40

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Chemistry

A Complete Course Book Term-I & Term-II

As per special scheme of assessment released by the CBSE dated July 05, 2021 vide Circular No. Acad-51/2021 for the session 2021-22

Compiled by:
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Term-I: MCQs (Including case- based & assertion reasoning based)
Term-II: Case-based/situation based, open ended-short answer/long answer

Class XII

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Syllabus

CENTRAL BOARD OF SECONDARY EDUCATION, NEW DELHI

CHEMISTRY (Theory)

CLASS–XII

Total Periods (Theory 160+ Practical 60)

One paper Time: 3 hours 70 marks

Unit	Title	No. of Periods	Marks
I	Solid State	10	23
II	Solutions	10	
III	Electrochemistry	12	
IV	Chemical Kinetics	10	
V	Surface Chemistry	08	
VI	General Principles and Processes of Isolation of Elements	08	19
VII	*p*-Block Elements	12	
VIII	*d*- and *f*-Block Elements	12	
IX	Coordination Compounds	12	
X	Haloalkanes and Haloarenes	10	28
XI	Alcohols, Phenols and Ethers	10	
XII	Aldehydes, Ketones and Carboxylic Acids	10	
XIII	Amines	10	
XIV	Biomolecules	12	
XV	Polymers	08	
XVI	Chemistry in Everyday Life	06	
Total		**160**	**70**

Unit I: Solid State (10 Periods)

Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties.

Band theory of metals, conductors, semiconductors and insulators and *n* and *p* type semiconductors.

Unit II: Solutions (10 Periods)

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties—relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit III: Electrochemistry (12 Periods)

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit IV: Chemical Kinetics (10 Periods)

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit V: Surface Chemistry (8 Periods)

Adsorption–physisorption and chemisorption, factors affecting adsorption of gases on solids, catalysis: homogenous and heterogenous, activity and selectivity of solid catalysts; enzyme catalysis, colloidal state: distinction between true solutions, colloids and suspension; lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion—types of emulsions.

Unit VI: General Principles and Processes of Isolation of Elements (8 Periods)

Principles and methods of extraction-concentration, oxidation, reduction—electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

Unit VII: *p*-Block Elements (12 Periods)

Group 15 Elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen preparation properties and uses; compounds of Nitrogen: preparation and properties of Ammonia and Nitric Acid, Oxides of Nitrogen (Structure only); Phosphorus-allotropic forms, compounds of Phosphorus: Preparation and properties of Phosphine, Halides and Oxoacids (elementary idea only).

Group 16 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: preparation, properties and uses, classification of Oxides, Ozone, Sulphur-allotropic forms; compounds of Sulphur: preparation properties and uses of Sulphur-dioxide, Sulphuric Acid: industrial process of manufacture, properties and uses; Oxoacids of Sulphur (Structures only).

Group 17 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation, properties and uses of Chlorine and Hydrochloric acid, interhalogen compounds, Oxoacids of halogens (structures only).

Group 18 Elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.

Unit VIII: *d*- and *f*-Block Elements (12 Periods)

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

Lanthanoids—Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.

Actinoids—Electronic configuration, oxidation states and comparison with lanthanoids.

Unit IX: Coordination Compounds (12 Periods)

Coordination compounds—Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit X: Haloalkanes and Haloarenes (10 Periods)

Haloalkanes: Nomenclature, nature of C-X bond, physical and chemical properties, mechanism of substitution reactions, optical rotation.

Haloarenes: Nature of C-X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).

Uses and environmental effects of—dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit XI: Alcohols, Phenols and Ethers (10 Periods)

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit XII: Aldehydes, Ketones and Carboxylic Acids (10 Periods)

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties, uses.

Unit XIII: Amines (10 Periods)

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit XIV: Biomolecules (12 Periods)

Carbohydrates: Classification (aldoses and ketoses), monosaccahrides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates.

Proteins: Elementary idea of—amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones—Elementary idea excluding structure.

Vitamins: Classification and functions.

Nucleic Acids: DNA and RNA.

Unit XV: Polymers (8 Periods)

Classification—natural and synthetic, methods of polymerization (addition and condensation), copolymerization, some important polymers: natural and synthetic like polythene, nylon polyesters, bakelite, rubber. Biodegradable and non-biodegradable polymers.

Unit XVI: Chemistry in Everyday Life (6 Periods)

Chemicals in medicines: analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines.

Chemicals in food: preservatives, artificial sweetening agents, elementary idea of antioxidants.

Cleansing agents: soaps and detergents, cleansing action.

Design of Question Paper

CHEMISTRY (Theory)

CLASS–XII (2020-21)

S. No.	Domains	Total Marks	%
1.	**Remembering and Understanding:** Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers. Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	28	40
2.	**Applying:** Solve problems to new situations by applying acquired knowledge, facts, techniques and rules in a different way.	21	30
3.	**Analysing, Evaluating and Creating:** Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations. Present and defend opinions by making judgments about information, validity of ideas or quality of work based on a set of criteria. Compile information together in a different way by combining elements in a new pattern or proposing alternative solutions.	21	30

Note:

1. No chapter wise weightage. Care to be taken to cover all the chapters.
2. Suitable internal variations may be made for generating various templates.

Choice(s):

- There will be no overall choice in the question paper.
- However, 33% internal choices will be given in all the sections.

The changes for classes XI-XII (2021-22) internal year-end/Board Examination are as under:		
Year-end Examination/Board Examination (Theory)	(2020-21) Existing	(2021-22) Modified
Composition	● Objective type Questions including Multiple Choice Question-20% ● Case-based/Source-based Integrated Questions-10% ● Short Answer/Long Answer Questions- Remaining 70%	● Competency Based Questions will be 20% ● These can be in the form of Multiple-Choice Questions, Case-based Questions, Source Based Integrated Questions or any other types ● Objective Questions will be 20 % ● Remaining 60% Short Answer/Long Answer Questions—(as per existing pattern)

Part-A

basic concepts

- NCERT Textbook Questions
- Multiple Choice Questions
- Assertion-Reason Questions
- Passage-based/Case-based Questions
- Very Short Answer Questions
- Short Answer Questions–I
- Short Answer Questions–II
- Long Answer Questions
- Self-Assessment Test

Chapter–1

The Solid State

basic concepts

The particles in solid are closely packed and held together by strong intermolecular forces. The building constituents have fixed positions and can only oscillate about their mean positions. They have definite shape and definite volume. The density of solids is high and they have low compressibility.

1. **Classes of Solids:** Two types of solids are known:

   (*i*) Amorphous solids, (*ii*) Crystalline solids.

   (*i*) Amorphous solids: In amorphous solids, the arrangement of building constituents is not regular but haphazard. They may have a short range order. Their melting points are not sharp. They are isotropic in nature, *i.e.*, their properties such as mechanical strength, electrical conductivity, etc. are same in all directions. Examples: rubber, quartz glass, etc.

   (*ii*) Crystalline solids: In crystalline solids, the arrangement of building constituents is regular throughout the entire three-dimensional network. A crystalline solid has sharp melting point and is anisotropic in nature *i.e.*, some of their physical properties such as electrical resistance or refractive index show different values when measured along different directions in the same crystal. It has a definite geometrical shape with flat faces and sharp edges. Examples: sodium chloride, quartz, etc.

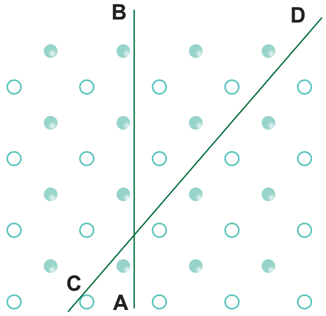


Fig. 1.1: Anisotropic behaviour of crystal

Table 1.1: Distinction between Crystalline and Amorphous Solids

Property	Crystalline Solids	Amorphous Solids
Shape	Definite characteristics and geometrical shape.	Irregular shape.
Melting point	Melt at a sharp and characteristic temperature.	Gradually soften over a range of temperature.
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces.
Heat of fusion	They have a definite and characteristic heat of fusion.	They do not have a definite heat of fusion.
Isotropy	Anisotropic in nature.	Isotropic in nature.
Nature	True solids.	Pseudo solids or super cooled liquids.
Order in arrangement of constituent particles	Long range order.	Only short range order.

Table 1.2: Different Types of Solids

	Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
1.	Molecular solids						
	(*i*) Non-polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
	(*ii*) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
	(*iii*) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
2.	Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
3.	Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
4.	Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN, C (graphite)	Hard Soft	Insulators Conductor (exception)	Very high

2. Space Lattice and Unit Cell

Space Lattice: It is the three-dimensional arrangement of identical points in the space which represent how the constituent particles (atoms, ions, molecules) are arranged in a crystal. Each particle is depicted as a point.

Unit Cell: A unit cell is the smallest portion of a space lattice which, when repeated in different directions, generates the entire lattice.

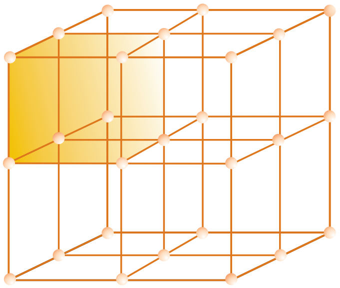


Fig. 1.2: A portion of a three dimensional cubic lattice and its unit cell

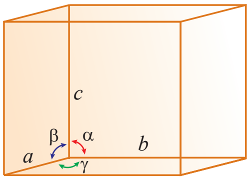


Fig. 1.3: Illustration of parameters of a unit cell

A unit cell is characterised by six parameters, *i.e.*, axial angles α, β and γ and axial lengths *a*, *b* and *c*. Thus, unit cell of a crystal possesses all the structural properties of a given crystal.

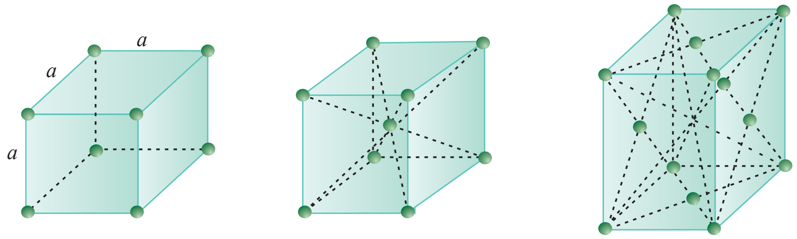
3. Crystal Systems: On the basis of the axial distances and the axial angles between the edges, the various crystals can be divided into seven systems. These are listed in Table 1.3.

Table 1.3: Seven Primitive Unit Cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu, KCl, Diamond
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2, $CaSO_4$

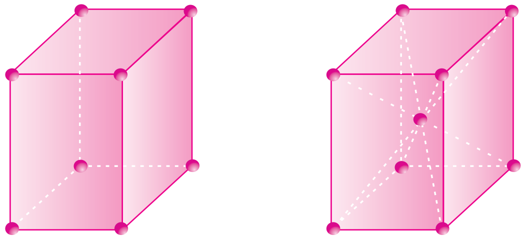
Orthorhombic or Rhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Graphite, ZnO, CdS, Mg, Zn
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$) HgS (cinnabar), ICl, As, Sb, Bi
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4.10H_2O$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3

There can be 14 different ways in which similar points can be arranged in a three-dimensional space. These are called **Bravais lattices**.



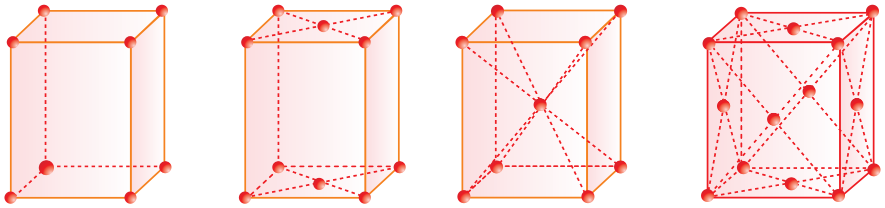
Primitive (or simple) Body-centred Face-centred

The three cubic lattices: all sides of same length, angles between faces all 90°



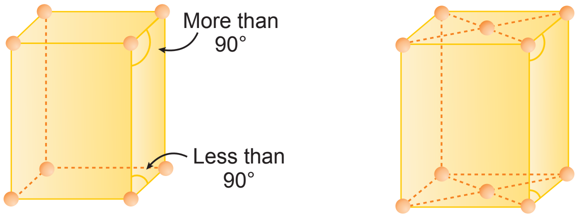
Primitive Body-centred

The two tetragonal: one side different in length from the other, two angles between faces all 90°



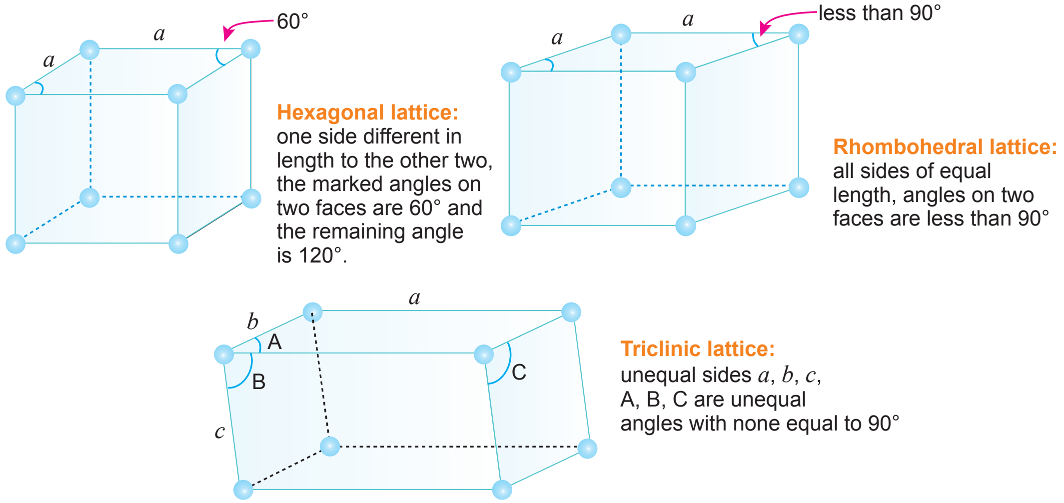
Primitive End-centred Body-centred Face-centred

The four orthorhombic lattices: unequal sides, angles between faces all 90°



Primitive End-centred

The two monoclinic lattices: unequal sides, two faces have angles other than 90°



Hexagonal lattice: one side different in length to the other two, the marked angles on two faces are 60° and the remaining angle is 120°.

Rhombohedral lattice: all sides of equal length, angles on two faces are less than 90°

Triclinic lattice: unequal sides a, b, c, A, B, C are unequal angles with none equal to 90°

Fig. 1.4: Unit Cells of 14 Types of Bravais Lattices

4. Number of Atoms in a Unit Cell

(*i*) An atom lying at the corner of a unit cell is shared equally by eight unit cells and therefore, only one-eighth (1/8) of an atom belongs to the given unit cell.

(*ii*) An atom present on an edge is distributed among the four unit cells, therefore only one-fourth (1/4) of an atom belongs to the given unit cell.

(*iii*) A face-centred atom is shared between two adjacent unit cells. Therefore, one-half (1/2) of an atom lies in each unit cell.

(*iv*) A body-centred atom belongs entirely to one unit cell since it is not shared by any other unit cell. Therefore, its contribution to the unit cell is one.

Applying above stated points, let us calculate the number of atoms in the different cubic unit cells.

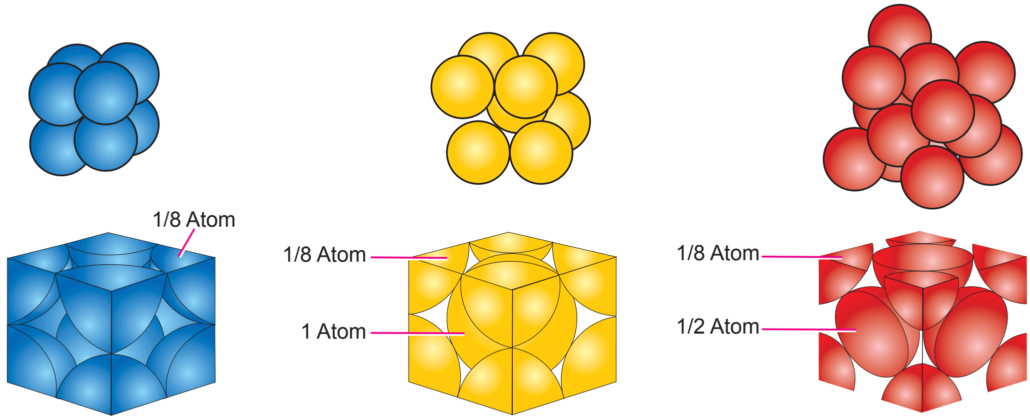
Simple cubic: 8 (corner atoms) × $\frac{1}{8}$ atom per unit cell = 1 atom

Body-centred cubic: 8 (corner atoms) × $\frac{1}{8}$ atom per unit cell + 1 (body centre atom) × 1 atom per unit cell

$$= 1 + 1 = 2$$

Face-centred cubic: 8 (corner atoms) × $\frac{1}{8}$ atom per unit cell

$$+ 6 \text{ (face atoms)} \times \frac{1}{2} \text{ atom per unit cell} = 1 + 3 = 4$$



Simple cubic

Body-centred cubic

Face-centred cubic

Fig. 1.5: Space-filling structures and actual portions of atoms belonging to one unit cell

Table 1.4: Number of Atoms per Unit Cell

Type of cell	Number of atoms at corners	Number of atoms in faces	Number of atoms in the body of cube	Total
Simple or primitive cubic	$8 \times \frac{1}{8} = 1$	0	0	1
Body-centred cubic (bcc)	$8 \times \frac{1}{8} = 1$	0	$1 \times 1 = 1$	2
Face-centred cubic (fcc)	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

5. **Density of Unit Cell:** Suppose edge of a unit cell of a cubic crystal is a, d is the density of the substance and M is the molar mass, then in case of cubic crystal,

$$\text{Mass of unit cell} = \text{Number of atoms in unit cell} \times \text{Mass of each atom}$$

$$= z \times m$$

$$\text{Mass of each atom } (m) = \frac{\text{Molar mass}}{\text{Avogadro number}}$$

$$m = \frac{M}{N_A}$$

$$\text{Mass of unit cell} = \frac{z \times M}{N_A}$$

$$\text{Volume of a unit cell} = a^3$$

Therefore, density of the unit cell,

$$d = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$d = \frac{z \times M}{a^3 \times N_A}, \text{ where } d \text{ is in g/cm}^3 \text{ and } a \text{ is in cm.}$$

6. **Other Parameters of a Cubic System**

   (*a*) **Atomic radius:** It is defined as half of the distance between nearest neighbouring atom in a crystal. It is expressed in terms of length of the edge (a) of unit cell of the crystal.

   (*i*) **Simple cubic structure (*sc*):** Radius of atom 'r' = $\frac{a}{2}$, as atoms touch each other along the edges.

   (*ii*) **Body-centred cubic structure (*bcc*):** Radius of atom 'r' = $\frac{\sqrt{3}\,a}{4}$, as the atoms touch each other along the cross diagonal of the cube.

   (*iii*) **Face-centred cubic structure (*fcc*):** Radius of atom 'r' = $\frac{a}{2\sqrt{2}}$, as the atoms touch each other along the face diagonal of the cube.

   (*b*) **Coordination number:** It is defined as the number of nearest neighbours that a particle has in a unit cell. It depends upon the structure of unit cell of the crystal.

   (*i*) **Simple cubic structure (*sc*):** Coordination number (C.N.) = 6

   (*ii*) **Body-centred cubic structure (*bcc*):** C.N. = 8

   (*iii*) **Face-centred cubic structure (*fcc*):** C.N. = 12

7. **Packing Efficiency**

   Packing efficiency is the percentage of total space filled by the particles.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by atoms in unit cell (v)}}{\text{Total volume of the unit cell } (V)} \times 100$$

   (*a*) **Packing efficiency in simple cubic structures:**

   Let 'a' be the cube edge and 'r' the atomic radius.

As the particles touch each other along the edge, therefore $a = 2r$

Volume of the unit cell = a^3

Since one atom is present in a unit cell, its volume

$$v = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

$$\therefore \text{ Packing efficiency} = \frac{v}{V} \times 100 = \frac{\pi a^3/6}{a^3} \times 100$$

$$= \frac{\pi}{6} \times 100 = \frac{3.14}{6} \times 100$$

$$= 52.36\% = 52.4\%$$

Therefore, 52.4% of unit cell is occupied by atoms and the rest 47.6% is empty space.

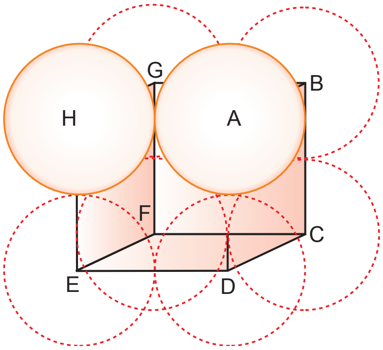


Fig. 1.6: Simple cubic unit cell. The spheres are in contact with each other along the edge of the cube.

(*b*) Packing efficiency in ccp and hcp structures: The efficiencies of both types of packing, *ccp* and *hcp*, are equally good since in both, atom spheres occupy equal fraction (74%) of the available volume. We shall now calculate the efficiency of packing in *ccp* structure. Let the unit cell length be '*a*' and face diagonal be '*b*' (represented as AC in Fig. 1.7). In this figure other sides are not shown for the sake of clarity.

In triangle ABC, ∠ABC is 90°, therefore,

$$AC^2 = b^2 = BC^2 + AB^2$$

$$= a^2 + a^2 = 2a^2$$

$$\therefore \quad b = \sqrt{2}\,a$$

If r is the radius of the sphere, we find

$$b = 4r = \sqrt{2}\,a$$

$$\text{or} \quad a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r \quad \text{or,} \quad r = \frac{a}{2\sqrt{2}}$$

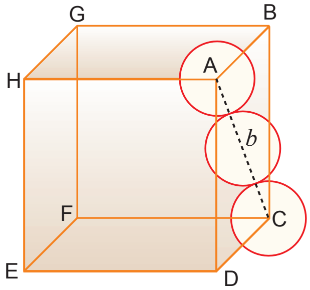


Fig. 1.7: Cubic close packing

As *ccp* structure has 4 atoms per unit cell, therefore the total volume of 4 spheres (v) is = $4 \times \frac{4}{3}\pi r^3$

Total volume of the unit cell $(V) = a^3 = (2\sqrt{2}\,r)^3$

$$\text{Packing efficiency} = \frac{v}{V} \times 100$$

$$= \frac{4 \times (4/3) \times \pi r^3}{(2\sqrt{2}\,r)^3} \times 100$$

$$= \frac{(16/3) \times \pi r^3}{16 \times \sqrt{2}\,r^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$$

Therefore, 74% of unit cell is occupied by atoms and the rest 26% is empty space.

(*c*) Efficiency of packing in bcc structures: In this case the atom at the centre is in touch with other two atoms which are diagonally arranged (see Fig. 1.8). The spheres along the body diagonal are shown with solid boundaries.

In ΔEFD,

$$b^2 = a^2 + a^2 = 2a^2$$

$$\therefore \quad b = \sqrt{2}\,a$$

In ΔAFD,

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$\therefore \quad c = \sqrt{3}a$$

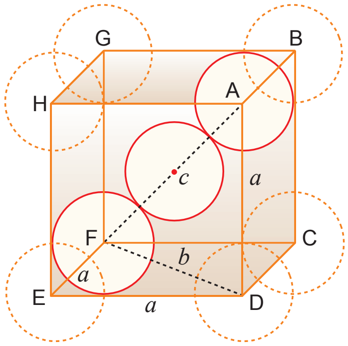


Fig. 1.8: Body-centred cubic unit cell

The length of the body diagonal c is equal to $4r$, r being the radius of the sphere (atom). As all the three spheres along the diagonal touch each other,

$$c = 4r$$

Therefore,

$$c = 4r = \sqrt{3}a$$

$$a = \frac{4r}{\sqrt{3}} \quad \text{or} \quad r = \frac{\sqrt{3}}{4}a$$

As already calculated, the total number of atoms associated with a *bcc* unit cell is 2, the volume (v) is, therefore,

$$2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$$

$$\text{Volume of the unit cell } (V) = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$\text{Packing efficiency} = \frac{\text{v}}{V} \times 100 = \frac{(8/3)\pi r^3}{(64/3\sqrt{3}) \times r^3} \times 100 = \frac{\sqrt{3}}{8}\pi \times 100 = 68\%$$

Therefore, 68% of unit cell is occupied by atoms and the rest 32% is empty space.

8. Close Packing of Constituents

(*a*) Close packing in one dimension

There is only one way of arranging spheres in a one-dimensional close packed structure, that is to arrange them in a row and touching each other. In one-dimensional close packed arrangement, the coordination number is 2.

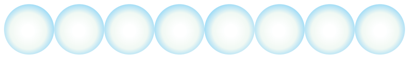


Fig. 1.9: Close packing of spheres in one dimension

(*b*) Close packing in two dimensions

Two-dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in two different ways as shown in Figs. 1.10(*a*) and (*b*).

(*i*) Square close packing [Fig. 1.10(*a*)]

(*ii*) Hexagonal close packing [Fig. 1.10(*b*)]

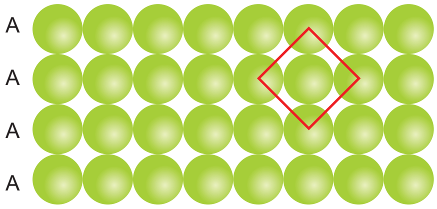


Fig. 1.10(a): AAA ..... type arrangement, C.N. = 4, Square close packing in 2-D

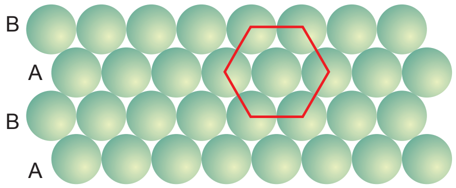


Fig. 1.10(b): ABAB.... type arrangement, C.N. = 6, Hexagonal close packing in 2-D

(*c*) Close packing in three dimensions

(*i*) Hexagonal close packing (*hcp*): The first layer is formed utilizing maximum space, thus wasting minimum space. In every second row the particles occupy the depressions (also called voids) between the particles of the first row (Fig. 1.11). In the third row, the particles are vertically aligned with those in the first row giving AB AB AB... arrangement. This structure has hexagonal symmetry and is known as hexagonal close packing (*hcp*). This packing is more efficient and leaves small space which is unoccupied by spheres. In *hcp* arrangement, the coordination number is 12 and only 26% space is free. A single unit cell has 4 atoms.

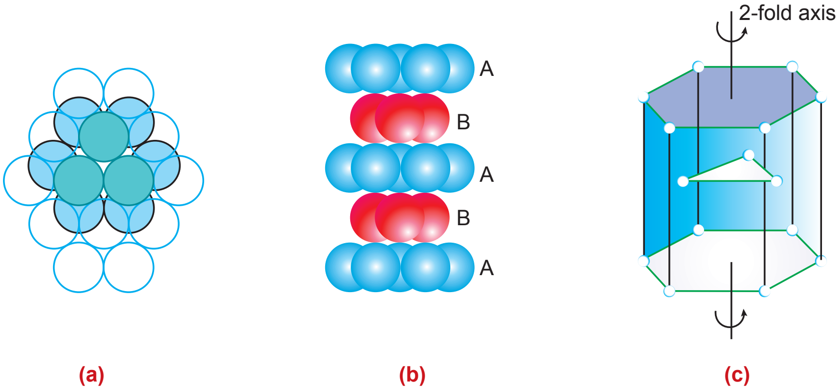


Fig. 1.11: Hexagonal close packing (*hcp*) of spheres in 3-D

(*ii*) Cubic close packing (*ccp*): Again, if we start with hexagonal layer of spheres and second layer of spheres is arranged by placing the spheres over the voids of the first layer, half of these holes can be filled by these spheres. Presume that spheres in the third layer are arranged to cover octahedral holes. This arrangement leaves third layer not resembling with either first or second layer, but fourth layer is similar to first, fifth layer to second, sixth to third and so on giving pattern ABCABCABC... . This arrangement has cubic symmetry and is known as cubic closed packed (*ccp*) arrangement. This is also called face-centred cubic (*fcc*) arrangement [Fig. 1.12(*a*) and (*b*)].

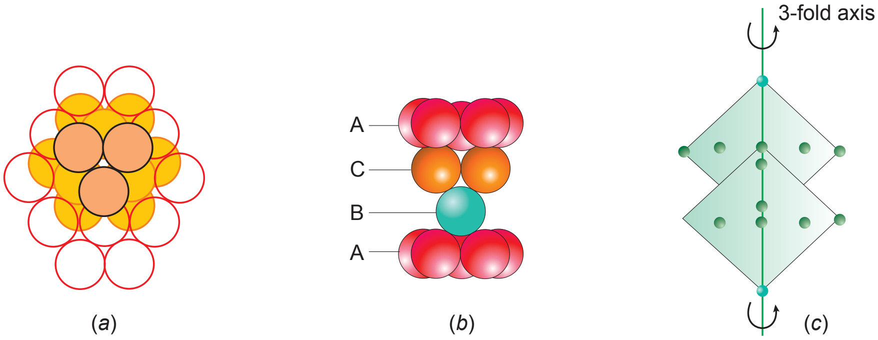


Fig. 1.12: Cubic close packing (*ccp*) of spheres in 3-D

The free space available in this packing is 26% and coordination number is 12.

9. **Voids or holes:** The empty spaces left between closed packed spheres are called voids or holes.

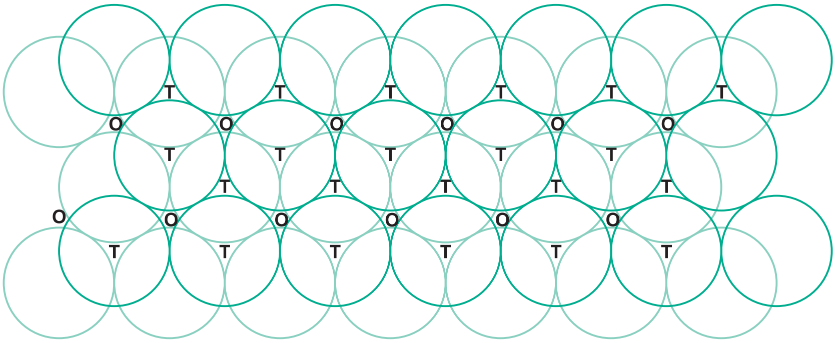


Fig. 1.13: Tetrahedral (T) and octahedral (O) voids

Voids are of three types:

(*a*) **Octahedral voids:** This void is surrounded by six spheres and formed by a combination of two triangular voids of the first and second layer. There is one octahedral void per atom in a crystal. The radius ratio $\left(\frac{r_{void}}{r_{sphere}}\right)$ is 0.414.

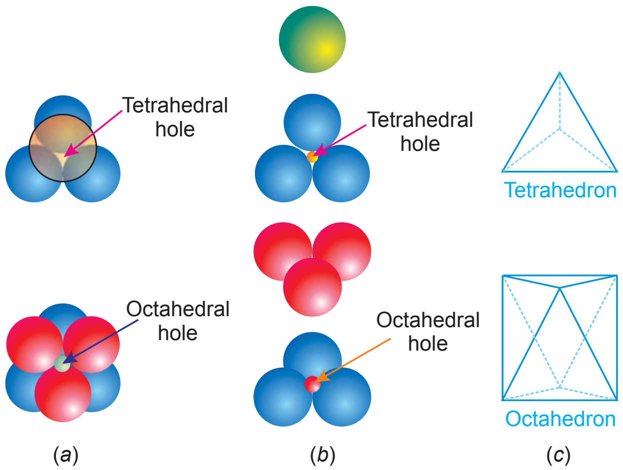


Fig. 1.14: Tetrahedral and octahedral voids (*a*) top view, (*b*) exploded side view, and (*c*) geometrical shape of the void

(*b*) **Tetrahedral voids:** These voids are surrounded by four spheres which lie at the vertices of a regular tetrahedron. There are 2 tetrahedral voids per atom in a crystal and the radius ratio is 0.225.

(*c*) **Trigonal voids:** The void, enclosed by three spheres in contact is called a trigonal void. There are 8 trigonal voids per atom in crystal and the radius ratio is 0.155.

