, secondary halide, primary halide, CH_3X

$\longleftarrow$

For S_N1 reaction

- For a given alkyl group reactivity of halide follows same order in both the mechanisms
  R – I > R – Br > R — Cl >> R – F

(iii) **Stereochemical aspects of nucleophilic substitution reaction :**

Some important concepts

(a) **Optical activity :**

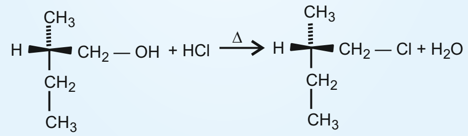
The compounds which rotate plane polarised light are optically active

- If a compound rotates plane polarised light in clockwise direction. It is called **dextrorotatory** and if it rotates in anti clock wise direction it is called **laevorotatory**.

(b) **Molecular asymmetry, Chirality and enantiomers:**

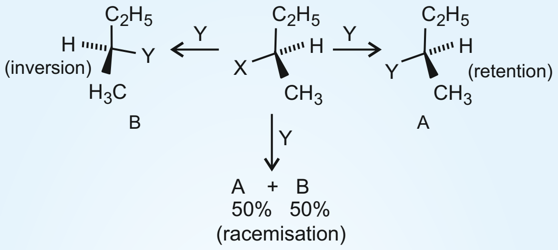
- If the spatial arrangement of four different groups around the central carbon is tetrahedral then the carbon is called **asymmetric carbon**
- The compounds which are non-superimposable on their mirror images are **Chiral** and are called enantiomers
- The stereoisomers having no mirror image relationship are called **diastereomers**.
- A mixture containing two enantiomers in equal proportions will have zero optical rotation. Such mixture is known as **racemic mixture**.

(c) **Retention :** In general, if during a reaction, no bond to the stereocentre is broken, the reaction is said to proceed with retention of configuration

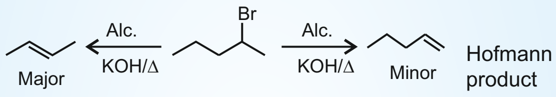


(–)-2-methylbutan-1-ol (+)-1-chloro-2-methylbutane

(d) Inversion, retention and recemisation



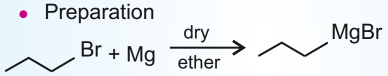
(B) Elimination reactions



Saytzeff product

(C) Reaction with metal

- Preparation



Grignard reagent
(Organometallic compound)

$RMgX + H_2O \longrightarrow \underset{\text{Hydrocarbon}}{RH} + Mg(OH)X$

Reaction of Haloarenes

(A) **Nucleophilic substitution :** Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to following reasons :

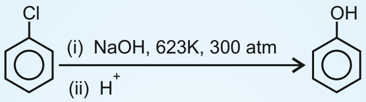
(i) Resonance effect : Lone pair of chlorine is in conjugation with benzene resulting in double bond character of C — Cl bond. As a result bond cleavage in haloarene is difficult.

(ii) Difference in hybridization of carbon atom in C– X bond

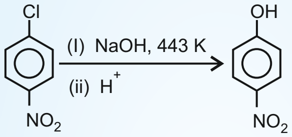
(iii) Instability of phenyl cation

(iv) Repulsion between haloarene and approaching nucleophile

- Replacement by hydroxyl group



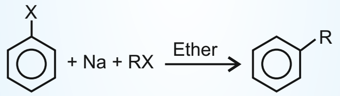
Presence of an electron with drawing group at o/p positions increases the reactivity of haloarenes



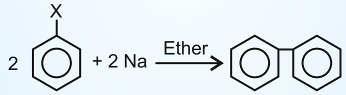
(B) **Electrophilic substitution reactions :** Haloarenes undergo electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and friedel crafts reaction.

Reaction with metals

(i) Wurtz-Fittig reaction



(ii) Fittig reaction



Diphenyl

Polyhalogen Compounds

$2CHCl_3 + O_2 \xrightarrow{h\nu} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$

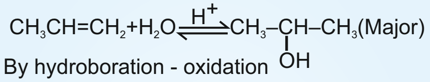
Alcohols, Phenols and Ethers

11
Chapter

① PREPARATION OF ALCOHOLS

(i) From alkenes

(a) By acid catalysed hydration :



$$CH_3CH{=}CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3{-}\underset{OH}{\underset{|}{CH}}{-}CH_3 \text{(Major)}$$

(b) By hydroboration - oxidation

$$CH_3{-}CH{=}CH_2 + (H{-}BH_2)_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}BH_2$$

$$CH_3{-}CH_2{-}CH_2{-}BH_2 \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_3B$$

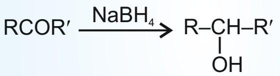
$$(CH_3CH_2CH_2)_3B \xrightarrow[H_2O]{3H_2O_2/\bar{O}H} 3CH_3CH_2CH_2OH + B(OH)_3$$

- The alcohol formed looks as if it has been formed by the addition of water to alkene in a way opposite to Markovnikov's rule.

(ii) From carbonyl compounds

(a) By reduction of aldehydes and ketones :

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$



$$RCOR' \xrightarrow{NaBH_4} R{-}\underset{OH}{\underset{|}{CH}}{-}R'$$

(b) By reduction of carboxylic acids and esters :

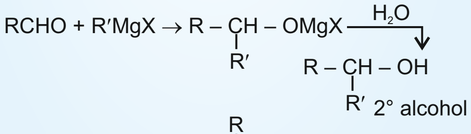
$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$$

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[Pd]{H_2} RCH_2OH + R'OH$$

(iii) From Grignard reagent

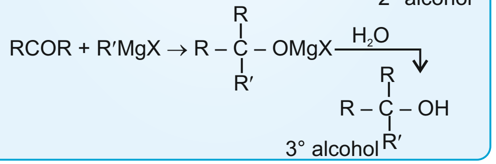
$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH$$

1° alcohol



$$RCHO + R'MgX \rightarrow R - \underset{R'}{\underset{|}{CH}} - OMgX \xrightarrow{H_2O} R - \underset{R'}{\underset{|}{CH}} - OH$$

2° alcohol

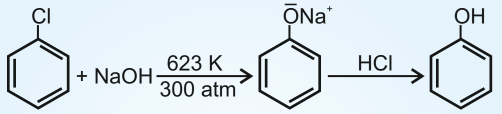


$$RCOR + R'MgX \rightarrow R - \overset{R}{\overset{|}{\underset{R'}{\underset{|}{C}}}} - OMgX \xrightarrow{H_2O} R - \overset{R}{\overset{|}{\underset{R'}{\underset{|}{C}}}} - OH$$

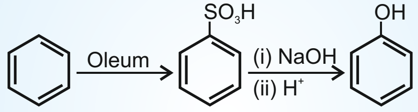
3° alcohol

② PREPARATION OF PHENOLS

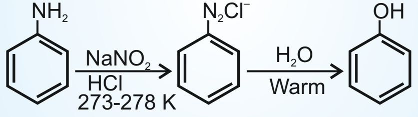
(a) From haloarenes



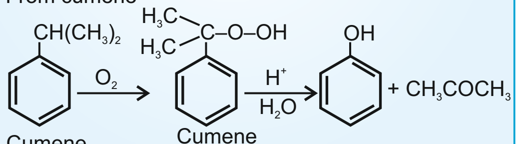
(b) From benzene sulphonic acid



(c) From diazonium salts



(d) From cumene



Cumene

Cumene hydroperoxide

③ PHYSICAL PROPERTIES

- High boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them.
- Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water.

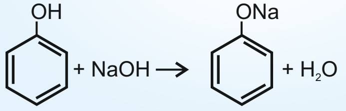
④ CHEMICAL REACTIONS :

[A] Reaction of alcohols

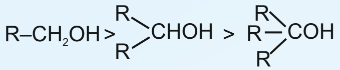
(a) Reactions involving cleavage of O-H bond

(i) Acidity of alcohols and phenols

- Reaction with metals
  $2R{-}O{-}H + 2Na \rightarrow 2R\bar{O}\overset{+}{Na} + H_2$
- Phenol reacts with aqueous NaOH

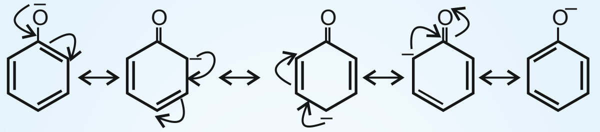


- Acidity of alcohols : Acidic strength order



$$R{-}CH_2OH > \begin{matrix}R\\R\end{matrix}{>}CHOH > \begin{matrix}R\\R\\R\end{matrix}{-}COH$$

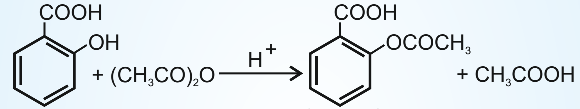
Acidity of phenols : Phenols are more acidic than alcohol because conjugate base of phenol (phenoxide ion) is resonance stabilised.



