

TOPPER SMART GUIRE-2013





Take the pathway to some high growth careers.



University of Petroleum & Energy Studies

Energy Acres, P.O. Bidholi, Via Prem Nagar, Dehradun - 248007.

ENROLLMENT OFFICES

Dehradun: Energy Acres, P.O. Bidholi, Via Prem Nagar, Dehradun-248007 Ph.: 0135-2102484/86, 2102549. Delhi: 1st Floor, 55 Community Centre, East of Kailash, New Delhi-110065. Ph.: 011-47173400.

Mumbai: A-345, 3rd Floor, Balaji Bhawan, Sector-11, CBD Belapur, Navi Mumbai-400614. Ph.: 022-67931912/13/14.

Ahmedabad: 206, 2nd Floor, President Plaza, Opp. Muktidham Derasar, Near Thaltej Cross Road, Ahmedabad-380054. Ph.: 079-40007933/34. Kolkata: 7K (Ground Floor- Part-A)

Cornfield Road, Ballygunj, Kolkata-700019. Ph.: 033-40075884/6.

Gear up for some path-breaking career opportunities with a new genre of undergraduate programs aimed at creating entry-level talent for India's Energy and Core Sector domains by stepping into University of Petroleum & Energy Studies.

•

Eligibility Criteria:

B.Tech.

- Applied Petroleum Engineering with specialization in Upstream
- Applied Petroleum Engineering with specialization in Gas Stream
- Chemical Engineering with specialization in Refining & Petrochemicals
- Geo Science Engineering
- Geo Informatics Engineering
- Aerospace Engineering
- Aerospace Engineering with specialization in Avionics
- Automotive Design Engineering
- **Electronics Engineering** •

*B.Tech. admissions through Board Merit/ AIEEE Merit Eligibility:

For Board Merit: Minimum 80% marks at Higher & Senior Secondary level (10th & 12th) and minimum 80% marks aggregate in PCM at Senior Secondary level (12th class) For AIEEE Merit: Minimum 60% marks at Higher & Senior Secondary level (10th & 12th), minimum 60% marks aggregate in PCM at Senior Secondary level (12th class) and AIEEE All India Rank upto 1 lakh.

Admission Criteria: Counseling through Merit Ranking.



- Oil & Gas Marketing
- **Aviation Operations**

Eligibility Criteria: Minimum 50% marks at Higher & Senior Secondary level (10th & 12th) Admission Criteria: Group Discussion & Interview

ech.+LLB

60% marks aggregate in PCM at Senior Secondary Level (12th)

Admission Criteria: UPES Engineering Aptitude Test (UPESEAT) followed by Centralized

Counseling/Board Merit*/ AIEEE Merit*/ CLAT Merit*/ LSAT-India Merit* admission based on Merit Ranking.

- B. Tech. Energy Technology + LLB with emphasis on Intellectual Property Rights
- B. Tech. Computer Science + LLB with emphasis on Cyber Laws

Computer Science Engineering

Material Science Engineering with

specialization in Nano Technology

Minimum 60% marks at Higher & Senior Secondary level (10th & 12th)
 Minimum 60% marks aggregate in PCM at Senior Secondary level (12th)

Admission Criteria: UPES Engineering Aptitude Test

100% Scholarship on Tuition Fee:

be as per the University policy.

Logistics Management

Auto Retailing

to 5% of seats in each B.Tech Program.

(UPESEAT) followed by Centralized counseling or Board Merit*/ AIEEE Merit* based on Merit Ranking.

1. Scholarship will be offered to students securing an

2. Scholarships will be given on the basis of Merit only. Continuation of Scholarship in the subsequent year will

aggregate of 85% marks in class XII & 90% marks in PCM for B.Tech (All Streams) in CBSE or ICSE Examination Board. Such Scholarships will be limited

Mechatronics Engineering

Power System Engineering

Infrastructure Engineering

Fire Safety Engineering

Eligibility Criteria: Minimum 60% marks at Higher & Senior Secondary Level (10th & 12th) and minimum

*Admissions through Board Merit / CLAT Merit/ LSAT Merit

CLAT Merit/ LSAT-India Merit: Candidates with minimum 60% Marks in Higher & Senior Secondary (10th & 12th), minimum 60% Marks in PCM at Senior Secondary Level (12th) and CLAT ranking upto 1500/ LSAT-India score of 60 percentile or above will be exempted from UL-SAT and admission will be process based on Merit Ranking. **Board Merit:** Candidates with minimum 80% marks in 10th, 12th and 12th PCM (Physics, Chemistry & Maths) are exempted from UL-SAT and admission process will be based on Merit Ranking.

AIEEE Merit: Minimum 60% marks at Higher & Senior Secondary level (10th & 12th), minimum 60% marks aggregate in PCM at Senior Secondary level (12th class) and AIEEE All India Rank upto 1 lakh and admission will be processed based on Merit Ranking



World-class Campus 4200 Students 42 Programs 212+ Faculty 2500 + Placements 350+ Recruiters

RECENT AWARDS & RECOGNITIONS

B-School Leadership Awards

B-School with Excellent Industry Interface Best Professor Teaching Marketing Management

Asia's Best B-School Awards

B School with Best Industry Interface Innovation Leadership Award

For application procedure and to apply online, Visit: www.upes.ac.in E-mail: enrollments@upes.ac.in or Call Toll Free: 1800-102-8737





Chapter : The Solid State

- Solid: Solid is a state of matter in which the constituting particles are arranged very closely. The constituent particles can be atoms, molecules or ions.
- 2. Properties of solids:
 - a. They have definite mass, volume and shape.
 - b. Intermolecular distances are short and hence the intermolecular forces are strong.
 - c. Their constituent particles have fixed positions and can only oscillate about their mean positions.
 - d. They are incompressible and rigid.
- 3. Classification of on the basis of the arrangement of constituent particles:
 - a. Crystalline solids: The arrangement of constituent particles is a regular orderly arrangement. Example: iron, copper, diamond, graphite
 - b. Amorphous solids: The arrangement of constituent particles is an irregular arrangement. Example: Glass, plastics, rubber
- 4. Properties of crystalline solids:
 - a. They have a definite characteristic geometrical shape
 - b. They have a long range order.
 - c. They have a sharp melting point.
 - d. They are anisotropic in nature i.e. their physical properties show different values when measured along different directions in the same crystal.
 - e. When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.
 - f. They have a definite and characteristic heat of fusion
 - g. They are called true solids
- 5. Polymorphic forms or polymorphs: The different crystalline forms of a substance are known as polymorphic forms or polymorphs. For example: graphite and diamond.







6. Types of crystalline solids:

	Type of Solid	Constitue nt Particles	Bonding/ Attractive Forces	Example s	Physical nature	Electrical conducti vity	Melting point
	Molecul ar solids	Molecules				Ô	
	1. Non polar		Dispersion or London forces	Ar, CCl ₄ , H ₂ , I ₂ , CO ₂	Soft	Insulator	Very low
	2. Polar		Dipole- dipole interaction s	HCl, solid SO ₂ , solid NH ₃	Soft	Insulator	Low
	3. Hydrog en bonded		Hydrogen bonding	H ₂ O (ice)	Hard	Insulator	Low
	Ionic solids	Ions	Coulombic or electrostat ic	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulator s in solid state but conducto rs in molten state and in aqueous solutions	High
	Metallic solids	Positive ions in a sea of delocalise d electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleabl e and ductile	Conducto rs in solid state as well as in molten state	Fairly high
h	Covale nt or networ k solids	Atoms	Covalent bonding	SiO ₂ (qu artz), SiC, C (diamon d), AIN	Hard	Insulator s	Very high







	C(graphi te)	Conducto r (exceptio n)	6
--	-----------------	----------------------------------	---

- 7. Characteristics of amorphous solids:
- a. They have an irregular shape.
- b. They have a short range order.
- c. They gradually soften over a range of temperature
- d. They are isotropic in nature i.e. their physical properties are the same in all directions.
- e. When cut with a sharp edged tool, they cut into two pieces with irregular surfaces.
- f. They do not have definite heat of fusion
- g. They are called pseudo solids or super cooled liquids. This is because they have a tendency to flow, though very slowly.
- 8. Crystal lattice: A regular ordered arrangement of constituent particles in three dimensions is called crystal lattice.
- Lattice points or lattice sites: The fixed positions on which the constituent particles are present are called lattice points or lattice sites. A group of lattice points which when repeated over and over again in 3 dimensions give the complete crystal lattice.
- 10. Unit cell: The unit cell is defined as the smallest repeating unit in space lattice which when repeated over and over again generates the complete crystal lattice. The crystal can consist of an infinite number of unit cells.
- 11. Parameters which characterize a unit cell:
 - a. Dimensions of the unit cell along the three edges, a, b and c: These edges may or may not be mutually perpendicular.
 - b. Inclination of the edges to each other: This is denoted by the angle between the edges α , β , and γ respectively. α is the angle between the edges b and c, β is the angle between the edges a and c, and γ is the angle between a and b.

12.Seven crystal systems:

- a. Cubic: $\alpha = \beta = \gamma = 90^{\circ}$, a = b = c
- b. Tetragonal: $\alpha = \beta = \gamma = 90^{\circ}$; $a = b \neq c$
- c. Orthorhombic: $\alpha = \beta = \gamma = 90^{\circ}$; $a \neq b \neq c$
- d. Monoclinic: $\alpha = \gamma = 90^{\circ}$, $\beta \neq 90^{\circ}$; $a \neq b \neq c$







- e. Hexagonal: $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$; $a = b \neq c$
- f. Rhombohedral or trigonal: $\alpha = \beta = \gamma \neq 90^{\circ}$; a = b = c
- g. Triclinic: $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$; $a \neq b \neq c$
- 13.Types of unit cells:
 - Primitive or simple unit cells have constituent particles only at its corners.
 - b. Centred unit cells are those unit cells in which one or more constituent particles are present at positions in addition to those present at the corners.

The centred unit cells are of three types:

- i. Face centred unit cell: A face centred unit cell consists of one constituent particle present at the centre of each face in addition to those present at the corners.
- ii. Body centred unit cell: A body centred unit cell consists of a one constituent particle is present at its body centre in addition to those present at the corners.
- iii. End centred unit cell: An end centred unit cells consists of one constituent particle present at the centre of any two opposite faces in addition to those present at the corners.
- 14.Number of particles at different lattice positions:
 - a. Corner: If an atom is present at any one corner, it is shared by eight unit cells. So, only one eighth of an atom actually belongs to the unit cell.
 - b. Face centre: If an atom is present at the centre of the face, it is shared by two unit cells. So, only half of the atom actually belongs to the unit cell.
 - c. Body centre: If an atom is present at the body centre, it is not shared by any other unit cell. So, that one atom completely belongs to the same unit cell.
 - d. End centre: If an atom is present at the edge centre, it is shared by four unit cells. So, only one fourth of an atom belongs to the unit cell.
- 15.Number of atoms in different unit cells:

a. Primitive unit cell: 1 atom

- b. Face centred unit cell: 4 atoms
- c. Body centred unit cell: 2 atoms

16.Coordination number is the number of nearest neighbours of a particle.







17.Close packed structures:

- a. Close packing in one dimension: Each sphere is in contact with two of its neighbours. Coordination number is two.
- b. Close packing in two dimensions: It is generated by stacking the rows of close packed spheres in two ways:
- i. Square close packing: When the spheres of the second row are placed exactly above those of the first row. This way the spheres are aligned horizontally as well as vertically. The arrangement is AAA type. Coordination number is 4.
- ii. Hexagonal close packing: When the spheres of the second row are placed above the first one in a staggered manner in such a way that its spheres fit in the depression of the first row. The arrangement is ABAB type. Coordination number is 6.
- c. Close packing in three dimensions: They can be obtained by stacking the two dimensional layers one above the other. It can be obtained in two ways:
- i. Three dimensional close packing from two dimensional square close packed layers: Here, The spheres of the upper layer are placed exactly over the first layer such the spheres of the layers are perfectly aligned horizontally and vertically. It has a AAAA.. type pattern. The lattice is simple cubic lattice.
- ii. Three dimensional close packing from two dimensional hexagonal close packed layers: There are two steps involved as:
 - i. Placing the second layer over the first layer: if a two dimensional layer is considered as A, the second layer which is placed above the first layer in such a way that the spheres of the second layer (considered as B) are placed in the depressions of the first layer. This gives rise to two types of voids: tetrahedral voids and octahedral voids.
 - ii. Placing the third layer over the third layer: There are two possibilities:
 - a. Covering the tetrahedral voids: Here, tetrahedral voids of the second layer may be covered by the spheres of the third layer. It gives rise to ABABAB... type pattern. The three dimensional structure is called hexagonal close packed structure. Coordination number is 12. Example: Mg, Zn
 - b. Covering the octahedral voids: Here, octahedral voids of the second layer may be covered by the spheres of the third layer. It gives rise to ABCABCABC... type pattern. The three dimensional structure is called cubic close packed structure or face centred cubic structure. Coordination number is12. Example: Cu, Ag



h





18. Types of voids:

- a. Tetrahedral voids: This type of void is formed at the centre when four spheres are joined in the form of a tetrahedron.
- b. Octahedral void: This type of void is surrounded by six spheres.
- 19.In hcp or ccp arrangement, octahedral and tetrahedral voids are present. The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids is twice the number of octahedral voids.

Example: If the number of close packed particles = nNumber of particles present in octahedral voids = nNumber of particles present in tetrahedral voids = 2n

20.Packing efficiency is the percentage of total space occupied by constituent particles (atoms, molecules or ions)

 $Packing efficiency = \frac{Volume \, occupied \, by \, spheres}{Total \, volume \, of \, unit \, cell} \times 100\%$

- a. Packing efficiency for face centred unit cell =74%
- b. Packing efficiency for body centred cubic unit cell =68%
- c. Packing efficiency for simple cubic unit cell =52.4%
- 21. Radius ratio in an octahedral void: For an atom to occupy an octahedral void, its radius must be 0.414 times the radius of the sphere.

 $\frac{r}{R} = 0.414$

22. Radius ratio for tetrahedral void: For an atom to occupy a tetrahedral void, its radius must be 0.225 times the radius of the sphere.



- 23.Density of a unit cell is same as the density of the substance.
- 24.Relationship between radius of constituent particle (r) and edge length(a):
 - a. Simple cubic unit cell: a= 2r
 - b. Face centred unit cell: $a = 2\sqrt{2} r$
 - c. Body centred unit cell: $a = \frac{4r}{\sqrt{3}}$





25.Volume of a unit cell = $(edge length)^3 = a^3$

- a. Simple cubic unit cell: Volume = $(2r)^3$
- b. Face centred unit cell: Volume = $(2\sqrt{2}r)^3$
- c. Body centred unit cell: Volume = $\left(\frac{4r}{\sqrt{3}}\right)^3$

26.Number of atoms in a unit cell (z):

- a. Simple cubic unit cell: z = 1
- b. Face centred unit cell: z = 4
- c. Body centred unit cell: z = 2
- 27.Density of unit cell:

Density of unit cell =
$$\frac{zM}{a^3.N_{\mu}}$$

- 28.Crystal defects are basically irregularities in the arrangement of constituent particles.
- 29.Defects are of two types:
 - a. Point defects Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.
 - b. Line defects Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.
- 30.Point defects are of three types:
 - a. Stoichiometric or intrinsic or thermodynamic defects: These are the point defects that do not disturb the stoichiometry of the solid.
 - b. Non stoichiometric defects: These are the point defects that disturb the stoichiometry of the solid.
 - c. Impurity defects: These are the defects in ionic solids due to the presence of impurities present in them.
- 31.Stoichiometric defects for non- ionic solids are of two types:

	/
Vacancy defect	Interstitial defect
A crystal is said to have vacancy defect when some of the lattice sites are vacant.	A crystal is said to have interstitial defect when some constituent particles (atoms or molecules) occupy an interstitial
This results in decrease in	This results in increase in
density of the substance.	density of the substance.







32. Stoichiometric defects for ionic solids are of two types:

Schottky defect	Frenkel or dislocation defect
In this defect equal number of	In this defect, the smaller ion
cations and anions are missing.	(usually cation) is dislocated from its normal site to an interstitial site.
It is basically a vacancy defect	It creates a vacancy defect at its
in ionic solids.	original site and an interstitial
	defect at its new location.
It decreases the density of a solid	It does not change the density of the solid
Schottky defect is shown by	Frenkel defect is shown by ionic
ionic substances in which the	substance in which there is a
cation and anion are of almost	large difference in the size of
similar sizes.	ions.
For example: NaCl, KCl, CsCl	For example: ZnS, AgCl, AgBr
and AgBr	and AgI

- 33. Non-stoichiometric defects are of two types:
 - a. Metal excess This type of defect is due to excess of metal cations. These may be due to:
 - i. Anionic vacancies: A compound may have an extra metal ion if the negative ion is absent from its lattice site. This empty lattice site is called a hole. To maintain electrical neutrality this site is occupied by an electron. The hole occupied by an electron is called f-centre or Farbenzenter centre . F- centre is responsible for the colour of the compound.
 - ii. Presence of extra cations: A compound is said to have extra cations if a cation is present in the interstitial site. An electron is present in the interstitial site to maintain the electrical neutrality.
 - b. Metal deficiency: This defect arises because of absence of metal ions from its lattice sites. The electrical neutrality is maintained by an adjacent ion having a higher positive charge.
- 34. Solids can also be classified into three types based on their electrical conductivities:
 - a. Conductors-The solids with conductivities ranging between 10^4 to $10^7 \ ohm^{-1}m^{-1}$ are called conductors.
 - b. Insulators These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm⁻¹m⁻¹.
 - a. Semi- conductors These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm⁻¹m⁻¹.







- 35. Band theory A metal is characterized by a band structure. The highest filled band is called valence band and the lowest unoccupied band is called conduction band. The gap between the two bands is called forbidden band.
- a. In case of conductors, the valence band and conduction band overlap
- b. In case of insulators, the forbidden gap is very large and the electrons are unable to excite to the conduction band.
- c. In case of semiconductors, forbidden gap is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.
- 36. Types of semiconductors:
- a. Intrinsic: These are those semiconductors in which the forbidden gap is small. Only some electrons may jump to conduction band and show some conductivity. They have very low electrical conductivity. Example: Silicon, germanium
- b. Extrinsic: When an appropriate impurity is added to an intrinsic semiconductor. Their electrical conductivity is high.
- 37.Doping: The process of adding an appropriate amount of suitable impurity to increase the conductivity of semiconductors.

n-type semiconductors	p -type semiconductors
)	
They are formed when silicon is	They are formed when silicon is
doped with electron rich impurity	doped with electron deficient
like group 15 elements.	impurity like group 13 elements.
The increase in conductivity is	The increase in conductivity is
due to the negatively charged	due to the positively charged
electrons.	holes.

38.Types of extrinsic semi conductors:

- **39.** Diode: It is a combination of n-type and p-type semiconductors and is used as a rectifier.
- 40.Transistors: They are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals.







- 41.12- 16 compounds These compounds are formed by the combination of group 12 and group 16 compounds. They possess an average valency of 4. Example: ZnS, CdS, CdSe and HgTe
- 42. 13- 15 compounds These compounds are formed by the combination of group 13 and group 15 compounds. They possess an average valency of 4. Example: InSb, AIP and GaAs
- 43. Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis.
- 44.On the basis of their magnetic properties, substances can be classified into five categories:
 - a. Paramagnetic: These are those substances which are weakly attracted by the magnetic field. It is due to presence of one or more unpaired electrons.
 - b. Diamagnetic: Diamagnetic substances are weakly repelled by a magnetic field. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons.
 - c. Ferromagnetic: These are those substances which are attracted very strongly by a magnetic field.
 - d. Antiferromagnetic: They have equal number of parallel and anti parallel magnetic dipoles resulting in a zero net dipole moment.
 - e. Ferrimagnetic: They have unequal number of parallel and anti parallel magnetic dipoles resulting in a net dipole moment.



WN.S.







 $i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$ $= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$ $= \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Total number of moles of particles before association/dissociation}}$ $14. \frac{p_1^{\circ} - p_1}{p_1^{\circ}} = i. \frac{n_2}{n_1}$ $15. \qquad \Delta T_b = i. \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$

16.
$$\Delta T_{f} = i \cdot \frac{K_{f} \times 1000 \times W_{2}}{M_{2} \times W_{1}}$$

17.
$$\pi = i \cdot \frac{n_2 RT}{V}$$

Key Learnings

- **1.** Solutions are the homogeneous mixtures of two or more than two components.
- **2.** Binary solution: A solution having two components is called a binary solution. Components of a binary solution are solute and solvent.
 - a. When the solvent is in solid state, solution is called solid solution.
 - b. When the solvent is in liquid state, solution is called liquid solution.
 - c. When the solvent is in gaseous state, solution is called gaseous solution.
- **3.** Concentration is the amount of solute in given amount of solution.
- **4.** Mass by volume percentage (w/v): Mass of the solute dissolved in 100 mL of solution.
- 5. Molality (m) is the number of moles of solute present in 1kg of solvent.
- **6.** Molarity (M) is the number of moles of solute present in 1L of solution.
- **7.** Normality is the number of gram equivalent of solute dissolved per litre of solution.
- **8.** Solubility is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- **9.** A solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.
- **10.** In a nearly saturated solution if dissolution process is an endothermic process, solubility increases with increase in temperature.
- **11.** In a nearly saturated solution if dissolution process is an exothermic process, solubility decreases with increase in temperature.
- **12.** Henry's Law: The law states at a constant temperature the solubility of gas in a liquid is directly proportional to the pressure of gas. Henry's law can also be stated as the partial pressure of gas in vapour phase is proportional to the mole fraction of the gas in the solution. $P = K_H x$







- **13.** When a non-volatile solute is dissolved in a volatile solvent, the vapour pressure of solution is less than that of pure solvent.
- **14.** According to Raoult's law for a solution of volatile liquids the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

 $p_1 = p_1^{o_1} x_1$; $p_2 = p_2^{o_2} x_2$

Using Dalton's law of partial pressure the total pressure of solution is calculated.