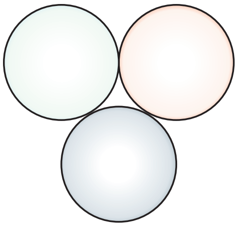


Fig. 1.15: Trigonal void

10. **Locating Tetrahedral and Octahedral Voids:** All closed packed structures have both octahedral and tetrahedral voids. In a ccp pattern, there is one octahedral void at the centre of body and 12 octahedral voids on each of the 12 edges of the cube. Each void on the edge is shared by four other unit cells.

Octahedral void at centre of cube = 1

Effective number of voids at edges = $12 \times \frac{1}{4} = 3$

Total number of octahedral voids = 1 + 3 = 4

In *ccp* structure, there are 8 tetrahedral voids. These are located at the body diagonals, two on each body diagonal at one-fourth of the distance from each end.

11. **Radius Ratio:** For ionic solids, the ratio of the radius of cation to that of anion is called radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r^+}{r^-}$$

12. **Crystal Defects:** The defects are basically irregularities in the arrangement of constituent particles. Broadly, crystal defects are of two types, namely, point defects and line defects. Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects.

13. **Point Defects**

Interstitials: Atoms or ions which normally occupy voids in a crystal are called interstitials.

Vacancy: When one of the constituent particles is missing from the crystal lattice, this unoccupied position is called vacancy.

Point defects can be classified into three types:

(A) Stoichiometric defects, (B) Impurity defects, and (C) Non-stoichiometric defects.

(A) **Stoichiometric Defects:** The point defects that do not disturb the stoichiometry of the solid are called stoichiometric defects. They are also called intrinsic or thermodynamic defects. These are of two types, vacancy defects and interstitial defects.

(*a*) **Vacancy defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect. It results in decrease in density of the substance. This defect can arise when a substance is heated.

(*b*) **Interstitial defect:** When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect. Due to this defect the density of the substance increases.

Vacancy and interstitial defects are generally shown by non-ionic solids because ionic solids must always maintain electrical neutrality. Ionic solids show these defects as Schottky and Frenkel defects as explained below:

(*i*) **Schottky defect:** This defect arises when equal number of cations and anions are missing from the lattice. It is a common defect in ionic compounds of high coordination number where both cations and anions are of the same size, *e.g.*, KCl, NaCl, KBr, etc. Due to this defect, density of crystal decreases and it begins to conduct electricity to a smaller extent [Fig. 1.16(*a*)].

(*ii*) **Frenkel defect:** This defect arises when some of the ions of the lattice occupy interstitial sites leaving lattice sites vacant. This defect is generally found in ionic crystals where anion is much larger in size than the cation, *e.g.*, AgBr, ZnS, etc. Due to this defect density does not change, electrical conductivity increases to a small extent and there is no change in overall chemical composition of the crystal [Fig. 1.16(*b*)].

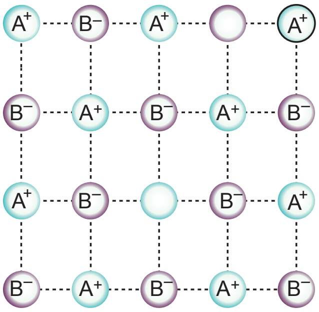


Fig. 1.16(*a*): Schottky defect

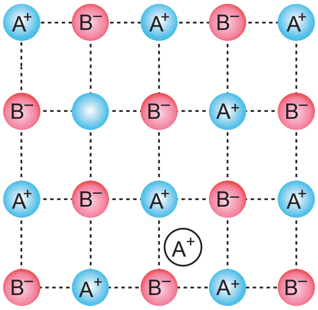


Fig. 1.16(*b*): Frenkel defect

(B) **Impurity Defects:** These defects arise when foreign atoms or ions are present in the lattice site (substitutional solid solutions) or in the interstitial sites (interstitial solid solutions). For example, when molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions.

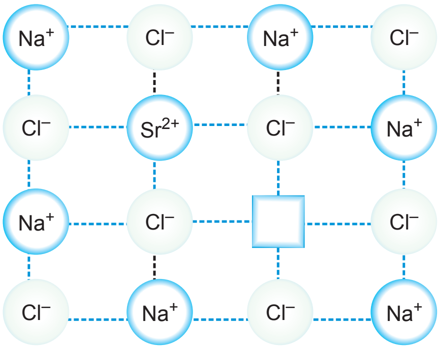


Fig. 1.17: Introduction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}.

(C) **Non-stoichiometric Defects:** These defects arise when stoichiometry of a substance is disturbed. These are of two types.

(*a*) **Metal excess defect:** This may occur in either of the following two ways:

(*i*) **Metal excess defect due to anion vacancies:** In this defect a negative ion from the crystal lattice may be missing from its lattice site leaving a hole or vacancy which is occupied by the electron originally associated with the anion. In this way crystal remains neutral. Alkali halides like NaCl and KCl show this type of defect.

➡ **F-centres:** These are the anionic sites occupied by unpaired electrons. F-centres impart colour to crystals. They impart yellow colour to NaCl crystals, violet colour to KCl crystals and pink colour to LiCl crystals. The colour results by the excitation of electrons when they absorb energy from the visible light falling on the crystal.

(*ii*) **Metal excess defect due to interstitial cation:** In this defect an extra positive ion occupies interstitial position in the lattice and the free electron is trapped in the vicinity of this interstitial cation. In this way crystal remains neutral. For example, zinc oxide on heating loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess of Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(*b*) **Metal deficiency defect:** This type of defect generally occurs when metal shows variable valency. The defect arises due to the missing of cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site. For example, Fe_xO, where $x = 0.93$ to 0.96.

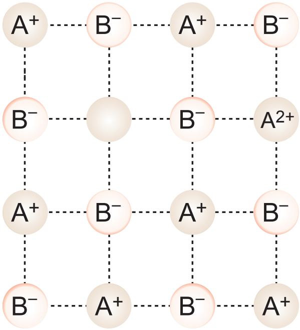


Fig. 1.18: Metal deficiency defect due to missing cations

14. (*a*) **13-15 Compounds:** When the solid state materials are produced by combination of elements of groups 13 and 15, the compounds thus obtained are called 13-15 compounds. For example, InSb, AlP, GaAs, etc.

(*b*) **12-16 Compounds:** Combination of elements of groups 12 and 16 yield some solid compounds which are referred to as 12-16 compounds. For example, ZnS, CdS, CdSe, HgTe, etc. In these compounds, the bonds have ionic character.

15. Magnetic Moments: The magnetic properties of substances result from their magnetic moments associated with individual electrons. Each electron has a magnetic moment, origin of which lies in two sources. It is a known fact that an electron shows two types of motions, *i.e.*, it rotates (spins) around its own axis and simultaneously revolves around the nucleus (orbital motion). An electron in motion is just like a small current loop. Two types of motions give rise to two types of magnetic moments—spin and orbital magnetic moments. Spin moment is directed along the spin axis and is shown in up or down direction [Fig. 1.19(*b*)]. Orbital motion also generates a magnetic field and thus gives rise to orbital moment along its axis of rotation [Fig. 1.19(*a*)]. In this way each electron of the atom behaves like a small bar magnet having permanent orbital and spin magnetic moments. Magnetic moments are measured in Bohr magneton (μ_B) unit (B.M.).

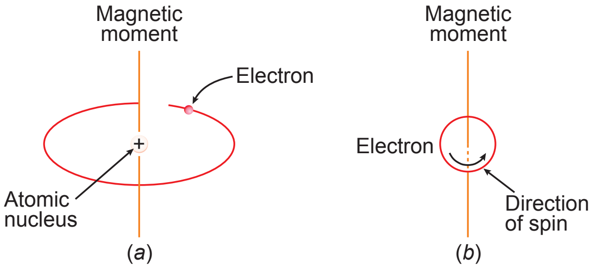


Fig. 1.19: Magnetic moment associated with (*a*) orbital motion and (*b*) spin motion of an electron

$$1 \text{ B.M.} = \frac{eh}{4\pi mc} = 9.27 \times 10^{-24} \text{ Am}^2 \text{ or } 9.27 \times 10^{-21} \text{ erg/gauss}$$

where e is charge on electron; h is Planck's constant; m is the mass of electron and c is the velocity of light.

Depending upon two spin motions (clockwise and anticlockwise), spin magnetic moment may acquire two values $\pm M_B$. Contribution of the orbital magnetic moment is equal to $M_L \cdot M_B$, where M_L is magnetic quantum number of electron.

16. **Magnetic Properties of Solids:** On the basis of their magnetic properties, substances can be classified into five categories.

(*a*) **Diamagnetic:** Diamagnetic substances are weakly repelled by the external magnetic field. The atoms of these substances have all paired up electrons. As pairing of electrons cancel their magnetic moments, they lose their magnetic character. NaCl, H_2O, TiO_2 and C_6H_6 are some examples of diamagnetic substances.

(*b*) **Paramagnetic:** Paramagnetic substances are weakly attracted by the external magnetic field. The atoms of these substances have one or more unpaired electrons. Paramagnetism is temporary and is present as long as external magnetic field is present. O_2, Fe^{3+}, Cr^{3+}, TiO, VO_2, Cu^{2+} are some examples of paramagnetic substances.

(*c*) **Ferromagnetic:** Ferromagnetic substances are strongly attracted by the external magnetic field. In solid state, the metal ions of these substances are grouped together into small regions called domains. Each domain acts as a tiny magnet. When such a substance is placed in a magnetic field all the domains get oriented in the direction of magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet. Thus, besides strong attractions, these substances can be permanently magnetised.

(*d*) **Antiferromagnetic:** These substances have domain structure similar to that of ferromagnetic substances but their domains are oppositely oriented and cancel out each other's magnetic moment. MnO is an antiferromagnetic substance.

(*e*) **Ferrimagnetic:** In ferrimagnetic substances due to unequal number of magnetic moment in parallel and antiparallel directions, the net magnetic moment is small. These substances lose ferrimagnetism on heating and become paramagnetic. Fe_3O_4 and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances.

Fig. 1.20: Schematic alignment of magnetic moments

➡ **Curie Temperature:** The temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism only is called curie temperature. For iron, the curie temperature is 1033 K, for Ni it is 629 K and for Fe_3O_4 it is 850 K. Below this temperature paramagnetic substances behave as ferromagnetic substances.

17. **Electrical Properties:** Solids are classified into three groups on the basis of their electrical conductivities:

(*a*) **Conductors:** These generally include metals. Their conductivity is of the order of 10^4–10^7 ohm^{-1} m^{-1}.

(*b*) **Semiconductors:** Those solids which have intermediate conductivities ranging from 10^{-6} to 10^4 ohm^{-1} m^{-1} are classified as semiconductors. As the temperature rises there is a rise in conductivity because electrons from the valence band jump to conduction band.

(*c*) **Insulators:** These are solids which have very low conductivity values ranging from 10^{-20} to 10^{-10} ohm^{-1} m^{-1}.

➡ **Causes of conductance in solids:** In most of the solids conduction takes place due to migration of electrons under the influence of electric field. However, in ionic compounds, it is the ions that are responsible for the conducting behaviour due to their movement.

In metals, conductivity strongly depends upon the number of valence electrons available in an atom. A band is formed due to closeness of molecular orbitals which are formed from atomic orbitals.

If this band is partially filled or it overlaps the higher energy unoccupied conduction band, the electrons can flow easily under applied electric field and the solid behaves as conductor [Fig. 1.21(*a*)]. If the gap between valence band and next higher unoccupied conduction band is large, electrons cannot jump into it and such a substance behaves as insulator. [Fig. 1.21(*b*)]

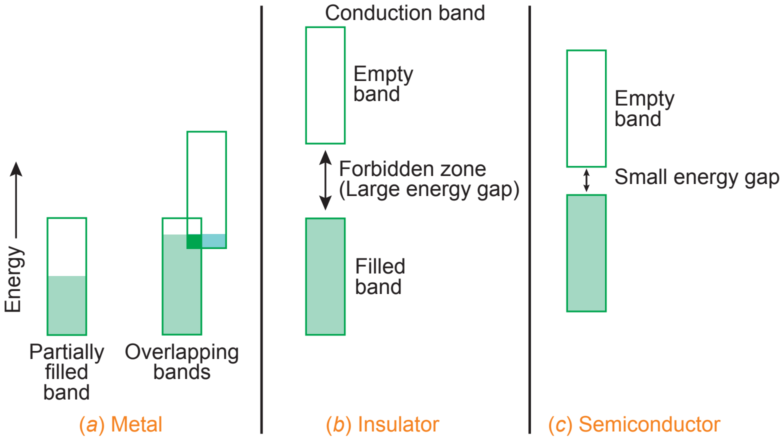


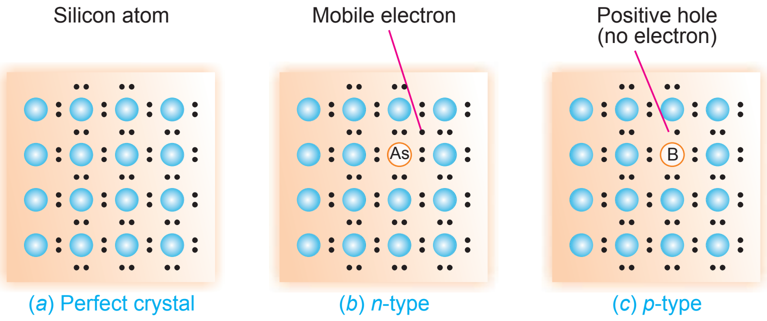
Fig. 1.21: Distinction among metals, insulators and semiconductors

If the gap between the valence band and conduction band is small, some electrons may jump from valence band to the conduction band. Such a substance shows some conductivity and it behaves as a semiconductor [Fig. 1.21(*c*)]. Electrical conductivity of semiconductors increases with increase in temperature, since more electrons can jump from valence to conduction band. Silicon and germanium show this type of behaviour and are called intrinsic semiconductors.

(*d*) **Doping:** It is a process by which impurity is introduced in semiconductors to enhance their conductivity.

➡ ***n*-type semiconductor:** When silicon or germanium crystal is doped with a Group 15 element like P or As, the dopant atom forms four covalent bonds like a Si or Ge atom but the fifth electron, not used in bonding, becomes delocalised and contributes its share towards electrical conduction. Thus, silicon or germanium doped with P or As is called *n*-type semiconductor, *n* indicates negative charge of electron since it is the electron that conducts electricity [Fig. 1.22(*b*)].

➡ ***p*-type semiconductor:** When silicon or germanium is doped with a group 13 element like B or Al, the dopant atom forms three covalent bonds, but at the place of fourth electron a hole is created. This hole moves through the crystal like a positive charge giving rise to electrical conductivity. Thus, Si or Ge doped with B or Al is called *p*-type semiconductor (*p* stands for positive hole), since it is the positive hole that is responsible for conduction [Fig. 1.22(*c*)].



(*a*) Perfect crystal (*b*) *n*-type (*c*) *p*-type

Fig. 1.22: Creation of *n*-type and *p*-type semiconductors

➡ **Diode:** Diodes are made by the combination of *n*-type and *p*-type semiconductors. They are used as rectifiers.

➡ **Transistors:** These are used to detect or amplify radio or audio signals. They consist of *pnp* or *npn* sandwich semiconductors.

➡ **Photodiode:** These are diodes which are capable of converting light energy into electrical energy and are used in solar cells.

18. Structure of Some Ionic Solids

(*a*) Ionic solids of the type AB

(*i*) NaCl (*fcc*): Cl^- in *ccp*, Na^+ occupy all the octahedral voids.

Coordination number is 6 : 6 and

$$\frac{r^+}{r^-} = 0.52$$

Number of formula units per unit cell = 4.

(*ii*) CsCl (*bcc*): Cl^- ions at the corners of a cube, Cs^+ ion at the body centre and vice-versa.

Coordination number is 8 : 8 and

$$\frac{r^+}{r^-} = 0.93$$

Number of formula units per unit cell = 1.

(*iii*) ZnS (Zinc blende): S^{2-} ions form *ccp* structure and Zn^{2+} ions occupy alternate tetrahedral voids, coordination number is 4 : 4 and

$$\frac{r^+}{r^-} = 0.4$$

Number of formula units per unit cell = 4.

(*iv*) ZnS (Wurtzite): S^{2-} ions form *hcp* structure and Zn^{2+} ions occupy alternate tetrahedral voids. Coordination number is 4 : 4 and

$$\frac{r^+}{r^-} = 0.4$$

Number of formula units per unit cell = 4.

(*b*) Ionic solid of the type AB_2

CaF_2 (Fluorite): Ca^{2+} ions form *ccp* structure and F^- ions occupy all tetrahedral voids. Coordination number is 8 : 4 and

$$\frac{r^+}{r^-} = 0.73$$

Number of formula units per unit cell = 4.

(*c*) Ionic solid of the type A_2B

Na_2O (Antifluorite structure): O^{2-} ions form *ccp* structure and Na^+ ions occupy all tetrahedral voids. Coordination number is 4 : 8.

Important Formulae

1. Density of unit cell (d) $= \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \dfrac{z \times M}{a^3 \times N_A}$

2. **Table 1.5: Different Parameters of Cubic System**

Unit cell	No. of atoms per unit cell	Distance between nearest neighbour (d)	C.N.	Radius (r)
Simple cubic	1	a	6	$\frac{a}{2}$
Face-centred cubic	4	$\frac{a}{\sqrt{2}}$	12	$\frac{a}{2\sqrt{2}}$
Body-centred cubic	2	$\frac{\sqrt{3}}{2}a$	8	$\frac{\sqrt{3}}{4}a$

3. Packing efficiency $= \dfrac{\text{Volume occupied by atoms in unit cell (v)}}{\text{Total volume of the unit cell } (V)} \times 100$

Table 1.6: Packing efficiency of different crystals

S.No.	Crystal system	Packing efficiency
(*i*)	Simple cubic	52.4%
(*ii*)	Body-centred cubic	68%
(*iii*)	Face-centred cubic	74%
(*iv*)	Hexagonal close-packed	74%

4. Radius ratio $= \dfrac{\text{Radius of the cation}}{\text{Radius of the anion}} = \dfrac{r^+}{r^-}$

Table 1.7: Structural arrangement of different radius ratios of ionic solids

Radius ratio (r^+/r^-)	Possible coordination number	Structural arrangement	Examples
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS, SiO_4^{4-}
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1.0	8	Body-centred cubic	CsCl

5. If R is the radius of the spheres in the close packed arrangement, then

(*i*) Radius of octahedral void, $r = 0.414\ R$

(*ii*) Radius of tetrahedral void, $r = 0.225\ R$

6. In a close packed arrangement:

(*i*) Number of octahedral voids = Number of atoms present in the close packed arrangement.

(*ii*) Number of tetrahedral voids = 2 × Number of atoms present in the close packed arrangement.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Why are solids rigid?

Ans. In solids, the constituent particles (atoms or molecules or ions) are not free to move but can only oscillate about their mean positions due to strong interatomic or intermolecular or interionic forces. This imparts rigidity.

Q. 2. Why do solids have a definite volume?

Ans. The constituent particles in solids are bound to their mean positions by strong forces of attraction. The interparticle distances remain unchanged at a given temperature and thus solids have a definite volume.

Q. 3. Classify the following as amorphous or crystalline solids:

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

Ans. **Amorphous solids:** Polyurethane, teflon, cellophane, polyvinyl chloride and fibre glass.

Crystalline solids: Naphthalene, benzoic acid, potassium nitrate and copper.

Q. 4. Why is glass considered a super cooled liquid?

Ans. Glass is an amorphous solid. Like liquids, it has a tendency to flow, though very slowly. This is evident from the fact that the glass panes in the windows of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Q. 5. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

Ans. Since the solid has the same value of refractive index along all directions, it is isotropic and hence, amorphous. Being an amorphous solid, it would not show a clean cleavage when cut with a knife. Instead, it would break into pieces with irregular surfaces.

Q. 6. Classify the following solids in different categories based on the nature of intermolecular forces operating in them:

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide.

Ans. **Ionic solids:** Potassium sulphate, zinc sulphide.

Covalent solids: Graphite, silicon carbide.

Molecular solids: Benzene, urea, ammonia, water, argon.

Metallic solids: Rubidium, tin.

Q. 7. Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

Ans. Covalent.

Q. 8. Ionic solids conduct electricity in molten state but not in solid state. Explain.

Ans. In the molten state, ionic solids ionise to give free ions and hence can conduct electricity. However, in the solid state, since the ions are not free to move about but remain held together by strong electrostatic forces of attraction, they behave as insulators.

Q. 9. What type of solids are electrical conductors, malleable and ductile?

Ans. Metallic solids.

Q. 10. Give the significance of a 'lattice point'.

Ans. Each lattice point represents one constituent particle of the solid. This constituent particle may be an atom, an ion, or a molecule.

Q. 11. Name the parameters that characterise a unit cell.

Ans. A unit cell is characterised by

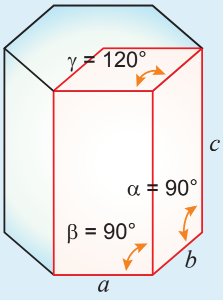
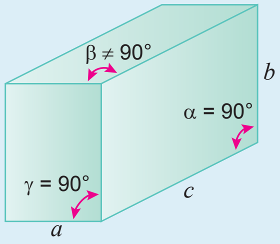
(*i*) its dimensions along the three edges, *a*, *b* and *c*.

(*ii*) angles between the edges, which are α (between *b* and *c*), β (between *a* and *c*) and γ (between *a* and *b*). Thus, a unit cell is characterised by six parameters, *a, b, c*, α, β and γ.

Q. 12. Distinguish between

(*i*) Hexagonal and monoclinic unit cells **(*ii*) Face-centred and end-centred unit cells**

Ans. (*i*) Hexagonal and monoclinic unit cells

System	Hexagonal	Monoclinic
		
No. of space lattices	1	2
Possible variations	Primitive	Primitive, End-centred
Axial distances	$a = b \neq c$	$a \neq b \neq c$
Axial angles	$\alpha = \beta = 90°, \gamma = 120°$	$\alpha = \gamma = 90°, \beta \neq 90°$
Examples	Graphite, ZnO, CdS	$Na_2SO_4.10H_2O$, monoclinic sulphur

(*ii*) Face-centred and end-centred unit cells

Unit cell	Face-centred	End-centred
Position of lattice points	At the corners and at the centre of each face	At the corners and at the centres of two end faces
No. of atoms per unit cell	$8\times\frac{1}{8}+6\times\frac{1}{2}=4$	$8\times\frac{1}{8}+2\times\frac{1}{2}=2$

Q. 13. Explain how much portion of an atom is located at (*i*) corner and (*ii*) body-centre of a cubic unit cell is part of its neighbouring unit cell.

Ans. (*i*) A point lying at the corner of a unit cell is shared equally by eight unit cells and therefore, only $\frac{1}{8}$ of each such point belongs to the given unit cell.

(*ii*) A body-centred point belongs entirely to one unit cell since it is not shared by any other unit cell.

Q. 14. What is the two dimensional coordination number of a molecule in square close packed layer? **[*CBSE (F) 2013*]**

Ans. 4.

Q. 15. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Ans. No. of atoms in the 0.5 mol close-packed structure $= 0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

No. of octahedral voids $= 1 \times$ No. of atoms in the close-packed structure $= 3.011 \times 10^{23}$

No. of tetrahedral voids $= 2 \times$ No. of atoms in the close-packed structure $= 2 \times 3.011 \times 10^{23}$

$= 6.022 \times 10^{23}$

Total number of voids $= 3.011 \times 10^{23} + 6.022 \times 10^{23} = \mathbf{9.033 \times 10^{23}}$

Q. 16. A compound is formed by two elements, *M* and *N*. The element *N* forms *ccp* and atoms of *M* occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

Ans. Suppose atoms of element N present in $ccp = x$

$\therefore$ Number of tetrahedral voids $= 2x$

Since $\frac{1}{3}$rd of the tetrahedral voids are occupied by atoms of element M,

$\therefore$ Number of atoms of element, $M = \frac{1}{3}\times 2x = \frac{2x}{3}$

$$\text{Ratio of } M : N = \frac{2x}{3} : x = 2:3$$

Hence, the formula of the compound $= \boldsymbol{M_2N_3}$.

Q. 17. Which of the following lattices has the highest packing efficiency?

(*i*) simple cubic

(*ii*) body-centred cubic

(*iii*) hexagonal close-packed lattice.

Ans. Hexagonal close-packed lattice has the highest packing efficiency (74%).

Q. 18. An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^{3} kg m^{-3}, what is the nature of the cubic unit cell?

Ans. Density, $d = \dfrac{z \times M}{a^3 \times N_A}$ or $z = \dfrac{d \times a^3 \times N_A}{M}$ ...(*i*)

Here, $M = 2.7 \times 10^{-2}$ kg mol^{-1}

$a = 405$ pm $= 405 \times 10^{-12}$ m $= 4.05 \times 10^{-10}$ m

$d = 2.7 \times 10^{3}$ kg m^{-3}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

Substituting these values in expression (*i*), we get

$$z = \frac{(2.7 \times 10^3 \text{ kg m}^{-3})\,(4.05 \times 10^{-10} \text{ m})^3\,(6.022 \times 10^{23} \text{mol}^{-1})}{2.7 \times 10^{-2} \text{ kg mol}^{-1}}$$

$$= \mathbf{4}$$

As there are 4 atoms of the element present per unit cell. Hence, the cubic unit cell must be face-centred.

Q. 19. What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

Ans. On heating a solid, vacancy defect is produced in the crystal. This is because on heating, some lattice sites become vacant. As a result of this defect, the density of the substance decreases because some atoms or ions leave the crystal completely.

Q. 20. What type of stoichiometric defect is shown by: (*i*) ZnS (*ii*) AgBr?

Ans. (*i*) ZnS shows Frenkel defect because its ions have a large difference in size.

(*ii*) AgBr shows both Frenkel and Schottky defects.

Q. 21. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

Ans. When a cation of higher valence is added as an impurity in an ionic solid, some of the sites of the original cations are occupied by the cations of higher valency. Each cation of higher valency replaces two or more original cations and occupies the site of one original cation and the other site(s) remains vacant.

$$\text{Cationic vacancies produced} = \left[\begin{array}{c}\text{Number of cations of higher valency} \\ \times \\ \text{Difference in valencies of the original cation} \\ \text{and cation of higher valency}\end{array}\right]$$

Q. 22. Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

Ans. In ionic solids with anionic vacancies due to metal excess defect, when the metal atoms deposit on the surface, they diffuse into the crystal and after ionisation, the metal ion occupies cationic vacancy while electron occupies anionic vacancy. Such anionic sites occupied by an electron are known as **F-centres**. These electrons get excited to higher energy levels by adsorption of suitable wavelengths from the visible white light and therefore appear coloured. When Na vapours are passed over NaCl crystals such defect is created and the crystals become yellow due to excess Na^+ and presence of F-centres.

Q. 23. A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

Ans. *n*-type semiconductor means conduction due to presence of excess of electrons. Therefore, to convert group 14 element into *n*-type semiconductor, it should be doped with group 15 element *e.g.*, As.

Q. 24. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic? Justify your answer.

Ans. Ferromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called 'domains'. Each domain acts as a tiny magnet. These domains are randomly oriented. When a ferromagnetic substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field and a strong magnetic field is produced. Such order of domains persists even when the external magnetic field is removed. Hence, the ferromagnetic substance becomes a permanent magnet. On the other hand, the net or resultant magnetic moment of ferrimagnetic substances is small.

NCERT Textbook Exercises

Q. 1. Define the term 'amorphous'. Give a few examples of amorphous solids.

Ans. An amorphous solid consists of particles of irregular shape. The arrangement of constituent particles in such a solid has only short range order. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Examples: Glass, rubber and plastics.

Q. 2. What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

Ans. Glass is an amorphous solid in which the constituent particles (SiO_4 tetrahedra) have only a short range order and there is no long range order. In quartz, the constituent particles (SiO_4 tetrahedra) have both short range as well as long range orders. On melting quartz and then cooling it rapidly, it is converted into glass.

Q. 3. Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.

(*i*) Tetra phosphorus decoxide (P_4O_{10}) **(*ii*) Ammonium phosphate $(NH_4)_3PO_4$**

(*iii*) SiC **(*iv*) I_2**

(*v*) P_4 **(*vi*) Plastic**

(*vii*) Graphite **(*viii*) Brass**

(*ix*) Rb **(*x*) LiBr**

(*xi*) Si

Ans. Ionic: $(NH_4)_3PO_4$ and LiBr; **Metallic:** Brass, Rb; **Molecular:** P_4O_{10}, I_2, P_4;

Network (covalent): Graphite, SiC, Si; **Amorphous:** Plastic.

Q. 4. (*i*) What is meant by the term 'coordination number'?

(*ii*) What is the coordination number of atoms:

(*a*) in a cubic close packed structure? **(*b*) in a body-centred cubic structure?**

Ans. (*i*) Coordination number is defined as the number of nearest neighbours in a close-packed structure. In ionic crystals, coordination number of an ion in the crystal is the number of oppositely charged ions surrounding that particular ion.

(*ii*) (*a*) 12 (*b*) 8.

Q. 5. How can you determine the atomic mass of an unknown metal if know its density and the dimension of its unit cell? Explain your answer.

Ans. Refer to Basic Concepts Point 5. $\left(\text{Atomic mass, } M = \dfrac{d \times a^3 \times N_A}{z}\right)$

Q. 6. 'Stability of a crystal is reflected in the magnitude of its melting point'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

Ans. Higher the melting point, stronger are the forces holding the constituent particles together and hence greater is the stability. In other words, stronger the lattice structure, higher will be lattice energy and more will be the stability of crystal, hence higher the melting point. The intermolecular forces in water and ethyl alcohol are mainly the hydrogen bonding. Higher melting point of water as compared to alcohol shows that hydrogen bonding in ethyl alcohol molecules is not as strong as in water molecules. Diethyl ether is a polar molecule and the intermolecular forces present in it is dipole–dipole attraction. Whereas methane is a non-polar molecule and the only forces present in it is the weak van der Waals' forces.

Q. 7. How will you distinguish between the following pairs of terms: *[CBSE (AI) 2014]*

(*i*) Hexagonal close packing and cubic close packing?

(*ii*) Crystal lattice and unit cell?

(*iii*) Tetrahedral void and octahedral void?

Ans. (*i*) Refer to Basic Concepts Points 8(*c*) (*i*) and (*ii*).

(*ii*) The regular three dimensional arrangement of identical points in the space which represent how the constituent particles (atoms, ions, molecules) are arranged in a crystal is called a crystal lattice.

A unit cell is the smallest portion of a crystal lattice, which when repeated over and again in different directions produces the complete crystal lattice.

(*iii*) A void surrounded by four spheres occupying the corners of tetrahedron is called a tetrahedral void. It is much smaller than the size of spheres in the close packing. A void surrounded by six spheres along the corners of an octahedral is called octahedral void. The size of the octahedral void is smaller than that of the spheres in the close packing but larger than the tetrahedral void.

Q. 8. How many lattice points are there in one unit cell of each of the following lattices?

(*a*) face-centred cubic (*b*) face-centred tetragonal (*c*) body-centred.

Ans. (*a*) 14 (*b*) 14 (*c*) 9.

Q. 9. Explain:

(*a*) The basis of similarities and differences between metallic and ionic crystals.

(*b*) Ionic solids are hard and brittle.

Ans. (*a*) Similarities:

(*i*) Both ionic and metallic crystals have electrostatic forces of attraction. In ionic crystals, these are between the oppositely charged ions. In metals, these are among the valence electrons and the kernels.

(*ii*) In both cases, the bond is non-directional.

Differences:

(*i*) In ionic crystals, the ions are not free to move. Hence, they cannot conduct electricity in the solid state. They can do so only in the molten state or in aqueous solution. In metals, the valence electrons are not bound but are free to move. Hence, they can conduct electricity in the solid state.

(*ii*) Ionic bond is strong due to electrostatic forces of attraction. Metallic bond may be weak or strong depending upon the number of valence electrons and the size of the kernels.

(*b*) Ionic solids are hard because there are strong electrostatic forces of attraction among the oppositely charged ions. They are brittle because ionic bond is non-directional.

Q. 10. Calculate the efficiency of packing in case of a metal crystal for

(*a*) simple cubic (*b*) body-centred cubic (*c*) face-centred cubic

(with the assumption that atoms are touching each other).

Ans. Refer to Basic Concepts Point 7.