(ii) Esterification :

$$Ar/R{-}O{-}H + R'COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

Ester



Salicylic acid

(Aspirin)

(b) Reactions involving cleavage of C-O bond in alcohols

(i) Reaction with hydrogen halides : (Lucas test)

$ROH + HX \rightarrow R{-}X + H_2O$

- Lucas reagent (Conc. HCl and $ZnCl_2$)
- Tertiary alcohol produce turbidity with Lucas reagent immediately
- Primary alcohols do not produce turbidity at room temperature.

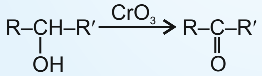
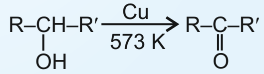
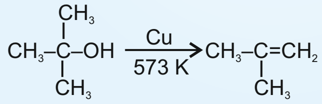
(ii) Reaction with phosphorus trihalides :

$3R{-}OH + PX_3 \rightarrow 3R{-}X + H_3PO_3$ (X = Cl, Br)

(iii) Dehydration : $C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$

Relative ease of dehydration : Tertiary > Secondary > Primary

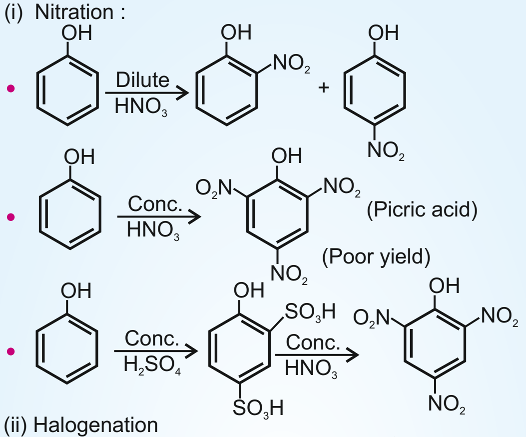
(iv) Oxidation

- $RCH_2OH \xrightarrow{CrO_3} RCHO$
- $CH_3{-}CH{=}CH{-}CH_2OH \xrightarrow{PCC} CH_3{-}CH{=}CH{-}CHO$
- 
  $R{-}\underset{OH}{\underset{|}{CH}}{-}R' \xrightarrow{CrO_3} R{-}\underset{O}{\underset{\|}{C}}{-}R'$
- $RCH_2OH \xrightarrow[573\ K]{Cu} RCHO$
- 
  $R{-}\underset{OH}{\underset{|}{CH}}{-}R' \xrightarrow[573\ K]{Cu} R{-}\underset{O}{\underset{\|}{C}}{-}R'$
- 
  $CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}OH \xrightarrow[573\ K]{Cu} CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$

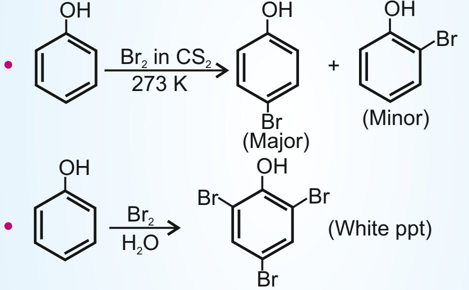
[B] Reaction of phenols :

(a) Electrophilic aromatic substitution

(i) Nitration :

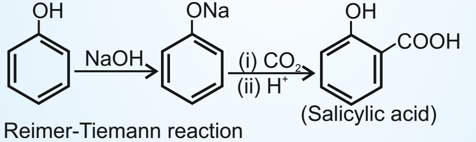


(ii) Halogenation

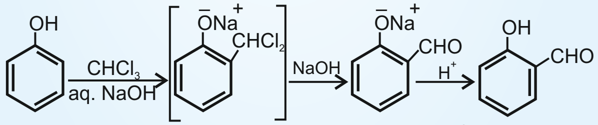


2, 4, 6-Tribromophenol

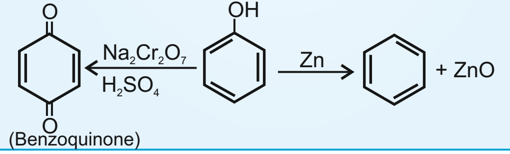
(b) Kolbe's reaction :



(c) Reimer-Tiemann reaction



(d) Reaction with Zinc dust and chromic acid



⑤ PREPARATION OF COMMERCIALLY IMPORTANT ALCOHOLS

Methanol : $CO + 2H_2 \xrightarrow[\text{200-300 atm, 573-673 K}]{ZnO-Cr_2O_3} CH_3OH$

Ethanol : $C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

- Ethanol is made unfit for drinking by mixing in it some copper sulphate and pyridine. It is known as denaturation of alcohol.

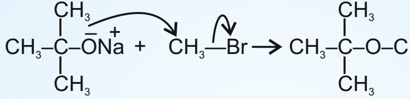
⑥ ETHERS

Preparation of ethers

(a) Dehydration of alcohols : $CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$

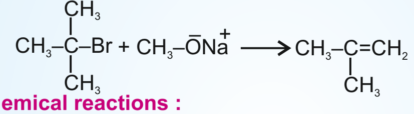
(b) Williamson synthesis : $R–X + R'–\bar{O}\overset{+}{Na} \xrightarrow{S_N2} R–O–R' + NaX$

- Alkyl halide is primary
- Alkoxide ion can be primary, secondary or tertiary.



$$CH_3–\underset{CH_3}{\overset{CH_3}{C}}–\bar{O}\overset{+}{Na} + CH_3–Br \rightarrow CH_3–\underset{CH_3}{\overset{CH_3}{C}}–O–CH_3$$

- If tertiary alkyl halide is used, then only alkene is formed.



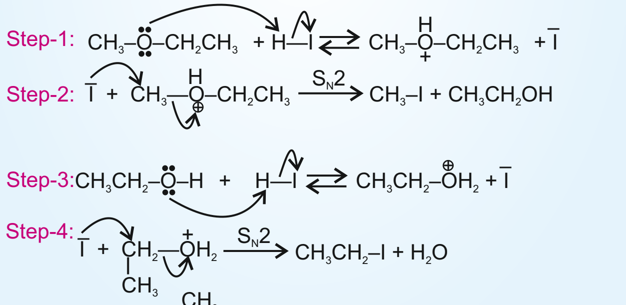
$$CH_3–\underset{CH_3}{\overset{CH_3}{C}}–Br + CH_3–\bar{O}\overset{+}{Na} \longrightarrow CH_3–\underset{CH_3}{C}=CH_2$$

Chemical reactions :

(i) Cleavage of C–O bond in ether : R–O–R + HX → RX + R–OH

- The order of reactivity of halogen halides HI > HBr > HCl
- Cleavage of ether takes place with concentrated HI or HBr at high temperature.

Example 1 : $CH_3–O–C_2H_5 \xrightarrow[HI]{\text{Excess}} CH_3–I + C_2H_5–I$

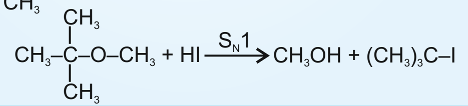


Step-1: $CH_3–\ddot{\underset{\bullet\bullet}{O}}–CH_2CH_3 + H–I \rightleftharpoons CH_3–\underset{+}{\overset{H}{O}}–CH_2CH_3 + \bar{I}$

Step-2: $\bar{I} + CH_3–\underset{\oplus}{\overset{H}{O}}–CH_2CH_3 \xrightarrow{S_N2} CH_3–I + CH_3CH_2OH$

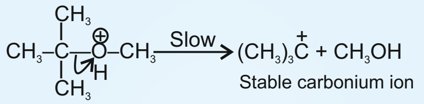
Step-3: $CH_3CH_2–\ddot{\underset{\bullet\bullet}{O}}–H + H–I \rightleftharpoons CH_3CH_2–\overset{\oplus}{O}H_2 + \bar{I}$

Step-4: $\bar{I} + \underset{CH_3}{CH_2}–\overset{+}{O}H_2 \xrightarrow{S_N2} CH_3CH_2–I + H_2O$



Example 2 : $CH_3–\underset{CH_3}{\overset{CH_3}{C}}–O–CH_3 + HI \xrightarrow{S_N1} CH_3OH + (CH_3)_3C–I$

Mechanism :

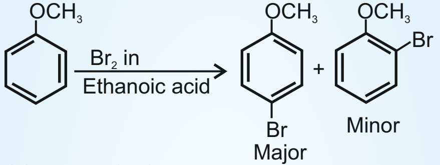


$$CH_3–\underset{CH_3}{\overset{CH_3}{C}}–\overset{\oplus}{\underset{H}{O}}–CH_3 \xrightarrow{\text{Slow}} (CH_3)_3\overset{+}{C} + CH_3OH$$