 $p_{total} = p_1^{o} + (p_2^{o} - p_1^{o}) x_2$

- **15.** On comparison of Raoult' law and Henry's law, it is observed that the partial pressure of volatile component or gas is directly proportional to its mole fraction in solution. In case of Henry's Law the proportionality constant is K_H and it is different from p_1^0 which is partial pressure of pure component. Raoult's Law becomes a special case of Henry's Law when K_H becomes equal to p_1^0 in Henry's law.
- **16.** Liquid –liquid solutions can be classified into ideal and non-ideal solutions on basis of Raoult's Law.

Ideal solutions	Non- ideal solutions
The solutions that obey Raoult's Law over the entire range of	When a solution does not obey Raoult's Law over the entire range
concentrations are known as ideal	of concentration, then it is called
solutions.	non-ideal solution.
Δ_{mix} H=0 and Δ_{mix} V=0	Λ_{min} H \neq 0 and Λ_{min} V \neq 0
The intermolecular attractive	The intermolecular attractive
forces between solute molecules	forces between solute molecules
and solvent molecules are nearly	and solvent molecules are not
equal to those present between	equal to those present between
solute and solvent molecules i.e.	solute and solvent molecules i.e.
A-A and B-B interactions are	A-A and B-B interactions are not
nearly equal to those between A-B	equal to those between A-B

17. Non- ideal solutions are of two types:

Non ideal solution showing	Non ideal solution showing	
positive deviation	negative deviation	
The vapour pressure of a solution	The vapour pressure of a solution	
is higher than that predicted by	is lower than that predicted by	
Raoult's Law	Raoult's Law	
The intermolecular attractive	The intermolecular attractive	
forces between solute-solvent	forces between solute-solvent	
molecules are weaker than those	molecules are stronger than those	
between solute-solute and	between solute-solute and	
solvent-solvent molecules i.e.	solvent-solvent molecules i.e.	
A-B < A-A and B-B interactions	A-B > A-A and $B-B$ interactions	







- **18.** Azeotropes are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. Liquids forming azeotrope cannot be separated by fractional distillation.
- **19.** There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope.
- **20.** The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.
- **21.** The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.
- **22.** Properties of solution which depends on only the number of solute particles but not on the nature of solute are called colligative properties.
- **23.** There are four colligative properties:
 - a. Relative lowering of vapour pressure

).

- b. Eleveation of boiling point
- c. Depression of freezing point
- d. Osmotic pressure
- **24.** Relative lowering of vapour pressure: Difference in the vapour pressure of pure solvent (p_1°) and solution (p_1) represents lowering in

vapour pressure $(p_1^{\circ} - p_1)$. Dividing lowering in vapour pressure by vapour pressure of pure solvent is called relative lowering of vapour

pressure
$$\left(\frac{p_1^{\circ} - p_1}{p_1^{\circ}}\right)$$

Relative lowering of vapour pressure is directly proportional to mole fraction of solute. Hence it is a colligative property.

$$\frac{p_1^{0} - p_1}{p_1^{0}} = x_2$$

25. Elevation of boiling point: The difference in boiling points of solution (T_b) and pure solvent (T_b^0) is called elevation in boiling point

$$\Delta T = T_{\rm b} - T_{\rm b}^{0}.$$

For a dilute solution elevation of boiling point is directly proportional to molal concentration of the solute in solution. Hence it is a colligative property.

$$\Lambda T_{b} = \frac{K_{b} \times 1000 \times W_{2}}{M_{2} \times W_{1}}$$





- **26.** Depression of freezing point: The lowering of vapour pressure of solution causes a lowering of freezing point compared to that of pure solvent. The difference in freezing point of the pure solvent (T_f^0) and
 - solution (T_f) is called the depression in freezing point. $\Delta T = T_f^0 T_f$ For a dilute solution depression in freezing point is a colligative property because it is directly proportional to molal concentration of solute.

$$\Delta T_{\rm f} = \frac{K_{\rm f} \times 1000 \times W_2}{M_2 \times W_1}$$

- **27.** Osmosis: The phenomenon of flow of solvent molecules through a semi permeable membrane from pure solvent to solution is called osmosis.
- **28.** Osmotic pressure: The excess pressure that must be applied to solution to prevent the passage of solvent into solution through a semi permeable membrane is called osmotic pressure.

Osmotic pressure is a colligative property as it depends on the number of solute particles and not on their identity.

For a dilute solution, osmotic pressure (π) is directly proportional to the molarity (C) of the solution i.e. $\pi = CRT$

29. Osmotic pressure can also be used to determine the molar mass of solute using the equation $M_2 = \frac{w_2 RT}{\pi V}$

30. Two solutions having same osmotic pressure at a given temperature are called isotonic solution.

- **31.** If a solution has more osmotic pressure than other solution it is called hypertonic solution.
- **32.** If a solution has less osmotic pressure than other solution it is called hypotonic solution.
- **33.** Reverse osmosis: The process of movement of solvent through a semi permeable membrane from the solution to the pure solvent by applying excess pressure on the solution side is called reverse osmosis.
- **34.** Colligative properties help in calculation of molar mass of solutes.
- **35.** Molar mass that is either lower or higher than expected or normal molar mass is called as abnormal molar mass.
- **36.** van't Hoff factor (i)accounts for the extent of dissociation or association .

_ Normal molar mass

Abnormal molar mass

Observed colligative property

Calculated colligative property

Total number of moles of particles after association/dissociation

Totalnumber of moles of particles before association/dissociation

Value of i is less than unity in case solute undergo association Value of i is greater than unity in case solute undergo dissociation



PPER



J

37. Inclusion of van't Hoff factor modifies the equations for colligative properties as:

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = i \cdot \frac{n_2}{n_1}$$

$$\Delta T_b = i \cdot \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$\Delta T_r = i \cdot \frac{n_2 RT}{V}$$



Annal is





Chapter : Electrochemistry.

Key Learnings

- **1.** Oxidation is defined as a loss of electrons while reduction is defined as a gain of electrons.
- **2.** In a redox reaction, both oxidation and reduction reaction takes place simultaneously.
- **3.** Direct redox reaction: In a direct redox reaction, both oxidation and reduction reactions take place in the same vessel. Chemical energy is converted to heat energy in a direct redox reaction.
- **4.** Indirect redox reaction: In indirect redox reactions, oxidation and reduction take place in different vessels. In an indirect redox reaction, chemical energy is converted into electrical energy.
- **5.** In an indirect redox reaction, the device which converts chemical energy into electrical energy is known as an electrochemical cell.
- 6. In an electrochemical cell:
 - a. The half cell in which oxidation takes place is known as oxidation half cell
 - b. The half cell in which reduction takes place is known as reduction half cell.
 - c. Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged.
 - d. Transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction.
 - e. An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt.
 - f. A salt bridge is a U shaped tube containing an inert electrolyte in agar-agar and gelatine.

7. A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.

- **8.** Representation of an electrochemical cell:
 - a. Anode is written on the left while the cathode is written on the right.
 - b. Anode represents the oxidation half cell and is written as: Metal/Metal ion (Concentration)
 - c. Cathode represents the reduction half cell and is written as: Metal ion (Concentration)/Metal
 - d. Salt bridge is indicated by placing double vertical lines between the anode and the cathode
 - Electrode potential is the potential difference that develops between the electrode and its electrolyte. The separation of charges at the equilibrium state results in the potential difference between the metal and the solution of its ions. It is the measure of tendency of an electrode in the half cell to lose or gain electrons.





- **9.** When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential. It is denoted as E^{Θ} .
- **10.** According to the present convention, standard reduction potentials are now called standard electrode potential.

11. There are 2 types of electrode potentials: Oxidation potential and reduction potential.

12. Oxidation potential is the tendency of an electrode to lose electrons or get oxidized.

13. Reduction potential is the tendency of an electrode to gain electrons or get reduced.

14. Oxidation potential is the reverse of reduction potential.

15. The electrode having a higher reduction potential has a higher tendency to gain electrons. So, it acts as a cathode.

16. The electrode having a lower reduction potential acts as an anode.

17. The standard electrode potential of an electrode cannot be measured in isolation.

18. According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures.

19. Standard calomel electrode can also be used as a reference electrode.

20. Standard hydrogen electrode consists of a platinum wire sealed in a glass tube and carrying a platinum foil at one end. The electrode is placed in a beaker containing an aqueous solution of an acid having 1 Molar concentration of hydrogen ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at 298 K. The oxidation or reduction takes place at the Platinum foil. The standard hydrogen electrode can act as both anode and cathode.

If the standard hydrogen electrode acts as an anode:

 $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

If the standard hydrogen electrode acts as a cathode:

 $2H^+$ (aq) + $2e^- \rightarrow H_2$ (g)

21. In the electrochemical series, various elements are arranged as per their standard reduction potential values.

22. A substance with higher reduction potential value means that it has a higher tendency to get reduced. So, it acts as a good oxidising agent.

23. A substance with lower reduction potential value means that it has a higher tendency to get oxidised. So, it acts as a good reducing agent.

24. The electrode with higher reduction potential acts as a cathode while the electrode with a lower reduction potential acts as an anode.





25. The potential difference between the 2 electrodes of a galvanic cell is called cell potential and is measured in Volts.

26. The cell potential is the difference between the reduction potential of cathode and anode.

 $E_{cell} = E_{cathode} - E_{anode}$

Cell potential is called the electromotive force of the cell (EMF) when no current is drawn through the cell.

27. Nernst studied the variation of electrode potential of an

electrode with temperature and concentration of electrolyte.

28. Nernst formulated a relationship between standard electrode potential E^e and electrode potential E.

$$E = E^{\theta} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$
$$E = E^{\theta} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \text{ (At 298 K)}$$

29. Electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.

30. Nernst equation when applied to a cell:

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303 \text{RT}}{\text{nF}} \log \frac{[\text{Anode ion}]}{[\text{Cathode ion}]}$$

This helps in calculating the cell potential

31. At equilibrium, cell potential E_{cell} becomes zero

32. Relationship between equilibrium constant K_c and standard cell potential E^{e}_{cell} :

$$\mathsf{E}^{\mathsf{e}}_{\mathsf{cell}} = \frac{0.059}{n} \log \mathsf{K}_{\mathsf{c}} \; (\mathsf{At} \; 298 \; \mathsf{K})$$

33. Work done by an electrochemical cell is equal to the decrease in Gibbs energy

 $\Delta G^{\theta} = -nFE^{\theta}_{cell}$

34. The substances which allow the passage of electricity through them are known as conductors.

35. Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.

36. The resistance of any object is directly proportional to its length I and inversely proportional to its area of cross section A.

$$\mathsf{R} = \rho \, \frac{l}{A}$$

 $\boldsymbol{\rho}$ is called specific resistance or resistivity. Its SI unit is ohm metre.





37. The inverse of resistance is known as conductance, G

 $G = \frac{1}{R}$

Unit of conductance is ohm⁻¹ or mho. It is also expressed in Siemens denoted by S.

38. The inverse of resistivity is known as conductivity. It is represented by the symbol κ . The SI unit of conductivity is Sm⁻¹. But it is also expressed in Scm⁻¹

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{l}{A}\right) = G \frac{l}{A}$$

So, conductivity = Conductance × Cell constant

39. For measuring the resistance of an ionic solution, there are 2 problems:

a) Firstly, passing direct current changes the composition of the solutionb) Secondly, a solution cannot be connected to the bridge like a metallic wire or a solid conductor.

44. This can be resolved by using a source of alternating current and the second problem is resolved by using a specially designed vessel called conductivity cell.

45. A conductivity cell consists of 2 Pt electrodes coated with Pt black.

They have area of cross section A and are separated by a distance I. Resistance of such a column of solution is given by the equation:

$$\mathsf{R} = \rho \, \frac{l}{A} = \frac{1}{\kappa} \frac{l}{A}$$

 $\frac{l}{A}$ is called cell constant and is denoted by the symbol G^{*}

46. Molar conductivity of a solution is defined as the conducting power of all the ions produced by dissolving 1 mole of an electrolyte in solution.

Molar conductivity $\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$

Where κ = Conductivity and M is the molarity Unit of Molar conductivity is Scm² mol⁻¹

47. Equivalent conductivity is the conductivity of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

Equivalent conductivity $\Lambda_{e} = \frac{\kappa \times 1000}{N}$ Unit of equivalent conductivity is S cm² (g equiv)⁻¹





48. Kohlrausch's Law of independent migration of ions: According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions.

If the limiting molar conductivity of the cations is denoted by λ^o_+ and

that of the anions by λ_{-}^{o} then the limiting molar conductivity of electrolyte is:

 $\wedge^0_m = v_+^{}\lambda^0_+ + v_-^{}\lambda^0_-$

Where $v_{\scriptscriptstyle +}$ and $v_{\scriptscriptstyle -}$ are the number of cations and anions per formula of electrolyte

49. Degree of dissociation: It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution. It is denoted by α .

$$a = \frac{\wedge_m^c}{\wedge_m^0}$$

50. $K_a = \frac{c a^2}{1-a}$ where K_a is acid dissociation constant , 'c' is concentration

of electrolyte, a is degree of ionization.

51. Faraday constant: It is equal to charge on 1 mol of electrons. It is equal to 96487 C mol⁻¹ or approximately equal to 96500 C mol⁻¹.

- **52.** Faraday's first law of electrolysis: The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed.
- **53.** Faraday's second law of electrolysis: If same charge is passed through different electrolytes, the mass of substance deposited will be proportional to their equivalent weights.
- **54.** Products of electrolysis: The products of electrolysis depend upon the nature of electrolyte being electrolyzed and the nature of electrodes. If electrode is inert like platinum or gold, they do not take part in chemical reaction i.e. they neither lose nor gain electrons. If the electrodes are reactive then they will take part in chemical reaction and products will be different as compared to inert electrodes. The products of electrolysis also depend upon the electrode potentials of oxidizing and reducing species. Some of the electrochemical processes although feasible but slow in their rates at lower voltage, these do not take place. They require extra voltage, i.e. over voltage at which these processes will take place. The products of electrolysis also differ in molten state and aqueous solution of electrolyte.
- **55.** Primary cells. A primary cell is a cell in which electrical energy is produced by the reaction occurring in the cell, e.g. Daniell cell, dry cell, mercury cell. It cannot be recharged.









TOPPER WWW.TOPPERLEARNING.COM



Top Formulae

DEPENDENTIFICATIONS COM
TOP FORMULE
1.
$$E_{cull} = E_{cuthode} - E_{anode}$$

2. $E = E^{\alpha} - \frac{0.059}{n} \log_2 \frac{1}{n [M^{\alpha+1}]}$ (At 298 K)
3. $E_{cull} = E^{\alpha}_{cult} - \frac{2.303F}{nF} \log \frac{[Anode ion]}{[Cathode ion]}$
4. $E^{\alpha}_{cull} = \frac{0.059}{n} \log K_{c}$ (At 298 K)
5. $\Delta G^{\alpha} = -nFE^{\alpha}_{cull}$
6. $R = p \frac{1}{A} = \frac{1}{K} \frac{1}{A}$
7. $G = \frac{1}{R}$
8. Conductivity = Conductance × Cell constant
9. $\kappa = \frac{1}{p} = \frac{1}{R} (\frac{1}{A}) = G \frac{1}{A}$
10. Cell constant and is denoted by the symbol G
11. $\Lambda_m = \frac{Specific conductance}{Molarity} = \frac{\kappa}{C}$
 $\Lambda_m = \frac{s \times 1000}{C}$
Remember:
12. $\alpha = \frac{\Lambda_m^{\alpha}}{\Lambda_m^{\alpha}}$
13. $K_a = \frac{G^2}{1-\alpha}$
14. $m = ZII$
15. $K_a = \frac{G^2}{1-\alpha}$
15. $K_a = \frac{G^2}{1-\alpha}$
16. $m = ZII$





Chapter : Chemical Kinetics

Key learnings:

- 1. Chemical kinetics: The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical kinetics.
- Rate of reaction: It is defined as the change in concentration of reactant (or product) in unit time. Unit of rate of reaction is mol L⁻¹s⁻¹.
- 3. Average rate: The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$.
- 4. Instantaneous rate: It is the rate of reaction when the average rate is taken over a particular moment of time. It is equal to dx/dt.
- 5. Rate law or rate equation: It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
- 6. Rate constant: When the concentration of reactants is unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
- 7. Molecularity of a reaction: Total number of atoms, ions or molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number. It is never more than three. It cannot be zero.
- Order of a reaction: The sum of the exponents (power) of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
- 9. Half- life of a reaction: The time taken for a reaction, when half of the starting material has reacted is called half- life of a reaction. For first

order reaction $t_{\frac{1}{2}} = \frac{0.693}{k}$, where k is rate constant.

It is independent of initial concentration for first order reaction.





10. Pseudo first order reaction: The reaction which is bimolecular but order is one is called pseudo first order reaction. This happens when one of the reactants is in large excess. E.g., acidic hydrolysis of ester (ethyl acetate).

 $CH_{3}COOC_{2}H_{5} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + C_{2}H_{5}OH$

- Activation energy (E_a): It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to the formation of product molecules.
- 12. Arrhenius equation of reaction rate: It gives the relation between rate of reaction and temperature.

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

where k = rate constant, A = frequency factor,

 E_a = energy of activation

R = gas constant, T = temperature in Kelvin,

 $\ln k = \ln A - E_a/RT$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

- Mechanism of reaction: The sequence of elementary processes leading to the overall stoichiometry of a chemical reaction is known as mechanism of a reaction.
- 14. Activated complex: It is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.
- 15. Rate determining step: The slowest step in the reaction mechanism is called rate determining step.
- 16. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).







Top Formulae:

- 1. Instantaneous rate = $\frac{dx}{dt}$, where dx is small change in conc. and dt is the smallest interval of time.
- 2. Average rate = $\frac{\Delta x}{\Delta t}$, where Δx is change in concentration and Δt is large interval of time.
- 3. $A + B \rightarrow C + D$

Rate of disappearance of A = $\frac{-d[A]}{dt}$, where d[A] is small change in

conc. of 'A' and dt is small interval of time

Rate of disappearance of B = $\frac{-d[B]}{dt}$,

Rate of appearance of C = $\frac{+d[C]}{dt}$

Rate of appearance of D = $\frac{+d[D]}{dt}$

Rate =
$$\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Unit of rate of reaction = mol $L^{-1}s^{-1}$

4. Order of reaction:

If rate law expression for a reaction is

Rate = k $[A]^{\times} [B]^{\gamma}$

Order of reaction = x + y

Remember: Order cannot be determined with a given balanced chemical equation. It can be experimentally determined.





5.

Integrated rate law for zero order reaction:

 $R \rightarrow P$ $\frac{\mathrm{d}x}{\mathrm{d}t} = \mathrm{k}[\mathrm{R}]^{0}$ Unit of 'k' is mol $L^{-1}s^{-1}$ $k = \frac{[R_o] - [R]}{t}$



If we plot a graph between concentration of R vs time, the graph is a straight line with slope equal to -k and intercept is equal to $[R_0]$

6. Half- life reaction for a for zero order reaction:

$$\mathsf{t}_{\frac{1}{2}} = \frac{[\mathsf{R}_0]}{2\,\mathsf{k}}$$

Rate law for Ist order reaction: 7.

$$R \rightarrow P$$

$$k = \frac{2.303}{t} \log \frac{[R_o]}{[R]}$$

where 'k' is rate constant or specific reaction rate, $[R_o]$ is initial molar conc., [R] is final molar conc. after time't'

If we plot a graph between In[R] with time, we get a straight line whose slope = -k and intercept ln[R_o]

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

where 'a' is initial conc. in mol L^{-1} , x mol L^{-1} have reacted in time 't' final conc., after time 't' is (a - x)

Half- Life for a first order reaction is: 8.



N



9. Formula to calculate rate constant for first order gas phase reaction of the type $A(a) \rightarrow B(a) + C(a)$

$$A(g) \rightarrow B(g) + C(g)$$

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_i)}$$

Where:

 p_i is initial pressure of A p_t is total pressure of gaseous mixture containing A , B, C Remember:

- $p_t = p_A + p_B + p_C$
- 10. Arrhenius equation:

 $k = A e^{-E_a/RT}$

11. $\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \text{ R}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

12. Rate =
$$PZ_{AB}$$
. $e^{\frac{-E_a}{RT}}$

Where:

NN.S.