Q. 11. Silver crystallises in *fcc* lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver. **[*CBSE (AI) 2010; (F) 2010*]**

Ans. $$M = \frac{d \times a^3 \times N_A}{z} = \frac{10.5 \text{ g cm}^{-3} \times (4.07 \times 10^{-8} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})}{4}$$

$$= \frac{10.5 \text{ g cm}^{-3} \times 67.419 \times 10^{-24} \text{ cm}^3 \times 6.02 \times 10^{23} \text{ mol}^{-1}}{4} = \mathbf{106.54 \text{ g mol}^{-1}}$$

Q. 12. A cubic solid is made up of two elements *P* and *Q*. Atoms of *Q* are at the corners of the cube and *P* at the body centre. What is the formula of the compound? What are the coordination numbers of *P* and *Q*?

Ans. Number of *P* atoms per unit cell = 1 (at the body centre) × 1 = 1

Number of *Q* atoms per unit cell = 8 (at the corners) × $\frac{1}{8}$ = 1

Hence the formula is ***PQ***.

Coordination number of each of *P* and *Q* = **8**.

Q. 13. Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93u. **[*CBSE (AI) 2008*]**

Ans. $d = 8.55$ g/cm^3, $M = 93$ g/mol

For *bcc*, $z = 2$, $a = ?$

$N_A = 6.02 \times 10^{23}$ mol^{-1}

$$d = \frac{z \times M}{a^3 \times N_A}$$

Substituting the values,

$$8.55 = \frac{2 \times 93}{a^3 \times 6.02 \times 10^{23}}$$

$$a^3 = \frac{2 \times 93}{8.55 \times 6.02 \times 10^{23}}$$

$$a = \left(\frac{930}{8.55 \times 3.01}\right)^{1/3} 10^{-8}$$

Let $$x = \left(\frac{930}{8.55 \times 3.01}\right)^{1/3}$$

$\therefore$ $$\log x = \log\left(\frac{930}{8.55 \times 3.01}\right)^{1/3}$$

$$= \frac{1}{3}(\log 930 - \log 8.55 - \log 3.01)$$

$$= \frac{1}{3}(2.9685 - 0.9320 - 0.4786)$$

$$\log x = \frac{1}{3}(1.5579) = 0.5193$$

$$x = \text{Antilog } (0.5193)$$

$$x = 3.306$$

$\therefore$ $$a = 3.306 \times 10^{-8} \text{ cm}$$

Now $$r = \frac{\sqrt{3}}{4} \times 3.306 \times 10^{-8} = \frac{1.732 \times 3.306 \times 10^{-8}}{4}$$

$$r = 1.4315 \times 10^{-8} \text{ cm} = \mathbf{143.15 \text{ pm}}$$

Q. 14. If the radius of the octahedral void is r and the radius of the atoms in close packing is R, derive relationship between r and R.

Ans. A sphere fitting into the octahedral void is shown by shaded circle. The spheres present above and below the void are not shown in the figure. As *ABC* is a right-angled triangle, Pythagoras theorem is applied.

$$AC^2 = AB^2 + BC^2$$

$$(2R)^2 = (R + r)^2 + (R + r)^2 = 2(R + r)^2$$

$$4R^2 = 2(R + r)^2$$

$$2R^2 = (R + r)^2$$

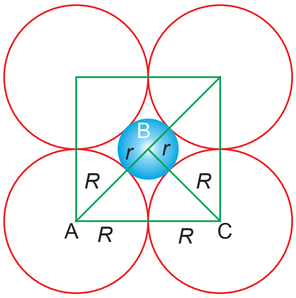
$$(\sqrt{2}\,R)^2 = (R + r)^2$$

$$\sqrt{2}\,R = R + r$$

$$r = \sqrt{2}\,R - R$$

$$r = (\sqrt{2} - 1)\,R = (1.414 - 1)R$$

$$\boldsymbol{r = 0.414\,R}$$



Q. 15. Copper crystallises into a *fcc* lattice with edge length 3.61 × 10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

Ans. $$d = \frac{z \times M}{a^3 \times N_A}$$

For *fcc* lattice of copper, $z = 4$

Atomic mass of copper, $M = 63.5 \text{ g mol}^{-1}$

$\therefore$ $$d = \frac{4 \times 63.5 \text{ g mol}^{-1}}{(3.61 \times 10^{-8} \text{ cm})^3 \times (6.022 \times 10^{23} \text{mol}^{-1})} = 8.97 \text{ g cm}^{-3}$$

which is in agreement with the measured value.

Q. 16. Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

Ans. 98 Ni atoms, are associated with 100 O atoms. Out of 98 Ni atoms, suppose Ni present as $Ni^{2+} = x$.

Then Ni present as $Ni^{3+} = 98 - x$.

Total charge on x Ni^{2+} and $(98 - x)$ Ni^{3+} should be equal to charge on 100 O^{2-} ions.

Therefore, $x \times 2 + (98 - x) \times 3 = 100 \times 2$

or $2x + 294 - 3x = 200$

or $x = 94$

$\therefore$ Fraction of Ni present as $Ni^{2+} = \frac{94}{98} \times 100 = \mathbf{96\%}$

Fraction of Ni present as $Ni^{3+} = \frac{4}{98} \times 100 = \mathbf{4\%}$

Q. 17. What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanisms.

Ans. Refer to Basic Concepts Point 17.

Q. 18. Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that this substance is a *p*-type semiconductor?

Ans. The ratio less than 2 : 1 in Cu_2O shows that some cuprous (Cu^+) ions have been replaced by cupric (Cu^{2+}) ions. For maintaining electrical neutrality, every two Cu^+ ions will be replaced by one Cu^{2+} ion thereby creating a hole. As conduction will be due to the presence of these positive holes, hence it is a *p*-type semiconductor.

Q. 19. Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Ans. Let the number of oxide ions (O^{2-}) in the close packing be x.

$\therefore$ Number of octahedral voids $= x$

As 2/3rd of the octahedral voids are occupied by ferric ions, number of ferric ions present

$$= \frac{2}{3} \times x = \frac{2x}{3}$$

$\therefore$ Ratio of $Fe^{3+} : O^{2-} = \frac{2x}{3} : x = 2 : 3$

Hence, the formula of ferric oxide is $\mathbf{Fe_2O_3}$.

Q. 20. Classify each of the following as being either a *p*-type or a *n*-type semiconductor:

(*i*) Ge doped with In (*ii*) Si doped with B.

Ans. (*i*) Ge is Group 14 element and In is Group 13 element therefore, an electron deficit hole is created. Thus, semiconductor is *p*-type.

(*ii*) Since Si is Group 14 element and B is Group 13 element, therefore, an electron deficit hole is created. Thus, semiconductor is *p*-type.

Q. 21. Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

Ans. For *fcc*, $a = 2\sqrt{2}\, r = 2 \times 1.414 \times 0.144$ nm $= 0.407$ nm.

Q. 22. In terms of band theory, what is the difference

(*i*) between a conductor and an insulator

(*ii*) between a conductor and a semiconductor?

Ans. (*i*) The energy gap between the valence band and conduction band in an insulator is very large while in a conductor, the energy gap is very small or there is overlapping between valence band and conduction band.

(*ii*) In a conductor, there is a very small energy gap or there is overlapping between valence band and conduction band whereas in semiconductor there is always a small energy gap between them.

Q. 23. Explain the following terms with suitable examples:

(*i*) Schottky defect (*ii*) Frenkel defect (*iii*) interstitials (*iv*) F-centres.

Ans. Refer to Basic Concepts Point 13.

Q. 24. Aluminium crystallises in a cubic close packed structure. Its metallic radius is 125 pm.

(*a*) What is the length of the side of the unit cell?

(*b*) How many unit cells are there in 1.00 cm^3 of aluminium? *[CBSE (F) 2011]*

Ans. (*a*) For a *fcc* unit cell, $r = \frac{a}{2\sqrt{2}}$

$$a = 2\sqrt{2}r = 2 \times 1.414 \times 125$$

$$= \mathbf{353.5\ pm}$$

(*b*) Volume of unit cell $= a^3 = (353.5 \times 10^{-10}\ \text{cm})^3$

$$= 442 \times 10^{-25}\ \text{cm}^3$$

$$\text{Number of unit cell} = \frac{1\ \text{cm}^3}{442 \times 10^{-25}\ \text{cm}^3} = \mathbf{2.26 \times 10^{22}\ unit\ cells}$$

Q. 25. If NaCl is doped with 10^{-3} mol % SrCl$_2$, what is the concentration of cation vacancies?

Ans. As NaCl is doped with 10^{-3} mol % of SrCl$_2$

i.e., 100 mol of NaCl are doped with 10^{-3} mol of SrCl$_2$

$\therefore$ 1 mol of NaCl is doped with $\text{SrCl}_2 = \frac{10^{-3}}{100}\ \text{mol} = 10^{-5}\ \text{mol}$

As each Sr^{2+} ion introduces one cation vacancy, therefore, concentration of cation vacancies

$$= 10^{-5} \times 6.02 \times 10^{23}\ \text{mol}^{-1}$$

$$= \mathbf{6.02 \times 10^{18}\ mol^{-1}}$$

Q. 26. Explain the following with suitable examples:

(*a*) Ferromagnetism **(*b*) Paramagnetism**

(*c*) Ferrimagnetism **(*d*) Antiferromagnetism**

(*e*) 12-16 and 13-15 group compounds.

Ans. Refer to Basic Concepts Points 16 (*c*), (*e*); 16 (*b*), (*d*) and 14 (*a*), (*b*).

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Which of the following conditions favours the existence of a substance in the solid state? *[NCERT Exemplar]*

(*a*) High temperature (*b*) Low temperature

(*c*) High thermal energy (*d*) Weak cohesive forces

2. Which of the following is not a characteristic of a crystalline solid? *[NCERT Exemplar]*

(*a*) Definite and characteristic heat of fusion.

(*b*) Isotropic nature.

(*c*) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal.

(*d*) A true solid

3. Which of the following is true about the value of refractive index of quartz glass? *[NCERT Exemplar]*

(*a*) Same in all directions (*b*) Different in different directions

(*c*) Cannot be measured (*d*) Always zero

4. Which of the following statement is not true about amorphous solids? **[*NCERT Exemplar*]**

(*a*) On heating they may become crystalline at certain temperature.
(*b*) They may become crystalline on keeping for long time.
(*c*) Amorphous solids can be moulded by heating.
(*d*) They are anisotropic in nature.

5. The sharp melting point of crystalline solids is due to ____________. **[*NCERT Exemplar*]**

(*a*) a regular arrangement of constituent particles observed over a short distance in the crystal lattice.
(*b*) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.
(*c*) same arrangement of constituent particles in different directions.
(*d*) different arrangement of constituent particles in different directions.

6. Which one of the following is a covalent crystal?

(*a*) Rock salt
(*b*) Ice
(*c*) Quartz
(*d*) Dry ice

7. Which of the following solids is not an electrical conductor?

(*i*) Mg(*s*) **(*ii*) TiO(*s*)** **(*iii*) $I_2(s)$** **(*iv*) $H_2O(s)$**

(*a*) (*i*) only
(*b*) (*ii*) only
(*c*) (*iii*) and (*iv*)
(*d*) (*ii*), (*iii*) and (*iv*)

8. The number of atoms in a face centred cubic unit cell is

(*a*) 2
(*b*) 4
(*c*) 5
(*d*) 6

9. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is:

(*a*) AB_2
(*b*) A_2B_3
(*c*) A_2B_5
(*d*) A_2B

10. The total number of tetrahedral voids in the face centred unit cell is ____________.

(*a*) 6
(*b*) 8
(*c*) 10
(*d*) 12

11. If Z is the number of atoms in the unit cell that represents the closest packing sequence—ABC ABC, the number of tetrahedral voids in the unit cell is equal to

(*a*) Z
(*b*) 2Z
(*c*) $\frac{Z}{2}$
(*d*) $\frac{Z}{4}$

12. In which pair most efficient packing is present?

(*a*) *hcp* and *bcc*
(*b*) *hcp* and *ccp*
(*c*) *bcc* and *ccp*
(*d*) *bcc* and simple cubic cell

13. The fraction of the total volume occupied by the atoms present in a simple cube is

(*a*) $\pi/4$
(*b*) $\pi/6$
(*c*) $\pi/(3\sqrt{2})$
(*d*) $\pi/(4\sqrt{2})$

14. A metallic crystal has the *bcc* type staking pattern. What percentage of volume of this lattice is empty space?

(*a*) 68%
(*b*) 32%
(*c*) 26%
(*d*) 74%

15. A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion (Y^-) will be

(*a*) 275.1 pm
(*b*) 322.5 pm
(*c*) 241.5 pm
(*d*) 165.7 pm

16. AB crystallizes in a body centred cubic lattice with edge length '*a*' equal to 387 pm. The distance between two oppositely charged ions in the lattice is

(*a*) 250 pm
(*b*) 200 pm
(*c*) 300 pm
(*d*) 335 pm

17. If a stands for the edge length of the cubic systems: simple cubic, body centred cubic and face centred cubic, then the ratio of the radius of the spheres in these systems will be respectively

(*a*) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$
(*b*) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
(*c*) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$
(*d*) $1a : 3a : \sqrt{2}a$

18. Which of the following crystals does not exhibit Frenkel defect?

(*a*) AgBr (*b*) AgCl (*c*) KBr (*d*) ZnS

19. The type of crystal defect is indicated in the diagram below

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-
Cl^-	○	Cl^-	Na^+	○	Na^+
Na^+	Cl^-	○	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+	○	Na^+

(*a*) Frenkel defect (*b*) Frenkel and Schottky defect

(*c*) Interstitial defect (*d*) Schottky defect

20. Which of the following is true about the charge acquired by *p*-type semiconductors?

(*a*) Positive (*b*) Neutral

(*c*) Negative (*d*) Depends on concentration of *p* impurity

Answers

1. (*b*) **2.** (*b*) **3.** (*a*) **4.** (*d*) **5.** (*b*) **6.** (*c*) **7.** (*c*) **8.** (*d*) **9.** (*c*) **10.** (*b*)
11. (*b*) **12.** (*b*) **13.** (*b*) **14.** (*b*) **15.** (*c*) **16.** (*d*) **17.** (*a*) **18.** (*c*) **19.** (*d*) **20.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***

(b) ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***

(c) ***Assertion (A) is correct, but Reason (R) is incorrect statement.***

(d) ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. Assertion (*A*) : Graphite is a good conductor of electricity however diamond belongs to the category of insulators.

Reason (*R*) : Graphite is soft in nature on the other hand diamond is very hard and brittle.

2. Assertion (*A*) : The total number of atoms present in a simple cubic unit cell is one.

Reason (*R*) : Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.

3. Assertion (*A*) : The coordination number of square close packing in two dimensions is 6.

Reason (*R*) : In square close packing, each sphere is in contact with four of its neighbours.

4. Assertion (*A*) : Total number of octahedral voids present in unit cell of cubic close packing including the one that is present at the body centre, is four.

Reason (*R*) : Besides the body centre there is one octahedral void present at the centre of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells.

5. Assertion (*A*) : The packing efficiency is maximum for the *fcc* structure.

Reason (*R*) : The coordination number is 12 in *fcc* structures.

6. Assertion (*A*) : Semiconductors are solids with conductivities in the intermediate range from $10^{-6} - 10^{4}$ ohm^{-1} m^{-1}.

Reason (*R*) : Intermediate conductivity in semiconductor is due to partially filled valence band.

7. **Assertion (*A*) :** Ferrimagnetic substances lose magnetism on heating.
Reason (*R*) : Fe_3O_4 and $MgFe_2O_4$ are examples of substances that show ferrimagnetism.

Answers

1. (*b*) **2.** (*a*) **3.** (*d*) **4.** (*c*) **5.** (*b*) **6.** (*c*) **7.** (*b*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Solid is that form of matter which possesses rigidity and hence a definite shape and a definite volume. If intermolecular forces are greater than thermal energy, substances exist as solid. Solids can be classified into two types: Crystalline solids and amorphous solids. Crystalline solids have regular arrangement of particles, definite geometric shapes, sharp melting points and definite heat of fusion. They are anisotropic and undergo clean cleavage. On the other hand, amorphous solids have no regular arrangement of particles, irregular shapes, melt over a range of temperature, no definite heat of fusion. They are isotropic and undergo irregular cleavage. Ionic solids, molecular solids, covalent solids and metallic solids are the types of crystalline solids.

1. **Solid A is very hard, electrical insulator in solid as well as molten state and melts at extremely high temperature. What type of solid is it?**

Ans. Covalent or network solid.

2. **Is polythene used in making polythene bags a crystalline material or an amorphous material?**

Ans. Polythene is a polymer and is an amorphous solid.

3. **Sodium metal is quite soft whereas sodium chloride crystals are quite hard. Why?**

Ans. In sodium metal, the atoms are held together by metallic bonds which are quite weak while sodium chloride is an ionic compound in which oppositively charged Na^+ and Cl^- ions are held together by strong electrostatic force of attraction. Hence, it is quite hard.

4. **Diamond and solid rhombic sulphur both are covalent solids but the latter has very low melting point than the former. Why?**

Ans. Diamond is a three dimensional covalent solid with strong interatomic forces whereas rhombic sulphur is a one dimensional covalent solid consisting of puckered eight membered (S_8) held together by weak van der Waal's forces.

5. **What type of interactions held the molecules in a polar molecular solid?**

Ans. Dipole-dipole interactions.

PASSAGE–2

Any departure from a perfectly ordered arrangement of constituent particles is called defect or imperfection. In solids, when the ratio between cations and anions remains the same after defect, it is termed as stoichiometric defects. Schottky and Frenkel defects are categorised into stoichiometric defects. In Schottky defect equal number of cations and anions are missing while in Frenkel defect cations are missing from lattice sites and occupy interstitial sites. In non-stoichiometric defects, the ratio of cations and anions changes as a result of the defect. Metal excess and metal deficiency defects are non-stoichiometric defects.

1. **Why are the defects of the crystalline solids called thermodynamic defects?**

Ans. In crystalline solids there is perfect arrangement of the constituent particles only at 0 K. With the increase in temperature, the number of defects increases so the defects are called thermodynamic defects.

2. **Why is Frenkel defect not found in pure alkali metal halides?**

Ans. Alkali metal ions have large size which cannot fit into the interstitial sites, so Frenkel defect is not found in pure alkali metal halides.

3. What type of defect can arise when a solid is heated?

Ans. Vacancy defect is produced in the crystal when a solid is heated.

4. Why is FeO(*s*) not formed in stoichiometric composition?

Ans. This is due to replacement of Fe^{2+} ions by Fe^{3+} ions.

5. What type of crystal defect is produced when sodium chloride is doped with $MgCl_2$?

Ans. Impurity defect.

Very Short Answer Questions [1 mark]

Q. 1. How can a material be made amorphous?

Ans. By melting the material and then cooling it rapidly.

Q. 2. Why does the window glass of the old buildings look milky? [*CBSE (F) 2016*]

Ans. It is due to heating during the day and cooling at night, *i.e.*, due to annealing over a number of years, glass acquires crystalline character.

Q. 3. 'Crystalline solids are anisotropic in nature.' What does this statement mean? [*CBSE Delhi 2011; (F) 2011*]

Ans. It means that some of their physical properties like electrical conductivity, refractive index, etc., are different in different directions.

Q. 4. What kind of attractive forces are present in the molecular crystalline solids?

Ans. Dispersion forces, dipole–dipole interactions and hydrogen bonds.

Q. 5. What type of interactions hold the molecules together in a polar molecular solid? [*CBSE (AI) 2010*]

Ans. The interactions which hold the molecules together in a polar molecular solid are dipole-dipole attractions.

Q. 6. Give an example each of a molecular solid and an ionic solid. [*CBSE Central 2016*]

Ans. **Molecular solids:** CO_2, I_2, HCl

Ionic solids: NaCl, ZnS, CaF_2

Q. 7. Write a feature which will distinguish a metallic solid from an ionic solid. [*CBSE Delhi 2010; (F) 2010*]

Ans. Metals are malleable and ductile whereas ionic solids are hard and brittle.

Q. 8. How many effective sodium ions are located at the edge centre of a unit cell in a sodium chloride crystal?

Ans. $12 \times \frac{1}{4} = 3.$

Q. 9. In NaCl crystal, Cl^- ions are in *fcc* arrangement. Calculate the number of Cl^- ions in its unit cell. [*HOTS*]

Ans. Cl^- ions per unit cell $= 8 \times \frac{1}{8}$ (from corners) $+ 6 \times \frac{1}{2}$ (from face centres) $=$ **4**

Q. 10. Express the relationship between atomic radius (*r*) and the edge length (*a*) in the *bcc* unit cell. [*CBSE (F) 2014*]

Ans. r (atomic radius) $= \frac{\sqrt{3}}{4}\, a$ (edge length of unit cell).

Q. 11. A cubic solid is made up of two elements A and B. Atoms A are present at the corners of the cube and B are at the alternate face centres. What is the formula of the solid? [*HOTS*]

Ans. Number of A atoms per unit cell $= 8 \times \frac{1}{8} = 1$

Number of B atoms per unit cell $= 2 \times \frac{1}{2} = 1$

$\therefore$ Formula of the compound = **AB**

Q. 12. A compound formed by elements *A* and *B* has a cubic structure in which *A* atoms are at the corners of the cube and *B* atoms are at the face centres. Derive the formula of the compound.

Ans. Number of A atoms per unit cell = 8 (at the corners) $\times \frac{1}{8} = 1$

Number of B atoms per unit cell = 6 (at the face centres) $\times \frac{1}{2} = 3$

$$\text{A} : \text{B} = 1 : 3$$

$\therefore$ The formula of the compound = $\mathbf{AB_3}$.

Q. 13. A metallic element crystallises into a lattice having a pattern of AB AB…… and packing of spheres leaves out voids in the lattice. What type of structure is formed by this arrangement?[*CBSE Delhi 2017 C*]

Ans. *hcp*.

Q. 14. What is the formula of a compound in which the element *P* forms *hcp* lattice and atoms of *Q* occupy 2/3rd of octahedral voids? [*CBSE (F) 2017*]

Ans. Let the number of atoms of P in *hcp* lattice = N

So, number of octahedral voids = N

$\therefore$ Number of Q atoms = $\frac{2}{3} \times N = \frac{2}{3}N$

$$Q : P = \frac{2}{3}N : N = 2 : 3$$

Hence, the formula of the compound is $\boldsymbol{Q_2P_3}$.

Q. 15. A compound is formed by two elements *X* and *Y*. Atoms of the element *Y* (as anions) make *ccp* and those of the element *X* (as cations) occupy all the octahedral voids. What is the formula of the compound?

Ans. Suppose the number of atoms Y in *ccp* = N

$\therefore$ Number of octahedral voids = $N \times 1 = N$

$\therefore$ Number of atoms of $X = N$

Ratio of $X : Y = N : N = 1 : 1$

Hence, formula of the compound = $\boldsymbol{XY}$

Q. 16. In corundum, oxide ions are arranged in hexagonal close packing and aluminium ions occupy two-third of the octahedral voids. What is the formula of corundum?

Ans. Let the number of oxide ions in the packing be N.

Then octahedral voids = N. Therefore, Al^{3+} ions = $\frac{2}{3} \times \text{N} = \frac{2N}{3}$.

$\therefore$ Ratio of $\text{Al}^{3+} : \text{O}^{2-} = \frac{2N}{3} : N = 2 : 3$

Hence, formula of corundum is $\mathbf{Al_2O_3}$.

Q. 17. What is the formula of a compound in which the element *P* forms *ccp* lattice and atoms of *Q* occupy 2/3rd of tetrahedral voids? [*CBSE (F) 2017*]

Ans. Let the number of atoms of P in *ccp* arrangement = N

So, number of tetrahedral voids = $2N$

$\therefore$ Number of Q atoms $= \frac{2}{3} \times 2\text{N} = \frac{4}{3}\text{N}$

$$\text{Q} : \text{P} = \frac{4}{3}\text{N} : \text{N} = 4 : 3$$

Hence, formula of the compound = $\mathbf{Q_4P_3}$

Q. 18. What is the formula of a compound in which the element *Y* forms *ccp* lattice and atoms of *X* occupy 2/3rd of tetrahedral voids? [*CBSE Allahabad 2015*]

Ans. Let the number of particles of element Y in *ccp* lattice = N

Number of tetrahedral voids = $2N$

Number of particles of element $X = \frac{2}{3} \times 2N = \frac{4}{3}N$

$$X : Y = \frac{4}{3}N : N$$

$$X : Y = 4 : 3$$

∴ Formula of the compound is $\boldsymbol{X_4Y_3}$.

Q. 19. A solid is made up of two elements *P* and *Q*. Atoms of *Q* are in *ccp* arrangement while atoms of *P* occupy all the tetrahedral sites. What is the formula of the compound?

Ans. Suppose number of atoms of Q in *ccp* arrangement = N

So, number of tetrahedral sites = 2 N

∴ Number of P atoms = 2 N

∴ $P : Q = 2N : N = 2 : 1$

Hence, formula of compound is $\mathbf{P_2Q}$.

Q. 20. A compound AB_2 possesses the CaF_2 type crystal structure. Write the coordination number of A^{2+} and B^- ions in its crystals. [*HOTS*]

Ans. Coordination no. of A = 8, Coordination no. of B = 4.

Q. 21. In spite of long range order in the arrangement of particles, why are the crystals usually not perfect? [*NCERT Exemplar*]

Ans. Crystals have long range repeated pattern of arrangement of constituent particles but in the process of crystallisation some deviations from the ideal arrangement (*i.e.*, defects) may be introduced. That is why crystals are usually not perfect.

Q. 22. What are the types of lattice imperfections found in crystals?

Ans. (*a*) Stoichiometric defects, *viz*., Schottky defect and Frenkel defect (*b*) Non-stoichiometric defects, *viz*., metal excess, metal deficiency, and (*c*) impurity defects.

Q. 23. Which point defect in its crystal units increases the density of a solid?
[*CBSE Delhi 2009, 2011; (AI) 2012*]

Ans. Interstitial defect.

Q. 24. Which crystal defect lowers the density of a solid? [*CBSE Delhi 2009, 2010; (AI) 2009*]

Ans. Schottky defect.

Q. 25. Which point defect in crystals does not alter the density of the relevant solid? [*CBSE Delhi 2009, 2010*]

Ans. Frenkel defect.

Q. 26. What type of stoichiometric defect is shown by AgCl? [*CBSE Delhi 2013*]

Ans. Frenkel defect.

Q. 27. What type of stoichiometric defect is shown by ZnS? [*CBSE (AI) 2017 C*]

Ans. ZnS shows Frenkel defect as its ions have a large difference in size.

Q. 28. Why does Frenkel defect not change the density of AgCl crystals?

Ans. Because of the Frenkel defect, no ion is missing from the crystal, therefore there is no change in density.

Q. 29. Why is FeO(*s*) not formed in stoichiometric composition? [*NCERT Exemplar*]

Ans. In the crystals of FeO, some of the Fe^{2+} cations are replaced by Fe^{3+} ions. Three Fe^{2+} ions are replaced by two Fe^{3+} ions to make up for the loss of positive charge. Eventually there would be less amount of metal as compared to stoichiometric proportion.

Q. 30. What type of crystal defect is produced when sodium chloride is doped with $MgCl_2$?

Ans. A cation vacancy is formed, so impurity defect is produced. A substitutional solid solution is formed (because $2Na^+$ ions are replaced by one Mg^{2+} ion at the lattice site).

Q. 31. Name the non-stoichiometric point defect responsible for colour in alkali metal halides.
[*CBSE Sample Paper 2016*]

Ans. Metal excess defect due to anionic vacancies.

Q. 32. Why does table salt, NaCl, sometimes appear yellow in colour? [*NCERT Exemplar*] [*HOTS*]

Ans. Yellow colour in sodium chloride is due to metal excess defect due to which unpaired electrons occupy anionic sites. These sites are called F-centres. These electrons absorb some energy from the visible white light for the excitation which makes crystal appear yellow.

Q. 33. Zinc oxide is white but it turns yellow on heating. Explain. [*CBSE North 2016*] [*HOTS*]

Ans. On heating ZnO loses oxygen according to the following reaction:

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Zn^{2+} ions are entrapped in the interstitial voids and electrons are entrapped in the neighbouring interstitial voids to maintain electrical neutrality. Due to presence of electrons in interstitial voids the colour is yellow.

Q. 34. What is meant by the term 'forbidden zone' in reference to band theory of solids? [*CBSE (F) 2012*]

Ans. The energy gap between valence band and conduction band is known as forbidden zone.

Q. 35. What would be the nature of solid if there is no energy gap between valence band and conduction band? [*CBSE East 2016*]

Ans. Conductor.

Q. 36. What is meant by an 'intrinsic semiconductor'? [*CBSE (F) 2011*]

Ans. Pure substances exhibiting conductivity similar to that of silicon and germanium are called intrinsic semiconductors.

Q. 37. Define superconductivity of a substance.

Ans. The property of a substance to offer no resistance to the flow of electricity at a particular temperature is known as superconductivity.

Q. 38. How does the electrical conductivity of metallic conductors vary with temperature?

Ans. Electrical conductivity decreases with rise in temperature because kernels begin to vibrate and create hindrance in the flow of electrons.

Q. 39. How does the electrical conductivity of semiconductors vary with temperature?

Ans. Electrical conductivity of semiconductors increases with increase in temperature as more electrons can jump from valence band to conduction band.

Q. 40. What is the difference between 13-15 and 12-16 compounds?

Ans. Group 13-15 compounds, *viz*., AlP, GaAs, etc. have large covalent character whereas Group 12-16 compounds, *viz*., ZnS, CdS, HgTe, etc. do not possess covalent character but have sufficient ionic character. However, all of them are semiconductors.

Q. 41. What type of semiconductor is obtained when silicon is doped with arsenic? [*CBSE (AI) 2010*]

Ans. *n*-type semiconductor.

Q. 42. Name the type of semiconductor obtained when silicon is doped with boron. [*CBSE Sample Paper 2017*]

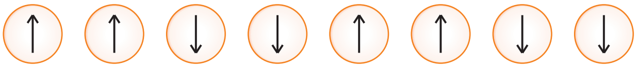
Ans. *p*-type semiconductor.

Q. 43. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic? [*CBSE Delhi 2013*]

Ans. Ferromagnetic.

Q. 44. What type of substances exhibit antiferromagnetism?

Ans. Substances in which domains are oppositely oriented and cancel out each other's magnetic moments exhibit antiferromagnetism.



Short Answer Questions–I [2 marks]

Q. 1. How will you distinguish between the following pairs of terms: [*CBSE (AI) 2014*]

(*i*) Tetrahedral and octahedral voids

(*ii*) Crystal lattice and unit cell

Ans. (*i*) A void surrounded by four spheres occupying the corners of tetrahedron is called a tetrahedral void. It is much smaller than the size of spheres in the close packing. A void surrounded by six spheres along the corners of an octahedral is called octahedral void. The size of the octahedral void is smaller than that of the spheres in the close packing but larger than the octahedral void.

(*ii*) The regular three dimensional arrangement of identical points in the space which represent how the constituent particles (atoms, ions, molecules) are arranged in a crystal is called a crystal lattice.

A unit cell is the smallest portion of a crystal lattice, which when repeated over and again in different directions produces the complete crystal lattice.

Q. 2. If three elements *A*, *B* and *C* crystallise in a cubic solid lattice with *A* atoms at the corners, B atoms at the cube centres and *C* atoms at the centre of the faces of the cube, then write the formula of the compound. **[*HOTS*]**

Ans. Atoms of A per unit cell $= 8 \times \frac{1}{8} = 1$

Atoms of B per unit cell $= 1$

Atoms of C per unit cell $= 6 \times \frac{1}{2} = 3$

Hence, the formula is $\boldsymbol{ABC_3}$.

Q. 3. A crystalline solid has a cubic structure in which tungsten (W) atoms are located at cube corners of the unit cell, oxygen atoms at the cube edges and sodium atom at the centre. What is the molecular formula of the compound? **[*HOTS*]**

Ans. Number of W atoms per unit cell = 8 (at the corners) $\times \frac{1}{8} = 1$

Number of O atoms per unit cell = 12 (at the edge centres) $\times \frac{1}{4} = 3$

Number of sodium atoms per unit cell = 1 (at the cube centre) × 1 = 1

Hence, the formula of the compound = $\mathbf{NaWO_3}$

Q. 4. In a cubic close packed structure of a mixed oxide; one-eighth of tetrahedral voids are occupied by divalent ions X^{2+}, while one half of the octahedral voids are occupied by trivalent ions Y^{3+}. What is the formula of the compound? **[*HOTS*]**

Ans. Let the number of O^{2-} ions in the crystal $= N$

$\therefore$ Number of tetrahedral voids $= 2N$

Number of octahedral voids $= N$

$\therefore$ Number of X^{2+} ions $= \frac{1}{8} \times 2N = \frac{N}{4}$

Number of Y^{3+} ions $= \frac{1}{2} \times N = \frac{N}{2}$

$$X^{2+} : Y^{3+} : O^{2-} = \frac{N}{4} : \frac{N}{2} : N = 1 : 2 : 4$$

Hence, the formula of the compound is $\mathbf{XY_2O_4}$.