$(CH_3)_3\overset{+}{C} + I^- \xrightarrow{\text{Fast}} (CH_3)_3C – I$

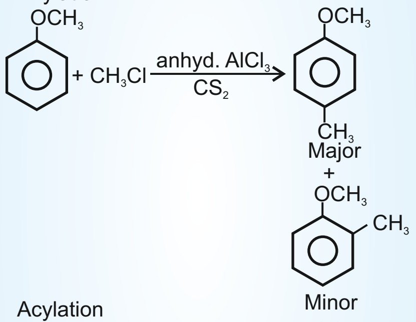
(ii) **Electrophilic substitution**

(a) Halogenation

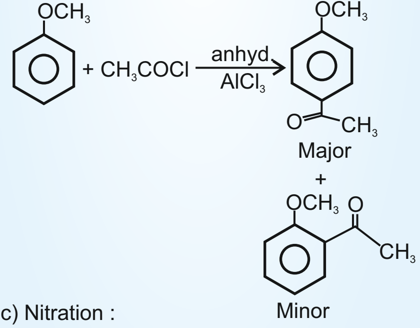


(b) Friedel-Crafts reaction :

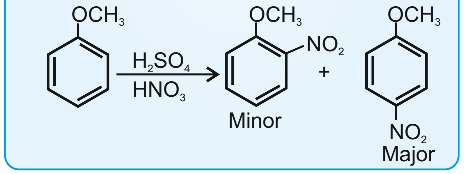
- Alkylation



- Acylation



(c) Nitration :



Aldehydes, Ketones and Carboxylic Acids

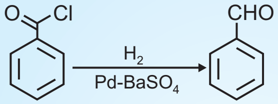
12

Chapter

ALDEHYDES AND KETONES

① PREPARATION OF ALDEHYDES

(i) From acyl chlorides (Rosenmund reduction)

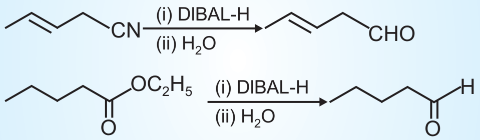


(ii) From Nitriles and Esters

- Stephen reaction

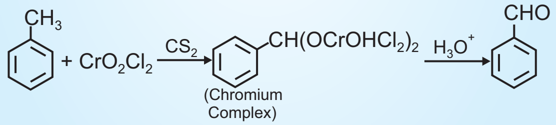
$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

(Reduction by DIBAL-H

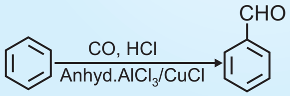


(iii) From Hydrocarbons

- Etard reaction



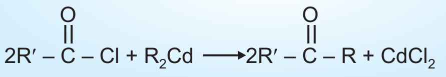
- Gatterman-Koch reaction



② PREPARATION OF KETONES

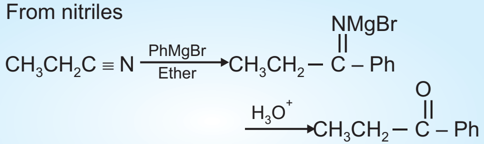
(i) From acyl chlorides

$$2R - Mg - X + CdCl_2 \longrightarrow R_2Cd + 2\ Mg(X)Cl$$



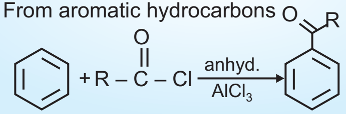
$$2R' - \overset{O}{\overset{\|}{C}} - Cl + R_2Cd \longrightarrow 2R' - \overset{O}{\overset{\|}{C}} - R + CdCl_2$$

(ii) From nitriles



$$CH_3CH_2C \equiv N \xrightarrow[\text{Ether}]{PhMgBr} CH_3CH_2 - \overset{NMgBr}{\overset{\|}{C}} - Ph \xrightarrow{H_3O^+} CH_3CH_2 - \overset{O}{\overset{\|}{C}} - Ph$$

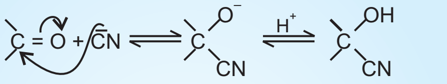
(iii) From aromatic hydrocarbons



③ CHEMICAL REACTIONS

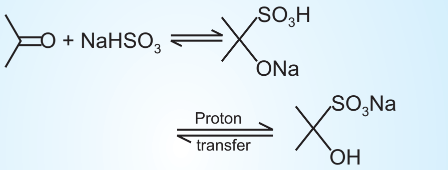
(i) **Nucleophilic addition reactions**

(a) Addition of hydrogen cyanide (HCN)



Cyanohydrin

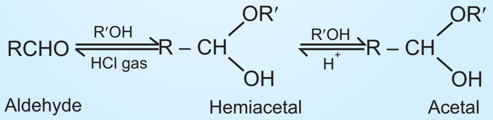
(b) Addition of $NaHSO_3$

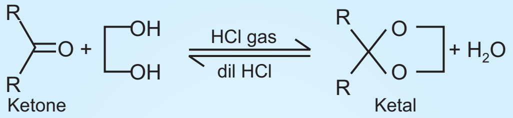


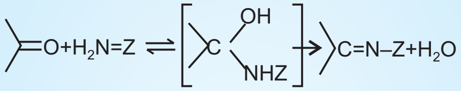
(Crystalline)

- Bisulphite addition product is crystalline
- It is water soluble and converted back to original carbonyl compound by treating it with acid or alkali
- It is useful for separation and purification of aldehydes.

(c) Addition of alcohols :

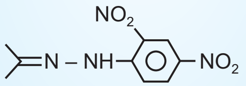






(d) Addition of ammonia and its derivative

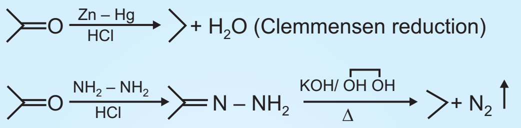
Z = alkyl, aryl, – OH, – NH_2, C_6H_5NH etc

Reagent	**Carbonyl derivative**	**Product name**
Ammonia	$>\!=NH$	Imine
Amine	$>\!=NR$	Schiff's base
Hydroxylamine	$>\!=N-OH$	Oxime
Hydrazine	$>\!=N-NH_2$	Hydrazone
2,4-DNP		2, 4- Dinitrophenyl-hydrazone
Semicarbazide	$>\!=N{-}NH-\overset{O}{\overset{\|}{C}}{-}NH_2$	Semicarbazone

(ii) Reduction

(a) Reduction to alcohols : Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$

(b) Reduction to hydrocarbons



(Wolff-Kishner reduction)

(iii) Oxidation

- Aldehydes are oxidised to carboxylic acids on treatment with common oxidising agents like HNO_3, $KMnO_4$, $K_2Cr_2O_7$ etc.
- Mild oxidising agents (Tests of aldehydes) **Tollen's test :** Silver mirror is formed on warming aldehyde with freshly prepared ammoniacal $AgNO_3$ solution (*Tollen's reagent*)

$RCHO + 2\,[Ag(NH_3)_2]^+ + 3\bar{O}H \rightarrow RCOO^- + 2Ag$

$2H_2O + 4NH_3$

Fehling's Test :

- On heating aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

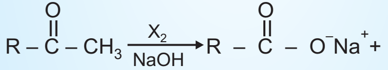
$R - CHO + 2Cu^{2+} + 5\bar{O}H \rightarrow RCOO^- + Cu_2O \downarrow + 3H_2O$

(red-brown ppt)

- Aromatic aldehydes do not respond to this test

Haloform reaction :

Oxidation of methyl ketones



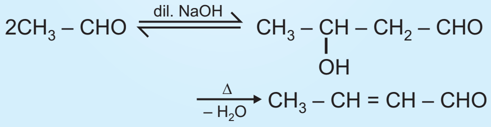
$R - \overset{O}{\overset{||}{C}} - CH_3 \xrightarrow[NaOH]{X_2} R - \overset{O}{\overset{||}{C}} - O^-Na^+ +$

$CHX_3 (X = Cl, Br, I)$

- Iodoform reaction with $I_2/NaOH$ is used for detection of CH_3CO or $CH_3CH(OH)$ groups which produces CH_3CHO group on oxidation.

(iv) Reaction due to α-hydrogen

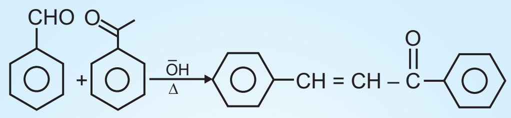
(i) Aldol condensation reaction :



$2CH_3 - CHO \underset{}{\overset{dil.\ NaOH}{\rightleftharpoons}} CH_3 - \underset{OH}{\underset{|}{CH}} - CH_2 - CHO$

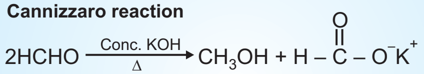
$\xrightarrow[-H_2O]{\Delta} CH_3 - CH = CH - CHO$

(ii) Cross aldol condenstation

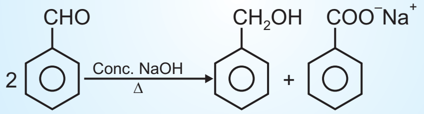


Other reactions

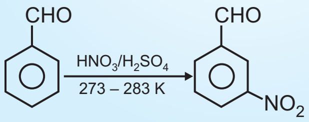
(v) Cannizzaro reaction



$2HCHO \xrightarrow[\Delta]{Conc.\ KOH} CH_3OH + H - \overset{O}{\overset{||}{C}} - O^-K^+$