 Z_{AB} represents the collision frequency of reactants, A and B $_{-E_a}^{-E_a}$

 $e^{\overrightarrow{RT}}$ represents the fraction of molecules with energies equal to or greater than E_a

P is called the probability or steric factor







Chapter : Surface Chemistry

Top Concepts / Key learnings:

- 1. Adsorption: The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed as adsorption.
- 2. Adsorbate: The substance which is being adsorbed on the surface of another substance is called adsorbate.
- Adsorbent: The substance present in bulk, on the surface of which 3. adsorption is taking place is called adsorbent.
- 4. Desorption: The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.
- 5. Absorption: It is the phenomenon in which a substance is uniformly distributed all over the surface.

•	Difference between adsorption and	absorption:
	Absorption	Adsorption
	(i) It is the phenomenon in which a	(i) The accumulation of

6

(i) It is the phenomenon in which a	(i) The accumulation of molecular	
substance is uniformly distributed	species at the surface rather than in the bulk of a solid or liquid is	
throughout the bulk of the solid.	termed as adsorption.	
(ii) It is a bulk phenomenon.	(ii) It is a surface phenomenon.	
(iii) The concentration is uniform throughout the bulk of solid.	(iii) The concentration of adsorbate increases only at the surface of the adsorbent.	

- Sorption: When adsorption and absorption take place simultaneously, 7. it is called sorption.
- 8. Enthalpy or heat of adsorption: Adsorption generally occurs with release in energy, i.e., it is exothermic in nature. The enthalpy change for the adsorption of one mole of an adsorbate on the surface of adsorbent is called enthalpy or heat of adsorption.





- 9. Types of adsorption:
 - a. Physical adsorption or physisorption: If the adsorbate is held on a surface of adsorbent by weak van der Waals' forces, the adsorption is called physical adsorption or physisorption.
 - Chemical adsorption or chemisorption: If the forces holding the adsorbate are as strong as in chemical bonds, the adsorption process is known as chemical adsorption of chemisorption.
- 10. Difference between Physical and chemical adsorption:

Physical adsorption (Physisorption)	Chemical adsorption (Chemisorption)		
(i) It is non-specific	(i) It is highly specific		
(ii) It is reversible	(ii) It is irreversible		
(iii) The amount of gas depends upon nature of gas, i.e., easily liquefiable gases like NH_3 , CO_2 , gas adsorbed to greater extent than H_2 and He. Higher the critical temperature of gas, more will be the extent of adsorption.	(iii) The amount of gas adsorbed is not related to critical temperature of the gas.		
(iv) The extent of adsorption increases with increase in surface area, e.g. porous and finely divided metals are good adsorbents.	(iv) It also increases with increase in surface area.		
(v) There are weak van der Waals' forces of attraction between adsorbate and adsorbent.	(v) There is strong force of attraction similar to chemical bond.		
(vi) It has low enthalpy of adsorption (20 – 40 kJ mol ⁻¹)	(vi) It has enthalpy heat of adsorption $(180 - 240 \text{ kJ mol}^{-1})$		
(vii) Low temperature is favourable.	(vii) High temperature is favourable.		
(viii) No appreciable activation energy is needed.	(viii) High activation energy is sometimes needed.		
(ix) It forms multimolecular layers.	(ix) It forms unimolecuar layers.		

11. Factors affecting adsorption of gases on solids:

- a. Nature of adsorbate: Physical adsorption is non-specific in
 - nature and therefore every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, easily liquefiable gases like NH₃. HCl, CO₂, etc. which have higher critical temperatures are absorbed to greater extent whereas H₂, O₂, N₂ etc. are adsorbed to lesser extent. The chemical







adsorption being highly specific, therefore, a gas gets adsorbed on specific solid only if it enters into chemical combination with it.

- b. Nature of adsorbent: Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents. They have their specific adsorption properties depending upon pores.
- c. Specific area of the adsorbent: The greater the specific area, more will be the extent of adsorption. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. The pores should be large enough to allow the gas molecules to enter.
- d. Pressure of the gas: Physical adsorption increases with increase in pressure.
- 12. Adsorption isotherm: The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve is termed as adsorption isotherm.
- 13. Freundlich Adsorption isotherm: The relationship between $\frac{x}{m}$ and pressure of the gas at constant temperature is called adsorption isotherm and is given by

 $\frac{x}{m} = k P^{1/n} (n > 1)$

Where x- mass of the gas adsorbed on mass m of the adsorbent and the gas at a particular temperature

k and n depends upon the nature of gas and the solid

 $\frac{x}{m}$ first increases with increase in pressure at low pressure but becomes

independent of pressure at high pressure.









The slope of the line is $\frac{1}{n}$ and intercept will be equal to log k.

14. Catalyst: Substances which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are known as catalysts and the phenomenon is known as catalysis.





15. Promoters: Those substances which increase the activity of catalyst are called promoters. Example: Mo is promoter whereas Fe is catalyst in Haber's Process.

 $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

- 16. Catalytic poisons (Inhibitors): The substances which decrease the activity of catalyst are called catalytic poisons or inhibitors e.g., arsenic acts as catalytic poison in the manufacture of sulphuric acid by `contact process.'
- 17. Types of catalysis:
 - a. Homogeneous catalysis: When the catalyst and the reactants are in the same phase, this kind of catalytic process is known as homogeneous catalysis.
 - b. Heterogeneous catalysis: When the catalyst and the reactants are in different phases, the catalytic process is said to be heterogeneous catalysis.
- 18. Activity of catalyst: The ability of a catalyst to increase the rate of a chemical reaction is called activity of a catalyst.
- 19. Selectivity of catalyst: It is the ability of catalyst to direct a reaction to yield a particular product (excluding others).

For example:

CO and H_2 react to form different products in presence of different catalysts as follows:

- a) $CO(g) + 3H_2(g) \xrightarrow{\text{Ni}} CH_4(g) + H_2O(g)$ b) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$ c) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$
- 20. Shape selective catalysis: The catalysis which depends upon the pore structure of the catalyst and molecular size of reactant and product molecules is called shape- selective catalysis. E.g. Zeolites are shape selective catalysts due to their honey- comb structure.





- 21. Enzymes: Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass. They are biochemical catalysts
- 22. Steps of enzyme catalysis:
 - (i) Binding of enzyme to substrate to form an activated complex

 $E + S \rightleftharpoons ES^{\neq}$

ii) Decomposition of the activated complex to form product

 $\mathsf{E} \,\, S^{\scriptscriptstyle \neq} \to \mathsf{E} + \mathsf{P}$

- 23. Characteristics of enzyme catalysis:
 - i) They are highly efficient. One molecule of an enzyme can transform 10⁶ molecules of reactants per minute.
 - ii) They are highly specific in nature, e.g., urease catalysis hydrolysis of urea only.
 - iii) They are active at optimum temperature (298 310 K). The rate of enzyme catalysed reaction becomes maximum at a definite temperature called the optimum temperature.
 - iv) They are highly active at a specific pH called optimum pH.
 - Enzymatic activity can be increased in presence of coenzymes which can be called as promoters.
 - vi) Activators are generally metal ions Na⁺, Co²⁺ and Cu²⁺ etc. They weakly bind to enzyme and increase its activity.
 - vii) Influence of inhibitors (poison): Enzymes can also be inhibited or poisoned by the presence of certain substances.



M




24. Distinction between true solution, colloids and Suspension.

True solution	Colloids	Suspension
It is homogeneous	It appears to be	It is heterogeneous
	homogeneous but is	
	actually heterogeneous	
The diameter of the	The diameter of the	The diameter of the
particles is less than 1	particles is 1 nm to	particles are larger that
nm	1000 nm	1000 nm
It passes through filter	It passes through	It does not pass through
paper	ordinary filter paper but	filter paper
	not through ultra-filters	
Its particles cannot be	Its particles can be seen	Its particles can be seen
seen under a	by a powerful	even with naked eye
microscope	microscope due to	
	scattering of light	

- 25. Colloids: A colloid is a heterogeneous system in which one substance is dispersed as very fine particles in another substance called dispersed medium.
- 26. Dispersed phase: The substance which is dispersed as very fine particles is called dispersed phase.
- 27. Dispersion medium: The substance present in larger quantity is called dispersion medium.
- 28. Classification of colloids on the basis of the physical state of dispersed phase and dispersion medium:

Dispersed phase	Dispersion medium	Name	Examples
Solid	Gas	Aerosol	Smoke, dust
Solid	Liquid	Sol	Paints
Solid	Solid	Solid sol	Coloured gem tones
Liquid	Solid	Gel	Jellies, cheese
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Whipped cream, froth



N



29. Classification of colloids on the basis of nature of interaction between dispersed phase and dispersion medium :

Lyophobic sols	Lyophilic sols
These colloids are liquid hating.	These colloids are liquid loving.
In these colloids the particles of	In these colloids, the particles of
dispersed phase have no affinity	dispersed phase have great
for the dispersion medium.	affinity for the dispersion medium.
They are not stable.	They are stable.
They can be prepared by mixing	They cannot be prepared by
substances directly.	mixing substances directly. They
	are prepared only by special
	methods
They need stabilizing agents for	They do not need stabilizing
their preservation.	agents for their preservation.
They are irreversible sols.	They are reversible sols.

- 30. Classification of colloids on the basis of types of particles of the dispersed phase:
 - Multimolecular colloids: The colloids in which the colloidal particles consist of aggregates of atoms or small molecules. The diameter of the colloidal particle formed is less than 1 nm.
 - b. Macromolecular colloids: These are the colloids in which the dispersed particles are themselves large molecules (usually polymers). Since these molecules have dimensions comparable to those of colloids particles, their dispersions are called
 - macromolecular colloids, e.g., proteins, starch and cellulose form macromolecular colloids.
 - c. Associated colloids (Micelles): Those colloids which behave as normal, strong electrolytes at low concentrations, but show colloidal properties at higher concentrations due to the formation of aggregated particles of colloidal dimensions. Such substances are also referred to as associated colloids.





- 31. Kraft Temperature (T_k): Micelles are formed only above a certain temperature called Kraft temperature.
- 32. Critical Micelle Concentration (CMC): Micelles are formed only above a particular concentration called critical micelle concentration.
- 33. Soaps: Soaps are sodium or potassium salts of higher fatty acids e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$
- 34. Methods of preparation of colloids:
 - a. Chemical methods: Colloids can be prepared by chemical reactions leading to the formation of molecules. These molecules aggregate leading to formation of sols.
 - b. Electrical disintegration or Bredig's Arc method: In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vaporizes the metal which then condenses to form particles of colloidal size.
 - c. Peptization: Peptization may be defined as the 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.
 - 35. Purification of colloids:
 - Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.
 - b. Electro dialysis. 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: 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 substances except the colloidal particles.
 - d. Ultracentrifugation: In this process, the colloidal solution is taken in a tube which is placed in ultracentrifuge. On rotating





the tube at very high speed, the colloidal particles settle down at the bottom of the tube and the impurities remain in solution. The settled particles are mixed with dispersion medium to regenerate the sol.

- 36.Properties of colloids:
 - a. Colour: The colour of colloidal solution depends upon the wavelength of light scattered by the colloidal particles which in turn depends upon the nature and size of particles. The colour also depends upon the manner in which light is received by the observer.
 - b. Brownian movement: Colloidal particles move in zig zag path. This type of motion is due to colliding molecules of dispersion medium constantly with colloidal particles.
 - c. Colligative properties: The values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at the same concentrations.
 - d. Tyndall effect: The scattering of a beam of light by colloidal particles is called Tyndall effect. The bright cone of light is called the Tyndall cone.
 - e. Charge on colloidal particles: Colloidal particles always carry an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative.

Positively charged colloids	Negatively charged colloids
Hydrated metallic oxides such as	Metallic sulphides like As_2S_3 , Sb_2S_3
Fe ₂ O ₃ .xH ₂ O, Cr ₂ O ₃ .xH ₂ O, Al ₂ O ₃ .xH ₂ O	sols
Basic dye stuff like malachite green,	Acid dye stuff like eosin, methyl
methylene blue sols	orange, Congo red sols
Hanmadahin (blood)	Starch sol, gum, gelatin, clay,
Haemoglobin (blobd)	charcoal, egg albumin, etc.





- f. Helmholtz electrical double layer: When the colloidal particles acquire negative or positive charge by selective adsorption of one of the ions, it attracts counter ions from the medium forming a second layer. The combination of these two layers of opposite charges around colloidal particles is called Helmholtz electrical double layer.
- g. Electrokinetic potential or zeta potential: The potential difference between the fixed layer and the diffused layer of opposite charges is called electrokinetic potential or zeta potential.
- h. Electrophoresis: The movement of colloidal particles under an applied electric potential is called electrophoresis.
- i. Coagulation or precipitation: The process of settling of colloidal particles as precipitate is called coagulation.

Hardy – Schulze rules:

i) Oppositely charged ions are effective for coagulation.

ii) The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation, e.g. $Al^{3+} > Ba^{2+} > Na^+$ for negatively charged colloids.

 $[Fe (CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$ for positively charged colloids 37. Types of emulsions:

- a. Water dispersed in oil: When water is the dispersed phase and oil is the dispersion medium. E.g. butter
- b. Oil dispersed in water: When oil is the dispersed phase and water is the dispersion medium. E.g. milk
- 38.Emulsification: The process of stabilizing an emulsion by means of an emulsifier.

39.Emulsifying agent: The substances which are added to stabilize the emulsions are called emulsifying agents or emulsifiers. E.g. soaps, gum







40. Demulsification: The process of breaking an emulsion into its constituent liquids is called demulsification by freezing, boiling, , ot. c centrifugation or some chemical methods.







<u>Chapter : General Principles & Processes</u> <u>Of Isolation of Elements</u>

Top concepts:

- 1. Minerals: The naturally occurring chemical substances in the earth's crust which are obtained by mining are known as minerals. Metals may or may not be extracted profitably from them.
- Ores: The rocky materials which contain sufficient quantity of mineral so that the metal can be extracted profitably or economically are known as ores.
- 3. Gangue: The earthy or undesirable materials present in ore are known as gangue.
- 4. Metallurgy: The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

5.	Chief Ores and Methods	of Extraction	of Some	Common	Metals:
----	------------------------	---------------	---------	--------	---------

Metals	Occurrence	Extraction Method	Remark
Sodium	Rock salt: NaCl Feldspar:Na ₃ AlSi ₃ O ₈	Electrolysis of fused NaCl or NaCl/ $CaCl_2$	Sodium is highly reactive, it reacts with water
Copper	Copper pyrites: $CuFeS_2$ Malachite: $CuCO_3$. $Cu(OH)_2$ Cuprite: Cu_2O Copper glance: Cu_2S	$\begin{array}{ll} \mbox{Roasting} & \mbox{of} & \mbox{sulphide} \\ \mbox{partially and reduction} \\ \mbox{2Cu}_2 \mbox{O} + \mbox{Cu}_2 \mbox{S} \rightarrow \mbox{6} \mbox{Cu} \\ & + \mbox{SO}_2 \end{array}$	It is self reduction in a specially designed converter. Sulphuric acid leaching is also employed.
Aluminium	Bauxite: AlO _x (OH) _{3-2x} where 0 <x<1 Cryolite: Na₃AlF₆ Kaolinite: [Al₂(OH)₄Si₂O₅]</x<1 	Electrolysis of Al ₂ O ₃ dissolved in molten cryolite or in Na ₃ AlCl ₆	A good source of electricity is needed in the extraction of Al
Zinc	Zinc blende or Sphalerite: ZnS Zincite: ZnO Calamine: ZnCO ₃	Roasting and then reduction with C	The metal may be purified by fractional distillation.
Lead	Galena: PbS	Roasting of the sulphide ore and then reduction of the oxide	Sulphide ore is concentrated by froth floatation process
Silver	Argentite: Ag ₂ S	Sodium cyanide leaching of the sulphide ore and finally replacement of Ag by Zn	It involves complex formation and displacement
Gold	Native, small amounts in many ores such as those of	Cyanide leaching, same as in case of silver	Gold reacts with cyanide to form complex





	copper and silver		
Iron	Haematite: Fe_2O_3 Magnetite: Fe_3O_4 Siderite: $FeCO_3$ Iron pyrites: FeS_2	Reduction with the help of CO and coke in blast furnace.	Limestone is added as flux which removes SiO ₂ as calcium silicate (slag) floats over molten iron and prevents its oxidation. Temperatures approaching 2170 K is required.

- 6. Steps of metallurgy:
 - a. Concentration of ore
 - b. Conversion of concentrated ore to oxide
 - c. Reduction of oxide to metal
 - d. Refining of metal
- 7. Concentration of ore: The process of removal unwanted materials like sand, clay, rocks etc from the ore is known as concentration, ore – dressing or benefaction. It involves several steps which depend upon physical properties of metal compound and impurity (gangue). The type of metal, available facilities and environmental factors are also taken into consideration.
- 8. Hydraulic washing (or gravity separation): It is based on difference in densities of ore and gangue particles. Ore is washed with a stream of water under pressure so that lighter impurities are washed away whereas heavy ores are left behind.
- 9. Magnetic separation: This method is based on the difference in magnetic and non magnetic properties of two components of ore (pure and impure). This method is used to remove tungsten ore particles from cassiterite (SnO_2). It is also used to concentrate magnetite (Fe_3O_4), chromite ($FeCr_2O_4$) and pyrolusite (MnO_2) from unwanted gangue.





- 10. Froth Floatation Process: The principle of froth floatation process is that sulphide ores are preferentially wetted by the pine oil, whereas the gangue particles are wetted by the water. Collectors are added to enhance the non-wettability of the mineral particles. Examples are pine oil, fatty acids and xanthates are added to it. Froth stabilizers are added to stabilize the froth. Examples are cresols, aniline. If two sulphide ores are present, it is possible to separate the two sulphide ores by adjusting proportion of oil to water or by adding depressants. For example- In the case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to froth but allows PbS to come with the froth.
- 11. Leaching (Chemical separation): It is a process in which ore is treated with suitable solvent which dissolves the ore but not the impurities.
- 12. Purification of Bauxite by Leaching: Baeyer's process:
 - Step 1:

 $AI_2O_3(s) + 2NaOH(aq) + 3H_2O(I) \rightarrow 2Na[AI(OH)_4](aq)$

Step 2:

 $2Na[AI(OH)_{4}](aq) + CO_{2}(g) \rightarrow AI_{2}O_{3}.xH_{2}O(s) + 2NaHCO_{3}(aq)$ Step 3:

 $AI_{2}O_{3}.xH_{2}O(s) \xrightarrow{Heatat1470K} AI_{2}O_{3}(s) + xH_{2}O(g)$

13. Concentration of Gold and Silver Ores by Leaching:

$$\begin{split} & 4\mathsf{M}(s) + 8\mathsf{CN}^{-}(\mathsf{aq}) + 2\mathsf{H}_2\mathsf{O}(\mathsf{aq}) + \mathsf{O}_2(\mathsf{g}) \to 4[\mathsf{M}(\mathsf{CN})_2]^{-}(\mathsf{aq}) + 4\mathsf{OH}^{-}(\mathsf{aq}) \\ & 2[\mathsf{M}(\mathsf{CN})_2]^{-}(\mathsf{aq}) + \mathsf{Zn}(s) \to [\mathsf{Zn}(\mathsf{CN})_4]^{2^{-}}(\mathsf{aq}) + 2\mathsf{M}(s) \\ & \mathsf{Where}: \\ & [\mathsf{M} = \mathsf{Agor}\,\mathsf{Au}] \end{split}$$



h



14. Conversion of ore into oxide: It is easier to reduce oxide than sulphide or carbonate ore. Therefore, the given ore should be converted into oxide by suitable method:

Roasting	Calcination
It is a process in which ore is	It is a process of heating ore in
heated in a regular supply of air	limited supply of air so as to
at a temperature below melting	convert carbonate ores into
point of the metal so as to	oxides.
convert the given ore into oxide	
ore.	
Sulphide ores are converted into	Carbonate ores are converted into
oxide by roasting	oxide by roasting
It is also used to remove	It is also used to remove moisture
impurities as volatile oxides	and volatile impurities
$E.g.: 2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$	E.g.: $CaCO_3 \xrightarrow{heat} CaO + CO_2$

- 15. Reduction of oxide to metal: The process of converting metal oxide into metal is called reduction. It needs a suitable reducing agent depending upon the reactivity or reducing power of metal. The common reducing agents used are carbon or carbon monoxide or any other metals like Al, Mg etc.
- 16. Thermodynamic principles of metallurgy: Some basic concepts of thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in metallurgical processes:
 - a. Gibbs free energy change at any temperature is given by $\Delta G = \Delta H T\Delta S$ where ΔG is free energy change, ΔH is enthalpy change and ΔS is entropy change.
 - b. The relationship between ΔG^{Θ} and K is $\Delta G^{\Theta} = -2.303$ RT log K where K is equilibrium constant. R = 8.314 JK⁻¹ mol⁻¹, T is temperature in Kelvin.