Q. 5. The radius of an atom of an element is 75 pm. If it crystallizes as a body-centred cubic lattice, what is the length of the side of the unit cell?

Ans. For *bcc*, $a = \frac{4}{\sqrt{3}} r = \frac{4}{\sqrt{3}} \times 75$

$$= \frac{4}{\sqrt{3}} \times 75 \times \frac{\sqrt{3}}{\sqrt{3}} = 100 \times 1.732 = \mathbf{173.2\ pm}$$

Q. 6. Tungsten crystallises in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of tungsten atom? **[*CBSE Delhi 2012*]**

Ans. $a = 316.5$ pm

For *bcc* unit cell, $r = \frac{\sqrt{3}}{4} a$

$$r = \frac{\sqrt{3}}{4} \times 316.5 \text{ pm} = \mathbf{137.04\ pm}$$

Q. 7. Calculate the efficiency of packing in case of a metal crystal for simple cubic (with the assumption that atoms are touching each other). **[*CBSE (AI) 2011*]**

Ans. Packing efficiency $= \dfrac{z \times \text{volume of one atom}}{\text{Volume of cubic unit cell}} \times 100 = \dfrac{z \times \frac{4}{3}\pi r^3}{a^3} \times 100$

For a simple cubic lattice, $a = 2r$ and $z = 1$

$\therefore$ Packing efficiency$= \dfrac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} \times 100 = \dfrac{\pi}{6} \times 100 = 52.36\% = \mathbf{52.4\%}$

Q. 8. Calculate the following

(*i*) Number of NaCl units in a unit cell of NaCl.

(*ii*) Number of CsCl unit in a unit cell of CsCl. **[*HOTS*]**

Ans. (*i*) Number of Na^+ ions = 12 (at edge centres) $\times \dfrac{1}{4}$ + 1 (at body centre) × 1 = 4

Number of Cl^- ions = 8 (at the corners) $\times \dfrac{1}{8}$ + 6 (at face centres) $\times \dfrac{1}{2}$ = 4

$\therefore$ Number of NaCl units per unit cell (*z*) = **4**

(*ii*) Number of Cs^+ ion = 1 (at the body centre) × 1 = 1

Number of Cl^- ions = 8 (at the corners) $\times \dfrac{1}{8}$ = 1

$\therefore$ Number of CsCl units per unit cell (*z*) = **1**

Q. 9. Calculate the following

(*i*) Number of ZnS units in a unit cell of ZnS.

(*ii*) Number of CaF_2 units in a unit cell of CaF_2. **[*HOTS*]**

Ans. (*i*) Number of Zn^{2+} ions = 4 (within the body) × 1 = 4

Number of S^{2-} ions = 8 (at the corners) $\times \dfrac{1}{8}$ + 6 (at face centres) $\times \dfrac{1}{2}$ = 4

$\therefore$ Number of ZnS units per unit cell (*z*) = **4**

(*ii*) Number of Ca^{2+} ions = 8 (at the corners) $\times \dfrac{1}{8}$ + 6 (at face centres) $\times \dfrac{1}{2}$ = 4

Number of F^- ions = 8 (within the body) × 1 = 8

Number of CaF_2 ions per unit cell (z) = **4**.

Q. 10. Lithium metal crystal has body-centred cubic structure. Its density is 0.53 g cm^{-3} and its molar mass is 6.94 g mol^{-1}. Calculate the volume of a unit cell of lithium metal. [N_A = 6.023 × 10^{23} mol^{-1}]

Ans. Volume of the crystal, $a^3 = \dfrac{z \times M}{d \times N_A}$

$$a^3 = \frac{2 \times 6.94}{0.53 \times 6.023 \times 10^{23}} = \mathbf{4.348 \times 10^{-23}\ cm^3}$$

Q. 11. An element with density 11.2 g cm^{-3} forms a f.c.c. lattice with edge length of 4 × 10^{-8} cm. Calculate the atomic mass of the element.

(Given: N_A = 6.022 × 10^{23} mol^{-1}) **[*CBSE Delhi 2014*]**

Ans. For *fcc* lattice number of atoms per unit cell, *z* = 4

Here, $d = 11.2\ \text{g cm}^{-3}$, $a = 4 \times 10^{-8}$ cm, $N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$

$$\text{Atomic mass, } M = \frac{d \times a^3 \times N_A}{z}$$

$$= \frac{11.2\text{g cm}^{-3} \times (4 \times 10^{-8}\ \text{cm})^3 \times 6.022 \times 10^{23}\text{mol}^{-1}}{4} = \mathbf{107.9\ g\ mol^{-1}} \text{ or } \mathbf{107.9\ u}$$

Q. 12. Account for the following: **[*CBSE (AI) 2013*]**

(*i*) Schottky defects lower the density of related solids.

(*ii*) Conductivity of silicon increases on doping it with phosphorus.

Ans. (*i*) In Schottky defect as the number of ions are missing from their normal lattice sites, the mass decreases whereas the volume remains the same. Due to this the density decreases.

(*ii*) This is due to availability of additional unpaired electrons on doping with phosphorous.

Q. 13. (*i*) Why does presence of excess of lithium makes LiCl crystals pink? **[*CBSE (AI) 2013*]**

(*ii*) A solid with cubic crystal is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound?

Ans. (*i*) Excess of lithium leads to metal excess defect. Lithium atoms lose electrons to form Li^+ ions. These electrons diffuse into the crystal and form F-centres. Therefore, LiCl crystals become pink.

(*ii*) Number of P atoms per unit cell = 1 (at the body centre) × 1 = 1

Number of Q atoms per unit cell = 8 (at the corners) $\times \frac{1}{8} = 1$

Hence, the formula of the compound = ***PQ*.**

Q. 14. (*i*) Based on the nature of intermolecular forces, classify the following solids: **[*CBSE (AI) 2014*]**

Sodium sulphate, Hydrogen

(*ii*) What happens when $CdCl_2$ is doped with AgCl?

Ans. (*i*) Sodium sulphate—Ionic solid, Hydrogen—Molecular solid (non-polar)

(*ii*) It results impurity defect. Each Cd^{2+} replaces two Ag^+ ions. It occupies the site of one ion and the other site remains vacant.

Short Answer Questions–II [3 marks]

Q. 1. Write the coordination number of each ion in the following crystals:

(*i*) ZnS **(*ii*) CaF_2**

(*iii*) Na_2O

Ans. (*i*) $Zn^{2+} = 4$, $S^{2-} = 4$

(*ii*) $Ca^{2+} = 8$, $F^- = 4$

(*iii*) $Na^+ = 4$, $O^{2-} = 8$

Q. 2. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number.

(At. mass of Fe = 55.845 u) **[*CBSE Delhi 2012; (F) 2012*]**

Ans. $a = 286.65$ pm $= 286.65 \times 10^{-10}$ cm; $M = 55.845$ g mol^{-1}; $d = 7.874$ g cm^{-3}

For *bcc* unit cell, $z = 2$

Substituting the values in the expression, $N_A = \frac{z \times M}{a^3 \times d}$, we get

$$N_A = \frac{2 \times 55.845 \text{ g mol}^{-1}}{(286.65 \times 10^{-10} \text{ cm})^3 \times 7.874 \text{ g cm}^{-3}}$$

$$N_A = \mathbf{6.000 \times 10^{23} \text{ mol}^{-1}}$$

Q. 3. An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05 × 10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the cubic unit cell? **[*CBSE Delhi 2015*]**

Ans. Number of atoms per unit cell, $z = \frac{d \times a^3 \times N_A}{M}$ …(*i*)

Here, $d = 2.7$ g cm^{-3}, $M = 27$ g mol^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1} and $a = 4.05 \times 10^{-8}$ cm

Substituting these values in the expression (*i*), we get

$$z = \frac{2.7\text{ g cm}^{-1} \times (4.05 \times 10^{-8}\text{ cm})^3 \times 6.022 \times 10^{23}\text{ mol}^{-1}}{27\text{ g/mol}}$$

$$z \simeq 4$$

As there are 4 atoms of the element present per unit cell therefore the cubic unit cell must be face-centered.

Q. 4. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom is 127.8 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face-centred cubic structure?

(Given: At. mass of Cu = 63.54 g mol^{-1} and $N_A = 6.022 \times 10^{23}$ mol^{-1}) ***[CBSE Delhi 2010; (AI) 2010]***

Ans. Suppose copper has *fcc* structure

∴ $z = 4, a = 2\sqrt{2}\,r$

$$d = \frac{z \times M}{a^3 \times N_A} \qquad \text{...}(i)$$

Here, $M = 63.54\text{ g mol}^{-1}$, $N_A = 6.022 \times 10^{23}\text{ mol}^{-1}$

$a = 2\sqrt{2}\,r = 2\sqrt{2} \times 127.8\text{ pm} = 2\sqrt{2} \times 127.8 \times 10^{-10}\text{ cm}$

$a = 3.614 \times 10^{-8}\text{ cm}$

Substituting these values in the expression (*i*), we get

$$d = \frac{4 \times 63.54\text{ g mol}^{-1}}{(3.614 \times 10^{-8}\text{ cm})^3 \times 6.022 \times 10^{23}\text{ mol}^{-1}}$$

$$= 8.94\text{ g cm}^{-3}$$

As the calculated value of density (8.94 g cm^{-3}) is in agreement with the given value (8.95 g cm^{-3}). Therefore, copper unit cell has face-centred cubic structure.

Q. 5. The density of lead is 11.35 g cm^{-3} and the metal crystallises with *fcc* unit cell. Estimate the radius of lead atom. ***[CBSE Delhi 2011]***

(At. mass of lead = 207 g mol^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1})

Ans. $d = \dfrac{z \times M}{a^3 \times N_A} \Rightarrow a^3 = \dfrac{z \times M}{d \times N_A}$ ...(*i*)

For a *fcc* unit cell, $z = 4$

$M = 207\text{ g mol}^{-1}$, $N_A = 6.02 \times 10^{23}\text{ mol}^{-1}$, $d = 11.35\text{ g cm}^{-3}$

Substituting these values in equation (*i*), we get

$$a^3 = \frac{4 \times 207\text{ g mol}^{-1}}{11.35\text{ g cm}^{-3} \times 6.02 \times 10^{23}\text{mol}^{-1}}$$

$$a^3 = \frac{4 \times 207 \times 10}{11.35 \times 6.02 \times 10^{24}}\text{ cm}^3$$

$$a = \left(\frac{8280}{11.35 \times 6.02}\right)^{1/3} \times 10^{-8}\text{ cm}$$

Let $$x = \left(\frac{8280}{11.35 \times 6.02}\right)^{1/3}$$

$$\log x = \frac{1}{3}[\log 8280 - \log 11.35 - \log 6.02]$$

$$= \frac{1}{3}[3.9180 - 1.0549 - 0.7796]$$

$$\log x = \frac{1}{3}[2.0835] = 0.6945$$

$$x = \text{Antilog}(0.6945) \Rightarrow x = 4.949$$

∴ $a = 4.949 \times 10^{-8}\text{ cm} \Rightarrow a = 494.9\text{ pm}$

For a *fcc* unit cell, $r = \frac{a}{2\sqrt{2}}$

$$r = \frac{494.9}{2\sqrt{2}} \text{ pm} = \frac{494.9\sqrt{2}}{4} \text{ pm} = \frac{494.9 \times 1.414}{4} \text{ pm}$$

$$r = \mathbf{174.95 \text{ pm}}$$

Q. 6. An element crystallizes in a *fcc* lattice with cell edge of 400 pm. Calculate the density if 200 g of this element contain 2.5 × 10^{24} atoms. **[*CBSE (F) 2016*]**

Ans. $$\text{Moles of the element} = \frac{\text{Atoms of the element}}{N_A}$$

or $$\frac{\text{Mass of the element}}{\text{Molar mass}} = \frac{2.5 \times 10^{24} \text{ atoms}}{6.022 \times 10^{23} \text{atoms mol}^{-1}}$$

$$\frac{200 \text{ g}}{\text{Molar mass}} = \frac{2.5 \times 10^{24}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\text{Molar mass} = \frac{200 \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{2.5 \times 10^{24}}$$

$$\text{Molar mass, } M = 48.18 \text{ g mol}^{-1}$$

Here, $z = 4$, $M = 48.18 \text{ g mol}^{-1}$, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

$a = 400 \text{ pm} = 400 \times 10^{-10} \text{ cm} = 4 \times 10^{-8} \text{ cm}$

Substituting these values in the expression,

$$d = \frac{z \times M}{a^3 \times N_A}, \text{ we get}$$

$$d = \frac{4 \times 48.18 \text{ g mol}^{-1}}{(4 \times 10^{-8} \text{ cm})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= \mathbf{5 \text{ g cm}^{-3}}$$

Q. 7. Sodium has a *bcc* structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23).

Ans. For the *bcc* structure, nearest neighbour distance (d) is related to the edge (a) as

$$d = \frac{\sqrt{3}}{2}a$$

or, $$a = \frac{2}{\sqrt{3}}d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

For *bcc* structure, $z = 2$

For sodium, $M = 23$

$$\text{Density, } d = \frac{z \times M}{a^3 \times N_A}$$

$$= \frac{2 \times 23 \text{ g mol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} = \mathbf{1.013 \text{ g/cm}^3}$$

Q. 8. Chromium crystallises in *bcc* structure. If its atomic diameter is 245 pm, find its density. Atomic mass of Cr = 52 amu and N_A = 6.02 × 10^{23} mol^{-1}.

Ans. Diameter = 245 pm

$$\therefore \quad \text{Radius} = \frac{245}{2} \text{ pm} = 122.5 \text{ pm}$$

In a *bcc* structure, $$r = \frac{\sqrt{3}}{4}a \quad \text{or} \quad a = \frac{4r}{\sqrt{3}}$$

$$a = \frac{4 \times 122.5}{\sqrt{3}} = \frac{490}{1.732} = 282.91 \text{ pm}$$

$$d = \frac{z \times M}{a^3 \times N_A} = \frac{2 \times 52}{(282.91 \times 10^{-10}\ \text{cm})^3 \times 6.02 \times 10^{23}}$$

$$= \frac{104}{2.264 \times 10^{-23} \times 6.02 \times 10^{23}} = \frac{104}{2.264 \times 6.02}$$

$$= \mathbf{7.63\ g\ cm^{-3}}$$

Q. 9. How would you account for the following? [*CBSE (AI) 2017*]

(*i*) Frenkel defects are not found in alkali metal halides.

(*ii*) Schottky defects lower the density of related solids.

(*iii*) Impurity doped silicon is a semiconductor.

Ans. (*i*) This is because alkali metal ions have larger size which cannot fit into interstitial sites.

(*ii*) As the number of ions decreases as a result of Schottky defect, the mass decreases whereas the volume remains the same.

(*iii*) This is due to additional electron or creation of an deficient hole on doping with impurity. Creation of deficient hole results in *p*-type semiconductor whereas additional electron results in *n*-type semiconductor.

Q. 10. Examine the given defective crystal:

X^+	Y^-	X^+	Y^-	X^+
Y^-	X^+	Y^-	X^+	Y^-
X^+	Y^-	X^+	e^-	X^+
Y^-	X^+	Y^-	X^+	Y^-

Answer the following questions:

(*i*) Is the above defect stoichiometric or non-stoichiometric?

(*ii*) Write the term used for the electron occupied site.

(*iii*) Give an example of the compound which shows this type of defect. [*CBSE Ajmer 2015*]

Ans. (*i*) Non-stoichiometric defect

(*ii*) F-centre

(*iii*) When crystals of NaCl are heated in an atmosphere of Na vapours or when crystals of KCl are heated in an atmosphere of K vapours.

Q. 11. (*i*) What is the radius of sodium atom if it crystallises in *bcc* structure with the cell edge of 400 pm?

(*ii*) Examine the given defective crystal:

X^+	Y^-	X^+	Y^-	X^+
Y^-	Z^{2+}	Y^-	X^+	Y^-
X^+	Y^-	○	Y^-	X^+
Y^-	X^+	Y^-	X^+	Y^-

(*a*) Write the term used for this type of defect.

(*b*) What is the result when XY crystal is doped with divalent (Z^{2+}) impurity? [*CBSE (F) 2017*]

Ans. (*i*) For a *bcc* structure, $r = \frac{\sqrt{3}}{4}a$

$$\therefore \qquad r = \frac{1.732}{4} \times 400\ \text{pm} = \mathbf{173.2\ pm}$$

(*ii*) (*a*) Impurity defect.

(*b*) Each Z^{2+} replaces two X^+ ions. It occupies the site of one X^+ ion and other site remain vacant. The vacancies results in the higher electrical conductivity of the solid.

Q. 12. What are the reasons of electrical conductivity in (*i*) metals, (*ii*) ionic solids, and (*iii*) semiconductors?

Ans. (*i*) It is due to flow of electrons.

(*ii*) It is due to flow of ions in solution or molten state and defects in the solid state.

(*iii*) It is due to the presence of impurities and defects.

Q. 13. (*i*) Based on the nature of intermolecular forces, classify the following solids:

Silicon carbide, Argon

(*ii*) ZnO turns yellow on heating. Why?

(*iii*) What is meant by groups 12-16 compounds? Give an example. [*CBSE (AI) 2017*]

Ans. (*i*) Silicon carbide: Covalent solid

Argon: Molecular solid (non-polar)

(*ii*) When ZnO is heated, it loses oxygen and turns yellow due to following reaction:

$$ZnO \xrightarrow{\text{Heat}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial voids.

(*iii*) These are the compounds prepared by combination of group 12 and 16 elements and behave like semiconductors, *e.g.*, ZnS, CdS, CdSe, etc. The bonds in these compounds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

Q. 14. (*i*) What type of stoichiometric defect is shown by KCl and why?

(*ii*) What type of semiconductor is formed when silicon is doped with As?

(*iii*) Which one of the following is an example of molecular solid: CO_2 or SiO_2?

(*iv*) What type of substances would make better magnets, ferromagnetic or ferrimagnetic?

[*CBSE (F) 2014*]

Ans. (*i*) KCl shows schottky defect as the cation, K^+ and anion, Cl^- are of almost similar sizes.

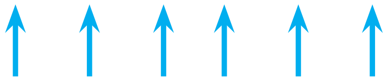
(*ii*) *n*-type semiconductor.

(*iii*) CO_2

(*iv*) Ferromagnetic

Q. 15. (*i*) What type of semiconductor is obtained when Ge is doped with In?

(*ii*) What type of magnetism is shown in the following alignment of magnetic moments?



(*iii*) What type of point defect is produced when AgCl is doped with $CdCl_2$?

Ans. (*i*) *p*-type semiconductor

(*ii*) Ferromagnetism

(*iii*) Impurity defect

Long Answer Questions [5 marks]

Q. 1. (*i*) An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

(*ii*) Write any two differences between amorphous solids and crystalline solids. [*CBSE Delhi 2017*]

Ans. (*i*) Number of atoms per unit cell, $z = \frac{d \times a^3 \times N_A}{M}$ ...(*i*)

Here, $d = 11.5$ g cm^{-3}, $M = 93$ g mol^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1},

$$a = 300 \text{ pm} = 300 \times 10^{-10} \text{ cm} = 3 \times 10^{-8} \text{ cm}$$

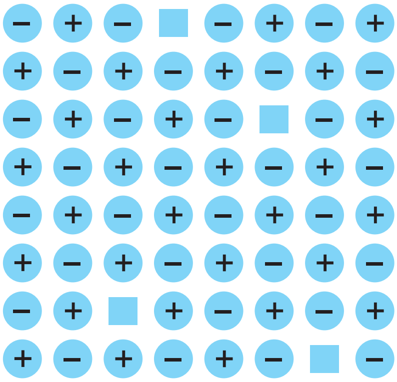
Substituting these values in the expression (*i*), we get

$$z = \frac{11.5 \text{ g cm}^{-3} \times (3 \times 10^{-8} \text{ cm})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{93 \text{ g mol}^{-1}} = 2.01$$

As there are 2 atoms of the element present per unit cell, therefore, the cubic unit cell must be body centred.

(*ii*) Refer to Basic Concepts Point 1, Table 1.1.

Q. 2. (*i*) Identify the type of defect shown in the following figure:



What type of substances show this defect?

(*ii*) A metal crystallizes in a body centred cubic structure. If '*a*' is the edge length of its unit cell, '*r*' is the radius of the sphere. What is the relationship between '*r*' and '*a*'?

(*iii*) An element with molar mass 63 g/mol forms a cubic unit cell with edge length of 360.8 pm. If its density is 8.92 g/cm^3. What is the nature of the cubic unit cell?

Ans. (*i*) Schottky defect.

It is shown by ionic substances in which the cation and anion are of almost similar sizes.

(*ii*) $r = \frac{\sqrt{3}}{4}a$

(*iii*) $d = \frac{z \times M}{a^3 \times N_A}$

or $$z = \frac{d \times a^3 \times N_A}{M} \quad ...(i)$$

Here, $d = 8.92 \text{ g cm}^{-3}$, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, $M = 63 \text{ g mol}^{-1}$

$a = 360.8 \text{ pm} = 360.8 \times 10^{-10} \text{ cm} = 3.608 \times 10^{-8} \text{ cm}$

Substituting these values in expression (*i*), we get

$$z = \frac{8.92 \text{ gcm}^{-3} \times (3.608{\times}10^{-8} \text{ cm})^3 \times 6.022{\times}10^{23} \text{ mol}^{-1}}{63 \text{ g mol}^{-1}} = 4$$

The unit cell is face centred cubic.

Q. 3. (*i*) (*a*) Why are crystalline solids anisotropic?

(*b*) What type of semiconductor is formed when silicon is doped with boron?

(*c*) Define the term coordination number. What is the coordination number of atoms in a cubic closed packed structure?

(*ii*) Sodium crystallises in a *bcc* unit cell. Calculate the approximate number of unit cells in 9.2 g of sodium. (Atomic Mass of Na = 23 u)

Ans. (*i*) (*a*) It arises from different arrangement of particles in different direction.

(*b*) Silicon is group 14 element and boron is group 13 element, therefore, an electron deficient hole is created. Thus, semiconductor is of *p*-type.

(*c*) Coordination number is defined as the number of nearest neighbours in a closed packed structure. The coordination number of an atom in *ccp* structure is 12.

(*ii*) No. of atoms per unit cell for *bcc* (z) = 2

$$\text{No. of atoms in 9.2 g of Na} = \frac{9.2\text{ g}}{23\text{ g mol}^{-1}} \times 6.022 \times 10^{23}\text{ atoms mol}^{-1}$$

$$= 2.4088 \times 10^{23}\text{ atoms}$$

$$\text{No. of unit cells} = \frac{2.4088 \times 10^{23}\text{ atoms}}{2\text{ atoms unit cell}^{-1}} = \mathbf{1.2044 \times 10^{23}\text{ unit cell}}$$

Q. 4. **(*i*) Name the non-stoichiometric point defect responsible for colour in alkali metal halides.**

(*ii*) An ionic compound made of atoms *X* and *Y* has a face centred cubic arrangement in which atoms X are at the corners and atoms *Y* are at the face centres. If one of the atoms is missing from the corner, what is the simplest formula of the compound?

(*iii*) What type of semiconductor is obtained when silicon is doped with arsenic?

(*iv*) Sodium metal crystallises in *bcc* lattice with the cell edge, 4.29 Å. What is the radius of sodium metal? What is the length of the body diagonal of the unit cell?

Ans. (*i*) Metal excess defect due to anion vacancies or F-centres.

(*ii*) Number of X atoms per unit cell = 7(at the corners) $\times \frac{1}{8} = \frac{7}{8}$

Number of Y atoms per unit cell = 6 (at the face centres) $\times \frac{1}{2} = 3$

$$X : Y = \frac{7}{8} : 3 = 7 : 24$$

∴ Formula of the compound = $\mathbf{X_7Y_{24}}$

(*iii*) *n*-type of semiconductor is obtained.

(*iv*) For *bcc* lattice,

$$r = \frac{\sqrt{3}}{4}a$$

$$r = \frac{1.732}{4} \times 4.29\text{ Å} = 1.86\text{ Å}$$

Length of the body diagonal $= 4r$

$= 4 \times 1.86\text{ Å} = \mathbf{7.44\text{ Å}}$

Q. 5. **(*i*) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol^{-1})**

(*ii*) Give reasons:

(*a*) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.

(*b*) Silicon on doping with phosphorus forms *n*-type semiconductor.

(*c*) Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

[*CBSE Delhi 2017*]

Ans. (*i*) $\text{Moles of aluminium} = \frac{\text{Mass of aluminium}}{\text{Molar mass}}$

$$= \frac{8.1\text{ g}}{27\text{ g mol}^{-1}} = 0.3\text{ mol}$$

Total number of Al atoms = 6.022×10^{23} atoms mol^{-1} × 0.3 mol

= 1.8066×10^{23} atoms

For *fcc*, $z = 4$

$$\text{Number of unit cells} = \frac{\text{Total number of atoms}}{4}$$

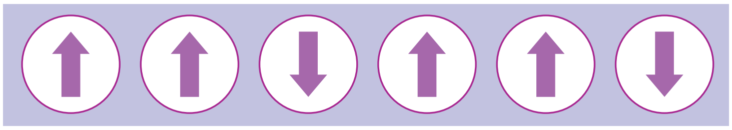
$$= \frac{1.8066 \times 10^{23}}{4} = \mathbf{4.5 \times 10^{22}}$$

(*ii*) (*a*) This is because Na^+ ion has large size so it cannot fit into interstitial sites.

(*b*) When Si is doped with P, which has five valence electrons, it forms four covalent bonds with four neighbouring Si atoms. The fifth extra electron becomes delocalised and increase the conductivity of Si. Here, the increase in conductivity is due to the negatively charged electron, hence Si doped with P is called *n*-type semiconductor.

(*c*) In ferrimagnetic substances, domains are aligned in opposite direction in unequal number and hence they have some net magnetic moment. On the other hand, in antiferromagnetic substances, the domains aligned in opposite directions are equal in number so they cancel magnetic moment completely and hence have zero magnetic moment. For diagram Refer to Fig. 1.20.

Q. 6. **(*i*) Following is the schematic alignment of magnetic moments:**



Identify the type of magnetism. What happens when these substances are heated?

(*ii*) If the radius of the octahedral void is '*r*' and radius of the atoms in close packing is '*R*'. What is the relation between '*r*' and '*R*'?

(*iii*) Tungsten crystallizes in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm. What is the radius of tungsten atom? **[*CBSE Sample Paper 2017*]**

Ans. (*i*) Ferrimagnetism.

These substances lose ferrimagnetism on heating and become paramagnetic. This is due to randomisation of domains (spins) on heating.

(*ii*) $r = 0.414\ R$

(*iii*) For *bcc* structure,

$$r = \frac{\sqrt{3}}{4}a$$

$$r = \frac{1.732}{4} \times 316.5 \text{ pm} = \mathbf{137.04\ pm}$$

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. **Lithium has a *bcc* structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of lithium metal. ($N_A = 6.02 \times 10^{23}$ mol^{-1})**

   (*a*) 154 pm (*b*) 352 pm

   (*c*) 527 pm (*d*) 264 pm

2. **The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is**

   (*a*) 6 (*b*) 4

   (*c*) 8 (*d*) 2

3. **How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g?**

   [Atomic masses: Na = 23 u, Cl = 35.5 u]

   (*a*) 2.57×10^{21} (*b*) 5.14×10^{21}

   (*c*) 1.28×10^{21} (*d*) 1.71×10^{21}

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.* **(3 × 1 = 3)**

4. **Assertion (*A*) :** KCl crystals appear violet in colour.

   Reason (*R*) : The violet colour is due to electrons trapped in anion vacancies.

5. **Assertion (*A*) :** Silicon forms ionic crystals.

   Reason (*R*) : The lattice of silicon consists of its atoms bonded together by covalent bonds in a three dimensional network.

6. **Assertion (*A*) :** In a rock salt structure, Cl^- ions form a close packed lattice and Na^+ ions occupy the octahedral voids.

   Reason (*R*) : NaCl possesses a face-centred cubic arrangement.

Answer the following questions:

7. What is the difference in the semiconductors obtained by doping silicon with Al and with P? **(1)**
8. Define the term void. **(1)**
9. Give packing efficiency and coordination number of the following crystal structures:

   (*i*) body centred cubic

   (*ii*) cubic close packing. **(2)**
10. How may the conductivity of an intrinsic semiconductor be increased? **(2)**

11. Define radius ratio? What is the coordination number if the radius ratio of the compound is 0.52? **(2)**

12. Answer the following questions:

(*i*) What are primitive unit cells and what are non-primitive unit cells?

(*ii*) What is the meaning of the term imperfections in solids? **(2)**

13. Write three differences between Schottky and Frenkel defect. **(3)**

14. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cm^3 then find the radius of metal atom.

($N_A = 6.022 \times 10^{23}$) **(3)**

15. An element has a body-centred cubic *bcc* structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?

[*CBSE Sample Paper 2016*] (3)

16. (*i*) How are the following properties of crystalline substances affected by Schottky and Frenkel defects?

(*a*) Density (*b*) Electrical conductivity

(*ii*) What is percentage efficiency of packing in case of *ccp* structure?

(*iii*) An element has *fcc* structure with a cell edge 200 pm. Calculate the density of element, if 200 g of the element contains 24×10^{23} atoms. **(5)**

Answers

1. (*b*) **2.** (*a*) **3.** (*a*) **4.** (*a*) **5.** (*d*) **6.** (*a*) **14.** 216.5 pm

15. 2.418×10^{24} atoms **16.** (*iii*) 41.6 g cm^{-3}

Solutions

basic concepts

1. **Solution:** A solution is a homogeneous mixture of two or more pure substances, the relative ratio of which can be changed within certain limits.

   When the constituents of the solution are two it is called binary, if three then ternary, if four then quaternary and so on.

   The two constituents of the solution are solvent and solute.

   Solvent (A): It is the component of the solution:

   (*i*) which is present in a relatively large proportion in the solution, and

   (*ii*) whose physical state is same as that of the resulting solution.

   Solute (B): It is the component of a solution which is present in relatively small proportion.

2. **Types of Solutions**

Table 2.1

Type of Solution	Solute	Solvent	Examples
	Gas	Gas	Mixture of oxygen and nitrogen gases
Gaseous Solutions	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
	Gas	Liquid	Oxygen dissolved in water
Liquid Solutions	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
	Gas	Solid	Solution of hydrogen in palladium
Solid Solutions	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

Amongst the nine types of solutions, the widely studied ones are:

(*a*) Solid–liquid (*b*) Liquid–liquid and (*c*) Gas–liquid solutions.

(*a*) Solid–liquid solutions: A small amount of solute (usually ionic solids) is dissolved in a large quantity of solvent. If the amount of solvent is large as compared to the solute, the solution is referred to as a dilute solution.

Saturated solution: A solution is said to be saturated if it holds the maximum amount of solute at a given temperature in a given quantity of the solvent.

Solubility: It may be defined as the maximum amount of solute that can be dissolved in 100 g of solvent at a specified temperature. The solubility of solid into liquid depends upon the following factors:

(*i*) Nature of solute (*ii*) Nature of solvent (*iii*) Temperature

Causes of solubility: The following types of forces of attraction are operated when a solute is mixed with a solvent:

(*i*) **Inter-ionic attraction in the solute molecules:** Ions are held together in the lattice due to electrostatic forces. Due to these forces molecules are stabilised and the energy released is called ***lattice energy***. This is defined as the energy released when 1 g mole of the compound is formed due to electrostatic attraction between the ions.

(*ii*) **Inter-molecular attraction between solvent molecules:** Water is a ***polar solvent*** because of the difference in electronegativity between hydrogen and oxygen atoms constituting water molecule. This difference gives rise to the development of a slight negative charge on oxygen and equal positive charge on hydrogen. A dipole is thus created giving rise to dipole–dipole attraction between water molecules.

(*iii*) **Solvation:** It represents force of attraction between solute and solvent molecules. If the solvent is water then the energy released is called **hydration energy**.

If hydration energy > lattice energy, then solution is easily formed. Both the ions of the solute get hydrated to overcome the lattice energy of the solute.