(vi) Electrophilic substitution reaction



④ CARBOXYLIC ACIDS

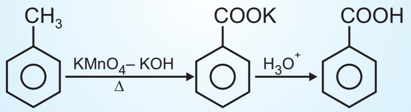
- Methods of Preparation

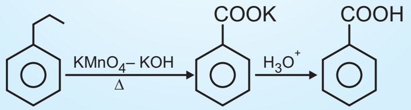
(a) From primary alcohols

$RCH_2OH \xrightarrow[(ii)\ H_3O^+]{(i)\ alkaline\ KMnO_4} RCOOH$

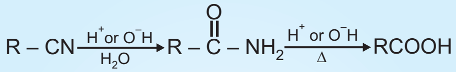
$CH_3(CH_2)_8CH_2OH \xrightarrow[Jones\ reagent]{CrO_3 - H_2SO_4} CH_3(CH_2)_8COOH$

(b) From alkylbenzenes

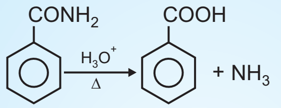




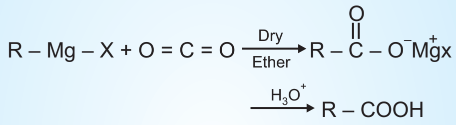
(c) From nitriles and amides



$R - CN \xrightarrow[H_2O]{H^+ or\ O^-H} R - \overset{O}{\overset{||}{C}} - NH_2 \xrightarrow[\Delta]{H^+ or\ O^-H} RCOOH$



(d) From Grignard reagents



$R - Mg - X + O = C = O \xrightarrow[Ether]{Dry} R - \overset{O}{\overset{||}{C}} - O^-\overset{+}{M}gx$

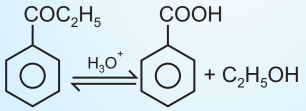
$\xrightarrow{H_3O^+} R - COOH$

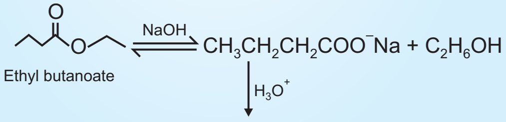
(e) From acyl halides and anhydrides

$RCOCl \xrightarrow{H_2O} R - COOH + Cl^-$

$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6O_5COOH$

(f) From esters





Butanoic acid

⑤ PHYSICAL PROPERTIES

- Due to extensive association by intermolecular H-bonding carboxylic acids have higher boiling point than aldehydes, ketones and alcohols of comparable molecular mass.
- In vapour phase or in aprotic solvent most carboxylic acids exist as dimer

⑥ CHEMICAL REACTIONS

(a) Reactions involving cleavage of O – H bond (Acidity)

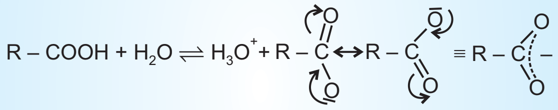
$2RCOOH + 2Na \rightarrow 2RCOO^-Na^+ + H_2$

$RCOOH + NaOH \rightarrow RCOO^-Na^+ + H_2O$

$RCOOH + NaHCO_3 \rightarrow RCOO^-Na^+ + H_2O + CO_2\uparrow$

- Carboxylic acids evolve CO_2 gas on reaction with $NaHCO_3$. This is used to detect the presence of carboxyl group in an organic compound.

  Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion



- Effect of substituents on the acidity of carboxylic acids :

EWG ← Electron withdrawing group (EWG) stabilises carboxylate anion and increases acidic stength

EDG ← Electron donating group (EDG) destablises the carboxylate anion and decreases acidic strength

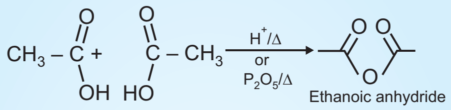
- Acidic strength order of some carboxylic acid

  $CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$

  Direct attachment of groups such as phenyl or vinyl to the carboxylic acid increases the acidity of corresponding carboxylic acid, Contrary to the decrease expected due to resonance effect.

(b) Reaction involving cleavage of C – OH bond

(i) Formation of anhydrides



(ii) Esterification

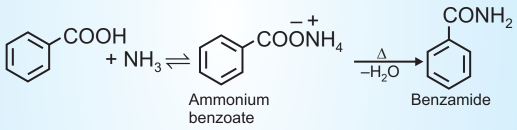
$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$

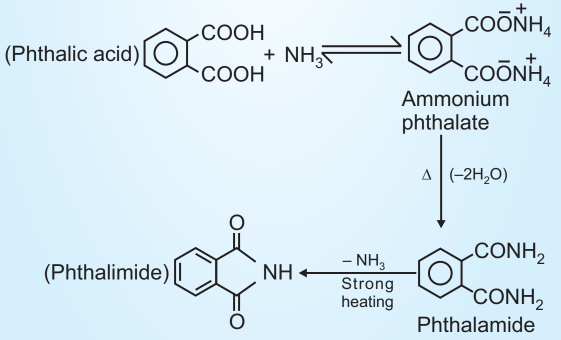
(iii) Reaction with PCl_5, and $SOCl_2$

$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

(iv) Reaction with ammonia





(c) Reactions involving – COOH group

(i) Reduction

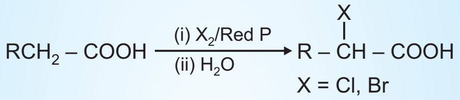
$RCOOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/ether\ or\ B_2H_6} RCH_2OH$

(ii) Decarboxylation

$RCOONa \xrightarrow[\Delta]{NaOH\ \&\ CaO} R - H + Na_2CO_3$

(d) Substitution reactions in the hydrocarbon part

(i) Halogenation (Hell - Volhard-Zelinsky reaction)

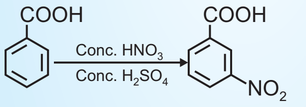


$RCH_2 - COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/Red\ P} R - \overset{X}{CH} - COOH$

X = Cl, Br

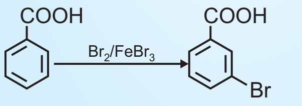
(ii) Ring substitution

- Aromatic carboxylic acids undergo electrophilic substitution reaction
- They do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and catalyst aluminum chloride gets bonded to carboxyl group
- Nitration



m-nirtobenzoic acid

- Bromination

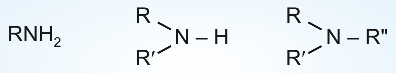


m-bromobenzoic acid

Amines

13
Chapter

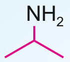
① CLASSIFICATION



Primary (1°) Secondary (2°) Tertiary (3°)

- Amines are said to be simple when all the alkyl groups are same and mixed when they are different.

② NOMENCLATURE

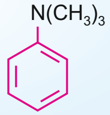


Propan-2-amine

$CH_3 – NH – CH_2CH_3$

N-methylethanamine

Propan-2-en-1-amine



N,N-Dimethylbenzenamine

③ PREPARATION OF AMINES

(i) Reduction of nitro compounds

a. $PhNO_2 \xrightarrow[\text{Ethanol}]{H_2/Pd} PhNH_2$

b. $PhNO_2 \xrightarrow[\text{or Fe + HCl}]{\text{Sn/HCl}} PhNH_2$

(ii) Ammonolysis of Alkyl Halides

$$\ddot{N}H_3 + R – X \longrightarrow R\overset{+}{N}H_3X \xrightarrow{NaOH} RNH_2$$

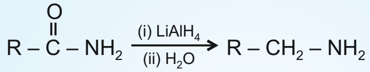
$$\underset{(1°)}{RNH_2} \xrightarrow{RX} \underset{(2°)}{R_2NH} \xrightarrow{RX} \underset{(3°)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}X}$$

- Ammonolysis has disadvantage of yielding a mixture of primary, secondary, tertiary amines and also quaternary ammonium salt
- Primary amine is obtained as major product by taking large excess of NH_3.

(iii) Reduction of Nitrites

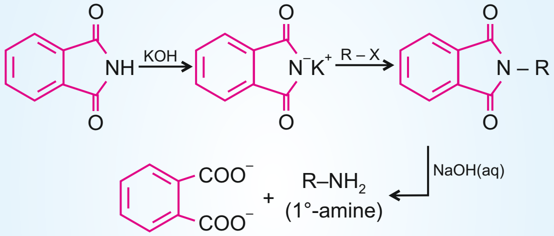
$$R–CN \xrightarrow[\text{or } H_2/Ni \text{ or } Na(Hg)/C_2H_5OH]{LiAlH_4} R–CH_2–NH_2$$

(iv) Reduction of amides



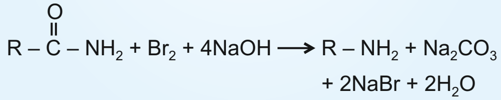
$$R – \overset{\overset{\large O}{||}}{C} – NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R – CH_2 – NH_2$$

(v) Gabriel phthalimide Synthesis



- This method is useful in the preparation of aliphatic primary amine
- Aromatic primary amine  is not prepared by this method because arylhalide donot undergo nucleophilic substitution reaction.