- c. A negative ΔG means +ve value of K i.e., products are formed more than the reactants. The reaction will proceed in forward direction.
- d. If ΔS is +ve, on increasing temperature the value of T ΔS increases so that T $\Delta S > \Delta H$ and ΔG will become negative.
- 17.Coupled reactions: If reactants and products of two reactions are put together in a system and the net ΔG of two possible reactions is -ve the overall reaction will take place. These reactions are called coupled reactions.
- 18. Ellingham diagrams: The plots between $\Delta_f G^{\circ}$ of formation of oxides of elements vs. temperature are called Ellingham diagrams. It provides a sound idea about selecting a reducing agent in reduction of oxides. Such diagrams help in predicting the feasibility of a thermal reduction of an ore. ΔG must be negative at a given temperature for a reaction to be feasible.
- 19. Limitations of Ellingham Diagrams: It does not take kinetics of reduction into consideration, i.e., how fast reduction will take place cannot be determined.
- 20. Reduction of iron oxide in blast furnace: Reduction of oxides takes place in different zones.

At 500 – 800 K (lower temperature range in blast furnace) $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$ $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$ $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$ At 900 – 1500 K (higher temperature range in blast furnace) $C + CO_2 \rightarrow 2CO$ $FeO + CO \rightarrow Fe + CO_2$ Limestone decomposes to CaO and CO₂ $CaCO_3 \xrightarrow{heat} CaO + CO_2$

Silica (impurity) reacts with CaO to form calcium silicate which forms slag. It floats over molten iron and prevents oxidation of



iron.

 $CaO + SiO_2 \rightarrow CaSiO_3$

Calcium silicate

(Slag)

- 21.Types of iron:
- a. Pig iron: The iron obtained from blast furnace is called pig iron. It is impure from of iron contains 4% carbon and small amount of S,.P, Si and Mn. It can be casted into variety of shapes.
- b. Cast iron: It is made by melting pig iron with scrap iron and coke using hot air blast. It contains about 3% of carbon content. It is extremely hard and brittle.
- c. Wrought iron: It is the purest form of commercial iron. It is also called malleable iron.

It is prepared by oxidative refining of pig iron in reverberatory furnace lined with haematite which oxidises carbon to carbon monoxide.

 $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

The substance which reacts with impurity to form slag is called flux e.g. limestone is flux.

 $S + O_2 \rightarrow SO_2$ $4P + 5O_2 \rightarrow 2P_2O_5$ $Si + O_2 \rightarrow SiO_2$ $CaO + SiO_2 \rightarrow CaSiO_3 (slag)$

 $3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ (slag)

The metal is removed and freed from slag by passing through rollers.



M





22. Electrolytic Reduction (Hall – Heroult Process): Purified bauxite ore is mixed with cryolite (Na_3AlF_6) or CaF_2 which lowers its melting point and increases electrical conductivity. Molten mixture is electrolysed using a number of graphite rods as anode and carbon lining as cathode.

The graphite anode is useful for reduction of metal oxide to metal.

 $2AI_2O_3 + 3C \rightarrow 4AI + 3CO_2$

 $AI_2O_3 \xrightarrow{\text{electrolysis}} 2AI^{3+} + 3O^{2-}$

At cathode: AI^{3^+} (melt) + $3e^- \rightarrow AI$ (I)

At anode: $C(s) + O^{2^{-}} (melt) \rightarrow CO(g) + 2e^{-}$

 $C(s) + 2O^{2^{-}} (melt) \rightarrow CO_2(g) + 4e^{-1}$

Graphite rods get burnt forming CO and CO_2 . The aluminium thus obtained is refined electrolytically using impure Al as anode, pure Al as cathode and molten cryolite as electrolyte.

At anode: $AI \rightarrow AI^{3^+} + 3e^-$ (Impure)

At cathode: $AI^{3^+} + 3e^- \rightarrow AI$ (pure)

23. Electrolysis of molten NaCl:

NaCl \rightarrow Na⁺+ Cl⁻ (Molten)

At cathode: $Na^+ + e^- \rightarrow Na$

At anode: $2CI^- \rightarrow CI_2 + 2e^-$

Thus sodium metal is obtained at cathode and $Cl_2(g)$ is liberated at anode.

- 24. Refining: It is the process of converting an impure metal into pure metal depending upon the nature of metal.
- 25. Distillation: It is the process used to purify those metals which have low boiling points, e.g., zinc, mercury, sodium, potassium. Impure metal is heated so as to convert it into vapours which changes into pure metal on condensation and is obtained as distillate.





- 26. Liquation: Those metals which have impurities whose melting points are higher than metal can be purified by this method. In this method, Sn metal can be purified. Tin containing iron as impurities heated on the top of sloping furnace. Tin melts and flows down the sloping surface where iron is left behind and pure tin is obtained.
- 27. Electrolytic refining: In this method, impure metal is taken as anode, pure metal is taken as cathode, and a soluble salt of metal is used as electrolyte. When electric current is passed, impure metal forms metal ions which are discharged at cathode forming pure metal.

At anode: Μ $M^{n+} + ne^{-}$ \rightarrow

(Impure)

At cathode: $M^{n+} + ne^- \rightarrow M$

(Pure)

Zone refining: It is based on the principle that impurities are more 28. soluble in the melt than in the solid state of the metal.

The impure metal is heated with the help of circular heaters at one end of the rod of impure metal. The molten zone moves forward along with the heater with impurities and reaches the other end and is discarded. Pure metal crystallizes out of the melt.

The process is repeated several times and heater is moved in the same direction. It is used for purifying semiconductors like B, Ge, Si, Ga and In.

29. Vapour phase refining: Nickel is purified by Mond's process. Nickel, when heated in stream of carbon monoxide forms volatile Ni(CO)₄ which on further subjecting to higher temperature decomposes to give pure metal.

 $330-350K \rightarrow Ni(CO)_4$ Ni + 4 CO -Ni + 4COPure

Impure





30. van- Arkel method: It is used to get ultra pure metals. Zr and Ti are purified by this process. Zr or Ti are heated in iodine vapours at about 870 K to form volatile ZrI_4 or TiI_4 which are heated over tungsten filament at 1800K to give pure Zr or Ti.

 $\begin{array}{ccc} \text{Ti} + 2\text{I}_2 & \longrightarrow & \text{TiI}_4 & \longrightarrow & \text{Ti} + 2\text{I}_2 \\ \text{Impure} & & \text{Pure} \\ \\ \text{Zr} + 2\text{I}_2 & \longrightarrow & \text{ZrI}_4 & \longrightarrow & \text{Zr} + 2\text{I}_2 \\ \text{Impure} & & \text{Pure} \end{array}$

31. Chromatographic method: It is based on the principle of separation or purification by chromatography which is based on differential adsorption on an adsorbent. In column chromatography, Al₂O₃ is used as adsorbent. The mixture to be separated is taken in suitable solvent and applied on the column. They are then eluted out with suitable solvent (eluant). The weakly adsorbed component is eluted first. This method is suitable for such elements which are available only in minute quantities and the impurities are not very much different in their chemical behaviour from the element to be purified.



MN. allino





Chapter : The p-Block Elements

Top concepts:

- 1. **p-Block elements:** Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.
- 2. **General electronic configuration of p-block elements:** The pblock elements are characterized by the ns²np¹⁻⁶ valence shell electronic configuration.
- 3. **Representative elements:** Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.
- 4. **Inert pair effect:** The tendency of ns² electron pair to participate in bond formation decreases with the increase in atomic size. Within a group the higher oxidation state becomes less stable with respect to the lower oxidation state as the atomic number increases. This trend is called 'inert pair effect'. In other words, the energy required to unpair the electrons is more than energy released in the formation of two additional bonds.
- 5. **Nitrogen family:** The elements of group 15 nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) belong to configuration is ns²np³.
- Oxygen family: Group 16 of periodic table consists of five elements oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their general electronic configuration is ns²np⁴.
- 7. **The halogen family:** Group 17 elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At), belong to halogen family. Their general electronic configuration is ns²np⁵.
- 8. **Group 18 elements:** Helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are Group 18 elements. They are also called noble gases. Their general electronic configuration is ns²np⁶ except helium which has electronic configuration 1s². They are called noble gases because they show very low chemical reactivity.



M'



GROUP 15 ELEMENTS

- 9. Atomic and ionic radii: Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.
- 10. **Ionisation energy:** It goes on decreasing down the group due to increase in atomic size. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements. Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half filled p-orbitals.
- 11. **Allotropy:** All elements of Group 15 except nitrogen show allotropy.
- 12. **Catenation:** Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent. The tendency to show catenation decreases down the group.
- 13. **Oxidation states:** The common oxidation states are +3, +5, -3. The tendency to show -3 oxidation state decreases down the group due to decrease in electronegativity which is due to increase in atomic size.

The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect.

Nitrogen shows oxidation states from -3 to +5.

Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.

 $3 \text{ HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2 \text{ NO}$

14. **Reactivity towards hydrogen:** All group 15 elements from trihydrides, MH₃. Hybridisation - sp³

The stability of hydrides decrease down the group due to decrease in bond dissociation energy down the group.

 $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Boiling point: $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

Boiling point increases with increase in size due to increase in van der Waals forces. Boiling point of NH_3 is more because of hydrogen bonding.

Bond angle: NH_3 (107.8°) > PH_3 (99.5°) > AsH_3 (91.8°) \approx SbH_3 (91.3°) > BiH_3 (90°)







Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.

Basicity decreases as $NH_3 > PH_3 > AsH_3 > SbH_3 < BiH_3$.

This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3 . It will decrease down the group as the electronegativity decreases down the group.

The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

15. **Reactivity towards oxygen:** All group 15 elements from trioxides (M_2O_3) and pentoxides (M_2O_5) .

Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small. It has a strong positive field in a very small area. Therefore, it attracts the electrons of water's O-H bond to itself and release H^+ ions easily. As we move down the group, the atomic size increases and hence the acidic character of oxides decreases and basicity increases down the group.

16. **Reactivity towards halogen:** Group 15 elements form trihalides and pentahalides.

Trihalides – covalent compounds and become ionic down the group.

sp³ hybridisation , pyramidal shape

Pentahalides - sp³d hybridisation, TBP shape

They are lewis acids because of the presence of vacant d – orbitals.

 $\mathsf{PCI}_5 + \mathsf{CI}^{\scriptscriptstyle -} \to [\mathsf{PCI}_6]^{\scriptscriptstyle -}$

 PCI_5 is ionic in solid state and exist as $[PCI_4]^+$ $[PCI_6]^-$

In PCl_5 , there are three equatorial bonds and two axial bonds. The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.

Nitrogen does not form pentahalides due to absence of *d*- orbitals.



Reactivity towards metals: All elements react with metals to form binary compounds in –3 oxidation state.





18. **Anomalous behaviour of nitrogen:** The behaviour of nitrogen differs from rest of the elements.

Reason:

- i. It has a small size.
- ii. It does not have d orbitals
- iii. It has high electronegativity
- iv. It has high ionization enthalpy

19. Dinitrogen:

Preparation:

 $NH_4CI(aq) + NaNO_2(aq) \xrightarrow{heat} N_2(g) + 2H_2O(I) + NaCI(aq)$

$$(NH_4)_2 Cr_2O_7 \xrightarrow{\text{heat}} N_2 + 4H_2O + Cr_2O_3$$

 $Ba(N_3)_2 \xrightarrow{heat} Ba + 3 N_2$

Properties:

It is a colouless, odourless, tasteless and non – toxic gas. It is chemically un-reactive at ordinary temperature due to triple bond in

 $N \equiv N$ which has high bond dissociation energy.

20. **Ammonia:** Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp³ hybridised.

Preparation:

Haber's process:

$$N_2$$
 (g)+3H₂ (g) \Longrightarrow 2 NH₃ (g)

 $\Delta_{\rm f} {\rm H}^{\rm o} = -$ 46.1 kJ mol⁻¹

 $Pressure = 200 \times 10^5 Pa$

Temperature = 773 K

Catalyst is FeO with small amounts of K₂O and Al₂O₃



PPER



21. Nitric Acid:

a. Ostwald Process:

 $4NH_3 + 5O_2 \xrightarrow{Pt/Rhgauge}{500 \text{ K},9\text{ bar}} 4NO + 6H_2O \dots(i)$

 $2 \text{NO} + \text{O}_2 \implies 2 \text{NO}_2 \dots \dots (\text{ii})$

 $3NO_2(g) + H_2O(I) \rightarrow 2HNO_3(aq) + NO(g) \dots$ (iii)

NO thus formed is recycled and the aqueous HNO₃ can be concentrated by distillation upto ~ 68% by mass. Further , ent in the con concentration to 98% can be achieved by dehydration with

Nitric acid is strong oxidizing agent in the concentrated as well as in



TOPPER www.topperlearning.com



Č.

22. Phosphorus:

- a. It shows the property of catenation to maximum extent due to most stable P P bond.
- b. It has many allotropes, the important ones are :
 - i. White phosphorus
 - ii. Red phosphorus
 - iii. Black phosphorus

White phosphorus	Red phosphorus	Black phosphorus	
Discrete tetrahedral P ₄ molecules	Polymeric structure consisting of chains of P ₄ units linked together	Exists in two forms - α black P and β black P	
Very reactive	Less reactive than white P	Very less reactive	
Glows in dark	Does not glow in dark	-	
Translucent waxy solid	Has an iron grey luster	Has an opaque monoclinic or rhombohedral crystals	
Soluble in CS ₂ but insoluble in water	Insoluble in water as well as CS_2	-	
It has low ignition temperature, therefore, kept under water		-	







TOPPER



Chlorides of Phosphorous: 24.

PCl ₃	PCI ₅
Colourless oily liquid	Yellowish white powder
$P_4 + 6 Cl_2 \rightarrow 4 PCl_3$	$P_4 + 10 \text{ Cl}_2 \rightarrow 4 \text{ PCl}_5$
$P_4 + 8 \text{SOCl}_2 \rightarrow 4 \text{PCl}_3 + 4 \text{SO}_2 + 2 \text{S}_2 \text{Cl}_2$	$P_4 + 10 SO_2CI_2 \rightarrow 4 PCI_5 + 10 SO_2$
Is hydrolysed in the presence of moisture $PCI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCI$	$PCI_{5} + H_{2}O \longrightarrow POCI_{3} + 2HCI$ $POCI_{3} + 3H_{2}O \longrightarrow H_{3}PO_{4} + 3HCI$
3 CH ₃ COOH + PCl ₃ \rightarrow 3 CH ₃ COCl + H ₃ PO ₃	3 CH_3COOH + $PCI_5 \rightarrow CH_3COCI$ + $POCI_3 + HCI$
$3 C_2H_5OH + PCI_3 \rightarrow 3 C_2H_5CI + H_3PO_3$	$\begin{array}{rrrr} C_2H_5OH \ + \ PCI_5 \ \rightarrow \ C_2H_5CI \ + \ POCI_3 \ + \\ HCI \end{array}$
Pyramidal shape, sp ³ hybridisation	TBP geometry, sp ³ d hybridisation
	$2Ag + PCI_5 \rightarrow 2 AgCI + PCI_3$ Sn + 2 PCI_5 \rightarrow SnCI ₄ + 2 PCI ₃

<u>It</u>







GROUP 16 ELEMENTS

25. Oxidation states: They show -2, +2, +4, +6 oxidation states. Oxygen does not show +6 oxidation state due to absence of d orbitals. Po does not show +6 oxidation state due to inert pair effect.

The stability of -2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity.

Oxygen shows -2 oxidation state in general except in OF_2 and O_2F_2

The stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.

- 26. **Ionisation enthalpy:** Ionisation enthalpy of elements of group 16 is lower than group 15 due to half filled p-orbitals in group 15 which are more stable. However, ionization enthalpy decreases down the group.
- 27. **Electron gain enthalpy:** Oxygen has less negative electron gain enthalpy than S because of small size of O.

From S to Po electron gain enthalpy becomes less negative to Po because of increase in atomic size.

28. **Melting and boiling point:** It increases with increase in atomic number. Oxygen has much lower melting and boiling points than sulphur because oxygen is diatomic (O_2) and sulphur is octatomic (S_8) .

29. Reactivity with hydrogen:

All group 16 elements form hydrides.

Bent shape

Bond angle: $H_2O > H_2S < H_2Se < H_2Te$

Intermolecular increase in van der Waals forces H bonding

Acidic nature: $H_2O < H_2S < H_2Se < H_2Te$

This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

Thermal stability: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$





This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

Reducing character: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

30. **Reactivity with oxygen:** EO₂ and EO₃

Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.

Acidity also decreases down the group.

 SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

31. Reactivity with halogens: EX₂ EX₄ and EX₆

The stability of halides decreases in the order $F^- > CI^- > Br^- > I^-$. This is because E-X bond length increases with increase in size.

Among hexa halides, fluorides are the most stable because of steric reasons.

Dihalides are sp³ hybridised, are tetrahedral in shape.

Hexafluorides are only stable halides which are gaseous and have $sp^{3}d^{2}$ hybridisation and octahedral structure.

 H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.



MN.S.





32. **Oxygen:**

Preparation:

$$2 \text{KCIO}_3 \xrightarrow{\text{heat}} 2 \text{KCI} + 3 \text{O}_2$$

$$2 \text{H}_2 \text{O}_2(aq) \xrightarrow{\text{finely divided metals}} 2 \text{H}_2 \text{O}(\text{I}) + \text{O}_2(\text{g})$$

$$2Ag_2O(s) \xrightarrow{\text{heat}} 4Ag(s) + O_2(g)$$

 $2 \text{HgO}(s) \xrightarrow{\Delta} 2 \text{Hg(I)} + O_2(g)$

$$2Pb_{3}O_{4}(s) \xrightarrow{\Delta} 6PbO(s) + O_{2}(g)$$
(Red lead)
$$2PbO_{2}(s) \xrightarrow{\Delta} 2PbO(s) + O_{2}(g)$$

33. **Oxides:**

The compounds of oxygen and other elements are called oxides.

Types of oxides:

a. Acidic oxides: Non- metallic oxides are usually acidic in nature.

 $SO_2 + H_2O \longrightarrow H_2SO_3$ (sulphurous acid)

b. Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,

$$\begin{split} &\mathsf{Na}_2\mathsf{O} + \mathsf{H}_2\mathsf{O} \longrightarrow 2\,\mathsf{NaOH} \\ &\mathsf{K}_2\mathsf{O} + \mathsf{H}_2\mathsf{O} \longrightarrow 2\,\mathsf{KOH} \\ &\mathsf{CaO} + \mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{Ca}\,(\mathsf{OH})_2 \end{split}$$

Amphoteric oxides: They show characteristics of both acidic as well as basic oxides.

$$\begin{aligned} \mathsf{AI}_2\mathsf{O}_3 + 6\,\mathsf{HCI}(aq) &\longrightarrow 2\,\mathsf{AICI}_3(aq) + 3\mathsf{H}_2\mathsf{O} \\ \mathsf{AI}_2\mathsf{O}_3 + 6\,\mathsf{NaOH}(aq) + 3\mathsf{H}_2\mathsf{O}(l) &\longrightarrow 2\mathsf{Na}_3[\mathsf{AI}(\mathsf{OH})_6](aq) \end{aligned}$$

d. Neutral oxides: These oxides are neither acidic nor basic.

Example: Co, NO and N_2O







34. **Ozone:**

Preparation:

i. It is prepared by passing silent electric discharge through pure and dry oxygen 10 - 15 % oxygen is coverted to ozone.

 $3O_2(g) \longrightarrow 2O_3(g); \Delta H = +142 \text{ kJ mol}^{-1}$

Structure of Ozone: Ozone has angular structure. Both O = O bonds are of equal bond length due to resonance.

35. Sulphur:

Sulphur exhibits allotropy:

- a. Yellow Rhombic (α sulphur):
- b. Monoclinic (β sulphur):

 α – Sulphur $\xrightarrow{369 \text{ K}} \beta$ – Sulphur

At 369 K both forms are stable. It is called transition temperature.

Both of them have S_8 molecules. The ring is puckered and has a crown shape.

Another allotrope of sulphur – cyclo S_6 ring adopts a chair form.

 S_2 is formed at high temperature (~ 1000 K). It is paramagnetic because of 2 unpaired electrons present in anti bonding π^* orbitals like O_2

36. Sulphuric acid:

Preparation: By contact process

$$\frac{1}{8}S_8 + O_2 \longrightarrow SO_2$$

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5}{2bar} 2SO_3(g) \qquad \Delta H^{\theta} = -196.6 \text{ kJ mol}^{-1}$$

Exothermic reaction and therfore low temperature and high pressure are favourable

$$SO_3(g) + H_2SO_4 \longrightarrow H_2S_2O_7$$
 (Oleum)





 $H_2S_2O_7 + H_2O \longrightarrow 2 H_2SO_4$ (96-98%)

It is dibasic acid or diprotic acid.

It is a strong dehydrating agent.

It is a moderately strong oxidizing agent.

GROUP 17 ELEMENTS

- 37. **Atomic and ionic radii:** Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.
- 38. **Ionisation enthalpy:** They have very high ionization enthalpy because of small size as compared to other groups.
- 39. **Electron gain enthalpy:** Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration.

Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.

40. **Eelctronegativity:** These elements are highly electronegative and electronegativity decreases down the group. They have high effective nuclear charge.

41. **Bond dissociation enthalpy:**

Bond dissociation enthalpy follows the order $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

This is because as the size increases bond length increases.

Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2 .

- 42. **Colour:** All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.
- 43. **Oxidising power:** All halogens are strong oxidisinga gents because they have a strong tendency to accept electrons.