(*iv*) **Temperature:** Saturated solution represents equilibrium between undissolved solute and dissolved solute.

$$\text{Undissolved solute} + \text{Solvent} \longrightarrow \text{Solution} \qquad \Delta_{\text{sol}}H = \pm x$$

If $\Delta_{\text{sol}} H < 0$, *i.e.*, (–ve), the dissolution is exothermic. In this case, as the temperature increases, solubility decreases (Le Chatelier's principle).

If $\Delta_{\text{sol}} H > 0$, *i.e.*, (+ve), there is endothermic dissolution. In this case, increase in temperature increases the solubility (Le Chatelier's principle).

(*b*) **Liquid–liquid solutions:** When two liquids are mixed, three different situations result:

(*i*) **Miscible liquids:** The two components are completely soluble. They are miscible only when they have similar nature or belong to the same homologous series. Example: water and alcohol (both polar), benzene–toluene (both belong to the same homologous series). There is a rule:

Like dissolves like – Polar solute is soluble in polar solvent and a non-polar one in a non-polar solvent.

(*ii*) **Partially miscible liquids:** This happens only when the intermolecular forces of one liquid is greater than that of the other is. Solubility, however, increases with increasing temperature. Examples: aniline-water, phenol-water.

(*iii*) **Immiscible liquids:** Two components are completely immiscible. This happens when one liquid is polar and the other is non-polar. Examples: Carbon tetrachloride-water; chloroform-water.

(*c*) **Gas–liquid solutions:** The gases are generally soluble in water and to a limited extent in other solvents too. Solubility, however, depends on the following factors:

(*i*) **Nature of gas:** Easily liquefiable gases are generally more soluble in common solvents.

(*ii*) **Nature of liquid:** Those gases which easily form ions in solution are more soluble in water than in other solvents. Ion formation in other solvents is not an easy process.

$$\text{HCl}(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)$$

(*iii*) **Pressure:** Pressure is an important factor affecting the solubility of gas in liquids. This is governed by Henry's law.

(*iv*) **Temperature:** With rise in temperature, the solubility generally decreases because gas is expelled. Some gases, however, find their solubility increased at a higher temperature.

➡ **Henry's law:** It states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

The most commonly used form of Henry's law states that the partial pressure (p) of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution and is expressed as

$$p = K_H\, x$$

Here K_H is the Henry's law constant and x is the mole fraction of the gas.

Note: Mole fraction is discussed in detail further in this chapter.

Limitations of Henry's Law:

Henry's law is applicable only when

- The pressure of the gas is not too high and temperature is not too low.
- The gas should not undergo any chemical change.
- The gas should not undergo association or dissociation in the solution.

Applications of Henry's Law:

- To increase the solubility of CO_2 in soda water and soft drinks, the bottle is sealed under high pressure.
- To avoid the toxic effects of high concentration of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- At high altitudes, low blood oxygen causes climbers to become weak and make them unable to think clearly, which are symptoms of a condition known as anoxia.

3. Methods of Expressing Concentration of Solutions:

The concentration of solution is the amount of the solute present in the given quantity of solution or solvent. It can be expressed in any of the following ways:

(*a*) **Mass percentage (*w/w*):** It may be defined as mass of solute per 100 g of solution.

$$\text{Mass\% of solute} = \frac{\text{Mass of solute}}{\text{Total mass of the solution}} \times 100$$

(*b*) **Volume percentage (*V/V*):** It may be defined as volume of solute per 100 mL of solution.

$$\text{Volume \% of solute} = \frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$$

(*c*) **Mass by volume percentage (*w/V*):** It may be defined as the mass of solute per 100 mL of the solution.

$$\text{Mass by volume \%} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(*d*) **Parts per million (ppm):** It is the parts of a component per million (10^6) parts of the solution.

$$\text{ppm} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

It is convenient to express concentration in ppm when a solute is present in trace quantities.

(*e*) **Mole fraction (*x*):** It may be defined as the ratio of the number of moles of one component (solute or solvent) to the total number of moles of all the components present in the solution.

If in a solution, n_A and n_B are the number of moles of solvent and solute, respectively, then

Mole fraction of solvent in the solution,

$$x_A = \frac{n_A}{n_A + n_B}$$

Mole fraction of solute in the solution,

$$x_B = \frac{n_B}{n_A + n_B}$$

In a solution, sum of the mole fractions of all the components is unity. For example, in a binary solution (having two components), $x_A + x_B = 1$.

(*f*) **Molarity (*M*):** It is defined as number of moles of solute dissolved in one litre of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$$

Unit of molarity is mol L^{-1} or M (molar). Molarity changes with change in temperature as volume changes with change in temperature.

(*g*) **Molality (*m*):** It is defined as the number of moles of the solute dissolved in one kilogram (kg) of the solvent and is expressed as:

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in grams)}} \times 1000$$

Unit of molality is mol kg^{-1} or molal (m).

Molality is independent of temperature.

4. Vapour Pressure of Pure Liquid and Solution

Vapour pressure: When a liquid is taken in a closed vessel, a part of the liquid evaporates and its vapours occupy the available empty space. These vapours cannot escape as the vessel is closed. They would rather have a tendency to condense into liquid form. In fact an equilibrium is established between vapour phase and liquid phase and the pressure that its vapour exert is termed as vapour pressure. Thus, vapour pressure of a liquid may be defined as the pressure exerted by the vapours above the liquid surface in equilibrium with the liquid phase at a given temperature.

The vapour pressure of a liquid depends on the following factors:

Nature of the liquid: Liquids having weak intermolecular forces are volatile and therefore have greater vapour pressure.

Temperature: Vapour pressure of a liquid increases with increase in temperature. This is because with increase in temperature, the kinetic energy of the molecules increases and therefore large number of molecules are available for escaping from the surface of the liquid.

(*a*) Vapour pressure of liquid–liquid solution:

Raoult's Law for solutions of volatile liquids: It states that for a solution of volatile liquids the partial pressure of each component of the solution is directly proportional to its mole fraction present in a solution. Mathematically,

$$p_A \propto x_A \qquad\qquad p_B \propto x_B$$
$$p_A = p^o_A x_A \qquad\qquad p_B = p^o_B x_B$$

where p_A and p_B are partial vapour pressures, x_A and x_B are mole fractions, p^o_A and p^o_B are the vapour pressure of pure components A and B respectively.

If p is total vapour pressure then according to Dalton's law of partial pressure,

$$\begin{aligned} p &= p_A + p_B \\ &= p^o_A x_A + p^o_B x_B \\ &= p^o_A (1 - x_B) + p^o_B x_B \\ &= p^o_A + (p^o_B - p^o_A)\, x_B \end{aligned}$$

As p^o_A and p^o_B are constants at a given temperature, it is evident from the above equations that the total vapour pressure varies linearly with the mole fraction x_B (or x_A since $x_A = 1 - x_B$).

The composition of the vapour phase in equilibrium with the solution can be determined from the partial pressure of the two components. If y_A and y_B are the mole fractions of components A and B respectively in the vapour phase, then

$$p_A = y_A\, p_{\text{total}}$$
$$p_B = y_B\, p_{\text{total}}$$

In general, $$p_i = y_i\, p_{\text{total}}$$

➡ **Raoult's law as a special case of Henry's law.**

In the solution of a gas in a liquid, if one of the components is so volatile that it exists as a gas, then it can be said that Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p^o_A.

(*b*) Vapour pressure of solutions of solids in liquids

Raoult's law for a solution containing a non-volatile solute and volatile solvent: It states that the relative lowering of vapour pressure is equal to mole fractions of solute which is non-volatile.

Mathematically, $$p = p_A + p_B$$

or, $$p = p_A \text{ (Since solute } B \text{ is non-volatile)}$$

$$p = p^o_A x_A$$

$$p = p^o_A(1 - x_B) = p^o_A - p^o_A x_B$$

$$p^o_A x_B = p^o_A - p$$

or $$\frac{p^o_A - p}{p^o_A} = x_B$$

or Relative lowering of vapour pressure = Mole fraction of solute

5. Ideal and Non-Ideal Solutions

(*a*) Ideal solution: A solution is called an ideal solution if it obeys Raoult's law over a wide range of concentration (Fig. 2.1) at a specified temperature.

For an ideal solution,

$$p = p_A + p_B = p^o_A x_A + p^o_B x_B$$

Liquids having similar nature and structure are likely to form ideal solutions. Examples are:

- Mixture of methanol and ethanol
- Mixture of *n*-hexane and *n*-heptane
- Mixture of benzene and toluene.

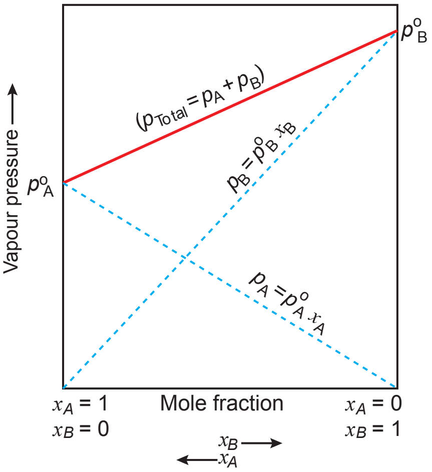


Fig. 2.1: Vapour pressure diagram for an ideal solution

Reasons for formation of ideal solutions: A solution of two miscible liquids *A* and *B* will be ideal if two essential conditions are fulfilled.

(*i*) If F_{A-A} is the force of attraction between molecules of *A* and F_{B-B} is that of molecules of *B*, then *A* and *B* will form an ideal solution only if,

$$F_{A-B} = F_{A-A} = F_{B-B}$$

(*ii*) The solution of *A* and *B* liquids will be ideal if *A* and *B* have similar structures and polarity. Methanol and ethanol have the same functional group and almost same polarity and therefore, form ideal solutions.

For an ideal solution

(*i*) Raoult's law is obeyed, *i.e.*, $p_A = p^o_A x_A$ and $p_B = p^o_B x_B$

(*ii*) $\Delta_{mix} H = 0$ and

(*iii*) $\Delta_{mix} V = 0$.

(*b*) Non-ideal solution: A solution which does not obey Raoult's law for all concentrations is called a non-ideal solution.

For a non-ideal solution

(*i*) Raoult's law is not obeyed,

i.e., $p_A \neq p^o_A x_A$ and $p_B \neq p^o_B x_B$

(*ii*) $\Delta_{mix} H \neq 0$ and

(*iii*) $\Delta_{mix} V \neq 0$.

A non-ideal solution can show either positive or negative deviation from Raoult's law.

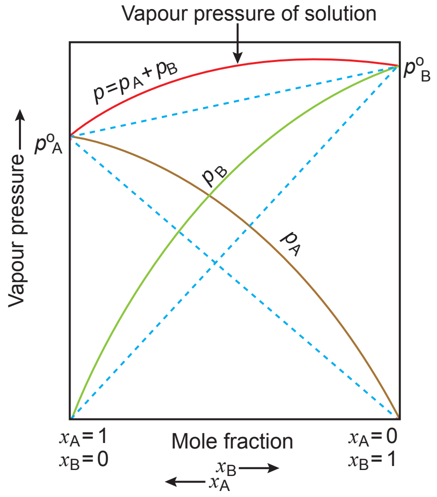


Fig. 2.2: Vapour pressure diagram showing positive deviation

(A) Positive Deviation: The deviation will be called positive when the partial pressure of each component and the resultant total pressure are greater than the pressure expected on the basis of Raoult's law (Fig. 2.2).

In such cases, the intermolecular forces between solvent–solute molecules (F_{A-B}) are weaker than those between solvent–solvent (F_{A-A}) and solute–solute (F_{B-B}) molecules. That is,

$$F_{A-B} < F_{A-A} \text{ and } F_{B-B}$$

This shows that the molecules of *A* or *B* will escape more easily from the surface of the solution, *i.e.*, the vapour pressure of solution will be higher.

Characteristics of a Solution Showing Positive Deviation

- $p_A > p^o_A x_A$; $p_B > p^o_B x_B$
- $\Delta_{mix} H > 0$, *i.e.*, + ve,
- $\Delta_{mix} V > 0$, *i.e.*, + ve,

Some examples of the solution exhibiting positive deviations are:

(*i*) Ethyl alcohol and water
(*ii*) Acetone and carbon disulphide
(*iii*) Carbon tetrachloride and benzene
(*iv*) Acetone and benzene

(B) Negative Deviation: The deviation is called negative deviation, if the partial pressure of each component (*A* and *B*) and resultant total vapour pressure are less than the pressure expected on the basis of Raoult's law. (Fig. 2.3)

This type of deviation is shown by the solutions in which

$$F_{A-B} > F_{A-A} \quad \text{and} \quad F_{B-B}$$

Due to this, there is decrease in the escaping tendency of *A* or *B* molecules from the surface of solution.

Consequently, the vapour pressure of the solution will be lower.

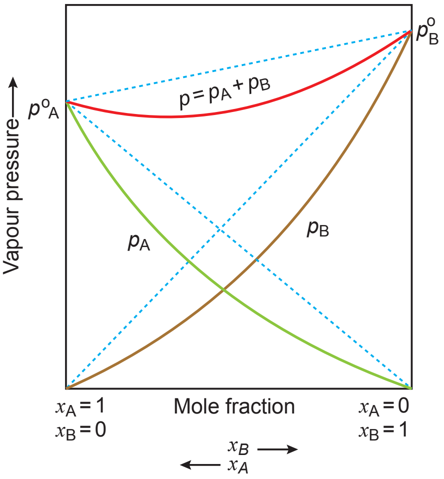


Fig. 2.3: Vapour pressure diagram showing negative deviation

Characteristics of a Solution Showing Negative Deviation

- $p_A < p^o_A x_A$; $p_B < p^o_B x_B$
- $\Delta_{mix} H < 0$, *i.e.*, –ve, because weak *A–A* and *B–B* bonds are broken and strong *A–B* bond is formed. Heat is consequently released.
- $\Delta_{mix} V < 0$, *i.e.*, –ve,

Some examples of the solution showing negative deviations are

(*i*) HNO_3 and water
(*ii*) Chloroform and acetone
(*iii*) Acetic acid and pyridine
(*iv*) Hydrochloric acid and water

Table 2.2: Characteristics of Ideal and Non-ideal Solutions

S.No.	Ideal Solutions	Non-ideal Solutions	
		Positive Deviation	Negative Deviation
(*i*)	$F_{A-A} = F_{B-B} = F_{A-B}$	$F_{A-B} < F_{A-A}$ and F_{B-B}	$F_{A-B} > F_{A-A}$ and F_{B-B}
(*ii*)	$p_A = p^o_A x_A$; $p_B = p^o_B x_B$	$p_A > p^o_A x_A$; $p_B > p^o_B x_B$	$p_A < p^o_A x_A$; $p_B < p^o_B x_B$
(*iii*)	$\Delta_{mix} H = 0$	$\Delta_{mix} H > 0$, *i.e.*, +ve	$\Delta_{mix} H < 0$, *i.e.*, –ve
(*iv*)	$\Delta_{mix} V = 0$	$\Delta_{mix} V > 0$, *i.e.*, +ve	$\Delta_{mix} V < 0$, *i.e.*, –ve

Azeotropes or Azeotropic mixture: Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Types of Azeotropes:

(*i*) Minimum boiling azeotropes: These are the binary mixtures whose boiling point is less than either of the two components. The non-ideal solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition, *e.g.*, a mixture of 94.5% ethyl alcohol and 4.5% water by volume.

(*ii*) **Maximum boiling azeotropes:** These are the binary mixtures whose boiling point is more than either of the two components. The solutions that show large negative deviation from Raoults's law form maximum boiling azeotrope at a specific composition, e.g., a mixture of 68% HNO_3 and 32% H_2O by mass.

6. Colligative Properties

Those properties which depend on the number of solute particles (molecules, atoms or ions) but not upon their nature are called colligative properties. The following are the colligative properties:

(*a*) Relative lowering of vapour pressure of the solvent,

(*b*) Elevation of boiling point of the solvent,

(*c*) Depression of freezing point of the solvent,

(*d*) Osmotic pressure of the solution.

(*a*) Relative lowering of vapour pressure: The addition of a non-volatile solute to a volatile solvent decreases the escaping tendency of the solvent molecules from the surface of solutions as some of the surface area is occupied by non-volatile solute particles. According to Raoult's law, the relative lowering of vapour pressure is equal to mole fraction of solute.

Thus, $$\frac{p_A^o - p}{p_A^o} = x_B = \frac{n_B}{n_A + n_B}$$

For a dilute solution, $n_B << n_A$, hence neglecting n_B in the denominator, we have

$$\frac{p_A^o - p}{p_A^o} = \frac{n_B}{n_A} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$M_B = \left(\frac{p_A^o}{p_A^o - p}\right) \times \frac{W_B \times M_A}{W_A}$$

(*b*) Elevation of boiling point: Boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure. When a non-volatile solute is added to a volatile solvent, the vapour pressure of the solvent decreases. In order to make this solution boil, its vapour pressure must be increased by raising the temperature above the boiling point of the pure solvent. The difference in the boiling point of solution (T_b^o) and that of pure solvent (T_b) is called elevation of boiling point (ΔT_b). Thus,

Elevation of boiling point = $\Delta T_b = T_b - T_b^o$ (Fig. 2.4)

For dilute solution, it has been found that the elevation of boiling point is directly proportional to the molal concentration of the solute in the solution. Thus,

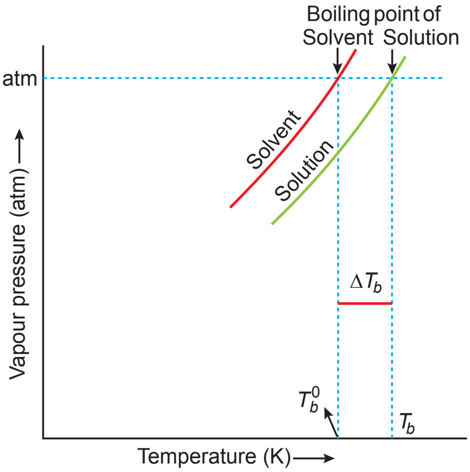


Fig. 2.4: Vapour pressure temperature curves showing elevation in boiling point of solution

$$\Delta T_b \propto m \text{ or } \quad \Delta T_b = K_b m$$

where K_b is a constant called molal elevation constant or ebullioscopic constant.

When $m = 1 \text{ mol kg}^{-1}$, $\Delta T_b = K_b$

Hence, molal elevation constant may be defined as the elevation in boiling point when one mole of a non-volatile solute is dissolved in one kilogram (1000 g) of solvent. The unit of K_b is K kg mol^{-1}.

As $$m = \frac{W_B \times 1000}{M_B \times W_A}$$

Therefore,
$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

(*c*) **Depression of freezing point:** Freezing point is defined as the temperature at which the vapour pressure of a substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution freezes when its vapour pressure equals the vapour pressure of the pure solid solvent. Whenever a non-volatile solute is added to the volatile solvent, its vapour pressure decreases and it would become equal to that of solid solvent at a lower temperature. The difference in the freezing point of pure solvent (T_f^o) and that of the solution (T_f) is known as depression of freezing point (ΔT_f). Thus,

Depression of freezing point = $\Delta T_f = T_f^o - T_f$.

It has been found that for a dilute solution, depression in freezing is directly proportional to molality of the solution.

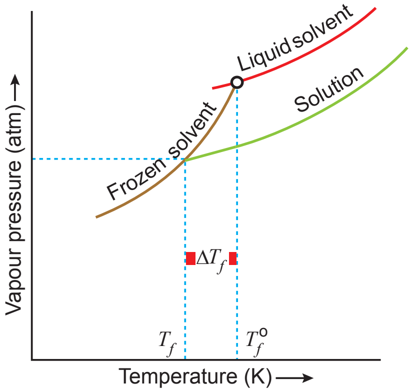


Fig. 2.5: Vapour pressure temperature curves showing depression in freezing point of solution

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m$$

where K_f is a constant called molal depression constant or cryoscopic constant.

When $m = 1$ mol kg^{-1}, $\quad \Delta T_f = K_f$

Hence, molal depression constant may be defined as the depression in freezing point when one mole of non-volatile solute is dissolved in one kilogram (1000 g) of solvent. The unit of K_f is K kg mol^{-1}.

Since,
$$m = \frac{W_B \times 1000}{M_B \times W_A}$$

$\therefore$
$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

or,
$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

The values of K_b and K_f which depend upon the nature of the solvent and concentration of the solution, can be ascertained from the following relations:

$$K_b = \frac{R \times M_A \times (T_b^o)^2}{\Delta_{vap} H \times 1000}$$

$$K_f = \frac{R \times M_A \times (T_f^o)^2}{\Delta_{fus} H \times 1000}$$

where,
R = Universal gas constant
M_A = Molecular mass of solvent
T_b^o = Boiling point of pure solvent
$\Delta_{\text{vap}} H$ = Enthalpy of vapourisation of solvent
T_f^o = Freezing point of pure solvent
$\Delta_{\text{fus}} H$ = Enthalpy of fusion of solid solvent

(*d*) **Osmosis:** When a solution is separated from its solvent by a semipermeable membrane (SPM) there is a spontaneous flow of solvent molecules from solvent compartment to solution compartment. The phenomenon is called osmosis. This movement of solvent is only in one direction. In diffusion, however, movement takes place in both the directions.

- **Semipermeable membrane (SPM):** A membrane through which only solvent molecules can pass but not the solute ones. Cellophane, parchment paper and the wall of living cell are the examples of SPM. It is also made of inorganic material, copper ferrocyanide $[Cu_2[Fe(CN)_6]]$.

- **Osmotic pressure (π):** The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, *i.e.*, to stop the passage of solvent molecules into it through semipermeable membrane (Fig. 2.6).

Osmotic pressure (π) is proportional to molarity (C) of the solution at a given temperature T. Thus,

$$\pi = CRT$$

or,
$$\pi = \frac{n_B}{V}RT = \frac{W_B \times R \times T}{M_B \times V}$$

or,
$$M_B = \frac{W_B \times R \times T}{\pi \times V}$$

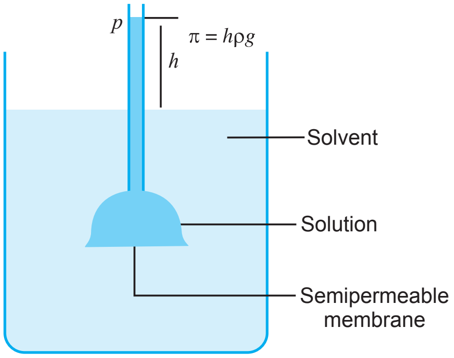


Fig. 2.6: The principle of measuring osmotic pressure: The pressure in excess of atmospheric pressure that must be applied to the solution to prevent it from rising in the tube is the osmotic pressure. This will also be equal to hydrostatic pressure of the liquid column of height, *h*.

- **Reverse osmosis:** If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent (or water) flows out of the solution through the semipermeable membrane. In this way the direction of osmosis is reversed and so the process is called reverse osmosis (Fig. 2.7).

Thus, we can say that reverse osmosis is just opposite to the osmosis when an extra pressure is applied. Reverse osmosis is used in desalination to get pure water from sea water.

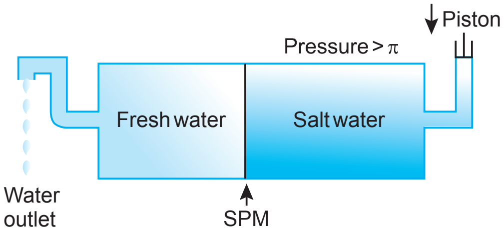


Fig. 2.7: Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution

- **Isotonic solutions:** Two solutions are said to be isotonic when they exert the same osmotic pressure because they have the same molar concentration. All intravenous injections must be isotonic with body fluids.

- **Isosmotic solutions:** When two isotonic solutions are separated by a semipermeable membrane, no osmosis occurs. The solutions are called **isosmotic solutions**.

- **Hypotonic solutions:** A solution having lower osmotic pressure than the other solution is said to be hypotonic with respect to the other solution.

- **Hypertonic solution:** A solution having higher osmotic pressure than the other solution is said to be hypertonic with respect to other solution.

- **Plasmolysis:** When the cell is placed in a hypertonic solution, the fluid comes out of the cell due to osmosis and as a result cell material shrinks gradually. This process is called *plasmolysis*.

7. Abnormal Molar Masses

- **Association:** Association of molecules leads to decrease in the number of particles in the solution resulting in a decrease in the value of colligative property. As colligative property is inversely related to the molecular mass. Therefore, higher value is obtained for molecular mass than normal values.

For example, when ethanoic acid is dissolved in benzene it undergoes dimerisation and shows a molecular mass of 120 (normal molecular mass is 60).

- **Dissociation:** Dissociation leads to increase in the number of solute particles in the solution resulting in an increase in the value of colligative property. Since colligative property is inversely related to the molecular mass, therefore, molecular mass of such a substance as calculated from colligative property will be less than its normal value. For example, KCl is an electrolyte. When it is dissolved in water it dissociates into K^+ and Cl^- ions and there would be double the number of particles if complete dissociation takes place. Hence, it is expected to have molecular mass 37.25 g or $\left(\frac{74.5}{2}\right)$ g.

$$KCl \rightleftharpoons K^+ + Cl^-$$

- **van't Hoff Factor (*i*):** It may be defined as the ratio of normal molecular mass to the observed molecular mass of the solute.

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

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

or, $$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of particles before association/dissociation}}$$

van't Hoff factor (i) expresses the extent of association or dissociation of the solute particles in the solutions.

In case of association, $i < 1$

In case of dissociation, $i > 1$

When there is neither association nor dissociation, $i = 1$

8. Modified Form of Colligative Properties

Inclusion of 'i' modifies the equation for colligative properties as follows:

- Relative lowering of vapour pressure of solvent

$$\frac{p_A^o - p_A}{p_A^o} = i\,\frac{n_B}{n_A}$$

- Elevation of boiling point, $\Delta T_b = i\, K_b\, m$
- Depression of freezing point, $\Delta T_f = i\, K_f\, m$
- Osmotic pressure, $\pi = i\, CRT$

Important Formulae

In the formulae given below, A represents solvent and B represents solute, also

M_A = Molar mass of solvent
W_A = Mass of solvent
V = Volume of solution
GEM = Gram Equivalent Mass

M_B = Molar mass of solute
W_B = Mass of solute
d = Density of solution
GMM = Gram Molecular Mass

1. Mass percentage $(w/w) = \dfrac{W_B}{W_A + W_B} \times 100$

   Volume percentage $(V/V) = \dfrac{V_B}{V_A + V_B} \times 100$

   Mass by volume percentage $\left(\dfrac{w}{V}\right) = \dfrac{W_B \times 100}{V\ (\text{mL})}$

   Parts per million $(ppm) = \dfrac{W_B}{W_A + W_B} \times 10^6$

2. Mole fraction of A, $x_A = \dfrac{n_A}{n_A + n_B}$

   Mole fraction of B, $x_B = \dfrac{n_B}{n_A + n_B}$

   $$x_A + x_B = 1$$

3. Molarity $(M) = \dfrac{\text{Moles of solute}}{\text{Volume of solution in litre}} = \dfrac{n_B}{V\ (\text{in } L)} = \dfrac{W_B}{M_B \times V\ (\text{in } L)}$

4. Molality $(m) = \dfrac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \dfrac{n_B}{W_A (\text{in kg})}$ or $m = \dfrac{W_B \times 1000}{M_B \times W_A\ (in\ g)}$

5. Normality $(N) = \dfrac{\text{Gram equivalents of solute}}{\text{Volume of solution in litre}} = \dfrac{W_B}{GEM \text{ of solute} \times V\ (\text{in } L)}$

6. **Relationship between Molarity and Normality**

   The normality (N) and molarity (M) of a solution are related as follows:

   Normality × Equivalent mass (solute) = Molarity × Molar mass (solute)

7. **Relationship between Molarity and Normality with Mass percentage (p)**

   If p is the mass percentage and d is the density of the solution then

   $$\text{Molarity} = \frac{p \times d \times 10}{\text{Molecular mass (solute)}};$$

   $$\text{Normality} = \frac{p \times d \times 10}{\text{Equivalent mass (solute)}}$$

8. **Relationship between Molarity (M) and Molality (m)**

   $$m = \frac{1000 \times M}{(1000 \times d) - (M \times GMM_B)}$$

9. **Relationship between Molality (m) and Mole fraction of solute (x_B)**

   $$x_B = \frac{m \times GMM_A}{1000 + m \times GMM_A}$$

   Also, $$m = \frac{1000 x_B}{x_A \times GMM_A}$$

10. **Dilution formula:** If the solution of some substance is diluted by adding solvent from volume V_1 to volume V_2 then

    $$M_1 V_1 = M_2 V_2$$

    Similarly, $$N_1 V_1 = N_2 V_2$$

11. **Molarity of a mixture:** If V_1 mL of a solution of molarity M_1 is mixed with another solution of same substance with volume V_2 and molarity M_2 then molarity of the resulting mixture of solution (M) can be obtained as:

$$M = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

12. **Relationship between molarity (M) and mole fraction of solute (x_B)**

$$x_B = \frac{M \times GMM_A}{M(GMM_A - GMM_B) + 1000d}$$

Also,

$$M = \frac{1000 \times d \times x_B}{x_A \times GMM_A + x_B \times GMM_B}$$

13. **Raoult's law for volatile solute**

$$p_A = p_A^o x_A \quad \text{and} \quad p_B = p_B^o x_B$$

where p_A and p_B are partial vapour pressures of component 'A' and component 'B' in the solution. p_A^o and p_B^o are vapour pressures of pure components 'A' and 'B' respectively.

$$\text{Total vapour pressure, } p = p_A + p_B = p_A^o x_A + p_B^o x_B$$

14. **Raoult's law for non-volatile solute**

$$\frac{p_A^o - p}{p_A^o} = x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} \quad \text{(For a dilute solution } n_B << n_A\text{)}.$$

$$M_B = \left(\frac{p_A^o}{p_A^o - p_A}\right)\frac{W_B \times M_A}{W_A}$$

where x_B is mole fraction of solute and $\frac{p_A^o - p_A}{p_A^o}$ is relative lowering of vapour pressure.

15. **Elevation in boiling point:**

$$\Delta T_b = K_b \times m$$

$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

or,

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

where,

$$\Delta T_b = T_b - T_b^o$$

16. **Depression in freezing point:**

$$\Delta T_f = K_f \times m$$

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

or,

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

17. **Osmotic pressure (π)**

$$\pi V = n_B RT$$

$$\pi V = \frac{W_B}{M_B} \times R \times T, \; M_B = \frac{W_B \times R \times T}{\pi \times V}$$

$$\pi = \frac{n_B}{V} \times R \times T \quad \text{or} \quad \pi = CRT \text{ where '}C\text{' is molarity.}$$

Osmotic pressure is related to the relative lowering of vapour pressure, elevation in boiling point and depression in freezing points according to the following relations:

$$\pi = \left(\frac{p_A^o - p_A}{p_A^o}\right) \times \frac{d \times R \times T}{M_B}$$

$$\pi = \frac{\Delta T_b \times d \times R \times T}{1000 \times K_b}$$

$$\pi = \frac{\Delta T_f \times d \times R \times T}{1000 \times K_f}$$

where d is the density of solution at temperature 'T'.

18. van't Hoff factor

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

or, $$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

or, $$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Modified forms of colligative properties:

(*a*) $\frac{p_A^o - p_A}{p_A^o} = i x_B$ (*b*) $\Delta T_b = i\,K_b m$

(*c*) $\Delta T_f = i\,K_f m$ (*d*) $\pi V = i\,n_B RT$

19. $\alpha = \frac{i-1}{n-1}$, where α is degree of dissociation, 'i' is van't Hoff factor, 'n' is number of ions produced per formula of the compound.

20. $\alpha = \frac{1-i}{1-\frac{1}{n}}$ **or** $\alpha = \frac{i-1}{\frac{1}{n}-1}$

where α is degree of association, n is the number of molecules of solute that associate to form an associated molecule, $\frac{1}{n} < 1$.