(vi) Hoffmann bromamide degradation reaction



$$R – \overset{\overset{\large O}{||}}{C} – NH_2 + Br_2 + 4NaOH \longrightarrow R – NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

- Primary amine formed contains one carbon less than that present in the amide.

④ PHYSICAL PROPERTIES

- Aniline and other arylamines are usually colourless but get colour on storage due to atmospheric oxidation
- Lower aliphatic amines are soluble in water because they form hydrogen bonds with water molecules.
- Order of boiling points of isomeric amines: Primary > Secondary > Tertiary

⑤ CHEMICAL REACTIONS

(i) Basic character of amines

- Order of bascity of amines in gaseous phase:

  tertiary amine > secondary amine > primary amine > NH_3
- Basic nature of amines in aqueous medium:

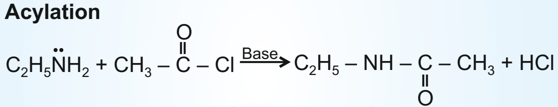
  (a) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

  (b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- Aryl amines are less basic than alkylamines because in arylamine the lone pair on nitrogen is involved in resonance.

(ii) Alkylation

$$R – NH_2 + CH_3 – Br \longrightarrow RNH – CH_3 + HBr$$

(iii) Acylation



$$C_2H_5\ddot{N}H_2 + CH_3 – \overset{\overset{\large O}{||}}{C} – Cl \xrightarrow{Base} C_2H_5 – NH – \underset{\underset{\large O}{||}}{C} – CH_3 + HCl$$

(iv) Carbylamine reaction (chemical test)

$$R – NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R – NC + 3KCl + 3H_2O$$

It is used as a test for primary amines

(v) Reaction with nitrous acid (With primary aliphatic amine)

$$R – NH_2 + HNO_2 \xrightarrow[HCl]{NaNO_2} [R – \overset{\oplus}{N}_2Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$$

(vi) Reaction with arylsulphonyl chloride (Hinsberg's reagent)

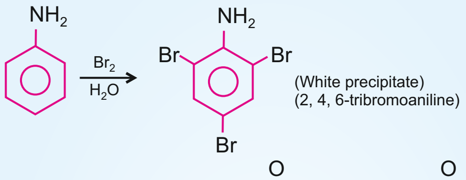
- Reaction with primary amine

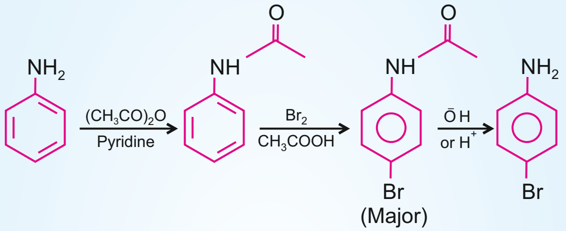
  $PhSO_2Cl + C_2H_5\ddot{N}H_2 \longrightarrow \underset{\text{(Soluble in alkali)}}{PhSO_2NHC_2H_5}$
- Reaction with secondary amine

  $PhSO_2Cl + (C_2H_5)_2\ddot{N}H \longrightarrow \underset{\text{(insoluble in alkali)}}{PhSO_2N(C_2H_5)_2}$
- Tertiary amines do not react with benzensulphonyl chlorides.

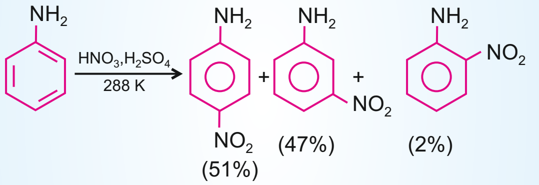
(vii) Electrophilic substitution reaction:

(a) Bromination

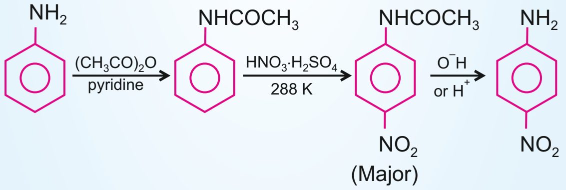




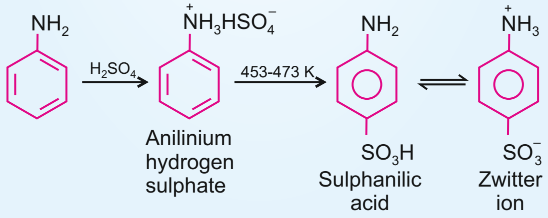
(b) Nitration



- Controlled nitration reaction

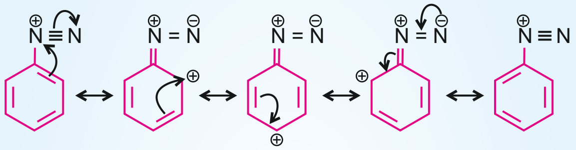


(c) Sulphonation



⑥ DIAZONIUM SALTS

- Primary aliphatic amines form highly unstable alkyldiazonium salts.
- Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperature (273-278 K) due to resonance



(i) Method of preparation of $C_6H_5\overset{\oplus}{N}_2\overset{\ominus}{Cl}$

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K} C_6H_5\overset{\oplus}{N}_2\overset{\ominus}{Cl}$$

(ii) Physical properties

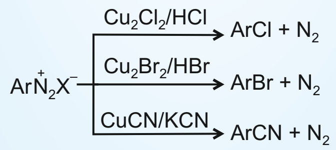
- Benzenediazonium chloride is colourless crystalline solid and readily soluble in water.
- It is stable in cold but reacts with water when warmed.
- Benzenediazonium Fluoroborate is water insoluble and stable at room temperature.

(iii) Chemical reactions

A. Reactions involving displacement of nitrogen

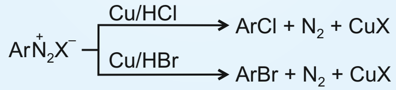
(a) Replacement by halide or cyanide ion

Sandmeyer reaction



$$Ar\overset{+}{N}_2X^- \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$$
$$Ar\overset{+}{N}_2X^- \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$$
$$Ar\overset{+}{N}_2X^- \xrightarrow{CuCN/KCN} ArCN + N_2$$

Gatterman reaction



$$Ar\overset{+}{N}_2X^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$$
$$Ar\overset{+}{N}_2X^- \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$$

(b) Replacement by iodide ion

$$Ar\overset{+}{N}_2Cl^- + KI \rightarrow ArI + KCl + N_2$$

(c) Replacement by fluoride ion

$$Ar\overset{+}{N}_2Cl^- + HBF_4 \rightarrow Ar\overset{+}{N}_2BF_4^- \xrightarrow{\Delta} Ar-F + BF_3 + N_2$$

(d) Replacement by Hydrogen

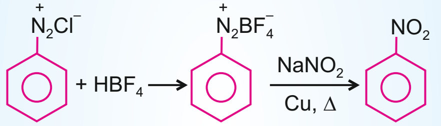
$$Ar\overset{+}{N}_2Cl^- + H_3PO_2 + H_2O \rightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N}_2Cl^- + CH_3CH_2OH \rightarrow ArH + N_2 + CH_3CHO + HCl$$

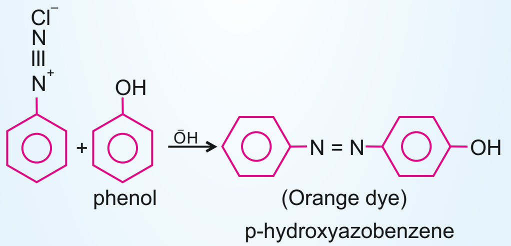
(e) Replacement by hydroxyl group

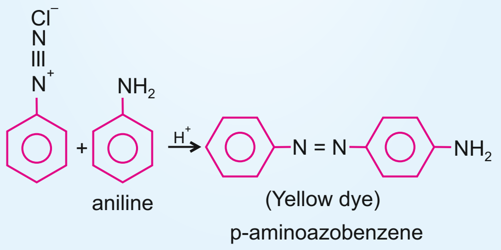
$$Ar\overset{+}{N}_2Cl^- + H_2O \xrightarrow{283\ K} ArOH + N_2 + HCl$$

(f) Replacement by $-NO_2$ group



B. Reactions involving retenation of diazo group (Coupling reaction)





Biomolecules

14
Chapter

① CARBOHYDRATES

Classification of Carbohydrates:

A. Monosaccharides: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. Examples: Glucose, fructose, arabinose etc.

B. Oligosaccharides: These carbohydrates yield two to ten monosaccharide units on hydrolysis. They are further classified as disaccharides, trisaccharides etc.

C. Polysaccharides: They yield a large number of monosaccharide units on hydrolysis.

Example : Starch, Cellulose etc.