Order of oxidizing power is $F_2 > Cl_2 > Br_2 > I_2$



44. Reactivity with H₂:



Stability: HF > HCl > HBr > HI

This is because of decrease in bond dissociation enthalpy.

Boiling point: HCl < HBr < HI < HF

HF has strong intermolecular H bonding

As the size increases van der Waals forces increases and hence boiling point increases.

% Ionic character: HF > HCl > HBr > HI

Dipole moment: HF > HCl > HBr > HI

Electronegativity decreases down the group.

Reducing power: HF < HCl < HBr < HI

45. **Reactivity with metals:** Halogens react with metals to form halides.

Ionic character: MF > MCl > MBr > MI

Halides in higher oxidation state will be more covalent than the one in the lower oxidation state.

46. Interhalogen compounds: Reactivity of halogens towards other halogens:

Binary compounds of two different halogen atoms of general formula

X X'_n are called interhalogen compounds where n = 1, 3, 5, or 7

These are covalent compounds.

All these are covalent compounds.

Interhalogen compounds are more reactive than halogens because X- X' is a more polar bond than X-X bond.

All are diamagnetic.

Their melting point is little higher than halogens.

XX' (CIF, BrF, BrCl, ICl, IBr, IF) (Linear shape)

XX'₃ (CIF₃, BrF₃, IF₃, ICl₃) (Bent T- shape)

XX'₅ – CIF₅, BrF₅, IF₅, (square pyramidal shape)







XX'₇ – IF₇ (Pentagonal bipyramidal shape)

47. Oxoacids of halogens:

Fluorine forms only one oxoacid HOF (Fluoric (I) acid or hypofluorous acid) due to high electronegativity.

Acid strength: $HOCI < HCIO_2 < HCIO_3 < HCIO_4$

Reason: $HCIO_4 \rightarrow H^+ + CIO_4^-$

most stable

Acid strength: HOF > HOCl > HOBr > HOI

This is because Fluorine is most electronegative.

GROUP 18 ELEMENTS:

48. **Ionisation enthalpy:** They have very high ionization enthalpy because of completely filled orbitals.

Ionisation enthalpy decreases down the group because of increase in size.

- 49. **Atomic radii:** Increases down the group because number of shells increases down the group.
- 50. **Electron gain enthalpy:** They have large electron gain enthalpy because of stable electronic configuration.
- 51. **Melting and boiling point:** Low melting and boiling point because only weak dispersion forces are present.
- 52. XeF₂ is linear, XeF₄ is square planar and XeF₆ is distorted octahedral. KrF₂ is known but no true compound of He Ne and Ar are known.

53. Compounds of Xe and F:

$$Xe + F_2 \xrightarrow{673 \text{ K, 1bar}} XeF_2$$

$$Xe + 2F_2 \xrightarrow{873 \text{ K}} 7bar \xrightarrow{} XeF_4$$

$$Xe + 3F_2 \xrightarrow{573 \text{ K}} 60-70 \text{ bar} \xrightarrow{} XeF_6$$

$$XeF_4 \xrightarrow{} 0 F_6 \xrightarrow{} 0 F_6$$

 $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$ XeF_2 , XeF_4 and XeF_6 are powerful fluorinating agents.













Chapter : The d and f-Block Elements

Top Concepts

- 1. d -Block elements: The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as d block elements. Their general electronic configuration is $(n 1)d^{1-10} ns^{1-2}$ where (n 1) stands for penultimate (last but one) shell.
- Transition element: A transition element is defined as the one which has incompletely filled *d* orbitals in its ground state or in any one of its oxidation states.
- 3. Zinc, cadmium, mercury are not regarded as transition metals due to completely filled d orbital.
- f-Block elements: The elements constituting the *f* -block are those in which the 4 *f* and 5 *f* orbitals are progressively filled in the latter two long periods.
- Lanthanoids: The 14 elements immediately following lanthanum, i.e., Cerium (58) to Lutetium (71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties. Therefore, it is studied along with lanthanoids.
- Actinoids: The 14 elements immediately following actinium (89), with atomic numbers 90 (Thorium) to 103 (Lawrencium) are called actinoids. They belong to second inner transition series. Actinium (89) has similar properties. Therefore, it is studied along with actinoids.
- 7. Four transition series:
 - a. 3d transition series. The transition elements with atomic number 21(Sc) to 30(Zn) and having incomplete 3d orbitals is called the first transition series.
 - b. 4d transition series. It consists of elements with atomic number 39(Y) to 48 (Cd) and having incomplete 4d orbitals. It is called second transition series.







- c. 5d transition series. It consists of elements with atomic number 57(La), 72(Hf) to 80(Hg) having incomplete 5d orbitals. It is called third transition series.
- d. 6d transition series. It consists of elements with atomic number 89(Ac), 104(Rf) to 112(Uub) having incomplete 6d orbitals. It is called fourth transition series.
- 8. General Characteristics of transition elements:
 - a. Metallic character: All transition elements are metallic in nature, i.e. they have strong metallic bonds. This is because of presence of unpaired electrons. This gives rise to properties like high density, high enthalpies of atomization, and high melting and boiling points.
 - b. Atomic radii: The atomic radii decrease from Sc to Cr because the effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increase in shielding effect. Cu and Zn have bigger size because the shielding effect increases and electron electron repulsions repulsion increases.
 - c. Lanthanoid Contraction: The steady decrease in the atomic and ionic radii of the transition metals as the atomic number increases. This is because of filling of 4f orbitals before the 5d orbitals. This contraction is size is quite regular. This is called lanthanoid contraction. It is because of lanthanoid contraction that the atomic radii of the second row of transition elements are almost similar to those of the third row of transition elements.
 - Ionisation enthalpy: There is slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 3d and 4d transition series because of Lanthanoid Contraction.





- e. Oxidation state: Transition metals show variable oxidation states due to tendency of (n-1)d as well as ns electrons to take part in bond formation.
- f. Magnetic properties: Most of transition metals are paramagnetic in nature due to presence of unpaired electrons. It increase s from Sc to Cr and then decreases because number of unpaired and then decrease because number of unpaired electrons increases from Sc to Cr and then decreases.
- g. Catalytic properties: Most of transition metals are used as catalyst because of (i) presence of incomplete or empty d – orbitals, (ii) large surface area, (iii) varuable oxidation state, (iv) ability to form complexes, e.g., Fe, Ni, V₂O₃, Pt, Mo, Co and used as catalyst.
- h. Formation of coloured compounds: They form coloured ions due to presence of incompletely filled d – orbitals and unpaired electrons, they can undergo d – d transition by absorbing colour from visible region and radiating complementary colour.
- Formation of complexes: Transition metals form complexes due to (i) presence of vacant d – orbitals of suitable energy (ii) smaller size (iii) higher charge on cations.
- j. Interstitial compounds: Transition metals have voids or interstitials in which C, H, N, B etc. can fit into resulting in formation of interstitial compounds. They are non – stoichiometric, i.e., their composition is not fixed, e.g., steel. They are harder and less malleable and ductile.

Alloys formation: They form alloys due to similar ionic size.
 Metals can replace each other in crystal lattice, e.g., brass, bronze, steel etc.





9. Preparation of Potassium dichromate (K₂Cr₂O₇):

It is prepared by fusion of chromate ore (FeCr₂O₄) with sodium carbonate in excess of air.

 $4\mathsf{FeCr}_2\mathsf{O}_4 + 8\mathsf{Na}_2\mathsf{CO}_3 + 7\mathsf{O}_2 \longrightarrow 8\mathsf{Na}_2\mathsf{CrO}_4 + 2\mathsf{Fe}_2\mathsf{O}_3 + 8\mathsf{CO}_2$

 $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$

Sodium Sodium

chromate dichromate

 $Na_2Cr_2O_7 + 2KCI \longrightarrow K_2Cr_2O_7 + 2NaCI$

10. Effect of pH on chromate and dichromate ions: The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2 \operatorname{CrO}_4^{2-} + 2\mathrm{H}^+ \rightarrow \operatorname{Cr}_2\mathrm{O}_7^{2-} + \mathrm{H}_2\mathrm{O}$$

 $\operatorname{Cr}_2\mathrm{O}_7^{2-} + 2 \operatorname{OH}^- \rightarrow 2 \operatorname{CrO}_4^{2-} + \mathrm{H}_2\mathrm{O}$

11. Potassium dichromate acts as a strong oxidizing agent in acidic medium.

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

12. Preparation of Potassium permanganate (KMnO₄):

a. Potassium permanganate is prepared by fusion of MnO_4 with alkali metal hydroxide (KOH) in presence of O_2 or oxidising agent like KNO₃. It produces dark green K_2MnO_4 which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

$$2MnO_{2} + 4KOH + O_{2} \longrightarrow 2K_{2}MnO_{4} + 2H_{2}O$$
$$4H^{+} + 3MnO_{4}^{2-} \longrightarrow 2MnO_{4}^{-} + MnO_{2} + 2H_{2}O$$
$$Or$$



M



Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

 $MnO_2 \xrightarrow{fused with KOH} MnO_2^{-} \xrightarrow{fused with KOH} MnO_4^{2-}$

(manganate ions)

 $MnO_4^{2-} \xrightarrow{\text{electrolytic oxidation in alkaline medium}} MnO_4^{-}$ (Green) (Purple)

(ii) In laboratory, Mn²⁺ salt can be oxidized by peroxodisulphate ion to permanganate ion.

 $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

13. Potassium permanganate acts as a strong oxidizing agent in acidic, neutral or faintly basic medium.

In acidic medium.

$$MnO_4^-$$
 + 8 H⁺ + 5 e⁻ \rightarrow Mn^{2+} + 4 H₂O

In neutral or faintly basic medium,

$$MnO_4^- + 3 e^- + 2 H_2O \rightarrow MnO_2 + 4OH^-$$

14. Properties of Lanthanoids and Actinoids.

Lanthanoids	Actinoids
+3 oxidation state is most common along with +2 and +4	Actiniods also show higher oxidation states such as $+4$, $+5$, $+6$ and $+7$.
	They are more reactive
Except Promethium, they are non -	They are radioactive
radioactive.	
The magnetic properties of	The magnetic properties of the
lanthanoids are less complex than	actinoids are more complex than
actinoids.	those of the lanthanoids

15. Mischmetall - It is a well known alloy which consists of a lanthanoid metal (\sim 95%) and iron (\sim 5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.






Chapter : Coordination Compounds

1. Difference between coordination compound and double bond:

Coordination compound	Double salt
A coordination compound contains a	When two salts in stoichiometric ratio
central metal atom or ion surrounded	are crystallised together from their
by number of oppositely charged ions	saturated solution they are called
or neutral molecules. These ions or	double salts
molecules re bonded to the metal	
atom or ion by a coordinate bond.	
Example: $K_4[Fe(CN)_6]$	Example:FeSO ₄ .(NH ₄) ₂ SO ₄ .6H ₂ O
	(Mohr's salt)
They do not dissociate into simple	They dissociate into simple ions when
ions when dissolved in water.	dissolved in water.

- Coordination entity: A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: in K₄[Fe(CN)₆], [Fe(CN)₆]⁴⁻ represents coordination entity.
- 3. Central atom or ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. E.g.: in K₄[Fe(CN)₆], Fe²⁺ is the central metal ion.
- Ligands: A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand. It may be neutral, positively or negatively charged. Example: H₂O, CN⁻, NO⁺ etc.
 - **Donor atom:** An atom of the ligand attached directly to the metal is called the donor atom. For example: in the complex K_4 [Fe(CN)₆], carbon is a donor atom.





- 6. Coordination number: The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example: in the complex K₄[Fe(CN)₆], the coordination number of Fe is 6.
- 7. Coordination sphere: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the coordination sphere. For example: in the complex K₄[Fe(CN)₆], [Fe(CN)₆]⁴⁻ is the coordination sphere.
- Counter ions: The ions present outside the coordination sphere are called counter ions. For example: in the complex K₄[Fe(CN)₆], K⁺ is the counter ion.
- 9. Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example: [PtCl₄]²⁻ is square planar, Ni(CO)₄ is tetrahedral while [Cu(NH₃)₆]³⁺ is octahedral.
- 10. **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.
- 11. **Denticity:** The number of ligating (linking) atoms present in ligand is called denticity.
- Unidentate ligands: The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands. Example: H₂O, NH₃, CO, CN⁻
- Didentate ligands: The ligands which contain two donor atoms or ions through which they are bonded to the metal ion. For example: ethylene diamine (H₂NCH₂CH₂NH₂) has two nitrogen atoms, oxalate ion

 $\begin{bmatrix} COO^{-} \\ | \\ COO^{-} \end{bmatrix}$ has two oxygen atoms which can bind with the metal atom.





- 14. Polydentate ligand: When several donor atoms are present in a single ligand, the ligand is called polydentate ligand. For example: in N(CH₂CH₂NH₂)₃, the ligand is said to be polydentate. Ethylenediaminetetraacetate ion (EDTA⁴⁻) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.
- 15. Chelate: An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points. An example is the complex ion formed between ethylene diamine and cupric ion, [Cu(NH₂CH₂NH₂)₂]²⁺.
- 16. Ambidentate ligand: Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligand. Example: NO₂⁻, and SCN⁻. NO₂⁻ can link through N as well as O while SCN⁻ can link through S as well as N atom.
- 17. Werner's coordination theory: Werner was able to explain the nature of bonding in complexes. The postulates of Werner's theory are:
 - a. Metal shows two different kinds of valencies: primary valence and secondary valence.

Primary valence	Secondary valence	
This valence is normally ionisable.	This valence is non – ionisable.	
It is equal to positive charge on	The secondary valency equals the	
central metal atom.	number of ligand atoms coordinated	
5	to the metal. It is also called	
	coordination number of the metal.	
These valencies are satisfied by	It is commonly satisfied by neutral	
negatively charged ions.	and negatively charged, sometimes	
1.	by positively charged ligands.	
Example: in $CrCl_3$, the primary		
valency is three. It is equal to		
oxidation state of central metal ion.		







- b. The ions/ groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
- c. The most common geometrical shapes in coordination compounds are octahedral, square planar and tetrahedral.
- 18. **Oxidation number of central atom:** The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.
- 19. **Homoleptic complexes:** Those complexes in which metal or ion is coordinate bonded to only one kind of donor atoms. For example: $[Co(NH_3)_6]^{3+}$
- Heteroleptic complexes: Those complexes in which metal or ion is coordinate bonded to more than one kind of donor atoms. For example: [CoCl₂(NH₃)₄]⁺, [Co(NH₃)₅Br]²⁺
- 21. **Isomers.** Two or more compounds which have same chemical formula but different arrangement of atoms are called isomers.
- 22. **Types of isomerism:**
 - a. Structural isomerism
 - i. Linkage isomerism
 - ii. Solvate isomerism or hydrate isomerism
 - iii. Ionisation isomerism
 - iv. Coordination isomerism
 - b. Stereoisomerism
 - i. Geometrical isomerism
 - ii. Optical isomerism
- 23. **Structural isomerism:** This type of isomerism arises due to the difference in structures of coordination compounds. Structural isomerism, or constitutional isomerism, is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.





- a. **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. Example: $[Co(NH_3)_5Br] SO_4$ and $[Co(NH_3)_5 SO_4] Br$
- b. Solvate isomerism: It is isomerism in which solvent is involved as ligand. If solvent is water it is called hydrate isomerism, e.g., [Cr(H₂O)₆]Cl₃ and [CrCl₂(H₂O)₄] Cl₂. 2H₂O
- c. Linkage isomerism: Linkage isomerism arises in a coordination compound containing ambidentate ligand. In the isomerism, a ligand can form linkage with metal through different atoms. Example: [Co(NH₃)₅ONO]Cl₂ and [Co(NH₃)₅NO₂]Cl₂
- d. Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. Example: [Co(NH₃)₆][Cr(C₂O₄)₃] and [Cr(NH₃)₆][Co(C₂O₄)₃]
- 24. **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.
 - a. **Geometrical isomerism:** It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.
 - b. **Optical isomerism:** Optical isomers are those isomers which are non superimposable mirror images.



MN. allin



25. Valence bond theory:

According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, and square planar.

These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination number	Type of hybridisation	Distribution of hybrid
		orbitals in space
4	sp ³	tetrahedral
4	dsp ²	Square planar
5	sp³d	Trigonal bipyramidal
6	sp ³ d ² (nd orbitals are	Octahedral
	involved – outer orbital	
	complex or high spin or	
	spin free complex)	
6	d ² sp ³ ((n-1) d orbitals are	Octahedral
	involved –inner orbital or	
	low spin or spin paired	
	complex)	

26. **Magnetic properties of coordination compounds:** A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

Magnetic moment $\mu = \sqrt{n(n+2)}$ where n is number of unpaired electrons.

27. **Crystal Field Theory:** It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. It is theoretical assumption.





28. **Crystal field splitting in octahedral coordination complexes:**



29. Crystal field splitting in tetrahedral coordination complexes:



30. For the same metal, the same ligands and metal-ligand distances, the difference in energy between e_g and t_{2g} level is

$$\Delta_t = -\frac{4}{9}\Delta_0$$





Metal carbonyls. Metal carbonyls are homoleptic complexes in which 31. carbon monoxide (CO) acts as the ligand. For example: $Ni(CO)_4$ The metal – carbon bond in metal carbonyls possesses both σ and π characters. The metal-carbon bond in metal carbonyls possess both s and p character. The M–C σ bond is formed by the donation of lone pair of electrons from 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 ind t etween Ct carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



MN.S.





Chapter : Haloalkanes and Haloarenes

- 1. Nature of C-X bond in alkyl halides: X is more electronegative than carbon. So, the C-X bond is polarized with C having a partial positive charge and X having a partial negative charge
- 2. Preparation of haloalkanes:



Halogen exchange method:

R-Br + AgF → R-F + AgBr

(Swarts reaction)

- 3. Preparation of haloarenes:
- a. By elecrophilic substitution reaction:

















e. Balz - Schiemann reaction:



- 4. Physical properties of haloalkanes:
 - a. Solubility. Although haloalkanes are polar in nature, yet they are practically very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. However Haloalkanes are not able to form hydrogen bonds with water and therefore, less energy is released when new attractions are set up between the haloalkane and the water molecules because these are not as strong as the original hydrogen bonds in water molecules. As a result, solubility of haloalkanes in water is low.
 - **b.** Density:
 - Simple fluoro and chloroalkanes are lighter than water while bromides and polychloro devrivatives are heavier than water.
 - With the increase in number of carbon atoms, the densities go on increasing.







- With the increase in number of halogen atoms, the densities go on increasing.
- The densities increase in the order:
- Fluoride < chloride < bromide < iodide
- The density also increases with increasing number and atomic mass of the halogen.
- **c.** Method and Boiling points:
 - Molecules of organic halogen compounds are generally polar.
 Due to the polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole dipole and van der Waals)
 between the molecules are stronger in halogen derivatives of alkanes. As a result melting and boiling points of chlorides, bromides and iodides are considerably higher than those of the parent hydrocarbon of comparable molecular mass.
 - Amongst themselves, the following trends are observed:
 - For the same alkyl group the boiling points of alkyl chlorides, bromides and iodides follow the order RI > RBr
 RCl > RF where R is an alkyl group. This is because with the increase in the size of the halogen, the magnitude of van der Waals force increase.
 - In general, the boiling points of chloro, bromo and iodo compounds increase with increase in the number of halogen atoms.
 - For the same halogen atom, the boiling points of haloalkanes increase with increase in the size of alkyl groups.







- For isomeric alkyl halides, the boiling points decrease with branching. This is because branching of the chain makes the molecule more compact and, therefore, decrease the surface area. Due to decrease in surface area, the magnitude of van der Waals forces of attraction decreases and consequently, the boiling points of the branched chain compound is less than those of the straight chain compounds.
- 5. Physical Properties of Haloarenes:
 - a. These are generally colourless liquids or crystalline solids.
 - b. These are heavier than water.
 - c. Melting and boiling points of haloarenes:
 - Melting and boiling points of haloarenes are nearly the same as those of alkyl halides containing the same number of carbon atoms.
 - The boiling points of monohalogen derivatives of benzene are in the order: iodo > bromo > chloro > fluoro
 - For the same halogen atom, the melting and boiling points increase as the size of the aryl group increases.
 - The melting point of para isomer is quite higher than that of ortho or meta isomers. This is due to the fast that is has symmetrical structure and there fore, its molecules can easily pack loosely in the crystal lattice. As a result intermolecular forces of attraction are stronger and therefore, greater energy is required to break its lattice and it melts at higher temperature.



h



- 5. Chemical properties of haloalkanes:
 - **a.** Nucleophilic substitution reaction:

$$N\bar{u} + -C X^{\delta^+} X^{\delta^-} \longrightarrow C Nu + X$$

Mechanism:

S _N I	S _N II	
First order reaction Rate =k [RX] [Nu]	Second order reaction Rate =k [RX]	
Racemic mixture	Inversion of configuration	
One step reaction	Two step reaction	
Order : $CH_3X < 1^{\circ} < 2^{\circ} < 3^{\circ}$	Order : CH ₃ X > 1° > 2° > 3°	

 $\label{eq:R-X+aq. KOH} \begin{array}{l} \rightarrow \mbox{R-OH} + \mbox{KX} \\ \mbox{R-X+NH}_3 \rightarrow \mbox{R-NH}_2 + \mbox{HX} \\ \mbox{R-X+KCN} \rightarrow \mbox{R-CN} + \mbox{KX} \\ \mbox{R-X+AgCN} \rightarrow \mbox{R-NC} + \mbox{KX} \end{array}$

b. Elimination reaction: Dehydrohalogentaion(β - elimination):

When a haloalkane with β -hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β -carbon and a halogen atom from the α -carbon atom. As a result, an alkene is formed as a product.