21. Molal elevation constant, $K_b = \frac{R \times M_A \times (T_b^o)^2}{1000 \times \Delta_{\text{vap}} H}$

22. Molal depression constant, $K_f = \frac{R \times M_A \times (T_f^o)^2}{1000 \times \Delta_{\text{fus}} H}$

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Ans. Mass percentage of benzene $= \frac{\text{Mass of benzene}}{\text{Mass of solution}} \times 100 = \frac{22\text{g}}{22\text{g} + 122\text{ g}} \times 100 = \mathbf{15.28\%}$

Mass percentage of carbon tetrachloride = 100 – Mass percentage of benzene

= 100 – 15.28 = **84.72%**

Q. 2. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Ans. Let the mass of solution be 100 g.

Mass of benzene = 30 g,

∴ Mass of carbon tetrachloride = 100 g – 30 g = 70 g

$$\text{Number of moles of benzene} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{30\text{ g}}{78\text{ g mol}^{-1}} = 0.385\text{ mol}$$

$$\text{Number of moles of carbon tetrachloride} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{70\text{ g}}{154\text{ g mol}^{-1}} = 0.455\text{ mol}$$

$$\text{Mole fraction of benzene} = \frac{\text{Moles of benzene}}{\text{Moles of benzene} + \text{Moles of carbon tetrachloride}}$$

$$= \frac{0.385\text{ mol}}{0.840\text{ mol}} = \mathbf{0.458}$$

Q. 3. Calculate the molarity of each of the following solutions:

(*a*) 30 g of $Co(NO_3)_2 . 6H_2O$ in 4.3 L of solution

(*b*) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL

Ans. (*a*) Mass of solute, $Co(NO_3)_2.6H_2O$ = 30 g

Molar mass of $Co(NO_3)_2.6H_2O = 59 + 2(14 + 3 \times 16) + 6 \times 18 = 291\text{ g mol}^{-1}$

$$\text{Number of moles of } Co(NO_3)_2.6H_2O = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{30\text{ g}}{291\text{ g mol}^{-1}} = 0.1\text{ mol}$$

Volume of solution = 4.3 L

$$\text{Molarity of solution} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}} = \frac{0.1\text{ mol}}{4.3\text{ L}} = \mathbf{0.023\text{ mol L}^{-1}}$$

(*b*) $M_1 = 0.5$ M $V_1 = 30$ mL

$M_2 = ?$ $V_2 = 500$ mL

Applying molarity equation, $M_1V_1 = M_2V_2$, we get

$0.5\text{ M} \times 30\text{ mL} = M_2 \times 500\text{ mL}$

$$M_2 = \frac{0.5 \times 30\text{ M}}{500} = \mathbf{0.03\text{ M}}$$

Alternatively,

Number of moles = Molarity × Volume of solution in litres

Number of moles of H_2SO_4 present in 0.5 M of 30 mL H_2SO_4 solution

$$= 0.5\text{ mol L}^{-1} \times 0.03\text{ L} = 0.015\text{ mol}$$

$$\text{Volume of solution} = 500\text{ mL} = \frac{500\text{ L}}{1000} = 0.5\text{ L}$$

$$\therefore \text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}} = \frac{0.015\text{ mol}}{0.5\text{ L}} = \mathbf{0.03\text{ mol L}^{-1}}$$

Q. 4. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

Ans. Mass of required aqueous solution = 2.5 kg = 2500 g

0.25 molal aqueous solution of urea means 0.25 mole of urea is dissolved in 1000 grams of water.

Mass of water = 1000 g

Moles of urea = 0.25 mol

Molar mass of urea (H_2NCONH_2) $= 4 \times 1 + 2 \times 14 + 1 \times 12 + 1 \times 16 = 60\text{ g mol}^{-1}$

Mass of urea = Number of moles of urea × Molar mass of urea

∴ Mass of 0.25 moles of urea $= 0.25\text{ mol} \times 60\text{ g mol}^{-1} = 15\text{ g}$

Mass of solution = 1000 g + 15 g = 1015 g

1015 g of aqueous solution contains urea = 15 g

$\therefore$ 2500 g of aqueous solution will require urea = $\frac{15\text{ g}}{1015\text{ g}} \times 2500\text{ g} = \mathbf{36.95\ g}$

Q. 5. Calculate (*i*) molality (*ii*) molarity and (*iii*) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}.

Ans. 20% (mass/mass) aqueous KI solution means that

Mass of KI = 20 g

Mass of solution = 100 g

$\therefore$ Mass of solvent (water) = 100 – 20 = 80 g

(*i*) Calculation of molality

Molar mass of KI = 39 + 127 = 166 g mol^{-1}

$$n_{\text{KI}} = \frac{20\text{ g}}{166\text{ g mol}^{-1}} = 0.120$$

$$\text{Molality of solution} = \frac{n_{\text{KI}}}{W_{\text{H}_2\text{O}}} \times 1000 = \frac{0.120}{80} \times 1000 = \mathbf{1.5\ m}$$

(*ii*) Calculation of molarity

Density of solution = 1.202 g mL^{-1}

$$\text{Volume of solution} = \frac{100\text{ g}}{1.202\text{ g mL}^{-1}} = 83.2\text{ mL} = 0.0832\text{ L}$$

$$\text{Molarity of solution} = \frac{n_{\text{KI}}}{\text{Volume of solution in L}} = \frac{0.120\text{ mol}}{0.0832\text{ L}} = \mathbf{1.44\ M}$$

Alternatively,

$$\text{Molarity} = \frac{\text{mass/mass }\% \times d \times 10}{\text{Molar mass of KI}} = \frac{20 \times 1.202 \times 10}{166} = \frac{240.4}{166} = \mathbf{1.45\ M}$$

(*iii*) Calculation of mole fraction of KI

$$n_{\text{KI}} = 0.120\text{ mol}$$

$$n_{\text{H}_2\text{O}} = \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{80\text{ g}}{18\text{ g mol}^{-1}} = 4.44\text{ mol}$$

$$x_{\text{KI}} = \frac{n_{\text{KI}}}{n_{\text{H}_2\text{O}} + n_{\text{KI}}} = \frac{0.120\text{ mol}}{4.44\text{ mol} + 0.12\text{ mol}} = \frac{0.120\text{ mol}}{4.560\text{ mol}} = \mathbf{0.0263}$$

Q. 6. H_2S, a toxic gas with rotten egg-like smell, is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Ans. 0.195 m aqueous solution of H_2S means 0.195 mole of H_2S is dissolved in 1000 g of water.

$$\text{Number of moles of water in 1000 g} = \frac{1000\text{ g}}{18\text{ g mol}^{-1}} = 55.55\text{ mol}$$

Number of moles of H_2S = 0.195 mol

$$x_{\text{H}_2\text{S}} = \frac{n_{\text{H}_2\text{S}}}{n_{\text{H}_2\text{S}} + n_{\text{H}_2\text{O}}} = \frac{0.195\text{ mol}}{0.195\text{ mol} + 55.55\text{ mol}} = \frac{0.195\text{ mol}}{55.745\text{ mol}} = 0.0035$$

According to Henry's law, $p_{\text{H}_2\text{S}} = K_{\text{H}} \times x_{\text{H}_2\text{S}}$

$\therefore$ 0.987 bar = $K_H \times 0.0035$

$$K_H = \frac{0.987\text{ bar}}{0.0035} = \mathbf{282\ bar}$$

Q. 7. Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Ans. $p_{CO_2} = 2.5 \text{ atm} = 2.5 \times 10^5 \text{ Pa}$

$K_H = 1.67 \times 10^8 \text{ Pa}$

According to Henry's law,

$$p_{CO_2} = K_H \times x_{CO_2}$$

$$\therefore \quad x_{CO_2} = \frac{p_{CO_2}}{K_H} = \frac{2.5 \times 10^5 \ Pa}{1.67 \times 10^8 \ Pa}$$

$$= 1.5 \times 10^{-3} \qquad ...(i)$$

$$\text{Mass of water} = \text{Density of water} \times \text{Volume of water}$$

$$= 1 \text{ g/mL} \times 500 \text{ mL} = 500 \text{ g}$$

Number of moles of water, (n_{H_2O})

$$= \frac{\text{Mass of water}}{\text{Molar mass}} = \frac{500 \text{ g}}{18 \text{ g/mol}} = 27.78 \text{ mol}$$

$$x_{CO_2} = \frac{n_{CO_2}}{n_{H_2O} + n_{CO_2}} = \frac{n_{CO_2}}{n_{H_2O}}$$

$$\Rightarrow \quad n_{CO_2} = x_{CO_2} \times n_{H_2O}$$

$$= 1.5 \times 10^{-3} \times 27.78 \text{ mol}$$

$$= 41.67 \times 10^{-3} \text{ mol}$$

$$\text{Mass of } CO_2 = \text{Number of moles of } CO_2 \times \text{Molar mass}$$

$$= 41.67 \times 10^{-3} \text{ mol} \times 44 \text{ g/mol}$$

$$= \mathbf{1.834 \text{ g}}$$

Q. 8. The vapour pressure of pure liquids *A* and *B* are 450 and 700 mm Hg respectively at 350 K. Find out the composition of the liquid mixture if the total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

Ans. According to Raoult's law,

$$p = p^o_A x_A + p^o_B x_B$$

$$= p^o_A x_A + p^o_B (1 - x_A) = p^o_B + (p^o_A - p^o_B)\, x_A$$

Here, $p^o_A = 450$ mm Hg; $p^o_B = 700$ mm Hg; $p = 600$ mm Hg

Substituting the values, we get

$$600 = 700 + (450 - 700)x_A$$

$$250x_A = 100 \qquad \text{or} \qquad x_A = \frac{100}{250} = \mathbf{0.4}$$

Also, $x_A + x_B = 1$ or $x_B = 1 - x_A = 1 - 0.4 = \mathbf{0.6}$

$p_A = p^o_A x_A$ and $p_B = p^o_B x_B$

$p_A = 450 \text{ mm Hg} \times 0.4$ and $p_B = 700 \text{ mm Hg} \times 0.6$

$p_A = 180$ mm Hg and $p_B = 420$ mm Hg

In vapour phase,

Mole fraction of *A*, $y_A = \dfrac{p_A}{p_A + p_B} = \dfrac{180 \text{ mm Hg}}{180 \text{ mm Hg} + 420 \text{ mm Hg}} = \mathbf{0.30}$

Mole fraction of *B*, $y_B = \dfrac{p_B}{p_A + p_B} = \dfrac{420 \text{ mm Hg}}{180 \text{ mm Hg} + 420 \text{ mm Hg}} = \mathbf{0.70}$

Q. 9. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea NH_2CONH_2 is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Ans. Here, $p^o_A = 23.8$ mm Hg

$W_B = 50$ g, M_B (urea) $= 60$ g mol^{-1}

$W_A = 850$ g, M_A (water) $= 18$ g mol^{-1}

Applying Raoult's law,

$$\frac{p^o_A - p_s}{p^o_A} = \frac{n_B}{n_A + n_B} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

$$= \frac{50/60}{850/18 + 50/60}$$

$$= \frac{0.83}{47.22 + 0.83} = \frac{0.83}{48.05} = \mathbf{0.017}$$

Thus, relative lowering of vapour pressure = **0.017**

Substituting $p^o_A = 23.8$ mm Hg, we get

$$\frac{23.8 - p_s}{23.8} = 0.017$$

On solving we get,

$$p_s = \mathbf{23.40\ mm\ Hg}$$

Hence, vapour pressure of water in the solution is **23.4 mm Hg.**

Q. 10. Boiling point of water at 750 mm Hg is 99.63ºC. How much sucrose is to be added to 500 g of water such that it boils at 100ºC?

Ans. Molecular mass of sucrose, ($C_{12}H_{22}O_{11}$), $M_B = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$ g mol^{-1}

Mass of water = 500 g

Elevation in boiling point, $\Delta T_b = 100\ °C - 99.63\ °C = 0.37\ °C = 0.37$ K

$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A} \quad \Rightarrow \quad W_B = \frac{\Delta T_b \times M_B \times W_A}{1000 \times K_b}$$

$$W_B = \frac{0.37 \times 342 \times 500}{1000 \times 0.52} = \mathbf{122\ g}$$

Q. 11. Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5ºC. $K_f = 3.9$ K kg mol^{-1}. ***[CBSE 2020 (56/1/1)]***

Ans. Molecular mass of ascorbic acid, $M_B = 6 \times 12 + 8 \times 1 + 6 \times 16 = 176$ g mol^{-1}

$$\Delta T_f = K_f \frac{1000 \times W_B}{M_B \times W_A}$$

or

$$W_B = \frac{\Delta T_f \times M_B \times W_A}{K_f \times 1000}$$

$$= \frac{1.5 \times 176 \times 75}{3.9 \times 1000} = \mathbf{5.08\ g}$$

Q. 12. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37ºC.

Ans.

$$\pi = CRT = \frac{n_B}{V} RT \qquad \text{...}(i)$$

Number of moles of solute dissolved, $n_B = \dfrac{1.0\ \text{g}}{185{,}000\ \text{g mol}^{-1}} = \dfrac{1}{185{,}000}$ mol

$V = 450$ mL $= 0.450$ L

$T = 37°C = 37 + 273 = 310$ K

$R = 8.314$ kPa K^{-1} mol^{-1} $= 8.314 \times 10^3$ Pa L K^{-1} mol^{-1}

Substituting these values in (*i*), we get

$$\pi = \frac{1}{185,000}\text{ mol} \times \frac{1}{0.45\text{ L}} \times 8.314 \times 10^3 \text{ Pa L K}^{-1}\text{ mol}^{-1} \times 310\text{ K}$$

$$= \mathbf{30.96\ Pa}$$

NCERT Textbook Exercises

Q. 1. Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

Ans. Refer to Basic Concepts Points 1 and 2.

Q. 2. Give an example of a solid solution in which the solute is a gas.

Ans. Solution of hydrogen in palladium

Q. 3. Define the following terms

(*i*) mole fraction **(*ii*) molality**

(*iii*) molarity **(*iv*) mass percentage**

Ans. Refer to Basic Concepts Point 3.

Q. 4. Concentrated nitric acid used in the laboratory is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1}?

Ans. Consider 100 g sample of HNO_3 solution. As solution is 68% (m/m),

∴ Mass of nitric acid = 68 g

Molar mass of HNO_3 = 63 g mol^{-1}

$$\therefore \text{ Number of moles of solute, } HNO_3 = \frac{68}{63}\text{ mol} = 1.079\text{ mol}$$

Density of solution = 1.504 g mL^{-1}

$$\therefore \text{ Volume of solution } = \frac{\text{Mass}}{\text{Density}} = \frac{100\text{ g}}{1.504\text{ g mL}^{-1}} = 66.5\text{ mL} = 0.0665\text{ L}$$

$$\text{Molarity of the solution } = \frac{\text{Moles of the solute}}{\text{Volume of solution in L}} = \frac{1.079\text{ mol}}{0.0665\text{ L}} = \mathbf{16.23\ mol\ L^{-1}}$$

Alternatively,

$$\text{Molarity of the solution} = \frac{\text{mass/mass }\% \times d \times 10}{\text{Molar mass of } HNO_3} = \frac{68 \times 1.504 \times 10}{63} = \frac{1022.723}{63} = \mathbf{16.23\ M}$$

Q. 5. A solution of glucose in water is labelled as 10 per cent w/w. What would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2 g mL^{-1}, what shall be the molarity of the solution? **[*CBSE (AI) 2014*]**

Ans. 10% w/w solution of glucose means 10 grams of glucose is present in 100 g of solution, *i.e.*, 90 g of water.

$$\text{Number of moles of glucose} = \frac{10\text{ g}}{180\text{ g mol}^{-1}} = 0.0555\text{ mol}$$

$$\text{Number of moles of water} = \frac{90\text{ g}}{18\text{ g mol}^{-1}} = 5\text{ mol}$$

$$\text{Molality of the solution} = \frac{\text{Number of moles of glucose}}{\text{Mass of water (in kg)}} = \frac{0.0555}{0.09\text{ kg}} = \mathbf{0.61\ mol\ kg^{-1}}$$

$$\text{Mole fraction of glucose, } x_{C_6H_{12}O_6} = \frac{n_{C_6H_{12}O_6}}{n_{C_6H_{12}O_6} + n_{H_2O}} = \frac{0.055\text{ mol}}{5\text{ mol} + 0.055\text{ mol}} = \mathbf{0.01}$$

$$\text{Mole fraction of water, } x_{H_2O} = 1 - x_{C_6H_{12}O_6} = 1.00 - 0.01 = \mathbf{0.99}$$

$$\text{Volume of 100 g glucose solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{100\text{g}}{1.2\text{ g mL}^{-1}} = \frac{1000}{12}\text{ mL} = \frac{1}{12}\text{L}$$

$$\text{Molarity of the solution} = \frac{\text{Number of moles of glucose}}{\text{Volume of solution}} = \frac{0.055 \text{ mol}}{\frac{1}{12}\text{L}} = \mathbf{0.660 \text{ mol L}^{-1}}$$

Q. 6. How many mL of a 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of both?

Ans. To calculate the number of moles of the components in the mixture.

Let Na_2CO_3 present in the mixture be x g

∴ $NaHCO_3$ present in the mixture = $(1 - x)$ g.

Molar mass of $Na_2CO_3 = 2 \times 23 + 12 + 3 \times 16 = 106 \text{ g mol}^{-1}$

Molar mass of $NaHCO_3 = 23 + 1 + 12 + 3 \times 16 = 84 \text{ g mol}^{-1}$

$$\therefore \quad n_{Na_2CO_3} = \frac{x}{106} \text{ mol}, \; n_{NaHCO_3} = \frac{1-x}{84} \text{ mol}$$

As mixture contains equimolar amounts of the two,

$$\therefore \quad \frac{x}{106} = \frac{1-x}{84} \quad \text{or} \quad 106 - 106x = 84x$$

$$\text{or} \quad x = \frac{106}{190} = 0.558 \text{ g}$$

$$\text{Thus,} \quad \text{moles of } Na_2CO_3 = \frac{0.558}{106} = 0.00526$$

$$\text{Moles of } NaHCO_3 = \frac{1-0.558}{84} = \frac{0.442}{84} = 0.00526$$

To calculate the moles of HCl required.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

1 mole of Na_2CO_3 requires HCl = 2 moles

∴ 0.00526 mole of Na_2CO_3 requires HCl = 0.00526 × 2 moles = 0.01052 mole

1 mole of $NaHCO_3$ requires HCl = 1 mole

∴ 0.00526 mole of $NaHCO_3$ requires HCl = 0.00526 mole

∴ Total HCl required = 0.01052 mol + 0.00526 mole = 0.01578 mole

To calculate volume of 0.1 M HCl.

0.1 mole of 0.1 M HCl are present in 1000 mL of HCl.

$$0.01578 \text{ mole of 0.1 M HCl will be present in HCl} = \frac{1000}{0.1} \times 0.01578 = \mathbf{157.8 \text{ mL}}$$

Q. 7. A solution is obtained by mixing 300 g of 25% and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Ans. $$300 \text{ g of 25\% solution contains solute} = \frac{300 \times 25}{100} = 75 \text{ g}$$

$$400 \text{ g of 40\% solution contains solute} = \frac{400 \times 40}{100} = 160 \text{ g}$$

Total mass of solute = 160 g + 75 g = 235 g

Total mass of solution = 300 g + 400 g = 700 g

$$\text{\% of solute in the final solution} = \frac{235}{700} \times 100 = \mathbf{33.5\%}$$

% of solvent in the final solution = 100 – 33.5 = **66.5%**

Q. 8. An antifreeze solution is prepared from 222.6 g of ethylene glycol, $C_2H_4(OH)_2$ and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1}, then what shall be the molarity of the solution?

Ans. Mass of ethylene glycol = 222.6 g

Molar mass of ethylene glycol, $C_2H_4(OH)_2 = 62 \text{ g mol}^{-1}$

$$\text{Number of moles of ethylene glycol} = \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59 \text{ mol}$$

$$\text{Mass of water} = 200 \text{ g} = 0.20 \text{ kg}$$

$$\text{Molality of solution} = \frac{\text{Moles of ethylene glycol}}{\text{Mass of solvent (in kg)}} = \frac{3.59 \text{ mol}}{0.20 \text{ kg}} = \mathbf{17.95 \text{ mol kg}^{-1}}$$

$$\text{Total mass of the solution} = 222.6 \text{ g} + 200 \text{ g} = 422.6 \text{ g}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} = 394.2 \text{ mL} = 0.3942 \text{ L}$$

$$\text{Molarity of solution} = \frac{\text{Moles of ethylene glycol}}{\text{Volume of solution (in L)}} = \frac{3.59 \text{ mol}}{0.3942 \text{ L}} = \mathbf{9.1 \text{ mol L}^{-1}}$$

Q. 9. A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$ which is supposed to be a carcinogen. The level of contamination was 15 ppm (by mass).

(*i*) Express this in percent by mass.

(*ii*) Determine the molality of chloroform in the water sample.

Ans. Let the mass of solution be 10^6 g.

Mass of solute, chloroform = 15 g

(*i*) $$\% \text{ by mass of chloroform} = \frac{\text{Mass of chloroform}}{\text{Mass of solution}} \times 100$$

$$= \frac{15 \text{ g}}{10^6 \text{ g}} \times 100 = \mathbf{15 \times 10^{-4} \%}$$

(*ii*) Mass of solvent, water = $10^6 \text{ g} - 15 \text{ g} \approx 10^6 \text{ g} \approx 10^3 \text{ kg}$

$$\text{Number of moles of chloroform, } CHCl_3 = \frac{\text{Mass of chloroform}}{\text{Molar mass}}$$

$$= \frac{15 \text{ g}}{119.5 \text{ g mol}^{-1}} = \mathbf{0.126 \text{ mol}}$$

$$\text{Molality of solution} = \frac{\text{Number of moles of chloroform}}{\text{Mass of water (in kg)}} = \frac{0.126 \text{ mol}}{10^3 \text{ kg}}$$

$$= \mathbf{1.26 \times 10^{-4} \text{ mol kg}^{-1}}$$

Q. 10. What role molecular interaction play in the solution of alcohol and water?

Ans. There is intermolecular hydrogen bonding in alcohol as well as in water. On mixing, the magnitude of attractive forces tends to decrease. Due to decrease in attractive forces, the solution shows positive deviations from ideal behaviour. As a result, the solution will have higher vapour pressure and lower boiling point as compared to that of pure water and pure alcohol separately.

Q. 11. Why do gases always tend to be less soluble in liquid as the temperature is raised?

Ans. $$\text{Gas} + \text{Liquid} \rightleftharpoons \text{Dissolved gas}; \Delta H = -\text{ ve}$$

Dissolution of gas in liquid is an exothermic process. As the temperature is increased, according to the Le Chatelier's principle the equilibrium will shift backward. This results in decrease of solubility of gases in liquid.

Q. 12. State Henry's law and mention some important applications.

Ans. Refer to Basic Concepts Point 2(*c*).

Q. 13. The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

Ans. According to Henry's law, $m = K_H \times p$

Case I. $6.56 \times 10^{-3} \text{g} = K_H \times 1 \text{ bar}$

or, $K_H = 6.56 \times 10^{-3} \text{ g bar}^{-1}$

Case II. $5.00 \times 10^{-2}\ \text{g} = (6.56 \times 10^{-3}\ \text{g bar}^{-1}) \times p$

or $$p = \frac{5.00 \times 10^{-2}\ \text{g}}{6.56 \times 10^{-3}\ \text{g bar}^{-1}} = \mathbf{7.62\ bar}$$

Q. 14. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}}H$ related to positive and negative deviations from Raoult's law?

Ans. Refer to Basic Concepts Point 5(*b*).

Q. 15. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

Ans. Vapour pressure of pure water at the boiling point ($p°$) = 1 atm = 1.013 bar

Vapour pressure of solution (p_s) = 1.004 bar

Mass of solute, $W_B = 2$ g

Mass of solution = 100 g

Mass of solvent, $W_A = 100\ \text{g} - 2\ \text{g} = 98$ g

Applying Raoult's law for dilute solution (being 2%)

$$\frac{p_A^{\circ} - p_s}{p_A^{\circ}} = x_B = \frac{n_B}{n_A + n_B} \simeq \frac{n_B}{n_A} = \frac{W_B/M_B}{W_A/M_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\frac{(1.013\ \text{bar} - 1.004\ \text{bar})}{1.013\ \text{bar}} = \frac{2\ \text{g} \times 18\ \text{g mol}^{-1}}{\text{M}_\text{B} \times 98\ \text{g}}$$

or $$M_B = \frac{2\ \text{g} \times 18\ \text{g mol}^{-1} \times 1.013\ \text{bar}}{98\ \text{g} \times 0.009\ \text{bar}} = \mathbf{41.35\ g\ mol^{-1}}$$

Q. 16. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?

Ans. Molar mass of heptane, $C_7H_{16} = 100\ \text{g mol}^{-1}$

Molar mass of octane, $C_8H_{18} = 114\ \text{g mol}^{-1}$

$$n_{C_7H_{16}} = \frac{26.0\ \text{g}}{100\ \text{g mol}^{-1}} = 0.26\ \text{mol}$$

$$n_{C_8H_{18}} = \frac{35.0\ \text{g}}{114\ \text{g mol}^{-1}} = 0.31\ \text{mol}$$

$$x_{C_7H_{16}} = \frac{n_{C_7H_{16}}}{n_{C_7H_{16}} + n_{C_8H_{18}}} = \frac{0.26}{0.26 + 0.31} = 0.456$$

$$x_{C_8H_{18}} = 1 - x_{C_7H_{16}}$$
$$= 1 - 0.456 = 0.544$$

$$p_{C_7H_{16}} = 105.2\ \text{kPa} \times 0.456$$
$$= 47.97\ \text{kPa}$$

$$p_{C_8H_{18}} = 46.8\ \text{kPa} \times 0.544 = 25.46\ \text{kPa}$$

$$p_{\text{total}} = p_{C_7H_{16}} + p_{C_8H_{18}}$$
$$= 47.97 + 25.46$$
$$= \mathbf{73.43\ kPa}$$

Q. 17. The vapour pressure of water is 12.3 kPa at 300 K. Calculate the vapour pressure of 1 molal solution of a non-volatile solute in it.

Ans. 1 molal solution means 1 mol of the solute is present in 1000 g of the solvent, H_2O (assuming the solution to be dilute).

$$n_{H_2O} = \frac{1000}{18} = 55.5\ \text{mol}$$

$$x_{\text{solute}} = \frac{1}{1+55.5} = 0.0177$$

Also, $$x_{\text{solute}} = \frac{p_A^o - p_s}{p_A^o} \Rightarrow 0.0177 = \frac{12.3 - p_s}{12.3}$$

or $$p_s = \mathbf{12.08\ kPa}$$

Q. 18. Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Ans. $p_s = 80\%$ of $p^o = \dfrac{80 \times p^o}{100} = 0.80\ p^o;\ n_B = \dfrac{W_B}{40}$ mol

$$n_{C_8H_{18}} = \frac{114\text{ g}}{114\text{ g mol}^{-1}} = 1\text{ mol (Molar mass of } C_8H_{18} = 114\text{ g mol}^{-1})$$

Now , $$\frac{p^o - p_s}{p^o} = x_B$$

$$\frac{p^o - 0.80p^o}{p^o} = \frac{n_B}{n_B + n_{C_8H_{18}}} = \frac{W_B/40}{W_B/40 + 1}$$

$$0.2\left(\frac{W_B}{40} + 1\right) = \frac{W_B}{40} \quad \text{or} \quad \frac{0.8\,W_B}{40} = 0.2$$

or $$W_B = \mathbf{10\ g}$$

Q. 19. A solution containing 30 g of a non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is then added to the solution, the new vapour pressure becomes 2.9 kPa at 298 K. Calculate (*i*) molar mass of the solute (*ii*) vapour pressure of water at 298 K.

Ans. (*i*) Suppose the molar mass of the solute = M_B g mol^{-1}

Number of moles of solute, $n_B = \dfrac{30}{M_B}$ mol

Number of solvent (water), $n_A = \dfrac{90\text{ g}}{18\text{ g mol}^{-1}} = 5$ mol

According to Raoult's law,

$$\frac{p_A^o - p_s}{p_A^o} = \frac{n_B}{n_A + n_B},\ i.e.,\ \frac{p_A^o - 2.8}{p_A^o} = \frac{30/M_B}{5 + (30/M_B)}$$

or $$1 - \frac{2.8}{p_A^o} = \frac{30/M_B}{5 + (30/M_B)}$$

or $$\frac{2.8}{p_A^o} = 1 - \frac{30/M_B}{5 + (30/M_B)} = \frac{5 + 30/M_B - 30/M_B}{5 + (30/M_B)} = \frac{5}{5 + (30/M_B)}$$

or $$\frac{p_A^o}{2.8} = \frac{5 + (30/M_B)}{5} = 1 + \frac{6}{M_B} \qquad \text{...}(i)$$

After adding 18 g of water,

Number of moles of water (n_A) = $\dfrac{108}{18}$ = 6 mol

According to Raoult's law,

$$\therefore \quad \frac{p_A^o - 2.9}{p_A^o} = \frac{30/M_B}{6 + (30/M_B)}$$

or $$1 - \frac{2.9}{p_A^o} = \frac{30/M_B}{6 + (30/M_B)}$$

or $$\frac{2.9}{p_A^o} = 1 - \frac{30/M_B}{6+(30/M_B)} = \frac{6+(30/M_B)-(30/M_B)}{6+(30/M_B)} = \frac{6}{6+(30/M_B)}$$

or $$\frac{p_A^o}{2.9} = \frac{6+(30/M_B)}{6}$$

or $$\frac{p_A^o}{2.9} = 1+\frac{5}{M_B} \qquad ...(ii)$$

Dividing equation (*i*) by equation (*ii*), we get

$$\frac{2.9}{2.8} = \frac{1+(6/M_B)}{1+(5/M_B)}$$

or $$2.9\left(1+\frac{5}{M_B}\right) = 2.8\left(1+\frac{6}{M_B}\right)$$

or $$2.9+\frac{14.5}{M_B} = 2.8+\frac{16.8}{M_B} \quad \text{or} \quad \frac{2.3}{M_B} = 0.1 \quad \text{or} \quad M_B = \mathbf{23\ g\ mol^{-1}}$$

(*ii*) Putting the value of M_B in equation (*i*), we get

$$\frac{p_A^o}{2.8} = 1+\frac{6}{23} = \frac{29}{23}$$

or $$p_A^o = \frac{29}{23} \times 2.8 = \mathbf{3.53\ kPa}$$

Q. 20. A 5% solution (by mass) of cane sugar in water has a freezing point of 271 K. Calculate the freezing point of a 5% glucose in water if the freezing point of pure water is 273.15 K.

Ans. Let the mass of solution = 100 g

∴ Mass of the cane sugar = 5 g

Mass of solvent, water = 100 g – 5 g = 95 g

$\Delta T_f = 273.15\ \text{K} - 271\ \text{K} = 2.15\ \text{K}$

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A} \quad \Rightarrow \quad K_f = \frac{\Delta T_f \times M_B \times W_A}{W_B \times 1000}$$

$$K_f = \frac{2.15 \times 342 \times 95}{5 \times 1000} = \mathbf{13.97\ K\ kg\ mol^{-1}}$$

For 5% solution of glucose in water

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A} = \frac{13.97 \times 5 \times 1000}{180 \times 95}$$

$$\Delta T_f = 4.08\ \text{K}$$

Freezing point of glucose solution, $T_f = \Delta T_f^o - \Delta T_f = 273.15\ \text{K} - 4.08\ \text{K} = \mathbf{269.07\ K}$

Q. 21. Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6). 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of *A* and *B*.

Ans. We know,

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

∴ $$M_{AB_2} = \frac{5.1 \times 1 \times 1000}{2.3 \times 20} = 110.87\ \text{g mol}^{-1}$$

Similarly, $$M_{AB_4} = \frac{5.1 \times 1 \times 1000}{1.3 \times 20} = 196.15\ \text{g mol}^{-1}$$

Suppose atomic masses of *A* and *B* are '*a*' and '*b*' respectively. Then

Molar mass of $AB_2 = a + 2b = 110.87$ g mol^{-1} ...(*i*)

Molar mass of $AB_4 = a + 4b = 196.15$ g mol^{-1} ...(*ii*)

Subtracting equation (*i*) from equation (*ii*), we get

$2b = 85.28$ or $b = 42.64$

Substituting the value of b in equation (*i*), we get

$a + 2 \times 42.64 = 110.87$ or $a = 25.59$

Thus, Atomic mass of A = **25.59 u**

Atomic mass of B = **42.64 u**

Q. 22. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

Ans. Osmotic pressure, $\pi = CRT$

First case:

$$\text{Number of moles of glucose, } C_6H_{12}O_6 = \frac{36\text{ g}}{180\text{ g mol}^{-1}} = 0.2\text{ mol}$$

$$\text{Molar concentration of solution, } C = \frac{0.2\text{ mol}}{1\text{ L}} = 0.2\text{ mol L}^{-1}$$

$$\therefore \quad 4.98\text{ bar} = 0.2\text{ mol L}^{-1} \times R \times 300\text{ K} \quad ...(i)$$

Second case:

$$1.52 = C \times R \times 300\text{ K} \quad ...(ii)$$

Dividing equation (*ii*) by equation (*i*), we get

$$\frac{1.52\text{ bar}}{4.98\text{ bar}} = \frac{C \times R \times 300\text{ K}}{0.2\text{ mol L}^{-1} \times R \times 300\text{ K}}$$

$$0.305 = \frac{C}{0.2\text{ mol L}^{-1}}$$

or $$C = \mathbf{0.0610\ mol\ L^{-1}}$$

Q. 23. Suggest the most important type of intermolecular interaction in the following pairs: (*i*) *n*-hexane and *n*-octane (*ii*) I_2 and CCl_4 (*iii*) $NaClO_4$ and water (*iv*) methanol and acetone (*v*) acetonitrile (CH_3CN) and acetone (C_3H_6O).