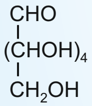
Monosaccharides:

- If a monosaccharide contains an aldehyde group, it is known as an aldose and if contains a keto group, it is called ketose

(a) Glucose: It is an aldohexose

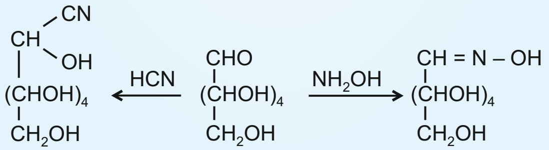
Structure of glucose

Glucose has been assigned the structure



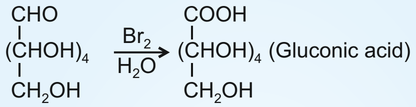
$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$ on the basis of following evidences:

- Its molecular formula is found to be $C_6H_{12}O_6$.
- On prolonged heating with HI, it forms n-hexane, suggesting carbons are linked in straight chain.
- Presence of carbonyl group is confirmed by the following reactions.



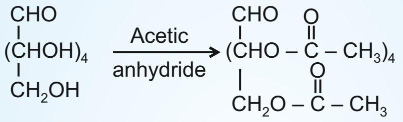
$\begin{array}{l}CH\begin{array}{l}\diagup CN\\ \diagdown OH\end{array}\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xleftarrow{HCN} \begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{NH_2OH} \begin{array}{l}CH = N - OH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$

- Carbonyl group present is an **aldehyde** is confirmed by the given reaction



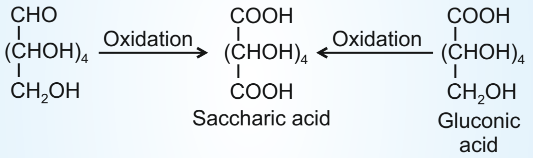
$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow[H_2O]{Br_2} \begin{array}{l}COOH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$ (Gluconic acid)

- Acetylation of glucose gives glucose pentaacetate which confirms presence of five OH groups



$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow[\text{anhydride}]{\text{Acetic}} \begin{array}{l}CHO\\ |\\ (CHO - \overset{O}{\overset{||}{C}} - CH_3)_4\\ |\\ CH_2O - \overset{O}{\overset{||}{C}} - CH_3\end{array}$

- Glucose and gluconic acid is oxidised to saccharic acid by nitric acid. This indicates presence of primary –OH group

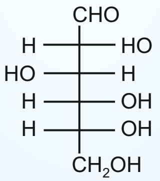


$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{\text{Oxidation}} \begin{array}{l}COOH\\ |\\ (CHOH)_4\\ |\\ COOH\end{array} \xleftarrow{\text{Oxidation}} \begin{array}{l}COOH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$

Saccharic acid

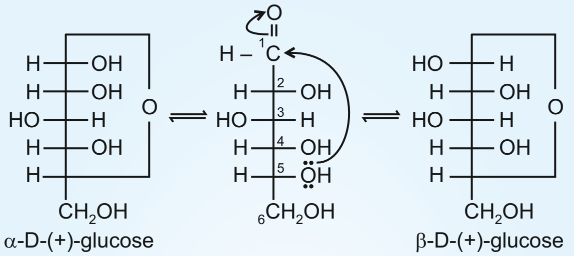
Gluconic acid

- Fischer suggested following configuration of D(+) glucose



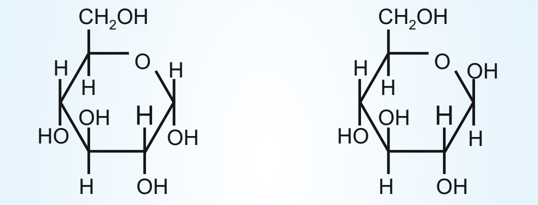
Cyclic Structure of Glucose

- The given observations could not explain chain structure of glucose
  (i) It does not react with $NaHSO_3$ or Schiff's reagent
  (ii) Pentaacetate of glucose does not react with NH_2OH.
  (iii) Glucose exist in two different crystalline forms, α and β forms.



α-D-(+)-glucose β-D-(+)-glucose

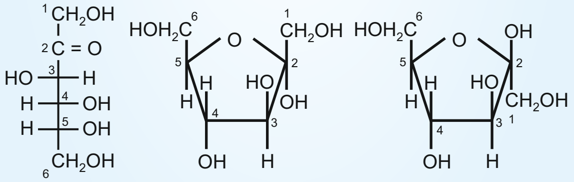
- α and β forms of glucose are called anomers. Six membered cyclic structure of glucose is called pyranose structure



α-D-(+) -Glucopyranose β-D-(+) -Glucopyranose

(b) Fructose

- Fructose is a ketohexose
- Following structures have been assigned to this molecule



D-(–)-fructose α-D-(–)-Fructofuranose β-D-(–)-Fructofuranose

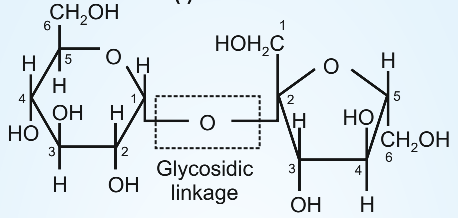
Tests of Glucose and Fructose

Both glucose and fructose reduce Tollen's reagent and Fehling's solution. They are also called reducing sugars.

② DISACCHARIDES

- Two monosaccharides are joined together by an oxide linkage formed by loss of water molecule forming a disaccharide. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

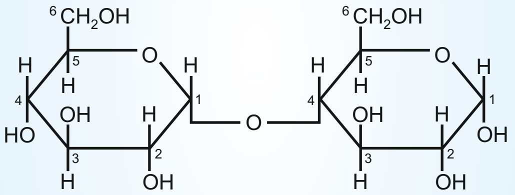
(i) Sucrose



α-D-glucose β-D-fructose

- It is dextrorotatory
- It is non reducing sugar

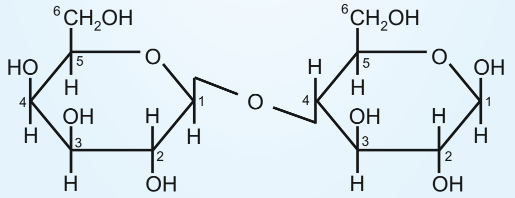
(ii) Maltose



α-D-glucose β-D-glucose

- It is dextrorotatory
- It is reducing sugar
- It gives positive test with Tollen's reagent and Fehling's solution

(iii) Lactose



α-D-galactose β-D-glucose

- It is dextrorotatory and is a reducing sugar
- It reduces Tollen's reagent and Fehling's solution

③ POLYSACCHARIDES

(i) Starch → Amylose (15-20% of starch)
→ Amylopectin (80-85% of starch)

- Amylose is water soluble component. It is long unbranched chain with 200-1000 α-D-(+) glucose units.
- Amylopectin is water insoluble component. It is branched chain polymer of α-D-glucose units.

(ii) Cellulose

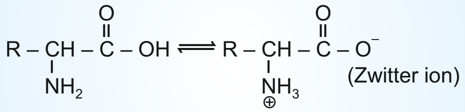
- It is a straight chain polysaccharide
- It is composed of β-D-glucose units

(iii) Glycogen

- It is called animal starch.
- Its structure is similar to amylopectin and is rather more highly branched.

④ PROTEINS

- All proteins are polymers of α-amino acid
- The amino acids which can be synthesised in the body, are known as non-essential amino acids.
- The amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids.
- In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion



$$R-\underset{NH_2}{CH}-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons R-\underset{\overset{\oplus}{NH_3}}{CH}-\overset{O}{\overset{\|}{C}}-O^- \quad \text{(Zwitter ion)}$$

Structure of Proteins

- Proteins can be classified into two types on the basis of their molecular shape

(a) Fibrous proteins:

- The polypeptide chains run parallel and held together by hydrogen and disulphides bonds giving fibre like structure
- They are insoluble in water e.g. keratin, myosin

(b) Globular proteins:

- In this case polypeptide chains coil around to give a spherical shape
- They are soluble in water e.g. insulin, globulin

⑤ VITAMINS

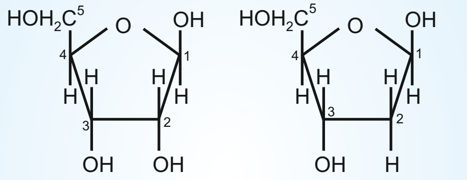
(i) Fat soluble vitamins: vitamins are soluble in fat. These are vitamins A, D, E and K.

(ii) Water soluble vitamins: B group vitamins and vitamin C are water soluble vitamins.

	Name of Vitamin	Deficiency Diseases
1.	Vitamin A	Xerophthalmia
2.	Vitamin B_1 (Thiamine)	Beri beri
3.	Vitamin B_2 (Riboflavin)	Cheilosis
4.	Vitamin B_{12}	Pernicious anaemia
5.	Vitamin C (Ascorbic acid)	Scurvy
6.	Vitamin D	Rickets (in children) osteomalacia (in adults)
7.	Vitamin K	Increased blood clotting time

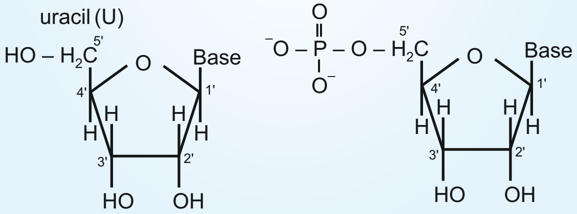
⑥ NUCLEIC ACIDS

- Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compound (called bases)
- In DNA molecule, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecules, it is β-D-ribose



β-D-ribose β-D-2-deoxyribose

- Bases in DNA: Adenine (A), guanine (G), Cytosine (C) and thymine (T)
- Bases in RNA: Adenine (A), guanine (G), cytosine (C) and uracil (U)



nucleoside nucleotide

Polymers

15

Chapter

① CLASSIFICATION OF POLYMERS

- **Classification based on source**
  - a. Natural polymers : These polymers are found in plants and animals. Examples are proteins, starch, rubber etc.
  - b. Semi-synthetic polymers : Cellulose derivatives as cellulose acetate and cellulose nitrate are semi-synthetic polymers.
  - c. Synthetic polymers : These are man made polymers examples are Buna-S, nylon 6,6, polythene etc.