Zaitsev rule (also pronounced as Saytzeff) is followed. It states that "In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms."































Chapter : Alcohols, Phenols And Ethers

Top concepts:

1. Structure of alcohols, phenols and ethers:











3. Preparation of phenols:



4. Physical properties of alcohols and phenols:

a. Boiling points:

 Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is because the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.



 The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. This is because of increase in van der Waals forces with increase in surface area.





 In alcohols, the boiling points decrease with increase of branching in carbon chain. This is because of decrease in van der Waals forces with decrease in surface area.

b. Solubility:

W.TOPPERLEARNING.COM

 Solubility of alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules.



• The solubility of alcohols decreases with increase in size of alkyl/aryl (hydrophobic) groups.

5. Chemical properties of alcohols:

- a. Reactions involving cleavage of O–H bond: Alcohols react as nucleophiles:
- b. Reactions involving cleavage of carbon oxygen (C–O) bond in

Alcohols: Protonated alcohols react as electrophiles:

- c. Dehydration
- d. Oxidation
- 6. Reactions of alcohols and phenols involving cleavage of O–H bond:

a. Reaction with metals:









b. Esterification:

 $Ar/RO - H + R' - COOH \stackrel{H^+}{\longleftarrow} Ar/ROCOR' + H_2O$ Phenol / Alcohol

 $Ar/R-OH + (R'CO)_2 O \xrightarrow{H^+} Ar/ROCOR'+R'COOH$ Phenol / Alcohol

 $R/ArOH + R'COCI \xrightarrow{Pyridine} R/ArOCOR + HC1$ Phenol / Alcohol

- Reactions of alcohols involving cleavage of carbon oxygen (C–O) bond:
 - a. Reaction with hydrogen halides:

 $ROH + HX \xrightarrow{conc.HCl + ZnCl_2}_{Lucas reagent} RX + H_2O$

b. Reaction with phosphorus trihalides:

3 ROH + $PX_3 \rightarrow 3 R-X + H_3PO_3$ (X = Cl, Br)

c. Dehydration:

















9. Acidic nature:

a. Phenol > H₂O > Primary alcohol > Secondary alcohol > Tertiary alcohol

The acidic character of alcohols is due to the polar nature of O–H bond.



Alkyl group is an electron-releasing group $(-CH_3, -C_2H_5)$ or it has electron releasing inductive effect (+I effect).

Due to +I effect of alkyl groups, the electron density on oxygen increases. This decreases the polarity of O-H bond.

And hence the acid strength decreases.

b. Phenol is more acidic than alcohol because:

- In phenol, the hydroxyl group is directly attached to the *sp*² hybridised carbon of benzene ring which acts as an electron withdrawing group. Whereas in alcohols, the hydroxyl group is attached to the alkyl group which have electron releasing inductive effect.
- In phenol, the hydroxyl group is directly attached to the *sp*² hybridised carbon of benzene ring. Whereas in alcohols, the hydroxyl group is attached to the *sp*³ hybridised carbon of the alkyl group. The *sp*² hybridised carbon has higher electronegativity than *sp*³ hybridised carbon. Thus, the polarity of O-H bond of phenols is higher than those of alcohols. Hence, the ionisation of phenols id higher than that of alcohols.
- The ionisation of an alcohol and a phenol takes place as follows:



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised.









The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.



c. In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. On the other hand, electron releasing groups, such as alkyl groups, in general, decreases the acid strength.

It is because electron withdrawing groups lead to effective delocalisation of negative charge in phenoxide ion.

10. How to distinguish between some important pair of organic compounds:

a. Phenol and alcohol:

Phenol on reaction with neutral $FeCl_3$ gives purple colour whereas alcohols do not give purple colour.

$$6 C_6H_5OH + Fe^{3+} \rightarrow [Fe(OC_6H_5)_6]^{3+} + 6 H^+$$

Purple colour

b. Primary, secondary and tertiary alcohol:

Lucas reagent test:

 $ROH + HCI \xrightarrow{conc.HCl + ZnCl_2} RCI + H_2O$

If it is a primary alcohol, no turbidity appears at room temperature. Turbidity appears only on heating.

If it is a secondary alcohol, turbidity appears in 5 minutes. If it is a tertiary alcohol, turbidity appears immediately.

c. Methanol and ethanol:

Iodoform test:

Ethanol when reacted with (I_2 and NaOH) or NaOI gives yellow ppt of iodoform since it has the presence of CH₃-CH (OH)- group.

C₂H₅OH +4I₂+ 6NaOH → CHI₃ + 5NaI + 5H₂O + HCOONa Yellow ppt. CH₃OH + I₂+ NaOH → NO YELLOW PPT







12. Physical properties of ethers: a. Miscibility:

Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule.



b. Boiling points:

Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bonding in alcohols. Hydrogen bonding is absent in ethers.





13.Chemical properties of ethers: a. Cleavage of C-O bond in ethers:

 $\begin{array}{rl} \text{R-O-R'} + & \text{HX} & \rightarrow \text{R-X} + \text{R'OH} \\ & \text{Excess} \end{array}$

- The order of reactivity of hydrogen halides is as follows: $\rm HI$ > HBr > HCl
- Alkyl halide formed is always the lower alkyl group.
- But if a tertiary alkyl group is present, the alkyl halide is always tertiary.
- In case of phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.

⇒ÖR +ÖR :ÖR :OR +ÖR IV V III I Π OCH. OCH, CH OCH₃ COCH₃ CH₃ + CH₃COCI COCH + CH_aCI In the (Major) (Minor) (Minor) (Major) presence of In the anhyd. AICI₃ presence of anhyd. AICI₃ and CS, OCH₃ Br, in ethanoic acid Anisole H₂SO₄, HNO₃ OCH₃ OCH₃ Br OCH₃ OCH₃ NO₂ MM Вr (Major) (minor) NO₂ (Minor) (Major)

b. Electrophilic substitution reaction in aromatic ethers:









14. Some important reactions for conversions:

a. Conversion 1:









Chapter: Aldehydes, Ketones and Carboxylic acids

Top concepts

Aldehydes:

1. Definition: Aldehydes are the organic compounds in which carbonyl group is attached to one hydrogen atom and one alkyl or aryl group.

2. General formula:



R can be an alkyl or aryl group

3. Preparation of aldehydes:

1. By oxidation of alcohols: Oxidation of primary alcohols in presence of oxidizing agent like $K_2 Cr_2 O_7 / H_2 SO_4$, KMnO₄, CrO₃ gives aldehydes

RCH ₂ OH	Oxidation	H R - C=O
1° Alcohol		Aldehyde

2. By dehydrogenation of alcohols: Vapours of primary alcohol when passed heated copper at 573 K forms aldehyde

 $\begin{array}{ccc} \text{RCH}_2\text{OH} & \xrightarrow{\text{Cu}} & \text{RCHO} \\ \hline 573\text{K} & \text{Aldehyde} \end{array}$

3. By hydration of alkynes: Ethyne on hydration with ${\rm HgSO}_{\rm _4}$ / dil ${\rm H_2SO}_{\rm _4}$ at 333 K forms acetaldehyde

HC = CH + H - OH
$$\xrightarrow{Hg^{2+}/H^{+}}$$
 CH₂ = C - H
Ethyne OH \downarrow Isomerisation CH₃ - C - H \parallel O
Ethanal







4. By Rosenmund reduction: Hydrogenation of acyl chloride over palladium on barium sulphate gives aldehyde



Benzoyl chloride

Benzaldehyde

5.By reduction of nitriles:

(a)Stephen Reaction: Reduction of nitriles in presence of stannous chloride in presence of HCl gives imine which on hydrolysis gives corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O} RCHO$$

(b) Nitriles are selectively reduced by DIBAL-H (Diisobutylaluminium hydride) to aldehydes

$$\operatorname{RCN} \xrightarrow{1. \operatorname{AlH}(i-\operatorname{Bu})_2}{2. \operatorname{H}_2 O} \operatorname{R-CHO}$$

 $CH_{3} - CH = CH - CH_{2}CH_{2} - CN \xrightarrow{1. AlH(i-Bu)_{2}} CH_{3} - CH = CH - CH_{2}CH_{2} - CHO$

6. By reduction of ester: Esters are reduced to aldehydes in presence of DIBAL-H (Diisobutylaluminium hydride)

$$CH_{3}(CH_{2})_{9} - \overset{O}{C} - OC_{2}H_{5} \xrightarrow{1. \text{ DIBAL-H}} CH_{3}(CH_{2})_{9} - \overset{O}{C} - H_{3}(CH_{2})_{9} - \overset{O}{C} - H_$$

8. From Hydrocarbons:

(i)By oxidation of methyl benzene:

(a) Etard Reaction: Chromyl chloride (CrO_2Cl_2) oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde







(b)Use of chromium oxide(CrO_3): Toluene or substituted toluene is converted to benzylidene in presence of chromic oxide in acetic anhydride.



(ii)By side chain chlorination followed by hydrolysis: Side chain halogenation of toluene gives benzal chloride which on hydrolysis gives benzaldehyde



(iii) Gatterman –Koch reaction: Benzene or its derivatives on treatment with carbon monoxide and HCl in presence of anhydrous aluminium chloride or cuprous chloride (CuCl) gives benzaldehyde or substituted benzaldehydes



Ketones:

1. Definition: Ketones are the organic compounds in which carbonyl group is attached to two alkyl group or aryl group or both alkyl and aryl group



R, R' may be alkyl or aryl

3. Preparation of ketones:

1. By oxidation of alcohols: Oxidation of secondary alcohols in presence of oxidizing agent like $K_2 Cr_2 O_7 / H_2 SO_4$, $KMnO_4$, CrO_3 gives ketones









2. By dehydrogenation of alcohols: When the vapours of a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and a ketone is formed

 $\begin{array}{ccc} R-CH-R' & \xrightarrow{Cu} & R-C-R' \\ I & 573K & I \\ OH & O \end{array}$

3. By hydration of alkynes:

Hydration of alkynes other than acetylene yields ketone. For example propyne on hydration with $HgSO_4$ / dilH₂SO₄ at 333 K forms propanone.



4. From acyl chloride: Acyl chloride on treatment with dialkyl cadmium (prepared by reaction of cadmium chloride with Grignard reagent) gives ketone

5. From nitriles: Nitriles on treatment with Grignard reagent followed by hydrolysis gives ketones

$$CH_{3} - CH_{2} - C = N + C_{6}H_{5}MgBr \xrightarrow{ether} CH_{3}CH_{2} - C \xrightarrow{NMgBr} \xrightarrow{H_{3}O^{+}} C_{2}H_{5} - C \xrightarrow{O} C_{6}H_{5}$$
Propiophenone
(1-Phenylpropanone)







6. By Friedel Crafts acylation reaction: Benzene or substituted benzene on treatment with acid chloride in presence of anhydrous aluminium chloride forms ketone



7. Preparation of aldehydes and ketones by ozonolysis of alkenes:



Aldehydes or Ketones

Reactions of aldehydes and ketones:

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons (or inductive effect).

Electronic Effect: Relative reactivities of aldehydes and ketones in nucleophilic addition reactions is due the positive charge on carbonyl carbon. Greater positive charge means greater reactivity. Electron releasing power of two alkyl groups in ketones is more than one in aldehyde. Therefore positive charge is reduced in ketones as compared to aldehydes. Thus ketones are less reactive than aldehydes.

Stearic Effect: As the number and size of alkyl group increase, the hindrance to the attack of nucleophile also increases and reactivity decreases. In aldehydes there is one alkyl group and one hydrogen atom, whereas in ketones there are two alkyl groups (same or different).

1. Nucleophilic addition reactions of aldehydes and ketones:

(a)Addition of hydrogen cyanide (HCN) to form cyanohydrins:



Tetrahedral intermediate







(b)Addition of sodium hydrogensulphite (NaHSO₃) to form bisulphate addition compound:





(ii)Ketones do not react with monohydric alcohols. Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals



(e)Addition of ammonia and its derivatives:

$$>C=O + H_2N-Z \iff \left[>C < OH \\ NHZ \right] \longrightarrow >C=N-Z + H_2O$$

Z=Alkyl, aryl, OH, NH2, $\mathrm{C_6H_5NH},$ NHCONH2, etc.





PPER





2. Reduction of aldehydes and ketones:

(a) Reduction to alcohols: Aldehydes and ketones on catalytic hydrogenation in presence of Ni, Pt or Pd by using lithium aluminium hydride (LiAlH₄) or

sodium borohydride (NaBH $_4$) forms primary and secondary alcohols respectively









(b) Reduction to hydrocarbons:

(i) Clemmensen reduction: Carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid

$$C = O \xrightarrow{Zn-Hg} CH_2 + H_2O$$

(ii) Wolff-Kishner reduction: Carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol

$$C = O \xrightarrow{\text{NH}_2\text{NH}_2} C = \text{NNH}_2 \xrightarrow{\text{KOH/ethylene glycol}} CH_2 + N_2$$

3. Oxidation of aldehydes and ketones:

(i) Aldehydes are oxidized to acids in presence of mild oxidising agents HNO_3 , $K_2Cr_2O_7$, $KMnO_4$

$$R-CHO \xrightarrow{[O]} R-COOH$$

(ii) Ketones are generally oxidized under drastic conditions i.e. with powerful oxidising agents like conc. HNO_3 , $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$ at elevated temperature

$$R \xrightarrow{1} CH_{2} \xrightarrow{2} CH_{2} \xrightarrow{3} CH_{2} \xrightarrow{[O]} R \xrightarrow{-COOH} + R' - CH_{2}COOH$$
(By cleavage of C₁-C₂ bond)
+
$$R \xrightarrow{-CH_{2}COOH} + R' \xrightarrow{-COOH}$$
(By cleavage of C₂-C₂ bond)

Important Note: In case of unsymmetrical ketones cleavage occurs in such a way that keto group stays with smaller alkyl group. This is known as Popoff's rule.

(iii)Haloform reaction: Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom i.e. methyl ketones are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform.









4. Reactions of aldehydes and ketones due to α -hydrogen: (i) Aldol condensation: Aldehydes and ketones having at least one α -hydrogen undergo a self condensation in the presence of dilute alkali as catalyst to form α -hydroxy aldehydes (aldol) or α -hydroxy ketones (ketol), respectively.

3-Hydroxybutanal (Aldol)

(Aldol condensation product)



(ii) Cross aldol condensation: Aldol condensation between two different aldehydes and ketones is called aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



NN.O.








2) Fehling's test: When an aldehyde is heated with Fehling's reagent it forms reddish brown precipitates of cuprous oxide.

Fehling's reagent: Fehling solution A (aqueous solution of CuSO₄) + Fehling solution B (alkaline solution of sodium potassium tartarate)

 $R-CHO + 2Cu^{2+} + 5\overline{O}H \longrightarrow RCO\overline{O} +$

Cu₂O + 3H₂C Red-brown ppt

Ketones do not give this test

Carboxylic Acids:

1. Definition: Carboxylic acids are the compounds containing the carboxyl functional group (-COOH)

2. General Formula



3. Preparation of carboxylic acid:

(i) From alcohols: Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMnO₄) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO₃) in acidic media.

 $\operatorname{RCH}_{2}\operatorname{OH} \xrightarrow{1. \text{ alkaline } \operatorname{KMnO}_{4}}_{2. \operatorname{H}_{3}\overset{+}{\operatorname{O}}} \operatorname{RCOOH}$

 $RCH_2OH \xrightarrow{CrO_3-H_2SO_4} RCOOH$

(ii) From aldehydes: Oxidation of aldehydes in presence of mild oxidizing agents like Tollen's reagent (ammoniacal solution of $AgNO_3$) or Fehling reagent (Fehling solution A (aqueous solution of $CuSO_4$) + Fehling solution B (aqueous solution of sodium potassium tartarate)) forms carboxylic acids

RCHO + $2[Ag(NH_3)_2]^+$ + $3 \overline{OH} \longrightarrow RCO\overline{O}$ + $2Ag + 2H_2O + 4NH_3$

 $\begin{array}{rcl} \text{R-CHO} + 2\text{Cu}^{2*} + 5\overline{\text{O}}\text{H} & \longrightarrow & \text{RCO}\overline{\text{O}} + \text{Cu}_2\text{O} + 3\text{H}_2\text{O} \\ & & \text{Red-brown ppt} \end{array}$



TOPPER www.topperlearning.com



(iii)From alkylbenzenes: Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate.



Benzoic acid

R is an alkyl group (primary or secondary)

(iv)From alkenes: Suitably substituted alkenes are oxidised to carboxylic acids on oxidation with acidic potassium permanganate or acidic potassium dichromate

 $\begin{array}{c} R-CH=CH-R & \xrightarrow{KMnO_4/H^+} & 2R-COOH \\ R-CH=CH-R_1 & \xrightarrow{KMnO_4/H^+} & R-COOH+R_1 - COOH \end{array}$

(v)From Nitriles: Nitriles on hydrolysis in presence of dilute acids or bases forms amide which on further hydrolysis gives carboxylic acid.

$$R-CN \xrightarrow{\stackrel{+}{H} \text{ or } \overline{OH}}_{H_2O} \xrightarrow{R} C-NH_2 \xrightarrow{\stackrel{+}{H} \text{ or } \overline{OH}}_{\Delta} RCOOH$$

(vi) From Grignard reagent: Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which on hydrolysis forms carboxylic acids

R-Mg-X + O=C=O
$$\xrightarrow{\text{Dry ether}}$$
 R \xrightarrow{O} \xrightarrow{O} $\xrightarrow{H_3O^+}$ RCOOH

(vii) From acyl halides and anhydrides: Acid chlorides when hydrolysed with water give carboxylic acids .On basic hydrolysis carboxylate ions are formed which on further acidification forms corresponding carboxylic acids. Anhydrides on hydrolysis forms corresponding acid(s)









$$(RCO)_2O \xrightarrow{H_2O} 2 RCOOH$$

(viii)From esters: Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.

$$R - COO - R' \xleftarrow{H_3 O'} R - COOH + R' - OH$$

$$R - COO - R' \xleftarrow{N_3 CH} R - COO - Na + R' - OH$$

$$\int H_3 O^*$$

4. Physical properties of carboxylic acids:

(i)Solubility: As the size of alky group increases solubility of carboxylic acid decreases because non-polar part of the acid increases

(ii)Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding





WWW.TOPPERLEARNING.COM



5. Acidity of carboxylic acids: Carboxylic acids are more acidic than phenols. Strength of acid depends on extent of ionization which in turn depends on stability of anion formed.

(i)Effect of electron donating substituents on the acidity of carboxylic acids: Electron donating substituent decreases stability of carboxylate ion by intensifying the negative charge and hence decreases acidity of carboxylic acids.

(ii)Effect of electron withdrawing substituent on the acidity of carboxylic acids: Electron withdrawing group increases stability of carboxylate ion by delocalizing negative charge and hence increases acidity of carboxylic acid

The effect of the following groups in increasing acidity order is

 $Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

(a)Effect of number of electron withdrawing groups: As the number of electron withdrawing groups increases –I effect increases, increasing the acid strength

(b)Effect of position of electron withdrawing group: As the distance between electron withdrawing group and carboxylic group increases, electron withdrawing influence decreases.

6. Reaction of carboxylic acids:

(a) Reactions involving cleavage of C-OH bond: Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride (i) Anhydride formation:



(ii) Esterification: Carboxylic acids are esterified with alcohols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst

RCOOH + R'OH $\xrightarrow{H^+}$ RCOOR' + H₂O

(iii) Carboxylic acids react with PCl_5 , PCl_3 and $SOCl_2$ to form acyl chlorides $RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$ $3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$ $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$



WWW.TOPPERLEARNING.COM



(iv) Reaction with ammonia (NH_3): Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature gives amides.



(b) Reactions involving COOH group:

(i)Reduction: Carboxylic acids are reduced to alcohols in presence of LiAlH₄ or B_2H_6 .

R-COOH
$$(i)$$
 LiAlH₄/ether or B₂H₆ \rightarrow R-CH₂OH (ii) H₃O⁺

(ii)Decarboxylation : Sodium or potassium salts of carboxylic acids on heating with soda lime (NaOH + CaO in ratio of 3:1) gives hydrocarbons which contain one carbon less than the parent acid.

R-COONa
$$\xrightarrow{\text{NaOH & CaO}}$$
 R-H + Na₂CO₃
Heat

(c)Reactions involving substitution reaction in hydrocarbon part:

(i) Hell-Volhard-Zelinsky reaction: Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids)

$$\begin{array}{ccc} \text{(i) } X_2/\text{Red phosphorus} \\ \hline \text{(ii) } H_2\text{O} \\ & & & & \\ & & &$$

α – Halocarboxylic acid

(ii)Ring substitution in aromatic acids: Aromatic carboxylic acids undergo electrophilic substitution reactions. Carboxyl group in benzoic acid is electron withdrawing group and is meta directing.