Ans. (*i*) Dispersion or London forces as both are non-polar.

(*ii*) Dispersion or London forces as both are non-polar.

(*iii*) Ion–dipole interactions as sodium chlorate gives Na^+ and ClO_4^- ions and water is a polar molecule.

(*iv*) Dipole–dipole interactions as both are polar molecules.

(*v*) Dipole–dipole interactions as both are polar molecules.

Q. 24. Based on solute–solvent interactions, arrange the following in order of increasing solubility in *n*-octane and explain.

Cyclohexane, KCl, CH_3OH, CH_3CN

Ans. (*i*) Cyclohexane and *n*-octane both are non-polar. Hence, they will mix completely in all proportions.

(*ii*) KCl is an ionic compound whereas n-octane is non-polar. Hence, KCl will not dissolve at all in *n*-octane.

(*iii*) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH. As *n*-octane is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane.

Therefore, the order of solubility in *n*-octane will be KCl < CH_3OH < CH_3CN < Cyclohexane.

Q. 25. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water: (*i*) phenol, (*ii*) toluene, (*iii*) formic acid, (*iv*) ethylene glycol, (*v*) chloroform, (*vi*) pentanol.

Ans. (*i*) Partially soluble as it has non-polar C_6H_5 group and polar —OH group which can form hydrogen bond with water.

(*ii*) Insoluble as toluene is non-polar while water is polar.

(*iii*) Highly soluble as formic acid can form hydrogen bonds with water.

(*iv*) Highly soluble as ethylene glycol can form hydrogen bonds with water.

(*v*) Insoluble as chloroform despite its polarity, cannot form hydrogen bonds with water.

(*vi*) Partially soluble as —OH group is polar but the bulky C_5H_{11} part is non-polar.

Q. 26. If the density of some lake water is 1.25 g mL^{-1} and contains 92 g of Na^+ ions per kg of water, calculate the molality of Na^+ ions in the lake.

Ans. Number of moles of Na^+ ion $= \dfrac{92 \text{ g}}{23 \text{ g mol}^{-1}} = 4$ mol

$$\text{Molality of } Na^+ \text{ ions} = \frac{\text{Number of moles of } Na^+ \text{ ions}}{\text{Mass of water in kg}}$$

$$= \frac{4 \text{ mol}}{1 \text{ kg}} = 4 \text{ mol kg}^{-1} = \mathbf{4\ m}$$

Q. 27. If the solubility product of CuS is 6 × 10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Ans. Maximum molarity of CuS in aqueous solution = Solubility of CuS in mol L^{-1}.

If S is the solubility of CuS in mol L^{-1} then

$$\underset{}{CuS} \rightleftharpoons \underset{S}{Cu^{2+}} + \underset{S}{S^{2-}}$$

$$K_{sp} = [Cu^{2+}][S^{2-}] = S \times S = S^2$$

∴ $S^2 = 6 \times 10^{-16}$

or $S = \sqrt{6 \times 10^{-16}}$ $= \mathbf{2.45 \times 10^{-8}\ mol\ L^{-1}}$

Maximum molarity of CuS in aqueous solution = $\mathbf{2.45 \times 10^{-8}\ mol\ L^{-1}}$

Q. 28. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN.

Ans. Mass of solution = 6.5 g + 450 g = 456.5 g

$$\text{Mass \% of aspirin} = \frac{\text{Mass of aspirin}}{\text{Mass of solution}} \times 100 = \frac{6.5}{456.5} \times 100 = \mathbf{1.424\%}$$

Q. 29. Nalorphene ($C_{19}H_{21}NO_3$) similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5 × 10^{-3} m aqueous solution required for the above dose.

Ans. 1.5 × 10^{-3} m solution means that 1.5 × 10^{-3} mole of nalorphene is dissolved in 1 kg of water.

Molar mass of $C_{19}H_{21}NO_3$ = 19 × 12 + 21 + 14 + 48 = 311 g mol^{-1}

1.5 × 10^{-3} mole of $C_{19}H_{21}NO_3$ = 1.5 × 10^{-3} × 311 g = 0.467 g

∴ Mass of solution = 1000 g + 0.467 g = 1000.467 g

∴ Thus, for 0.467 g of nalorphene, solution required = 1000.467 g

Hence, for 1.5 × 10^{-3} g of nalorphene, solution required $= \dfrac{1000.467\text{g}}{0.467} \times 1.5 \times 10^{-3}$ g $= \mathbf{3.21\ g}$

Q. 30. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 mol L^{-1} solution in methanol.

Ans.
$$\text{Molarity} = \frac{\text{Mass of solute/Molar mass}}{\text{Volume of solution (in litres)}}$$

Mass of benzoic acid = Molarity × Volume of solution × Molar mass

Volume of solution $= 250 \text{ mL} = \dfrac{250}{1000} \text{ L} = 0.25$ L

Molar mass of benzoic acid, C_6H_5COOH = 7 × 12 + 6 × 1 + 2 × 16 = 122 g mol^{-1}

Mass of benzoic acid = 0.15 mol L^{-1} × 0.25 L × 122 g mol^{-1} = **4.575 g**

Q. 31. The depression in freezing point of water observed for the same amount of acetic acid, tri-chloroacetic acid and trifluoroacetic acid increases in the order as given. Explain briefly.

Ans. The depression in freezing points are in the order:

$$CH_3COOH < Cl_3CCOOH < F_3CCOOH$$

Fluorine, being the most electronegative, has the highest negative inductive effect. As a result of this, trifluoroacetic acid is the strongest acid while acetic acid is the weakest acid. Hence, trifluoroacetic acid ionises to the largest extent while acetic acid ionises to the minimum extent to give ions in their solutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is the maximum for the trifluoroacetic acid and minimum for acetic acid.

Q. 32. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water; $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol^{-1}.

Ans. Number of moles of $CH_3CH_2CHClCOOH = \dfrac{10\text{ g}}{122.5\text{ g mol}^{-1}} = 8.16 \times 10^{-2}$ mol

$$\text{Molality of the solution} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (in grams)}} \times 1000$$

$$= \frac{8.16 \times 10^{-2}}{250} \times 1000 = 0.3264 \text{ mol kg}^{-1}$$

If α is the degree of dissociation of $CH_3CH_2CHClCOOH$, then

$$\begin{array}{llll} & CH_3CH_2CHClCOOH & \rightleftharpoons \; CH_3CH_2CHClCOO^- & + \; H^+ \\ \text{Initial conc.} & C \text{ mol L}^{-1} & 0 & 0 \\ \text{At equilibrium} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{C\alpha \,.\, C\alpha}{C(1-\alpha)} = C\alpha^2 \qquad [\text{Considering } (1-\alpha) = 1 \text{ for dilute solution}]$$

or $$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

Calculation of van't Hoff factor:

$$\begin{array}{llll} & CH_3CH_2CHClCOOH & \rightleftharpoons \; CH_3CH_2CHClCOO^- & + \; H^+ \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{Moles at equilibrium} & 1-\alpha & \alpha & \alpha \end{array}$$

Total number of mole of particles after dissociation = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{\text{Total number of moles of particles after dissociation}}{\text{Number of particles before dissociation}}$$

or, $$i = \frac{1+\alpha}{1} = 1 + \alpha = 1 + 0.065 = 1.065$$

$\therefore$ $$\Delta T_f = i\,K_f\,m$$

$$= (1.065)\,(1.86)\,(0.3264) = \mathbf{0.65\ K}$$

Q. 33. 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

OR

When 19.5 g of F—CH$_2$—COOH (Molar mass = 78 g mol^{-1}) is dissolved in 500 g of water, the depression in freezing point is observed to be 1°C. Calculate the degree of dissociation of F—CH$_2$—COOH. (Given: K_f of water = 1.86 K kg mol^{-1}) ***[CBSE 2020 (56/3/1)]***

Ans. Calculation of van't Hoff factor (*i*):

Number of moles of fluoroacetic acid = $\dfrac{19.5\text{ g}}{78\text{ g mol}^{-1}} = 0.25$ mol

$$\text{Molality, } m = \frac{\text{Number of moles of fluoroacetic acid}}{\text{Mass of water in kg}} = \frac{0.25 \text{ mol}}{0.5 \text{ kg}}$$

$$= 0.5 \text{ mol kg}^{-1}$$

$$\Delta T_f = i \times K_f \times m \quad \Rightarrow \quad i = \frac{\Delta T_f}{K_f \times m}$$

Here, $\Delta T_f = 1.0$ K; $K_f = 1.86$ K kg mol^{-1}; $m = 0.5$ mol kg^{-1}

$$i = \frac{1.0 \text{ K}}{1.86 \text{ K kg mol}^{-1} \times 0.5 \text{ mol kg}^{-1}} = \mathbf{1.0753}$$

Calculation of dissociation constant, K_a:

$$FCH_2COOH \rightleftharpoons FCH_2COO^- + H^+$$

Initial conc.	0.5	0	0
At equilibrium	$0.5\,(1-\alpha)$	$0.5\,\alpha$	$0.5\,\alpha$

$$\text{Total} = 0.5\,(1+\alpha)$$

$$i = \frac{0.5(1+\alpha)}{0.5} = 1+\alpha \quad \text{or} \quad \alpha = i - 1 = 1.0753 - 1 = 0.0753$$

$$K_a = \frac{0.5\alpha + 0.5\alpha}{0.5\,(1-\alpha)} = \frac{0.5\,\alpha^2}{1-\alpha} = \frac{0.5 \times (0.0753)^2}{1 - 0.0753}$$

$$K_a = \mathbf{3.07 \times 10^{-3}}$$

Q. 34. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.

Ans. $p_A^0 = = 17.535$ mm Hg; $W_B = 25$ g; $W_A = 450$ g

$M_B = 180$ g mol^{-1}; $M_A = 18$ g mol^{-1}

Substituting the values in the expression

$$\frac{p_A^o - p_s}{p_A^o} = \frac{W_B \times M_A}{M_B \times W_A}, \text{ we get}$$

$$\frac{17.535 - p_s}{17.535} = \frac{25 \times 18}{180 \times 450} \quad \text{or} \quad 1 - \frac{p_s}{17.535} = \frac{1}{180}$$

$$\frac{179}{180} = \frac{p_s}{17.535} \quad \text{or} \quad p_s = \mathbf{17.44 \text{ mm Hg}}$$

Q. 35. Henry's law constant for the molality of methane in benzene at 298 K is 4.27 × 10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Ans. Here, $K_H = 4.27 \times 10^5$ mm Hg,

$p = 760$ mm Hg

According to Henry's law, $p = K_H \times x_{CH_4}$

$$\therefore \quad x_{CH_4} = \frac{p}{K_H} = \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{ mm Hg}} = 1.78 \times 10^{-3}$$

Mole fraction of methane in benzene, $x_{CH_4} = \mathbf{1.78 \times 10^{-3}}$

Q. 36. 100 g of liquid *A* (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid *B* (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid *B* was found to be 500 torr. Calculate the vapour pressure of pure liquid *A* and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.

Ans. $$n_A = \frac{100 \text{ g}}{140 \text{ g mol}^{-1}} = \frac{5}{7} \text{ mol} \quad \text{and } n_B = \frac{1000 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{50}{9} \text{ mol}$$

$$x_A = \frac{n_A}{n_A + n_B}$$

$$\therefore \qquad x_A = \frac{5/7}{5/7 + 50/9} = \frac{5/7}{395/63} = \frac{5}{7} \times \frac{63}{395} = \frac{45}{395} = 0.114$$

$$\therefore \qquad x_B = 1 - 0.114 = 0.886$$

Also, given $P_B^0 = 500$ torr

According to Raoult's law,

$$p_A = x_A p_A^{\circ} = 0.114 \times p_A^{\circ} \qquad \text{...}(i)$$

$$p_B = x_B p_B^{\circ} = 0.886 \times 500 = 443 \text{ torr}$$

$$P = p_A + p_B$$

$$475 = 0.114 \; p_A^{\circ} + 443$$

or $$p_A^{\circ} = \frac{475 - 443}{0.114} = \mathbf{280.7 \text{ torr}}$$

Substituting this value in equation (i), we get

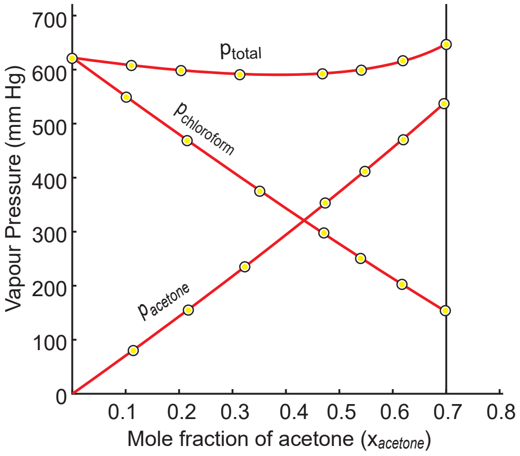
$$P_A = 280.7 \times 0.114 = \mathbf{32 \text{ torr}}$$

Q. 37. Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total}, $p_{\text{chloroform}}$ and p_{acetone} as a function of x_{acetone}, the experimental data observed for different compositions of mixture is:

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
p_{acetone} / mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}$ / mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

Ans.



x_{acetone}	0	0.118	0.234	0.360	0.508	0.582	0.645	0.721
p_{acetone} / mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}$ / mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
p_{total}	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8

Since the plot for p_{total} dips downwards, the solution shows negative deviation from the ideal behaviour.

Q. 38. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressures of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in the vapour phase if 80 g of benzene is mixed with 100 g of toluene.

Ans. Molar mass of benzene (C_6H_6) = 78 g mol^{-1}

Molar mass of toluene (C_7H_8) = 92 g mol^{-1}

$$n_{C_6H_6} = \frac{80 \text{ g}}{78 \text{ g mol}^{-1}} = 1.026 \text{ mol}$$

$$n_{C_7H_8} = \frac{100}{92 \text{ g mol}^{-1}} = 1.087 \text{ mol}$$

$$\therefore \quad x_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{C_7H_8}} = \frac{1.026}{1.026 + 1.087} = \frac{1.026}{2.113} = 0.486$$

$$x_{C_7H_8} = 1 - 0.486 = 0.514$$

$$p^o_{C_6H_6} = 50.71 \text{ mm Hg}, p^o_{C_7H_8} = 32.06 \text{ mm Hg}$$

Applying Raoult's law

$$p_{C_6H_6} = x_{C_6H_6} \times p^o_{C_6H_6} = 0.486 \times 50.71 \text{ mm Hg} = 24.65 \text{ mm Hg}$$

$$p_{C_7H_8} = x_{C_7H_8} \times p^o_{C_7H_8} = 0.514 \times 32.06 \text{ mm Hg} = 16.48 \text{ mm Hg}$$

$\therefore$ Mole fraction of benzene in the vapour phase $= \dfrac{p_{C_6H_6}}{p_{C_6H_6} + p_{C_7H_8}}$

$$= \frac{24.65}{24.65 + 16.48} = \frac{24.65}{41.13} = \mathbf{0.60}$$

Q. 39. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

Ans. Partial pressure of oxygen, $p_{O_2} = \dfrac{20}{100} \times 10 \text{ atm} = 2 \text{ atm} = 2 \times 760 \text{ mm Hg} = 1520 \text{ mm Hg}$

Partial pressure of nitrogen, $p_{N_2} = \dfrac{79}{100} \times 10 \text{ atm} = 7.9 \text{ atm} = 7.9 \times 760 \text{ mm Hg} = 6004 \text{ mm Hg}$

$K_H(O_2) = 3.30 \times 10^7$ mm, $K_H(N_2) = 6.51 \times 10^7$ mm

Applying Henry's law, $p_{O_2} = K_H \times x_{O_2}$

or $$x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm}}{3.30 \times 10^7 \text{ mm}} = \mathbf{4.61 \times 10^{-5}}$$

$$p_{N_2} = K_H \times x_{N_2}$$

or $$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm}}{6.51 \times 10^7 \text{ mm}} = \mathbf{9.22 \times 10^{-5}}$$

Q. 40. Determine the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C.

Ans. $$\pi = \frac{i \times W_B \times R \times T}{M_B \times V} \quad \text{or} \quad W_B = \frac{\pi \times M_B \times V}{i \times R \times T}$$

Molar mass of $CaCl_2$, $M_B = 40 + 2 \times 35.5 = 111 \text{ g mol}^{-1}$

$$\text{Mass of } CaCl_2, W_B = \frac{0.75 \text{ atm} \times 111 \text{ g mol}^{-1} \times 2.5 \text{ L}}{2.47 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$= \mathbf{3.42 \text{ g}}$$

Q. 41. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25°C, assuming that it is completely dissociated. ***[CBSE Delhi 2013, 2019 (56/5/2)]***

Ans. K_2SO_4 dissolved = 25 mg = 0.025 g

Volume of solution = 2 L, T = 25°C = 298 K

Molar mass of $K_2SO_4 = 2 \times 39 + 32 + 4 \times 16 = 174 \text{ g mol}^{-1}$

Since K_2SO_4 dissociates completely as $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

$$i = \frac{\text{Number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}} = \frac{3}{1} = 3$$

Applying van't Hoff equation,

$$\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$$

$$= \frac{3 \times 0.025\ \text{g} \times 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{174\ \text{g mol}^{-1} \times 2\ \text{L}} = \mathbf{5.27 \times 10^{-3}\ atm}$$

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. A solution of amalgam of mercury with sodium contains

	Solute	Solvent		Solute	Solvent
(*a*)	Solid	Solid	(*b*)	Solid	Liquid
(*c*)	Liquid	Solid	(*d*)	Liquid	Liquid

2. One kilogram of sea water sample contains 6 mg of dissolved O_2. The concentration of O_2 in ppm in the sample is

(*a*) 0.06 (b) 60 (*c*) 6 (d) 0.6

3. Mole fraction of the solute in a 1.0 molal aqueous solution is:

(*a*) 0.1770 (*b*) 0.0177 (*c*) 0.0344 (*d*) 1.7700

4. At what concentration does the solution of ethylene glycol used as an antifreeze?

(*a*) 35% volume by volume (*b*) 35% mass by volume

(*c*) 35% mass by mass (*d*) 35 ppm

5. On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid? [*NCERT Exemplar*]

(*a*) Sugar crystals in cold water. (*b*) Sugar crystals in hot water.

(*c*) Powdered sugar in cold water. (*d*) Powdered sugar in hot water.

6. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is __________. [*NCERT Exemplar*]

(*a*) less than the rate of crystallisation (*b*) greater than the rate of crystallisation

(*c*) equal to the rate of crystallisation (*d*) zero

7. Which of the following factor(s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent? [*NCERT Exemplar*]

(*i*) nature and solute (*ii*) temperature (*iii*) pressure

(*a*) (*i*) and (*iii*) at constant *T* (*b*) (*i*) and (*ii*) at constant *P*

(*c*) (*ii*) and (*iii*) only (*d*) (*iii*) only

8. The value of Henry's constant K_H is _____________. [*NCERT Exemplar*]

(*a*) greater for gases with higher solubility. (*b*) greater for gases with lower solubility.

(*c*) constant for all gases. (*d*) not related to the solubility of gases.

9. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to ____________. [*NCERT Exemplar*]

(*a*) low temperature (*b*) low atmospheric pressure

(*c*) high atmospheric pressure (*d*) both low temperature and high atmospheric pressure

10. A solution of chloroform in diethylether:

(*a*) obeys Raoult's law (*b*) shows a positive deviation from Raoult's law

(*c*) shows a negative deviation from Raoult's law (*d*) behaves like a near ideal solution

11. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law? [*NCERT Exemplar*]

(*a*) Methanol and acetone. (*b*) Chloroform and acetone.

(*c*) Nitric acid and water. (*d*) Phenol and aniline.

12. Intermolecular forces between two benzene molecules are nearly of same strength as those between two toluene molecules. For a mixture of benzene and toluene, which of the following are not true? [*NCERT Exemplar*]

(*a*) $\Delta_{mix}H$ = zero (*b*) $\Delta_{mix}V$ = zero

(*c*) These will form minimum boiling azeotrope (*d*) These will not form ideal solution

13. The system that forms maximum boiling azeotropes is:

(*a*) ethyl alcohol-water (*b*) benzene-toluene

(*c*) acetone-chloroform (*d*) carbon disulphide-acetone

14. At a given temperature, osmotic pressure of a concentrated solution of a substance ____________. [*NCERT Exemplar*]

(*a*) is higher than that of a dilute solution.

(*b*) is lower than that of a dilute solution.

(*c*) is same as that of a dilute solution.

(*d*) cannot be compared with osmotic pressure of dilute solution.

15. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because ____________. [*NCERT Exemplar*]

(*a*) it gains water due to osmosis. (*b*) it loses water due to reverse osmosis.

(*c*) it gains water due to reverse osmosis. (*d*) it loses water due to osmosis.

16. If we place the blood cells in a solution containing less than 0.9% (m/V) sodium chloride. They would swell. This is because

(*a*) the solution is hypotonic (*b*) the solution is isotonic

(*c*) the solution is hypertonic (*d*) none of these

17. Which of the following colligative property is used to calculate the molar mass of biomolecules?

(*a*) Relative lowering of vapour pressure (*b*) Elevation in boiling point

(*c*) Depression in freezing point (*d*) Osmotic pressure

18. Which of the following statements is false? [*NCERT Exemplar*]

(*a*) Units of atmospheric pressure and osmotic pressure are the same.

(*b*) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.

(*c*) The value of molal depression constant depends on nature of solvent.

(*d*) Relative lowering of vapour pressure, is a dimensionless quantity.

19. The values of Van't Hoff factors for KCl, NaCl and K_2SO_4, respectively, are ____________. [*NCERT Exemplar*]

(*a*) 2, 2 and 2 (*b*) 2, 2 and 3 (*c*) 1, 1 and 2 (*d*) 1, 1 and 1

20. The value of van't Hoff factor for ethanoic acid in benzene is

(*a*) 1.0 (*b*) 1.5 (*c*) 0.5 (*d*) 2

21. Which of the following aqueous solutions should have the highest boiling point? [*NCERT Exemplar*]

(*a*) 1.0 M NaOH (*b*) 1.0 M Na_2SO_4 (*c*) 1.0 M NH_4NO_3 (*d*) 1.0 M KNO_3

22. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is ____________. [*NCERT Exemplar*]

(*a*) the same (*b*) about twice (*c*) about three times (*d*) about six times

23. Molal elevation constant is calculated from the enthalpy of vapourisation ($\Delta_{vap}H$) and boiling point of the pure solvent (T_0) using the relation:

(*a*) $K_b = \dfrac{M_A R T_0^2}{1000\,\Delta_{vap}H}$ (*b*) $K_b = \dfrac{1000\,R T_0^2}{M_A \Delta_{vap}H}$

(*c*) $K_b = \dfrac{\Delta_{vap}H}{1000\,M_A R T_0^2}$ (*d*) $K_b = \dfrac{1000\,M_A T_0^2}{\Delta_{vap}HR}$

24. Which of the following statements is false? [*NCERT Exemplar*]

(*a*) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.

(*b*) The osmotic pressure of a solution is given by the equation $\pi = CRT$ (where C is the molarity of the solution).

(*c*) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is

$$BaCl_2 > KCl > CH_3COOH > \text{sucrose.}$$

(*d*) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.

Answers

1. (*c*) **2.** (*c*) **3.** (*b*) **4.** (*a*) **5.** (*d*) **6.** (*c*) **7.** (*a*), (*b*) **8.** (*b*) **9.** (*b*) **10.** (*c*)
11. (*a*) **12.** (*c*), (*d*) **13.** (*c*) **14.** (*a*) **15.** (*d*) **16.** (*a*) **17.** (*d*) **18.** (*b*) **19.** (*b*) **20.** (*c*)
21. (*b*) **22.** (*c*) **23.** (*d*) **24.** (*a*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement.

1. Assertion (*A*) : Molarity of a solution in liquid state changes with temperature.
Reason (*R*) : The volume of a solution changes with change in temperature.

2. Assertion (*A*) : The solubility of a gas in a liquid increases with increase of pressure.
Reason (*R*) : The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

3. Assertion (*A*) : Raoult's law is a special case of Henry's law.
Reason (*R*) : Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

4. Assertion (*A*) : Non-ideal solutions always form azeotropes.
Reason (*R*) : Boiling point of an azeotrope may be higher or lower than boiling points of both components.

5. Assertion (*A*) : If more volatile liquid is added to another liquid, vapour pressure of solution will be greater than that of pure solvent.
Reason (*R*) : Vapour pressure of solution is entirely due to solvent molecules.

6. Assertion (*A*) : The vapour pressure of a liquid decreases if some non-volatile solute is dissolved in it.
Reason (*R*) : The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

7. Assertion (*A*) : The boiling point of pure solvent is always higher than the boiling point of solution.
Reason (*R*) : The vapour pressure of the solvent decreases in the presence of non-volatile solute.

8. Assertion (*A*) : When NaCl is added to water a depression in freezing point is observed.
Reason (*R*) : The lowering of vapour pressure of a solution causes depression in the freezing point.

9. Assertion (*A*) : When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.

Reason (*R*) : Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

10. Assertion (*A*) : Lowering of vapour pressure is directly proportional to osmotic pressure of the solution.

Reason (*R*) : Osmotic pressure is a colligative property.

11. Assertion (*A*) : Molecular mass of polymers cannot be calculated using boiling point or freezing point method.

Reason (*R*) : Polymers solutions do not possess a constant boiling point or freezing point.

12. Assertion (*A*) : The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.

Reason (*R*) : Elevation of boiling point is directly proportional to the number of species present in the solution.

Answers

1. (*a*) **2.** (*a*) **3.** (*b*) **4.** (*d*) **5.** (*c*) **6.** (*b*) **7.** (*d*) **8.** (*a*) **9.** (*c*) **10.** (*b*)
11. (*c*) **12.** (*a*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The spontaneous flow of the solvent through a semipermeable membrane from a pure solvent to a solution or from a dilute solution to a concentrated solution is called osmosis. The phenomenon of osmosis can be demonstrated by taking two eggs of the same size. In an egg, the membrane below the shell and around the egg material is semi-permeable. The outer hard shell can be removed by putting the egg in dilute hydrochloric acid. After removing the hard shell, one egg is placed in distilled water and the other in a saturated salt solution. After some time, the egg placed in distilled water swells-up while the egg placed in salt solution shrinks.

The external pressure applied to stop the osmosis is termed as osmotic pressure (a Colligative property). Reverse osmosis takes place when the applied external pressure becomes larger than the osmotic pressure.

1. What do you expect to happen when red blood corpuscles (RBC's) are placed in 0.5% NaCl solution?

Ans. RBC's are isotonic with 0.9% NaCl solution, so they will swell and may even burst when placed in 0.5% NaCl solution.

2. Which one of the following will have higher osmotic pressure in 1 M KCl or 1 M urea solution?

Ans. 1 M KCl will have higher osmotic pressure because its dissociates to give K^+ and Cl^- ions while urea does not dissociate into ions in the solution.

3. Name one SPM which can be used in the process of reverse osmosis.

Ans. Cellulose acetate placed on a suitable support.

4. What are isotonic solutions?

Ans. Solutions having equal osmotic pressure are called isotonic solutions.

5. Write van't Hoff equation for dilute solution.

Ans. $\pi V = nRT$,

Where, π = Osmotic pressure, n = Number of moles, V = Volume of solution in litre, R = Gas constant, T = Temperature

PASSAGE–2

A solution which obeys Raoult's law strictly is called an ideal solution, while a solution which shows deviations from Raoult's law is called a non-ideal solution or real solution. Suppose the molecules of the solvent and solute are represented by A and B respectively, and let γ_{AB}, γ_{AA} and γ_{BB} are the attractive forces between A—B, A—A and B—B respectively. An ideal solution of the components A and B is defined as the solution in which the intermolecular interactions between the components A—B are of the same magnitude as the intermolecular interactions found in the pure components A—A and B—B. Similarly,a non- ideal solution of the components A and B is defined as the solution in which the intermolecular interactions between the components A—B are of the different magnitude as the intermolecular interactions found in the pure components A—A and B—B.

1. What type of liquids form the ideal solution?

Ans. Liquids that have similar structures and polarities form ideal solutions.

2. Give one example of an ideal solution.

Ans. Benzene + Toluene

3. Write two characteristics of non-ideal solution.

Ans. $\Delta H_{\text{mix}} \neq 0$, $\Delta V_{\text{mix}} \neq 0$.

4. On mixing liquid A and liquid B, volume of the resulting solution decreases, what type of deviation from Raoult's law is shown by?

Ans. The solution will show negative deviation from Raoult's law.

5. Which type of deviation will be shown by the solution, if $\gamma_{AB} < \gamma_{AA}$.

Ans. Solution will show positive deviation.

Very Short Answer Questions [1 mark]

Q. 1. Define mole fraction. [*CBSE Delhi 2012*]

Ans. Mole fraction of a component in a solution may be defined as the ratio of moles of that component to the total number of moles of all the components present in the solution.

Q. 2. How does the molarity of a solution change with temperature?

Ans. Molarity decreases with increase in temperature as volume of solution increases with increase in temperature.

Q. 3. When and why is molality preferred over molarity in handling solutions in chemistry?

Ans. Molality is preferred in studies that involves changes in temperature as in some of the colligative properties of solutions. This is because molality depends on masses of solvent which do not change with temperature.

Q. 4. The dissolution of ammonium chloride in water is an endothermic process but still it dissolves in water readily. Why? [*HOTS*]

Ans. This is because of entropy change. In this case, ΔS is +ve.

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

The ions that were held together in crystalline solid are free and moving in all possible directions. Its entropy has increased and this makes $T\Delta S > \Delta H$, *i.e.*, $\Delta G = -$ve.

Q. 5. Why are the aquatic species more comfortable in cold water in comparison to warm water? [*CBSE 2019 (56/2/3), (56/4/1)*]

Ans. At a given pressure, the solubility of oxygen in water increases with decrease in temperature. Presence of more oxygen at lower temperature makes the aquatic species more comfortable in cold water.

Q. 6. What is the similarity between Raoult's law and Henry's law? [*CBSE Delhi 2014*]

Ans. The similarity between Raoult's law and Henry's law is that in both the laws, the partial vapour pressure of the volatile component or gas is directly proportional to its mole fraction in the solution.

Q. 7. What type of liquids form ideal solutions?

Ans. Liquids that have similar structures and polarities form ideal solutions.

Q. 8. Write two characteristics of non-ideal solution. *[CBSE 2019 (56/5/2)]*

Ans. $\Delta_{mix}H \neq 0$ and $\Delta_{mix}V \neq 0$

Q. 9. Under what condition do non-ideal solutions show negative deviations?

Ans. When the new forces of interaction between the components are stronger than those in the pure components, then non-ideal solutions show negative deviations.

Q. 10. What are maximum boiling azeotropes? Give one example.

Ans. Maximum boiling azeotropes are those which boil at higher temperature than boiling point of each component in pure state, *e.g.*, 68% nitric acid and 32% water by mass.

Q. 11. Why is the vapour pressure of a solution of glucose in water lower than that of water? *[NCERT Exemplar]*

Ans. This is due to decrease in the escaping tendency of the water molecules from the surface of solution as some of the surface area is occupied by non-volatile solute, glucose particles.

Q. 12. Define molal depression constant or cryoscopic constant.

Ans. It is the depression in freezing point when 1 mole of non-volatile solute is dissolved in 1000 g of solvent.

Q. 13. What do you understand by the term that K_f for water is 1.86 K kg mol^{-1}?

Ans. It means that the freezing point of water is lowered by 1.86 K when 1 mole of non-volatile solute is dissolved in 1 kg of water.

Q. 14. What is an antifreeze?

Ans. A substance such as ethylene glycol which is added to water to lower its freezing point is called an antifreeze. It is named so as it delays freezing.