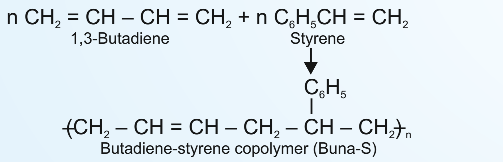
② TYPE OF POLYMERISATION REACTION

A. Addition polymerisation or chain growth polymerisation

- The molecules of the same monomer or different monomers add together on a large scale to form a polymer.
- Monomers used are unsaturated compounds, e.g. alkenes, alkadienes and their dirivatives
- Chain growth can take place through the formation of either free radicals or ionic species.
- The addition polymers formed by the polymerisation of a single monomeric species are known as **homopolymers**.

  Example : Polythene
- The polymers made by addition polymerisation from two different monomers are termed as **copolymers**.

  Example : Buna-S



$$n\,CH_2 = CH - CH = CH_2 + n\,C_6H_5CH = CH_2 \longrightarrow -\!\!\left(CH_2 - CH = CH - CH_2 - \underset{\displaystyle|}{\overset{C_6H_5}{CH}} - CH_2\right)\!\!-_n$$

1,3-Butadiene Styrene

Butadiene-styrene copolymer (Buna-S)

- **Preparation and uses** of important addition polymers

  i. **Polythene:** There are two types of polythene

  Low density polythene:
  - It is obtained by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in presence of a peroxide initiator.
  - It is obtained through free radical addition and H-atom abstraction.
  - It has highly branched structure.
  - They are chemically inert, tough but flexible and poor conductor of electricity

- **High density polythene:**

  $$nCH_2 = CH_2 \xrightarrow[(333\text{-}343)\ K\ (6\text{-}7)\ atm]{TiCl_4,(C_2H_5)_3Al} -\!\!\left(CH_2 - CH_2\right)\!\!-_n$$

  High density polythene
- Catalyst $TiCl_4$, $(C_2H_5)_3Al$ is called Ziegler-Natta catalyst
- The polymer obtained has high density due to close packing.
- These are also called linear polymers.
- It is also chemically inert, more tough and hard.

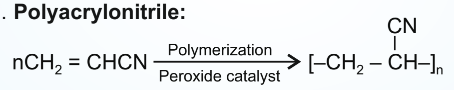
ii. **Polytetrafluoroethene** (Teflon)

$$nCF_2 = CF_2 \xrightarrow[\text{high pressure}]{\text{Catalyst}} \left[CF_2 - CF_2\right]_n$$

Teflon

Uses: It is used in making oil seals, gaskets and non-stick surface coated utensils.

iii. **Polyacrylonitrile:**



$$nCH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerization}} [-CH_2 - \overset{\displaystyle CN}{\overset{|}{CH}}-]_n$$

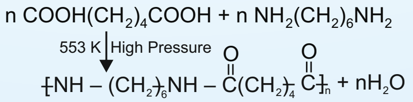
Uses: It is used as a substitute for wool in making commercial fibers as orlon or acrilan.

B. Condensation polymerisation or step growth polymerisation

- It generally involves a repetitive condensation reaction between two bi-functional or tri-functional monomeric units.
- This is also called step growth polymerisation.

  Preparation and uses of some polymers obtained by condensation polymerisation.

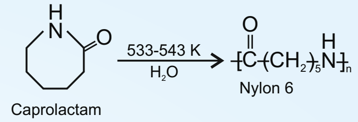
  i. **Polyamides:** These polymers possess amide linkages and are called nylons.
- **Nylon 6,6**:



$$n\,COOH(CH_2)_4COOH + n\,NH_2(CH_2)_6NH_2 \xrightarrow[\text{High Pressure}]{553\ K} \left[NH - (CH_2)_6NH - \overset{\displaystyle O}{\overset{\|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}\right]_n + nH_2O$$

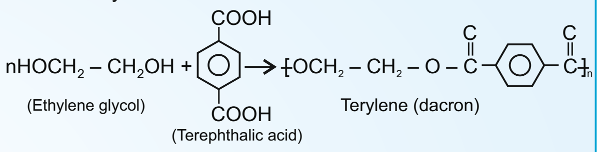
Uses: It is used in making sheets, bristles for brushes and in textile industry

- Nylon 6:



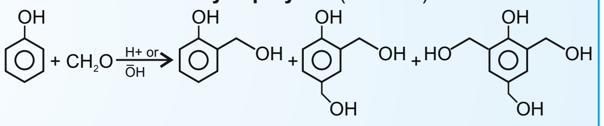
Use: It is used in manufacture of tyre cords, fabrics and ropes.

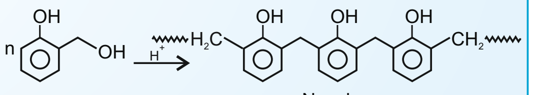
ii. **Polyesters:** These are condensation products of dicarboxylic acids and diols.



Use: It is used in blending with cotton and wool fibres.

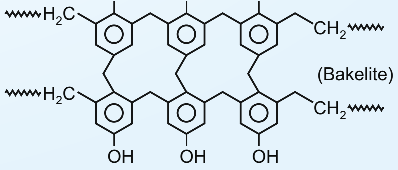
iii. **Phenol formaldehyde polymer** (Bakelite)





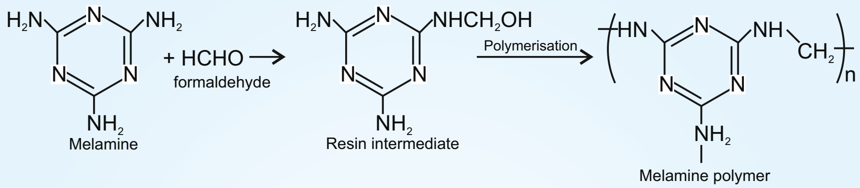
Novolac

- Novolac on heating with formaldehyde undergoes cross linking to form bakelite
- Bakelite is thermosetting polymer which can not be reused or remoulded



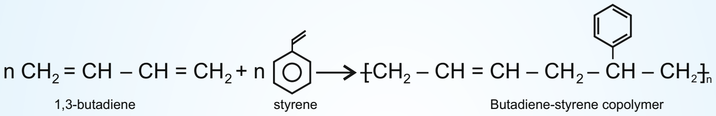
Uses: It is used for making combs, electrical switches and handles of various utensils.

iv. **Melamine-formaldehyde polymer**



Use: It is used in the manufacture of unbreakable crockery

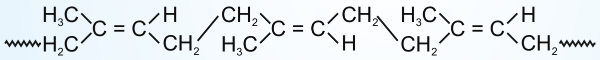
- **Copolymerization:**
  - Here a mixture of more than one monomeric species are allowed to polymerise and form a copolymer
  - The copolymer can be made both by chain growth and by step growth polymerisation.



Uses: It is used in manufacture of autotyres, floortiles, cable insulation etc.

- **Rubber** (Elastomer)

i. Natural rubber: It is a linear polymer of isoprene (2. methyl - 1, 3 - butadiene) and is also called as cis-1, 4- polyisoprene

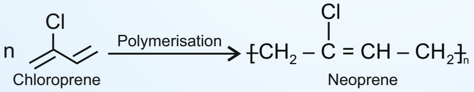


Vulcanisation of rubber: This process consists of heating a mixture of raw rubber with sulphur and appropriate additive at 273 K to 415 K.

- Sulphur forms cross links at the reactive sites of double bond.
- Due to valucanisation rubber gets stiffened

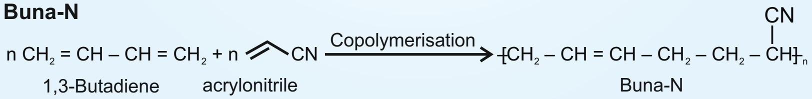
ii. **Synthetic rubbers**

- Neoprene



Uses: It is used for the manufacture of conveyor belts, gaskets and hoses.

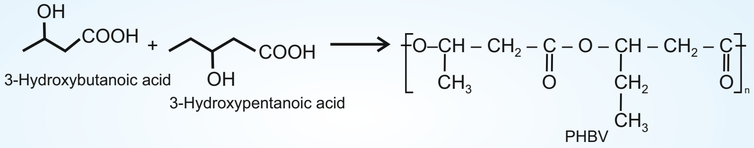
- **Buna-N**



Uses: It is used in making oil seals, tank lining etc.