PPER WWW.TOPPERLEARNING.COM











Chapter: Amines

Top concepts

1. Amines are regarded as derivatives of ammonia in which one, two or all three hydrogen atoms are replaced by alkyl or aryl group

2. Classification of amines:



R,R' and R" can be alkyl or aryl group

3. Preparation of amines:

(i)By reduction of nitro compounds:

Nitro compounds can be catalytically reduced by passing hydrogen gas in presence of Raney Ni, finely divided Pt or Pd as catalyst at room temperature.

$$R - NO_2 + 3H_2 \xrightarrow{Ni, Pt or Pd} R - NH_2 + 2H_2O$$

$$Ar - NO_2 + 3H_2 \xrightarrow{NI, Pt \text{ or } Pd} Ar - NH_2 + 2H_2O$$

Nitro compounds can also be reduced with active metals such as Fe, Sn, Zn etc. with conc. HCl

$$R - NO_{2} + 3H_{2} \xrightarrow{Sn/HCl} R - NH_{2} + 2H_{2}O$$

$$Ar - NO_{2} + 3H_{2} \xrightarrow{Sn/HCl} or Fe/HCl} Ar - NH_{2} + 2H_{2}O$$



WWW.TOPPERLEARNING.COM



(ii)By Hoffmann's method (Ammonolysis of alkyl halides): Reaction of alkyl halides with an ethanolic solution of ammonia in a sealed tube at 373 K forms a mixture of primary, secondary and tertiary amine and finally quarternary ammonium salt. Process of cleavage of C-X bond by ammonia is called ammonolysis.



The free amine can be obtained from the ammonium salt by treatment with a strong base:

NH_3	+	RX	$\rightarrow \text{RNH}_3^+ \text{X}^-$ -	NaOH →	RNH ₂	+	H ₂ O	+	Na^+X^-
					(1° amine)				
RNH ₂	+	RX	$\rightarrow R_2 N H_2^+ X^-$	NaOH →	R ₂ NH (2° amine)	Ŧ	H ₂ O	+	Na^+X^-
R ₂ NH	+	RX	$\rightarrow \text{R}_3\text{NH}^+\text{X}^-$	NaOH →	R ₃ N (3° amine)	+	H ₂ O	+	Na^+X^-

Order of reactivity of halides is: RI> RBr> RCl Larger the size of halogen atom easier is the cleavage of R-X bond

Limitations of Hoffmann's method:

Method gives mixture of amines which are difficult to separate in a laboratory

Methods to get only one product by Hoffmann's method:

(i)When ammonia is taken in excess primary amine is formed as main product

(ii)When alkyl halide is used in excess quarternary ammonium salt is formed as main product

Important Note: Method is not suitable for preparation of aryl amines because aryl amines are relatively less reactive than alkyl halides towards nucleophilic substitution reactions

(iii) By reduction of nitriles: Nitriles can be reduced to amines using $\rm H_2$ /Ni , LiAlH_4 or Na(Hg)/C_2H_5OH







$$\begin{array}{ccc} R-C\equiv N & \xrightarrow{H_2/Ni} & R-CH_2-NH_2 \\ & & & \\ &$$

(iii)By reduction of amides: Amides are reduced to corresponding amines by LiAlH₄

$$\begin{array}{c} O \\ \parallel \\ R-C-NH_2 \xrightarrow{(i) \text{ LiA1H}_4} R-CH_2-NH_2 \end{array}$$

(iv) By Gabriel phthalimide synthesis: Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine



Important Note: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with potassium phthalimide

(v) By Hoffmann bromamide degradation reaction: Primary amines can be prepared from amides by treatment with Br_2 and KOH. Amine contains one carbon atom less than the parent amide

$$O \\ || \\ R - C - NH_2 + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$







4. Physical properties of amines:

(i)Solubility: Lower aliphatic amine is soluble in water because they can form hydrogen bonding with water. Solubility decreases with increases in molar mass of amines due to increase in size of hydrophobic group

(ii)Boiling points: Among the isomeric amines primary and secondary amines have high boiling point because they can form hydrogen bonding. Tertiary amine cannot form hydrogen bonding due to the absence of hydrogen atom available for hydrogen bond formation. Hence order of boiling of isomeric amines is Primary>Secondary> Tertiary

5. Chemical properties of amines:

(a)Basic character of amines:

Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base. Basic character of amines can be better understood in terms of their K_{h} and pK_{h} values

$$R - NH_{2} + H_{2}O \rightleftharpoons R - NH_{3} + \overline{O}H$$

$$K = \frac{\left[R - NH_{3}\right]\left[O\overline{H}\right]}{\left[R - NH_{2}\right]\left[H_{2}O\right]}$$
or $K[H_{2}O] = \frac{\left[R - NH_{3}\right]\left[\overline{O}H\right]}{\left[R - NH_{2}\right]}$
or $K_{b} = \frac{\left[R - NH_{3}\right]\left[\overline{O}H\right]}{\left[R - NH_{2}\right]}$

$$pK_{b} = -\log K_{b}$$

NN

Greater K_{b} value or smaller pK_{b} indicates base is strong

(b)Comparison of basic strength of aliphatic amines and ammonia: Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom









(c) Comparison of basic strength of primary, secondary and tertiary amines (i)The order of basicity of amines in the gaseous phase follows the expected order on the basis of +I effect: tertiary amine > secondary amine > primary amine > NH_3

(ii)In aqueous solution it is observed that tertiary amines are less basic than either primary or secondary amines. This can be explained on basis of following factors:

(a) Solvation effect: Greater is the stability of the substituted ammonium cation formed, stronger is the corresponding amine as a base. Tertiary ammonium ion is less hydrated than secondary ammonium ion which is less hydrated than primary amine. Thus tertiary amines have fewer tendencies to form ammonium ion and consequently are least basic.



Maximum hydration

Minimum hydration

On the basis of solvation effect order of basicity of aliphatic amines should be primary amine>secondary amine>tertiary amine.

(b) Steric factor: As the crowding of alkyl group increases from primary to tertiary amine hinderance to hydrogen bonding increases which eventually decreases the basic strength. Thus there is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.



WWW.TOPPERLEARNING.COM



When the alkyl group is small like CH_3 there is no steric hindrance to hydrogen bonding. In this case order of basicity in aqueous medium is

 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ When alkyl group is ethyl group order of basicity in aqueous medium is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

(c)Comparison of basic strength of aryl amines and alkanamines: Generally aryl amines are considerably less basic than alkyl amines. Taking an example of aniline and ethylamine it is observed that ethyl amine is more basic than aniline. In aniline $-NH_2$ group is directly attached to benzene ring. Hence unshared pair of electron on nitrogen is less available for protonation because of resonance. Below mentioned are resonating structures of aniline.



In the above resonating structures there is a positive charge on nitrogen atom making the lone pair less available for protonation. Hence aniline is less basic than ethyl amine which has no resonating structures. Less basicity of aniline can also be explained by comparing the relative stability of aniline and anilinium ion obtained by accepting a proton. Greater the number of resonating structures, greater is the stability of that species.

Aniline is resonance hybrid of five resonating structures whereas anilinium ion has only two resonating structures.



Thus aniline has less tendency to accept a proton to form anilinium ion.









(d)Effect of substituent on basic character of amines: Electron donating or electron releasing group/groups (EDG) increases basic strength.

Electron withdrawing (EWG) decreases basic strength

(a) Acylation Reaction: Aliphatic and aromatic primary and secondary amines (which contain replaceable hydrogen atoms) react with acid chlorides, anhydrides and esters to form substituted amide. Process of introducing an acyl group (R-CO-) into the molecule is called acylation. The reaction is carried out in the presence of a stronger base than the amine, like pyridine, which removes HCl formed and shifts the equilibrium to the product side

Base $R - NH_{2}$ RNHCOR HCI RCOCI + +Acid Substituted chloride amide Ο \cap 11 Base R '- NH. **R**−C−O−C−R R'NHCOR RCOOH +Acid Substituted anhydride amide Base R₂NCOR RCOCI HCI R_NF +

Important Note: Since tertiary amine do not contain replaceable hydrogen atom they do not undergo acylation reaction



TOPPER www.topperlearning.com



(b) Carbylamine reaction: Only aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines

 $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$ Important Note: Secondary and tertiary amines do not give the above test

(c)Reaction of primary amine with nitrous acid:

(i)Primary aliphatic amine on reaction with nitrous acid (HNO_2) forms aliphatic diazonium salt which being unstable decomposes to form alcohol and evolve nitrogen

 $R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

(ii)Primary aromatic amines on reaction with nitrous acid (HNO_2) in cold (273-278 K) forms diazonium salt

 $\begin{array}{ccc} \mathrm{C_6H_5-NH_2} & \xrightarrow{\mathrm{NaNO_2+2HCl}} & \mathrm{C_6H_5-N_2Cl} & + \mathrm{NaCl+2H_2O} \\ \mathrm{Aniline} & & \mathrm{Benzenediazonium} \\ & & & \mathrm{chloride} \end{array}$

(d)Reaction with benzene sulphonyl chloride: Hinsberg's reagent-Benzene sulphonyl chloride ($C_6H_5SO_2CI$) reacts with primary and secondary amines to form sulphonamides



(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide formed by primary amine is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.









Since sulphonamide formed by secondary amine does not contain any hydrogen atom attached to nitrogen atom, so it is not acidic. Hence it is insoluble in alkali.



3° a min e

7. Ring substitution in aromatic amine: Aniline is more reactive than benzene and undergoes electrophilic substitution reaction preferably at ortho and para position.

(i) Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline



2,4,6-Tribromoaniline

Important Note: In order to stop reaction at monosubstitution activating effect of $-NH_2$ group is reduced by acetylation. This prevents di and tri substituted products. Acetyl group is removed by hydrolysis.



(ii) Nitration:

(a)Under strongly acidic medium aniline gets protonated to form anilinium ion, which is deactivating group and is meta directing. Hence minitroaniline is also formed in 47 % along with ortho and para products.









Important Note: Aromatic amines cannot be nitrated directly because HNO_3 being a strong oxidising agent oxidises it forming black mass

(b) Nitration by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride:



(iii) Sulphonation: Aniline reacts with conc. H_2SO_4 to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product









8. Reactions of benzene diazonium chloride:(a) Reactions involving displacement of nitrogen

$$\begin{array}{c} \begin{array}{c} CuCl/HCl \rightarrow ArCl + N_{2} \\ \hline CuBr/HBr \rightarrow ArBr + N_{2} \\ \hline CuCN /KCN \rightarrow ArCN + N_{2} \\ \hline Cu/HCl \rightarrow ArCl + N_{2} + CuCl \\ \hline Cu/HBr \rightarrow ArBr + N_{2} + CuCl \\ \hline Cu/HBr \rightarrow ArBr + N_{2} + CuCl \\ \hline KI \rightarrow ArI + KCl + N_{2} \\ \hline HBF_{4} \rightarrow Ar - \overset{+}{N_{2}}BF_{4} \xrightarrow{\Delta} Ar - F + BF_{3} + N_{2} \\ \hline H_{3}PO_{2} + H_{2}O \\ \hline \rightarrow ArH + N_{2} + H_{3}PO_{3} + HCl \\ \hline H_{2}O \rightarrow ArOH + N_{2} + HCl \\ \hline CH_{3}CH_{2}OH \\ \rightarrow ArH + N_{2} + CH_{3}CHO + HCl \\ \hline HBF_{4} \rightarrow \overset{+}{N_{2}}BF_{4} \\ \hline MaNO_{3} \\ \hline Cu, \Delta \end{array} + N_{2} + NaBF_{4} \end{array}$$

(b) Reactions involving retention of diazo group, coupling reactions: Diazonium ion acts as an electrophile because there is a positive charge on terminal nitrogen. Therefore benzene diazonium chloride couples with electron rich compounds like phenol and aniline to give azo compounds. Azo compounds contain -N=N- bond and reaction is coupling reaction.













Chapter : Biomolecules

Top Concepts:

1. Definition of carbohydrates: Polyhydroxy aldehydes or polyhydroxy ketones or compounds which give these on hydrolysis.

2. Classification of carbohydrates:

- a. Monosaccharides
- Simplest carbohydrates
- Cannot be hydrolysed into simpler compounds
- E.g. Glucose, mannose
- b. Oligosaccharides
- Carbohydrates which give 2 to 10 monosaccharide units on hydrolysis
- E.g. Sucrose, Lactose, Maltose
- c. Polysaccharides
- Carbohydrates which on hydrolysis give large number of monosaccharide units.
- E.g. Cellulose, starch

3. Anomers: Such pairs of optical isomers which differ in configuration only around C₁ atom are called anomers. E.g. α -D-glucopyranose and β -D-glucopyranose

4. Epimers: Such pairs of optical isomers which differ in configuration around any other C atom other than C_1 atom are called epimers. E.g. D-glucose and D- mannose are C_2 epimers.





D - Mannose



























Glucose does not give Schiff's test and does not react with sodium bisulphite and NH_3 .

Pentaacetyl glucose does not react with hydroxyl amine. This shows the absence of –CHO group and hence the presence of ring structure.

7. Cyclic structure of glucose:





m







 $HC = N NH C_{e}H_{e}$ $HC = NNHC_{e}H_{e}$ сн он [']C = 0 CHO с₆н₅nнnн₂ -nн₃ с₆н₅ nнnh₂ -н₂0 → (ĊH OH)₃ (ĊHOH) → (ĊHOH) ҁҥ҄ѻн ĊH_OH ĊH_OH $\downarrow C_{G}H_{NHNH_{2}}$ $HC = NNHC_6H_5$ $\dot{C} = NNHC_6H_5$ (ĊHOH)₃ ĊH_OH

Glucos azone or Fructosazone

Glucose and fructose gives the same osazone because the reaction takes place at C_1 and C_2 only.



MNN?





10. Lobry De Bruyn Van Ekenstein Rearrangement:



- Same results are obtained when fructose or mannose is reacted with an alkali.
- It is because of form of ene diol intermediate.
- It explains why fructose acts as a reducing sugar.

11. Mutarotation: The spontaneous change in specific rotation of an optically active compound is called mutarotation. E.g. α -D-glucose (m.p. = 146°C) with specific rotation $[\alpha]_D = +111^\circ$ and β -D-glucose (m.p. = 150°C) with specific rotation $[\alpha]_D = +19.2^\circ$ When either form is dissolved in water & allowed to stand, the specific rotation of the solution changes slowly and reaches or constant value of +52.5°.

 $\begin{array}{ccc} \alpha \text{-D-glucose} & & & \\ \hline & & \\ \text{sp. rot}^n = 111^\circ & & \\ \text{sp. rot}^n = +52.5^\circ & & \\ \text{sp. rot}^n = +19^\circ \end{array}$

12. Haworth projection: Representation for ring structure:

6 membered ring is called pyranose ring.

5 membered ring is called furanose ring.

How to write the projection: Groups projected to the right in the Fischer projection are written below the plane and those to the left are written above the plane.

Haworth projection of Glucose:





TOPPER www.topperlearning.com













13. Glycosidic linkage: The oxide linkage formed by the loss of a water molecule when two monosaccharides are joined together through oxygen atom is called glycosidic linkage.

14. Sucrose (invert sugar): Sucrose is dextrorotatory but on hydrolysis it gives dextrorotatory & laevorotatory and the mixture is laevorotatory.

$C_{12}H_{22}O_{11}$	+	H_2O	$\xrightarrow{H^+} C_6H_{12}O_6 +$	$C_6H_{12}O_6$
Sucrose $[\alpha]_D = + 66.5^\circ$			D – glucose $[\alpha]_D = +52.5^\circ$	D – fructose $[\alpha]_{D} = -92.4^{\circ}$

Sucrose is a non-reducing sugar because the two monosaccharide units are held together by a glycosidic linkage between C1 of α -glucose and C2 of β -fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.



Haworth Projection of Sucrose:



WWW.TOPPERLEARNING.COM





one glucose is linked to C4 of another glucose unit. The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.









16. Lactose (Milk sugar): It is composed of β-D-galactose and β -D-glucose. The linkage is between C1 of galactose and C4 of

glucose. Hence it is also a reducing sugar.









17. Starch: It is a polymer of α -glucose and consists of two components — Amylose and Amylopectin.

Amylose	Amylopectin
Water soluble component	Water insoluble component
It is a long unbranched chain polymer	It is a branched chain polymer
Contains 200 – 1000 α -D-(+)- glucose units held by α - glycosidic linkages involving C1 – C4 glycosidic linkage	It is a branched chain polymer of α - D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.
Constitutes about 15-20% of starch	Constitutes about 80- 85% of starch

18. Amino acids:

R – CH – COOH NH₂

Where R – Any side chain

Most naturally occurring amino acids have L – Config.



19. Essential amino acids: Those amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids. Example: Valine, Leucine

20. Non- essential amino acids: The amino acids, which can be synthesised in the body, are known as non-essential amino acids. Example: Glycine, Alanine







21. Zwitter ion form of amino acids: Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.

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. This is neutral but contains both positive and negative charges.

In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.



22. Isoelectronic point: The pH at which the dipolar ion exists as neutral ion and does not migrate to either electrode cathode or anode is called isoelectronic point.

23. Proteins: Proteins are the polymers of α -amino acids and they are connected to each other by peptide bond or peptide linkage. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein.

24. Peptide linkage: Peptide linkage is an amide linkage formed by condensation reaction between -COOH group of one amino acid and -NH₂ group of another amino acid.

$$H_2N - CH - COOH + H_2N - CH - COOH \rightarrow H_2N - CH - CH - COOH$$

$$R_1 \qquad R_2 \qquad R_1 \qquad R_2$$
Peptide linkage

25. Primary structure of proteins: The sequence of amino acids is said to be the primary structure of a protein.

26. Secondary structure of proteins: It refers to the shape in which long polypeptide chain can exist. Two different types of structures:

a. α – Helix:

• Given by Linus Pauling in 1951



 Right handed screw with the NH group of each amino acid residue H – bonded to – C = O of adjacent turn of the helix.



WWW.TOPPERLEARNING.COM



- Also known as 3.6_{13} helix since each turn of the helix has approximately 3.6 amino acids and a 13 membered ring is formed by H bonding.
- C = O and N H group of the peptide bonds are trans to each other.
- Ramchandran angles (Φ and Ψ) Φ angle which C_{α} makes with N H and Ψ angle which C_{α} makes with C = O.

b. β – pleated sheet:

- Exists when R group is small.
- In this conformation all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by hydrogen bonds.

27. Tertiary structure of proteins: It represents the overall folding of the polypeptide chain i.e., further folding of the 2° structure.

Types of bonding which stablise the 3° structure -

- i. Disulphide bridge (-S S-)
- ii. H bonding (C = O ... H N)
- iii. Salt bridge ($COO^- \dots {}^+NH_3$)
- iv. Hydrophobic interactions
- v. van der Waals forces

Two shapes are possible:

Fibrous proteins	Globular proteins		
When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre- like structure is formed.	This structure results when the chains of polypeptides coil around to give a spherical shape.		
Such proteins are generally insoluble in water	These are usually soluble in water.		
Examples: keratin (present in hair, wool, silk) and myosin (present in muscles), etc	Examples: Insulin and albumins		







28. Quaternary structure of proteins: Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure of proteins.

29. Denaturation of proteins:

The loss of biological activity of proteins when a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH. This is called denaturation of protein. Example: coagulation of egg white on boiling, curdling of milk

30. Nucleoside:



31. Nucleotide:

Base + sugar + phosphate group



32. Nucleic acids (or polynucletides): Long chain polymers of nucleotides. Nucleotides are joined by phosphodiester linkage between 5' and 3' C atoms of a pentose sugar.

33. Two types of nucleic acids:

Deoxyribonucleic Acid (DNA)	Ribonucleic Acid (RNA)		
It has a double stranded α -helix	It has a single stranded α -helix		
structure in which two strands are	structure.		
coiled spirally in opposite directions.			
Sugar present is β -D-2-deoxyribose	Sugar present is β -D-ribose		
Bases:	Bases:		
Purine bases: Adenine (A) and	Purine bases: Adenine (A) and		
Guanine (G)	Guanine (G)		
Pyrimidine bases : Thymine (T) and	Pyrimidine bases: Uracil (U) and		







cytosine (C)	cytosine (C)	
It occurs mainly in the nucleus of the	It occurs mainly in the cytoplasm of	
cell.	the cell.	
It is responsible for transmission for	It helps in protein synthesis.	
heredity character.		

34. Double helix structure of DNA:

- It is composed of 2 right handed helical polynucleotide chains coiled spirally in opposite directions around the same central axis.
- Two strands are anti-parallel i.e. their phosphodiester linkage runs in opposite directions.
- Bases are stacked inside the helix in planes \perp to the helical axis.
- Two strands are held together by H bonds (A = T, G ≡ C).
- The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.
- Diameter of double helix is 2 nm.
- Double helix repeats at intervals of 3.4 nm. (One complete turn)
- Total amount of purine (A + G) = Total amount of pyramidine (C + T)

35. Vitamins: Vitamins are organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

36. Classification of vitamins: Vitamins are classified into two groups depending upon their solubility in water or fat.

Fat soluble vitamins	Water soluble vitamins		
These vitamins are soluble in fat and	These vitamins are soluble in water.		
oils but insoluble in water.			
They are stored in liver and adipose	Water soluble vitamins must		
(fat storing) tissues	be supplied regularly in diet because		
	they are readily excreted in urine and		
	cannot be stored (except vitamin		
	B12) in our body.		
Example: Vitamin A, D, E and K	Example: Vitamin C, B group		
	vitamins		







37. Important vitamins, their sources and their deficiency diseases:

Name of vitamin	Source	Deficiency diseases
Vitamin A	Fish liver oil, carrots,	erophthalmia
	butter and milk	(hardening of cornea of
		eye)
		Night blindness
	Yeast, milk, green	Beri beri (loss of
(Thiamine)	vegetables and cereals	appetite,
	NATIL LIT	retarded growth)
Vitamin B_2	Milk, egg white, liver,	Chellosis (fissuring at
(Ridoflavin)	kidney	corners of mouth and
		lips), digestive disorders
		and burning sensation
Vitancia D	Venet mills and wells	or the skin.
Vitamin B_6	reast, milk, egg yolk,	Convuisions
(ryilduxille)	Cereals and grams	Dornicious anacmia
	Meat, fish, egg and	Permicious andernia
	curu	(RDC deficient in
Vitamin C	Citrus fruits amla and	Source (blooding gume)
(Ascorbic acid)	green leafy vegetables	Scarvy (bleeding gams)
Vitamin D	Exposure to suplight	Pickets (bone
Vitamin D	fish and equivale	deformities
	hish and egg yonk	in children) and
	X	osteomalacia
		(soft bones and
	V	ioint pain in adults)
Vitamin E	Vegetable oils like	Increased fragility of
	wheat	RBCs and muscular
	germ oil, sunflower oil,	weakness
	etc.	
Vitamin K	Green leafy vegetables	Increased blood clotting
		time
Vitamin K	Green leafy vegetables	Increased blood clott time
NN.		







Chapter : Polymers

Top concepts

1. Polymers are high molecular mass substance consisting of large number of repeating structural units. As polymers are single, giant molecules i.e. big size molecules, they are also called macromolecules

2. Simple molecules which combine to form polymers are called monomers

3. Process of formation of polymers from respective monomers is called polymerization

				_
No.	Classification	l	bes	Examples
	based on			
		1. Natural polymers:	Polymers obtained	Cellulose, starch, etc.
		from nature, mostly	y plants and animals	
1.	Source of	2. Synthetic polymers	s: Polymers prepared	Teflon,
	availability	in laboratory		Nylon 6,6,
				Synthetic rubber (Buna -
				S) etc.
		3. Semi synthetic	polymers: Polymers	Rayon (cellulose
		derived from	naturally occurring	acetate),
		polymers by car	rying out chemical	cellulose nitrate, etc.
		modifications		
2.	Structure of	1. Linear polymers:	Polymer consist of	High density polythene,
	polymer	long and straight cha	ins	polyvinyl chloride, etc.
		2.Branched chain		
		contains linear ch	Low density polythene	
		branches		
		3. Cross linked or network polymers:		
	(Polymers in which monomer units are		Bakelite, melamine, etc.
		cross linked together		
		dimensional network		
3.	Mode of	1.Addition polymers	1.Homopolymers:	
	polymerisation	:Polymers are	Polymers formed by	
		formed by the	the polymerisation	Polythene,
		repeated addition of	of a single	Polystyrene
		monomers with monomeric spec		
		double and triple 2.Copolymers:		
		bonds	Polymers formed by	
			addition	Buna-S,
			polymerisation of	Buna -N
			two different	

4. Classification of Polymers


TOPPER www.topperlearning.com



		monomers	
		Condensation polymers: Polymers formed by repeated condensation reaction between two different bi-functional or tri- functional monomeric units with elimination of simple molecules	Nylon 6, 6, Nylon 6
4.	Molecular forces	1. Elastomers: Polymer chains are held together by weakest intermolecular forces. Polymers are rubber – like solids with elastic properties	Buna – S, Buna – N, Neoprene
		2. Fibre: Polymers have strong intermolecular force like hydrogen bonding. Fibres are the thread forming solids which possess high tensile strength and high modulus	Nylon 6, 6, Polyesters
		3. Thermoplastic polymers: Polymers are held by intermolecular forces which are in between those of elastomers and fibres. These polymers are capable of repeated softening on heating and hardening on cooling	Polythene, Polystyrene
		4. Thermosetting polymers: Polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and eventually undergoes a permanent	Bakelite, Urea-formaldelyde resins

5. Addition Polymerisation or Chain Growth Polymerisation: Most common mechanism for addition polymerisation reactions is free radical mechanism Steps involved are:

Step 1: Chain initiating step: Organic peroxides undergo homolytic fission to form free radicals which acts as initiator. Initiator adds to C-C double bond of an alkene molecule to form a new free radical

 $C_{6}H_{5}-C-O-O-C-C_{6}H_{5} \longrightarrow 2C_{6}H_{5}-C-O \longrightarrow 2\dot{C}_{6}H_{5} + 2CO_{2}$ $\dot{C}_{6}H_{5}+CH_{2}=CH_{2} \longrightarrow C_{6}H_{5}-CH_{2}-\dot{C}H_{2}$







Step 2: Chain propagating step: Free radicals formed by homolytic cleavage adds to a double bond of monomer to form a larger free radical. Radical formed adds to another alkene molecule to form a larger free radical. This process continues until the radical is destroyed. These steps are called propagation steps.

Step 3: Chain terminating step: For termination of the long chain, free radicals combine in different ways to form polythene. One mode of termination of chain is shown as under:

$$C_{6}H_{5} + CH_{2} - CH_{2} - \dot{C}H_{2} - \dot{C}H_{2} - \dot{C}H_{2}$$

$$C_{6}H_{5} + CH_{2} - \dot{C}H_{2} - \dot{C}H_{2} - \dot{C}H_{2} - \dot{C}H_{2}$$

$$\longrightarrow C_{6}H_{5} + CH_{2} - CH$$

Addition polymerisation is called chain growth polymerisation because it takes place through stages leading to increase in chain length and each stage produces reactive intermediates for use in next stage of the growth of chain

No.	Name of polymer	Polymerisation Re	eaction & Uses	
1	Low density polythene (LDP)	$nCH_2 = CH_2$	350–570K 	$+CH_2-CH_2$
		Ethene Uses: It is used ir wires and manufa flexible pipes	n the insulation of ele acture of squeeze bot	Polythene ectricity carrying tles, toys and
2	High density polythene(HDP)	nCH ₂ = CH ₂	333-343 K ────→ 67atm Zieglar Natta catalyst	$+CH_2-CH_2$
		Ethene		Polythene

6 .Important Addition Polymers:





		Uses: It is used for manufacturing buckets, dustbins, bottles, pipes, etc.			
3	Polytetrafluoroethene (Teflon)	n $CF_2 = CF_2$ High pressure $-CF_2 - CF_2$ Tetrafluoroethene Teflon			
		Uses: It is used in making oil seals and gaskets and also used for non – stick surface coated utensils			
4	Polyacrylonitrile	n $CH_2 = CHCN$ $\xrightarrow{Polymerisation}$ \xrightarrow{CN} Acrylonitrile $\xrightarrow{Polymerisation}$ $\xrightarrow{CH_2 - CH}_n$ Polyacrylonitrile $\xrightarrow{Polymerisation}$ Polyacrylonitrile $\xrightarrow{Polymerisation}$ $Polymerisat$			

7. Condensation Polymerisation or Step Growth polymerization: Polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. In condensation reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalised species and is independent of each other, this process is also called as step growth polymerisation.

8 .Important Condensation Polymers:

1. Polyamides: Polymers possess amide linkage (-CONH-) in chain. These polymers are popularly known as nylons. Examples:

(a) Nylon 6, 6: It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.

 $n \operatorname{HOOC}(\operatorname{CH}_2)_4\operatorname{COOH} + n \operatorname{H}_2\operatorname{N}(\operatorname{CH}_2)_6\operatorname{NH}_2 \xrightarrow{553\mathrm{K}}$

 $\begin{bmatrix} \mathbf{H} & \mathbf{H} & \mathbf{O} \\ \mathbf{I} & \mathbf{I} & \mathbf{I} \\ \mathbf{N} - (\mathbf{C}\mathbf{H}_2)_6 - \mathbf{N} - \mathbf{C} (\mathbf{C}\mathbf{H}_2)_4 - \mathbf{C} \end{bmatrix}$ Nylon 6,6







Uses: Nylon 6, 6 is used in making sheets, bristles for brushes and in textile industry

(b) Nylon 6: It is obtained by heating caprolactum with water at a high temperature



Uses: Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes

(2) Polyesters: These are the polycondensation products of dicarboxylic acids and diols

Example: Terylene or Dacron

Terylene or Dacron: It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of zinc acetateantimony trioxide catalyst

- OCH₂-CH n HOH₂C - CH₂OH + n HOOC-- COOH Ethylene glycol Terephthalic acid Terylene or dacron (Ethane-1, 2 - diol) (Benzene-1,4 - di

Uses: Dacron fibre (terylene) is crease resistant and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.

3. Phenol - formaldehyde polymer (Bakelite and related polymers)

Bakelite: These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst. The initial product could be a linear product – Novolac used in paints.









 $\begin{array}{c|c} & \label{eq:charge} & \label{eq:charge} CH_2 & \label{eq:charg$

Uses: It is used for making combs, phonograph records, electrical switches and handles of various utensils

4. Melamine – formaldehyde polymer: Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde







Examples of synt	hetic rubber:
------------------	---------------

No.	Name of	Polymerisation Reaction and uses
	polymer	
1	Neoprene or polychloropre ne	













10. Biodegradable Polymers: Polymers which are degraded by microorganisms within a suitable period so that biodegradable polymers and their degraded products do not cause any serious affects on environment

Examples of biodegradable polymer:

1. Poly - β -hydroxybutyrate – co- β -hydroxy valerate (PHBV): It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 - hydroxypentanoic acid



M





ð.



2. Nylon 2-nylon 6: It is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid $(H_2N (CH_2)_5 COOH)$

nH₂N – CH₂ – COOH

+ $nH_2N - (CH_2)_5 - COOH$

glycine

amino caproic acid

 $(H_{N}-CH_{2}-C-H_{N}-(CH_{2})_{5}-C)$

Ļ



MM?





11. Some commercially important polymers along with their structures and lises

	uses			
	Name of Polymer	Monomer	Structure	Uses
	Polypropene	Propene	$(-CH_{2}-CH_{2}-CH)$	Manufacture of ropes, toys, pipes, fibres, etc.
-	Polystyrene	Styrene	(C_6H_5)	As insulator, wrapping material, manufacture of toys, radio and television cabinets
	Polyvinyl chloride (PVC)	Vinyl chloride		Manufacture of rain coats, hand bags, vinyl flooring, water pipes
	Glyptal	(a) Ethylene glycol Manufacture of (b) Phthalic acid		Manufacture of paints and lacquers
Š				
	2			





Chapter : Chemistry in Everyday Life

Top concepts

1. Drugs are low molecular mass (\sim 100-500 u) substances which interact with targets in the body and produce a biological response

2. Medicines are chemicals that are useful in diagnosis, prevention and treatment of diseases

3. Desirable or beneficial effect of a drug like treatment of symptoms and cure of a disease on a living body is known as therapeutic effect

4. Proteins which perform the role of biological catalysts in the body are called enzymes

5. Functions of enzymes:



(a) Enzyme (b) Substrate (c) Enzyme holding substrate (i) The first function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively

(ii) The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction

6. Main role of drugs is to either increase or decrease role of enzyme catalysed reactions. Inhibition of enzymes is a common role of drug action. Enzyme inhibitor is drug which inhibits catalytic activity of enzymes or blocks the binding site of the enzyme and eventually prevents the binding of substrate with enzyme. Drug can inhibit attachment of substrate on active site of enzymes in following ways.









(a) Competitive Inhibition: Competitive Inhibitors are the drugs that compete with the natural substrate for their attachment on the active sites of enzymes



(b) Non-Competitive Inhibition: Some drugs do not bind to the enzyme's active site, instead bind to a different site of enzyme called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognise it. If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently. The body then degrades the enzyme-inhibitor complex and synthesizes the new enzyme



Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site









7. Receptors as Drug Targets:

Proteins which are vital for communication system in the body are called receptors. In the body, message between two neurons and that between neurons to muscles is communicated through chemical messengers. They are received at the binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes which brings about the transfer of message into the cell. Chemical messenger gives message to the cell without entering the cell



Receptors show selectivity for one chemical messenger over the other because their binding sites have different shape, structure and amino acid composition.

Drugs that bind to the receptor site and inhibit its natural function are called antagonists. These are useful when blocking of message is required. Drugs that mimic the natural messenger by switching on the receptor are called agonists. These are useful when there is lack of natural chemical messenger.

8. Therapeutic action of different classes of drugs

(i) Antacid: Chemical substances which neutralize excess acid in the gastric juices and give relief from acid indigestion, acidity, heart burns and gastric ulcers

Examples: Eno, gelusil, digene etc.

(ii) Antihistamines: Chemical substances which diminish or abolish the effects of histamine released in body and hence prevent allergic reactions Examples: Brompheniramine (Dimetapp) and terfenadine (Seldane)







(iii) Neurologically Active Drugs: Drugs which have a neurological effect i.e. affects the message transfer mechanism from nerve to receptor

(a) Tranquilizers: Chemical substances used for the treatment of stress and mild or severe mental diseases

Examples: Derivatives of barbituric acids like veronal, amytal, nembutal, luminal, seconal

(b) Analgesics: Chemical substances used to relieve pain without causing any disturbances in the nervous system like impairment of consciousness, mental confusion, incoordination or paralysis etc.

Classification of Analgesics:

Non-narcotic analgesics:	Narcotic analgesics:
They are non-addictive drugs	When administered in medicinal doses, these drugs relieve pain and produce sleep
Examples: Aspirin, Ibuprofen, Naproxen, Dichlofenac Sodium	Examples: Morphine and its derivatives

(iv) Antimicrobials: Drugs that tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively

Types of antimicrobial drugs

(a) Antibiotics: Chemical substances produced by microorganisms that kill or prevent the growth of other microbes

Classification of antibiotics on basis of mode of control of microbial diseases:

Bactericidal	Bacteriostatic
Drugs that kills organisms in body	Drugs that inhibits growth of
	organisms
Examples:	Examples:
Penicillin, Aminoglycosides,	Erythromycin, Tetracycline,
Ofloxacin	Chloramphenicol







Classification of antibiotics on basis of its spectrum of action:

Broad spectrum antibiotics	Narrow spectrum	Limited spectrum
	antibiotics	antibiotics
Antibiotics which kill or	Antibiotics which are	Antibiotics effective
inhibit a wide range of	effective mainly	against a single
Gram-positive and Gram-	against Gram-positive	organism or disease
negative bacteria	or Gram-negative	\cap
	bacteria	
Examples:	Examples:	
Ampicillin and Amoxycillin	Penicillin G	

(b) Antiseptics: Chemical substances that kill or prevent growth of microorganisms and can be applied on living tissues such as cuts, wounds etc.

Examples: Soframicine, dettol

(c) Disinfectants: Chemical substances that kill microorganisms but cannot be applied on living tissues such as cuts, wounds etc. Examples: Chlorine (Cl_2), bithional, iodoform etc.

(v) Antifertility Drugs: Chemical substances used to prevent conception or fertilization

Examples: Norethindrone, ethynylestradiol (novestrol)

9. Food additives are the substances added to food to preserve its flavour or improve its taste and appearance

Different types of food additives:

No.	Name of food additive	Examples
1	Artificial Sweetening Agents: Chemical compounds which gives sweetening effect to the food and enhance its flavour	Aspartame, Sucrolose and Alitame
2	Food preservatives: Chemical substances which are added to food material to prevent their spoilage due to microbial growth	Sugar, Salts, Sodium benzoate
3	Food colours: Substances added to food to increase the acceptability and attractiveness of the food product	Allura Red AC, Tartrazine
4	Nutritional supplements: Substances added to food to improve the nutritional value	Vitamins, minerals etc.



PPER



5	Fat emulsifiers and stabilizing agents: Substances added to food products to give texture and desired consistency	Egg yolk (where the main emulsifying chemical is Lecithin)
6	Antioxidants :Substances added to food to prevent oxidation of food materials	Butylated Hydroxy Toluene (BHT), Butylated Hydroxy Anisole (BHA)

10. Soaps:

(i)Soap: It is a sodium or potassium salts of long chain fatty acids like stearic, oleic and palmitic acid.

$CH_2 - O - C - C_{17}H_{35}$			СН ₂ –ОН 	
$CH - O - C - C_{17}H_{35} +$	- 3NaOH →	3C17H35COONa +	CH –OH	
$\begin{vmatrix} & O \\ H_2 - & O - C - C_{17}H_{35} \end{vmatrix}$		(Soap)	∣ CH₂−OH	ls
Glyceryl ester of stearic acid (Fat)	Sodium hydroxide	Sodium stearate	Glycerol	15

····/·// ··· ·····

No.	Descriptions
2.	Medicated soaps: These soaps are the soft soaps containing substances with medicinal properties. Neem soap, carbolic soaps are some common examples of medicated soaps.
3.	Shaving soaps: These soaps are potassium sodium stearates and produce lasting lather. These contain glycerol to prevent rapid drying. A gum called rosin is added in these soaps which forms sodium rosinate which lathers well
4.	Transparent soaps: These soaps are prepared by dissolving the soap in ethanol and then evaporating the excess solvent
5.	Floating soaps: These soaps float in water and are prepared by beating tiny air bubbles into the product before it hardens
6.	Soap chips: These are prepared by running a thin sheet of melted soap onto a cool cylinder and scrapping off the soaps in small broken pieces







7.	Soap granules: These are dried miniature soap bubbles
8.	Soap powder and scouring soaps: These substances contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand and builders like sodium carbonate and trisodium phosphate. Builders help the soaps in its cleaning action

(iv) Advantages of using soaps: Soap is a good cleansing agent and is 100% biodegradable i.e., micro- organisms present in sewage water can completely oxidize soap. Therefore, soaps do not cause any pollution problems

(v) Disadvantages of using soaps:

 Soaps cannot be used in hard water because hard water contains metal ions like Ca²⁺ and Mg²⁺ which react with soap to form white precipitate of calcium and magnesium salts

2C ₁₇ H ₃₅ COONa	+	CaCl_2	\longrightarrow	2NaCl	+ (C ₁₇ H ₃₅ COO) ₂ Ca
Soap					Insoluble calcium stearate (Soap)

 $2C_{17}H_{35}COONa + MgCl_2 \longrightarrow 2NaCl + (C_{17}H_{35}COO)_2 Mg$

Soap

Insoluble magnesium stearate (Soap)

These precipitates stick to the fibres of the cloth as gummy mass and block the ability of soaps to remove oil and grease from fabrics. Therefore, it interferes with the cleansing ability of the soap and makes the cleansing process difficult.

• In acidic medium, the acid present in solution precipitate the insoluble free fatty acids which adhere to the fabrics and hence block the ability of soaps to remove oil and grease from the fabrics. Hence soaps cannot be used in acidic medium







11. Detergents:

(i)Detergents are sodium salts of long chain of alkyl benzene sulphonic acids or sodium salts of long chain of alkyl hydrogen sulphates

CH₃(CH₂)₁₀CH₂OSO₃⁺Na

Sodium laurylsulphate

CH₃(CH₂) Na

Sodium dodecylbenzenesulphonate

(ii)Classification of detergents:

(a)Anionic detergents:

Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogensulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali

Example:



Uses: They are used in household cleaning like dishwasher liquids, laundry liquid detergents, laundry powdered detergents etc.







Advantage: They are effective in slightly acidic solutions where soaps do not work efficiently

(b)Cationic detergents: Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic parts possess a long hydrocarbon chain and a positive charge on nitrogen atom.

Example:

$$\begin{bmatrix} CH_{3} \\ I \\ CH_{3}(CH_{2})_{15} - N - CH_{3} \\ I \\ CH_{3} \end{bmatrix}^{+} Br^{-}$$

Cetyltrimethyl ammonium bromide

Cationic detergents are termed so because a large part of molecule is a cation

Use: Since they possess germicidal properties, they are used as germicides

Advantage: They has strong germicidal action

Disadvantage: These detergents are expensive

(c) Non- ionic detergents: They do not contain any ion in their constitution. They are like esters of high molecular mass.

Example: Detergent formed by condensation reaction between stearic acid reacts and polyethyleneglycol

CH₃(CH₂)₁₆COOH + HO(CH₂CH₂O)_nCH₂CH₂OH

Polyethyleneglycol

- H_C

Stearic acid

CH₃(CH₂)₁₆COO(CH₂CH₂O)_nCH₂CH₂OH

Use: Making liquid washing detergents

Advantage: They have effective H- bonding groups at one end of the alkyl chain which make them freely water soluble.







12. Biodegradable detergents: Detergents having straight hydrocarbon chains that are easily decomposed by microorganisms.

rsoalet and a second

Example: Sodium lauryl sulphate

13. Non-Biodegradable detergents: Detergents having branched hydrocarbon chains that are not easily decomposed by microorganisms



MN.S.