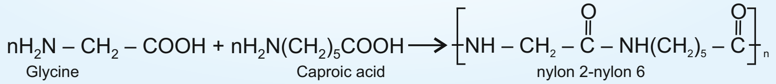
③ BIODEGRADABLE POLYMERS

- Poly β-hydroxybutyrate – co – β-hydroxy valerate (PHBV)



Uses: It is used in orthopaedic devices and in controlled release of drugs.

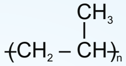
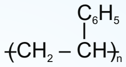
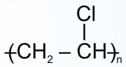
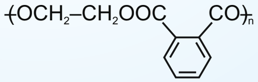
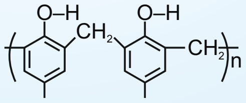
- Nylon 2-nylon 6



$$nH_2N - CH_2 - COOH + nH_2N(CH_2)_5COOH \longrightarrow \left[NH - CH_2 - \overset{O}{\overset{||}{C}} - NH(CH_2)_5 - \overset{O}{\overset{||}{C}} \right]_n$$

④ POLYMERS OF COMMERCIAL IMPORTANCE

- Some commercially important polymers along with their structures and uses are given below in table.

Name of polymer	Monomer	Structure	Uses
Polypropene	Propene	 $-\!(CH_2 - \overset{CH_3}{\overset{\vert}{C}H})_n\!-$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	 $-\!(CH_2 - \overset{C_6H_5}{\overset{\vert}{C}H})_n\!-$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	 $-\!(CH_2 - \overset{Cl}{\overset{\vert}{C}H})_n\!-$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$-\!(NH - CO - NH - CH_2)_n\!-$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid		Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde		For making combs, electrical switches, handles of utensils and computer discs.

Chemistry in Everyday Life

16

Chapter

① SOME IMPORTANT TERMS

- **Drugs :** Drugs are chemicals of low molecular masses (100-500u). These interact with macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these are called medicines.
- **Enzymes :** Proteins which perform the role of biological catalysts in the body are called enzymes.
- **Receptors :** Proteins which are crucial to communication system in the body are called receptors.
- **Enzyme inhibitors:** Drugs can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of enzyme. Such drugs are called enzyme inhibitors
- **Competitive inhibitors :** Drugs compete with natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.
- **Allosteric site :** Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site.
- **Chemical messengers :** In human body, message between two neurons and that between neurons to muscles is communicated through certain chemicals. These are called chemical messengers.
- **Antagonists :** Drugs that bind to the receptor site and inhibit its natural function are called antagonists.
- **Agonists :** Drugs that mimic the natural messenger by switching on the receptor are called agonists.

② THERAPEUTIC ACTION OF DIFFERENT CLASSES OF DRUGS

(i) Antacids :

- Over production of acid in the stomach causes irritation and pain
- Histamine stimulates the secretion of pepsin and HCl in the stomach
- Antacids prevent the interaction of histamine with receptors present in the stomach wall. This results in the release of lesser amount of acid.

Examples of antacids :

Cimetidine (Tegamet), ranitidine (Zantac)

(ii) **Antihistamines :**

- Histamine is a potent vasodilator
- Histamine is also responsible for the nasal congestion associated with common cold and allergic response to pollen
- Synthetic drugs, brompheniramine (Dimetapp) and terfenadine (Seldane), act as antihistamines

(iii) **Neuologically active drugs :**

Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

(a) **Tranquilizers :**

- These drugs are used for the treatment of stress, and mild or even severe mental diseases.
- These relieve anxiety, stress, irritability or excitement by inducing a sense of well being.
- They form an essential component of sleeping pills.
- **Examples are :** Iproniazid, phenelzine (Nardil), Meprobamate, Chlordiazepoxide, Equanil
- Derivatives of barbituric acids also constitute important class of tranquilizers. **Examples:** Veronal, amytal, nembutal, luminal and seconal

(b) **Analgesics :** These drugs reduce or abolish pain. These are of two types

(i) **Non-narcotic analgesics :** These drugs inhibit synthesis of prostaglandins which stimulate inflammation in the tissue and cause pain.
Examples: Aspirin and paracetamol

(ii) **Narcotic analgesics:**

- Morphine when administered in medicinal dose, relieve pain and produce sleep.

(iv) **Antimicrobials :**

- An antimicrobial destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria, fungi, virus, parasites selectively
- Antibiotics, antiseptics and disinfectants are antimicrobial drugs

(A) **Antibiotics :** Antibiotics are used as drugs to treat infections because of their low toxicity for humans and animals.

- Arsphenamine also known as salvarsan was used to treat syphilis caused by bacteria spirochete.
- Antibiotics are of two types :
  - (a) **Bactericidal :** These antibiotics have killing effect on microbes
    Examples: Penicillin, Aminoglycosides, Ofloxacin
  - (b) **Bacteriostatic :** These antibiotics have inhibitory effect on microbes.
    Examples : Erythromycin, Tetracycline, chloramphenicol
- Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be **broad spectrum antibiotics**.
  Examples: Ampicillin, Amoxycillin, Chloramphenicol, vancomycin, ofloxacin.
- Antibiotics effective mainly against Gram-positive or Gram-negative bacteria are **narrow spectrum antibiotics**.
  Example: Penicillin G

(B) **Antiseptics and disinfectants**

(a) **Antiseptics:** These are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
Examples: Furacine, soframicine

- Dettol is a mixture of chloroxylenol and terpineol.
- Bithional is added to soaps to impart antiseptic properties.
- 2-3 per cent solution in alcohol-water mixture is known tincture of iodine. It is applied on wounds.
- Boric acid in dilute aqueous solution is weak antiseptic for eyes.
- 0.2 per cent solution of phenol is an antiseptic.

(b) **Disinfectants :**

- These are applied to inanimate objects such as floors, drainage system, instruments etc.
- 1% solution of phenol is used as disinfectant
- Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and SO_2 in very low concentrations, are disinfectants.

(v) **Antifertility drugs :**

- Antifertility drugs are used to control birth in human beings.
- Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives.
- Norethindrone and novestrol are used as antifertility drugs.

③ CHEMICALS IN FOOD

(i) **Artificial sweetening agents :** Natural sweeteners, e.g., sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners.

	Artificial sweetener	Sweetness value in comparison to cane sugar
(a)	Aspartame	100
(b)	Saccharin	550
(c)	Sucralose	600
(d)	Alitame	2000

- Aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.
- Alitame is high potency sweetener. It is more stable than aspartame.
- Sucralose is trichloro derivative of sucrose. It is stable at cooking temperature.

(ii) **Food preservatives:**

- Food preservatives prevent spoilage of food due to microbial growth.

  Examples : Table salt, sugar, vegetable oils, C_6H_5COONa etc.

(iii) **Antioxidants in Food**

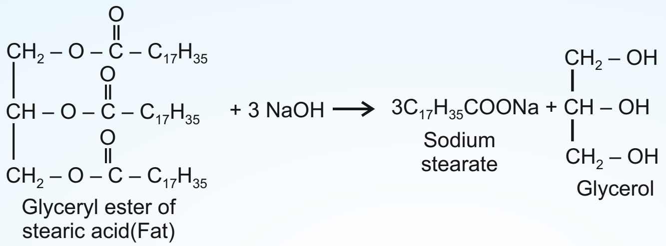
- These help in food preservation by retarding the action of oxygen on food.
- These are more reactive towards oxygen than food materials which they are protecting.
- Butylated hydroxytoluene (BHT) and butylated hydroxy anisole (BHA) are most familiar antioxidants.
- SO_2 and sulphite are useful antioxidants for wine and beer, sugar syrups and cut, peeled or dried fruits and vegetables.

④ CLEANSING AGENTS

Two types of detergents are used as cleansing agents.

(i) **Soaps :**

- Soaps are sodium or potassium salts of long chain fatty acids.
- Soaps containing sodium salts are formed by heating fat with aqueous NaOH. This reaction is called saponification



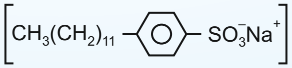
(ii) **Synthetic Detergents :** These are cleansing agents which have all the properties of soaps, but can be used both in soft and hard water.

- These are of three types

  (a) **Anionic detergents :** Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons.

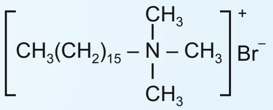
  Examples : Sodium laurylsulphate $(CH_3(CH_2)_{10}CH_2OSO_3^-Na^+)$,

  Sodium dodecylbenzene sulphonate



  (b) **Cationic detergents :** Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions.

  Example : Cetyltrimethyl ammonium bromide



$$\left[CH_3(CH_2)_{15}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_3\right]^+ Br^-$$

  (c) **Non-ionic detergents :** Non-ionic detergents do not contain any ion in their constitution.

  Examples : Detergent formed when stearic acid reacts with polyethylene glycol.

$$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethylene glycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH}$$

$$\Big\downarrow -H_2O$$

$$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

- Liquid dishwashing detergents are non-ionic type
- Detergents and soap remove grease and oil by micelle formation