Q. 15. What is de-icing agent? How does it work?

Ans. Common salt is called de-icing agent as it lowers the freezing point of water to such an extent that it does not freeze to form ice. Thus, it is used to clear snow from roads.

Q. 16. Why is glycol and water mixture used in car radiators in cold countries? *[HOTS]*

Ans. Ethylene glycol lowers the freezing point of water. Due to this, coolant in radiators will not freeze. Otherwise, radiator will burst due to freezing of coolant (water).

Q. 17. What are isotonic solutions? *[CBSE Delhi 2012, 2014]*

Ans. The solutions of the same osmotic pressure at a given temperature are called isotonic solutions.

Q. 18. How is it that measurement of osmotic pressures is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions? *[CBSE (AI) 2009]*

Ans. The osmotic pressure method has the advantage over elevation in boiling point or depression in freezing point for determining molar masses of macromolecules because

(*i*) Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.

(*ii*) Compared to other colligative properties, its magnitude is large even for very dilute solutions.

Q. 19. What is the van't Hoff factor for a compound which undergo dimerisation in an organic solvent?

Ans.

$$2X \longrightarrow X_2$$

$$i = \frac{\text{Number of moles of particles after association}}{\text{Number of moles of particles before association}} = \frac{1}{2}$$

Q. 20. What would be the value of van't Hoff factor for a dilute solution of K_2SO_4 in water?

Ans. In dilute solution, $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

$$\text{van't Hoff factor, } i = \frac{\text{Number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}} = \frac{3}{1} = 3.$$

Q. 21. Out of two 0.1 molal aqueous solutions of glucose and of potassium chloride, which one will have a higher boiling point and why? *[CBSE (F) 2013, 2019 (56/3/2)]*

Ans. 0.1 m KCl solution will have higher boiling point as KCl dissociates in the solution.

Q. 22. What will happen to freezing point of a potassium iodide aqueous solution when mercuric iodide is added to solution? **[*HOTS*]**

Ans. $$HgI_2 + 2KI \longrightarrow K_2HgI_4$$

Mercuric iodide forms a complex with potassium iodide, therefore, the number of solute particles (KI) in the solution decreases resulting in the decrease in the value of ΔT_f, *i.e.*, depression in the freezing point. As a result, the freezing point ($T_f = T_f^o + \Delta T_f$) of the solution will increase.

Q. 23. Why is osmotic pressure of 1 M KCl higher than 1 M urea solution?

Ans. This is because KCl dissociates to give K^+ and Cl^- ions while urea being a molecular solid does not dissociate into ions in the solution.

Short Answer Questions–I [2 marks]

Q. 1. Explain the solubility rule "like dissolves like" in terms of intermolecular forces that exist in solutions.

Ans. A substance (solute) dissolves in a solvent if the intermolecular interactions are similar in both the components; for example, polar solutes dissolve in polar solvents and non polar solutes in non polar solvents and thus we can say "like dissolves like".

Q. 2. State Henry's law. Write its one application. What is the effect of temperature on solubility of gases in liquid? **[*CBSE (F) 2016*]**

Ans. It states that the partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$$p \propto x \quad \text{or} \quad p = K_H x \qquad \text{where } K_H \text{ is the Henry's constant.}$$

Application of Henry's law:

To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

Effect of temperature on solubility:

As dissolution is an exothermic process, therefore, according to Le Chatelier's principle solubility should decrease with rise in temperature.

Q. 3. Henry's law constant (K_H) for the solution of methane in benzene at 298 K is 4.27 ×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg. **[*CBSE (F) 2013*]**

Ans. Here, $K_H = 4.27 \times 10^5$ mm Hg, $p = 760$ mm Hg

According to Henry's law, $p = \mathrm{K_H} x_{\mathrm{CH_4}}$

$$\therefore \qquad x_{\mathrm{CH_4}} = \frac{p}{\mathrm{K_H}} = \frac{760 \text{ mm Hg}}{4.27 \times 10^5 \text{mm Hg}} = 1.78 \times 10^{-3}$$

Mole fraction of methane in benzene, $x_{\mathrm{CH_4}}$ **= 1.78 × 10^{-3}**.

Q. 4. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law? **[*CBSE Delhi 2014; 2020 (56/5/1)*]**

Ans. It states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction. According to Raoult's law, for a volatile component, A of the solution $P_A \propto x_A$ or $P_A = P_A^0 x_A$, where P_A^0 is the vapour pressure of pure component A.

If one of the component is so volatile that it exist as a gas then according to Henry's law $p = K_H x$, where K_H is the Henry law constant *i.e.*, the partial vapour pressure of the volatile component (gas) is directly proportional to its mole fraction in the solution.

Thus the similarity between Raoult's law and Henry's law is that in both the laws, the partial vapour pressure of the volatile component or gas is directly proportional to its mole fraction in the solution.

Q. 5. State the following:

(*i*) Raoult's law in its general form in reference to solutions.

(*ii*) Henry's law about partial pressure of a gas in a mixture. **[*CBSE (AI) 2011*]**

Ans. (*i*) **Raoult's law:** It states that for any solution, the partial pressure of each volatile component in the solution is directly proportional to its mole fraction.

(*ii*) **Henry's law:** It states that the partial pressure of a gas in vapour phase (P) is proportional to its mole fraction (x) in the solution.

Q. 6. Define an ideal solution and write one of its characteristics. **[*CBSE Delhi 2014*]**

Ans. A solution which obeys Raoult's law over the entire range of concentration is called ideal solution. The important characteristics of an ideal solution are

(*i*) The enthalpy of mixing of pure components to form the solution is zero *i.e.*, $\Delta_{\text{mix}}H = 0$

(*ii*) The volume of mixing is zero *i.e.*, $\Delta_{\text{mix}}V = 0$

Q. 7. State Raoult's law for the solution containing volatile components. Write two differences between an ideal solution and a non-ideal solution. **[*CBSE Panchkula 2015*]**

Ans. Raoult's law states that for a solution of volatile liquids the partial vapour pressure of each component is directly proportional to its mole fraction.

Differences between Ideal and non-Ideal solutions

S.No.	Ideal solution	Non-Ideal solution
(*i*)	Obeys Raoult's law over entire range of concentration *i.e.*, $P_A = P^o_A x_A$; $P_B = P^o_B x_B$	Does not obey Raoult's law over entire range of concentration, *i.e.*, $P_A \neq P^o_A x_A$; $P_B \neq P^o_B x_B$
(*ii*)	$\Delta_{\text{mix}}H = 0$; $\Delta_{\text{mix}}V = 0$	$\Delta_{\text{mix}}H \neq 0$; $\Delta_{\text{mix}}V \neq 0$
(*iii*)	Does not form azeotrope.	Forms azeotrope.

(*Any two*)

Q. 8. Write two differences between a solution showing positive deviation and a solution showing negative deviation from Raoult's law. **[*CBSE East 2016*]**

Ans.

Solutions showing positive deviation from Raoult's law	Solution showing negative deviation from Raoult's law
(*i*) $P_A > P^o_A x_A$ and $P_B > P^o_B x_B$	(*i*) $P_A < P^o_A x_A$ and $P_B < P^o_B x_B$
(*ii*) $\Delta_{\text{mix}}H > 0$, $\Delta_{\text{mix}}V > 0$	(*ii*) $\Delta_{\text{mix}}H < 0$, $\Delta_{\text{mix}}V < 0$
(*iii*) Form minimum boiling azeotropes.	(*iii*) Form maximum boiling azeotropes.

(*Any two*)

Q. 9. State Raoult's law for a solution containing non-volatile solute. What type of deviation from Raoult's law is shown by a solution of chloroform and acetone and why? **[*CBSE (F) 2017*]**

Ans. It states that the relative lowering of vapour pressure is equal to mole fraction of solute when solvent alone is volatile and is expressed as

$$\frac{p^o_A - p_{\text{Total}}}{p^o_A} = x_{\text{B}}$$

A solution of chloroform and acetone shows negative deviation from Raoult's law. This is because chloroform molecule is able to form H–bond with acetone molecule as shown below.

It decreases the escaping tendency of molecules of each component from the surface of solution and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law.

Q. 10. **(*i*) Why is an increase in temperature observed on mixing chloroform and acetone?** **[*CBSE 2019 (56/2/3)*]**

(*ii*) Why does sodium chloride solution freeze at a lower temperature than water? **[*CBSE (F) 2013*]**

Ans. (*i*) The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules, they start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

(*ii*) When a non-volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.

Q. 11. Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. **[*CBSE Delhi 2015*]**

Ans. Azeotropes are binary liquid mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Maximum boiling azeotrope is formed by negative deviation from Raoult's law. A mixture of 68% nitric acid and 32% water by mass is an example of maximum boiling azeotrope.

Q. 12. What type of deviation is shown by a mixture of ethanol and acetone? What type of azeotrope is formed by mixing ethanol and acetone? **[*CBSE (F) 2013*]**

Ans. A mixture of ethanol and acetone shows positive deviation and the azeotrope formed by this mixture is minimum boiling azeotrope.

Q. 13. **(*i*) Gas (*A*) is more soluble in water than Gas (*B*) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why?**

(*ii*) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? **[*CBSE Central 2016*]**

Ans. (*i*) According to Henry's law, $p = K_H x$, *i.e.*, higher the value of K_H lower is the solubility of the gas in the liquid. Therefore, Gas *B* will have higher value of K_H than gas A.

(*ii*) Negative deviation from Raoult's law.

Q. 14. Derive the relationship between relative lowering of vapour pressure and molar mass of the solute. **[*CBSE Chennai 2015*]**

Ans. From Raoult's law we have, $p = p_A + p_B$

If solute B is non-volatile, then

$$p = p_A \quad \text{or} \quad p = p_A^{\circ} x_A$$

$$p = p_A^{\circ}(1 - x_B) = p_A^{\circ} - p_A^{\circ} x_B$$

$$p_A^{\circ} x_B = p_A^{\circ} - p$$

$$\frac{p_A^{\circ} - p}{p_A^{\circ}} = x_\text{B} \quad \text{or} \quad \frac{\Delta p}{p_A^{\circ}} = \frac{n_B}{n_A + n_B}$$

For a dilute solution $n_B << n_A$, so n_B can be neglected in denominator in comparison to n_A.

$$\frac{\Delta p}{p_A^{\circ}} = \frac{n_B}{n_A} = \frac{W_B/M_B}{W_A / M_A} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$M_B = \frac{p_A^{\circ} \times W_B \times M_A}{\Delta p \times W_A}$$

Q. 15. When 1.5 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point of benzene raised from 353.23 K to 353.93 K. Calculate the molar mass of the solute.

(K_b for benzene = 2.52 K kg mol^{-1}) **[*CBSE Chennai 2015*]**

Ans. $\Delta T_b = 353.93 \text{ K} - 353.23 \text{ K} = 0.7 \text{ K}$

Substituting $W_B = 1.5$ g, $W_A = 90$ g, $\Delta T_b = 0.7$ K, $K_b = 2.52$ K kg mol^{-1} in the expression

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}, \text{ we get}$$

$$M_B = \frac{2.52 \times 1.5 \times 1000}{0.7 \times 90}$$

$$\mathbf{M_B = 60 \text{ g mol}^{-1}}$$

Q. 16. Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol^{-1}) in 250 g of water. (K_f of water = 1.86 K kg mol^{-1}) **[*CBSE Delhi 2018*]**

Ans. Here, $W_B = 60$ g, $M_B = 180$ g mol^{-1}, $W_A = 250$ g, $K_f = 1.86$ K kg mol^{-1}

Substituting these values in the expression

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}, \text{ we get}$$

$$\Delta T_f = \frac{1.86 \times 60 \times 1000}{180 \times 250} = 2.48 \text{ K}$$

Freezing point of solution, $T_f = T_f^{\circ} - \Delta T_f = 273.15 \text{ K} - 2.48 \text{ K} = \mathbf{270.67 \text{ K}}$

Q. 17. Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure. *[CBSE Delhi 2012]*

Ans. Osmotic pressure (π) is defined as the extra pressure that must be applied to the solution side in order to prevent the flow of solvent molecules into it through a semipermeable membrane.

According to van't Hoff equation

$$\pi = \frac{n_B}{V} RT$$

where π is the osmotic pressure, R is the gas constant and V is the volume of solution in litres containing n_B moles of the solute.

If W_B grams of the solute of molar mass, M_B is present in the solution, then

$$n_B = \frac{W_B}{M_B} \text{ and we can write}$$

$$\pi = \frac{W_B \times R \times T}{M_B \times V} \quad \text{or} \quad M_B = \frac{W_B \times R \times T}{\pi \times V}$$

Thus, knowing W_B, T, π and V, the molecular mass of the solute, M_B can be calculated.

Q. 18. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass. *[CBSE (AI) 2011]*

Ans. $$M_B = \frac{W_B \times R \times T}{\pi \times V} \quad \text{....}(i)$$

Here, $W_B = 8.95 \text{ mg} = 8.95 \times 10^{-3}\text{g}$, $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$T = 25°\text{C} = (25 + 273) \text{ K} = 298 \text{ K}, \pi = 0.335 \text{ torr} = \frac{0.335}{760} \text{ atm}$

$V = 35 \text{ mL} = 35 \times 10^{-3} \text{ L}$

Substituting these values in the equation (*i*), we get

$$M_B = \frac{8.95 \times 10^{-3} \text{g} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298\text{K} \times 760}{0.335 \text{ atm} \times 35 \times 10^{-3} \text{ L}} = \mathbf{14193.3 \text{ g mol}^{-1}}$$

Q. 19. Give reasons: *[CBSE 2019 (56/2/1)]*

(*i*) Cooking is faster in pressure cooker than in cooking pan.

(*ii*) Red Blood Cells (RBC) shrink when placed in saline water but swell in distilled water.

Ans. (*i*) The use of pressure cooker reduces cooking time because the weight over the lid does not allow the steam to go out. As a result, pressure inside the cooker becomes high. Higher the pressure, higher is the boiling point and faster is the cooking.

(*ii*) As the concentration of saline solution is higher than the concentration inside the cell. Thus water will move outside the cytoplasm and the cell will shrink while, distilled water is hypotonic, when RBCs are placed in distilled water, water will enter the cell through simple diffusion and lead to cell swelling.

Q. 20. (*i*) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y?

(*ii*) What happens when we place the blood cell in water (hypotonic solution)? Give reason. *[CBSE Allahabad 2015]*

Ans. (*i*)
- The solution will show negative deviation from Raoult's law.
- Temperature will rise.

(*ii*) Due to osmosis water enters into the cell and blood cell will swell.

Q. 21. Define the following terms:

(*i*) Abnormal molar mass

(*ii*) van't Hoff factor (*i*) **[*CBSE Delhi 2017*]**

Ans. (*i*) When the molar mass of a substance determined by using any of the colligative properties comes out to be different than the theoretically expected molar mass, the substance said to show abnormal molar mass.

(*ii*) van't Hoff factor (*i*) gives the extent of association or dissociation of the solute particles in the solution. It may be defined as the ratio of observed colligative property to calculated colligative property.

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

Q. 22. Will the elevation in boiling point be same if 0.1 mol of sodium chloride or 0.1 mol of sugar is dissolved in 1 L of water? Explain. **[*CBSE Sample Paper 2016*] [*HOTS*]**

Ans. No, the elevation in boiling point is not the same. NaCl, being an electrolyte, dissociates almost completely to give Na^+ and Cl^- ions whereas glucose, being non-electrolyte does not dissociate. Hence, the number of particles in 0.1 M NaCl solution is nearly double than 0.1 M glucose solution. Elevation in boiling point being a colligative property, is therefore, nearly twice for 0.1 M NaCl solution than for 0.1 M glucose solution.

Short Answer Questions–II [3 marks]

Q. 1. At 25°C the saturated vapour pressure of water is 3.165 kPa (23.75 mm Hg). Find the saturated vapour pressure of a 5% aqueous solution of urea (carbamide) at the same temperature.

(Molar mass of urea = 60.05 g mol^{-1}) **[*CBSE (F) 2012*]**

Ans. $W_B = 5$ g, $W_A = 95$ g, $M_B = 60.05$ g mol^{-1}, $M_A = 18$ g mol^{-1}, $p^o_A = 3.165$ kPa

Substituting the values in the expression

$$\frac{p^o_A - p}{p^o_A} = \frac{W_B \times M_A}{M_B \times W_A}\text{, we get}$$

$$\frac{3.165\text{ kPa} - p}{3.165\text{ kPa}} = \frac{5\text{ g} \times 18\text{ g mol}^{-1}}{60.05\text{ g mol}^{-1} \times 95\text{ g}} = 0.015$$

$$p = 3.165\text{ kPa} - 0.015 \times 3.165\text{ kPa}$$

$$p = \mathbf{3.118\text{ kPa}}$$

Q. 2. Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionisation.

(K_b for water = 0.52 K kg mol^{-1}) **[*CBSE North 2016*]**

Ans. $i = \frac{3}{1} = 3 \left(Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}\right)$

Given, $W_B = 2$ g, $W_A = 50$ g, $M_B = 142$ g mol^{-1}, $K_b = 0.52$ K kg mol^{-1}

Substituting the values in the expression, $\Delta T_b = \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A}$

$$\Delta T_b = \frac{3 \times 0.52 \times 2 \times 1000}{142 \times 50} = 0.439\text{ K}$$

So, boiling point of solution, $T_b = T_b^0 + \Delta T_b$

$= 373.15\text{ K} + 0.439\text{ K} = \mathbf{373.589\text{ K}}$

Q. 3. A solution of glucose (Molar mass = 180 g mol^{-1}) in water has a boiling point of 100.20°C. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 K kg mol^{-1} and 0.512 K kg mol^{-1} respectively. **[*CBSE (F) 2017*]**

Ans. $\Delta T_b = 100.20°C - 100°C = 0.20°C$ or 0.20 K

$\Delta T_b = K_b \, . \, m \qquad \Rightarrow \qquad m = \Delta T_b / K_b$

$$m = \frac{0.20\text{ K}}{0.512\text{ K kg mol}^{-1}} \text{ or } m = 0.39\text{ mol kg}^{-1}$$

$$\Delta T_f = K_f\, m$$

$$\Delta T_f = 1.86\text{ K kg mol}^{-1} \times 0.39\text{ mol kg}^{-1} = 0.725\text{ K}$$

$$T_f = T_f^0 - \Delta T_f$$

$$= 273.15\text{ K} - 0.725\text{ K} = \mathbf{272.425\text{ K}}$$

Q. 4. Calculate the freezing point of a solution when 3 g of $CaCl_2$ ($M = 111$ g mol^{-1}) was dissolved in 100 g of water, assuming $CaCl_2$ undergoes complete ionisation. (K_f for water = 1.86 K kg mol^{-1}) **[*CBSE East 2016*]**

Ans. Here, $W_B = 3$ g, $i = \frac{3}{1} = 3\,(CaCl_2 \rightarrow Ca^{2+} + 2Cl^-)$, $W_A = 100$ g, $K_f = 1.86$ K kg mol^{-1}, $M_B = 111$ g mol^{-1}

Substituting these values in the expression,

$$\Delta T_f = \frac{i \times K_f \times W_B \times 1000}{M_B \times W_A}\text{, we get}$$

$$\Delta T_f = \frac{3 \times 1.86 \times 3 \times 1000}{111 \times 100} = 1.508\text{ K}$$

Freezing point of solution,

$$T_f = T_f^o - \Delta T_f$$

$$= 273.15\text{ K} - 1.508\text{ K} = \mathbf{271.642\text{ K}}$$

Q. 5. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated). (Given: Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1}) **[*CBSE Delhi 2015*]**

Ans. The given quantities are

$W_B = 3.9$ g, $W_A = 49$ g, $\Delta T_f = 1.62$ K, $M_B = 122$ g mol^{-1} and $K_f = 4.9$ K kg mol^{-1}

Substituting these values in the equation,

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}\text{, we get}$$

$$M_B = \frac{4.9 \times 3.9 \times 1000}{1.62 \times 49}$$

$$M_B = 240.74\text{ g mol}^{-1}$$

Thus, observed molecular mass of benzoic acid in benzene = 240.74 g mol^{-1}

Normal molecular mass of benzoic acid = 122 g mol^{-1}

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{122\text{ g mol}^{-1}}{240.74\text{ g mol}^{-1}} = \mathbf{0.507}$$

As $i < 1$, therefore, benzoic acid will undergo association in benzene.

Q. 6. Calculate the mass of NaCl (molar mass = 58.5 g mol^{-1}) to be dissolved in 37.2 g of water to lower the freezing point by 2°C, assuming that NaCl undergoes complete dissociation. (K_f for water = 1.86 K kg mol^{-1}) **[*CBSE (F) 2015*]**

Ans. $NaCl \longrightarrow Na^+ + Cl^-,\ i = \frac{2}{1} = 2$

Substituting $K_f = 1.86$ K kg mol^{-1}, $W_A = 37.2$ g, $M_B = 58.5$ g mol^{-1}, $i = 2$, $\Delta T_f = 2$°C or 2 K in the equation,

$$W_B = \frac{\Delta T_f \times M_B \times W_A}{i \times K_f \times 1000}\text{, we get}$$

$$W_B = \frac{2 \times 58.5 \times 37.2}{2 \times 1.86 \times 1000} = \mathbf{1.17\text{ g}}$$

Q. 7. At 300 K, 30 g of glucose, $C_6H_{12}O_6$ present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of another glucose solution is 1.52 bar at the same temperature, calculate the concentration of the other solution. [*CBSE 2019 (56/4/2)*]

Ans.
$$\pi = \frac{W_B \times R \times T}{M_B \times V} = CRT$$
$$4.98 = \frac{30 \times R \times 300}{180 \times 1} = 50R \quad ...(i)$$
$$1.52 = C \times R \times 300 = 300CR \quad ...(ii)$$

Dividing equation (*ii*) by (*i*), we get
$$\frac{300CR}{50R} = \frac{1.52}{4.98} \quad \Rightarrow \quad C = \mathbf{0.051\ M}$$

Q. 8. A solution containing 1.9 g per 100 mL of KCl ($M = 74.5$ g mol^{-1}) is isotonic with a solution containing 3 g per 100 mL of urea ($M = 60$ g mol^{-1}). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature. [*CBSE 2019 (56/2/1)*]

Ans. Isotonic solutions are those solutions which have the same osmotic pressure. If the osmotic pressures are equal at the same temperature, concentrations must also be equal. So,

For non-electrolyte Urea; $\pi = CRT$

For electrolyte KCl; $\pi = i\,CRT$

Thus, $C_{\text{urea}}RT = iC_{\text{KCl}}RT$

$C_{\text{urea}} = iC_{\text{KCl}}$

$$C_{\text{urea}} = \frac{3 \times 1000}{60 \times 100} = 0.5\text{ M}$$
$$C_{\text{KCl}} = \frac{1.9 \times 1000}{74.5 \times 100} = 0.25\text{ M}$$

So, $0.5 = i \times 0.25$

$i = 2.0$

Now,
$$\begin{array}{lcc} KCl \longrightarrow & K^+ & + \ Cl^- \\ 0.25 & 0 & 0 \\ 0.25 - \alpha & \alpha & \alpha \end{array}$$

Total moles after dissociation = $0.25 - \alpha + \alpha + \alpha$

$$i = \frac{\text{Total number of moles after dissociation}}{\text{Total number of moles before dissociation}}$$
$$i = \frac{0.25 + \alpha}{0.25} \quad \Rightarrow \quad 2.0 = \frac{0.25 + \alpha}{0.25}$$

$\alpha = 0.25$ or $\alpha = \mathbf{25\%}$

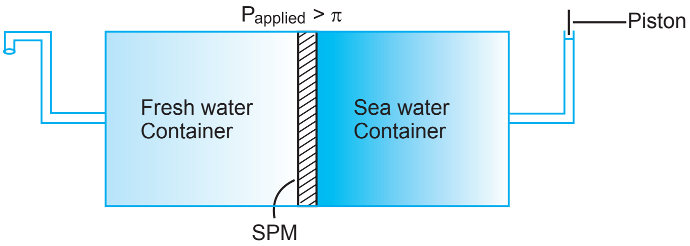
Q. 9. Given alongside is the sketch of a plant for carrying out a process.

(*i*) Name the process occurring in the given plant.

(*ii*) To which container does the net flow of solvent take place?

(*iii*) Name one SPM which can be used in this plant.

(*iv*) Give one practical use of the plant.



Ans. (*i*) Reverse osmosis.

(*ii*) Fresh water container.

(*iii*) Cellulose acetate placed on a suitable support.

(*iv*) Desalination of sea water.

Long Answer Questions [5 marks]

Q. 1. **(*i*) Define the following terms:**

(*a*) Molarity

(*b*) Molal elevation constant (K_b)

(*ii*) A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution.

[CBSE (AI) 2014]

Ans. (*i*) (*a*) Molarity may be defined as number of moles of solute dissolved in one litre of solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$$

(*b*) Molal elevation constant may be defined as the elevation in boiling point when one mole of solute is dissolved in 1000 grams of the solvent.

(*ii*) Osmotic pressure, $\pi = \dfrac{W_B \times R \times T}{M_B \times V}$

Osmotic pressure of urea solution $= \dfrac{15 \times R \times T}{60 \times 1}$

Osmotic pressure of glucose solution $= \dfrac{W_B \times R \times T}{180 \times 1}$

As, Osmotic pressure of urea solution = Osmotic pressure of glucose solution

Therefore, $\dfrac{15 \times R \times T}{60 \times 1} = \dfrac{W_B \times R \times T}{180 \times 1}$

Mass of glucose, $W_B = \dfrac{15 \times 180}{60} = \mathbf{45\ g}$

Q. 2. **(*i*) Explain why on addition of 1 mol glucose to 1 litre water the boiling point of water increases.**

(*ii*) Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the number of moles of CO_2 in 500 ml of soda water when packed under 2.53×10^5 Pa at the same temperature. *[CBSE (AI) 2017C]*

Ans. (*i*) On addition of glucose, a non-volatile solute to water (a volatile solvent) the vapour pressure of water decreases. In order to make the solution boil, its vapour pressure must be increased by raising the temperature above the boiling point of pure water. In other words, there is an increase in the boiling point of water.

(*ii*) According to Henry's law, $p_{CO_2} = K_H \times x_{CO_2}$ or $x_{CO_2} = \dfrac{p_{CO_2}}{K_H}$

$$\therefore \quad x_{CO_2} = \frac{2.53 \times 10^5 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.51 \times 10^{-3}$$

$$\text{Mass of water} = \text{Density of water} \times \text{volume of water}$$
$$= 1 \text{ g mL}^{-1} \times 500 \text{ mL} = 500 \text{ g}$$

$$\text{Moles of water, } n = \frac{\text{Mass of water}}{\text{Molar mass}} = \frac{500 \text{ g}}{18 \text{ g mol}^{-1}} = 27.78 \text{ mol}$$

$$x_{CO_2} = \frac{n_{CO_2}}{n_{H_2O} + n_{CO_2}} = \frac{n_{CO_2}}{n_{H_2O}} \quad \text{or} \quad n_{CO_2} = x_{CO_2} \times n_{H_2O}$$

$$n_{CO_2} = 1.51 \times 10^{-3} \times 27.78 \text{ mol}$$
$$= \mathbf{0.042\ mol}$$

Q. 3. **(*i*) Define the following terms:**

(*a*) Azeotrope **(*b*) Osmotic pressure**

(*c*) Colligative properties

(*ii*) Calculate the molarity of 9.8% (w/w) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1}. (Molar mass of H_2SO_4 = 98 g mol^{-1}) **[*CBSE (F) 2014*]**

Ans. (*i*) (*a*) The binary mixtures of liquids having same composition in liquid and vapour phase and boil at a constant temperature are called azeotropes.

(*b*) The excess of pressure which must be applied to the solution side to prevent the passage of solvent into it through a semipermeable membrane is called osmotic pressure.

(*c*) The properties of solutions which depend only on the number of solute particles in the solution but independent of their nature are called colligative properties.

(*ii*) Let the mass of solution = 100 g

∴ Mass of H_2SO_4 = 9.8 g

$$\text{Number of mole of } H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar Mass}} = \frac{9.8 \text{ g}}{98 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{100 \text{ g}}{1.02 \text{ g mL}^{-1}} = \frac{100}{1.02}\text{mL}$$

$$= \frac{100}{1.02}\text{mL} \times \frac{1}{1000 \text{ mL L}^{-1}} = \frac{1}{10.2}\text{L}$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$$

$$= \frac{0.1 \text{ mol}}{\frac{1 \text{ L}}{10.2}} = \mathbf{1.02 \text{ mol L}^{-1} \text{ or } 1.02 \text{ M}}$$

Q. 4. **Discuss biological and industrial importance of osmosis.**

Ans. The process of osmosis is of great biological and industrial importance as is evident from the following examples:

(*i*) Movement of water from soil into plant roots and subsequently into upper portion of the plant occurs partly due to osmosis.

(*ii*) Preservation of meat against bacterial action by adding salt.

(*iii*) Preservation of fruits against bacterial action by adding sugar. Bacterium in canned fruit loses water through the process of osmosis, shrivels and dies.

(*iv*) Reverse osmosis is used for desalination of water.

Q. 5. **(*i*) When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).**

[K_f for CS_2 = 3.83 K kg mol^{-1}, Atomic mass of Sulphur = 32 g mol^{-1}]

(*ii*) Blood cells are isotonic with 0.9 % sodium chloride solution. What happens if we place blood cells in a solution containing

(*a*) 1.2% sodium chloride solution?

(*b*) 0.4% sodium chloride solution? **[*CBSE Delhi 2016*]**

Ans. (*i*) Here, $W_B = 2.56$ g, $W_A = 100$ g, $\Delta T_f = 0.383$ K, $K_f = 3.83$ K kg mol^{-1}

Substituting these values in the expression, we get

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

$$M_B = \frac{3.83 \times 2.56 \times 1000}{100 \times 0.383} = 256 \text{ g mol}^{-1}$$

Now, molecular mass of $S_x = x \times 32 = 256$

$$x = \frac{256}{32} = 8$$

Therefore, formula of sulphur = $\mathbf{S_8}$

(*ii*) (*a*) Water will flow out of the cell and they would shrink.

(*b*) Water will flow into the cell and they would swell.

Q. 6. (*i*) Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?

(*ii*) 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution? *[CBSE 2019 (56/5/2)]*

Ans. (*i*) Osmotic pressure is directly proportional to the concentration of the solutes. Our body fluid contains a number of solutes. On taking large amount of common salt, Na^+ and Cl^- ions enter into the body fluid thereby raising the concentration of the solutes. As a result, osmotic pressure increases which may rupture the blood cells.

(*ii*) The given quantities are

$W_B = 2$ g, $W_A = 25$ g, $\Delta T_f = 1.62$ K, $K_f = 4.9$ K kg mol^{-1}

Substituting these values in equation $M_B = \dfrac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$, we get

$$M_B = \frac{4.9 \times 2 \times 1000}{1.62 \times 25} = 241.98 \text{ g mol}^{-1}$$

Thus, observed molecular mass of benzoic acid in benzene = 241.98 g mol^{-1}

Normal molecular mass of C_6H_5COOH = 122 g mol^{-1}

$$\therefore \quad i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}} = 0.504$$

$$i = 0.504 \qquad \text{...}(i)$$

If α represents the degree of association of solute then we would have $(1 - \alpha)$ mole of benzoic acid left in unassociated form and corresponding $\frac{\alpha}{2}$ as associated moles of benzoic acid at equilibrium.

Now, consider the following equilibrium for the acid:

$$\begin{array}{ccc} 2(C_6H_5COOH) & \rightleftharpoons & (C_6H_5COOH)_2 \\ 1 \text{ mol} & & 0 \\ (1-\alpha) \text{ mol} & & \frac{\alpha}{2} \text{ mol} \end{array}$$

Thus, total number of moles of particles at equilibrium

$$= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$i = \frac{\text{Total number of moles of particles after association}}{\text{Number of moles of particles before association}}$$

$$i = \frac{1 - \frac{\alpha}{2}}{1} = 1 - \frac{\alpha}{2} \qquad \text{...}(ii)$$

From (*i*) and (*ii*), we have

$$0.504 = 1 - \frac{\alpha}{2}$$

$$\frac{\alpha}{2} = 1 - 0.504 = 0.496$$

or $\quad \alpha = 0.496 \times 2 = \mathbf{0.992}$

Therefore, degree of association of benzoic acid in benzene is **99.2%**.

Q. 7. **(*i*) Give reasons for the following:**

(*a*) At higher altitudes, people suffer from a disease called anoxia. In this disease, they become weak and cannot think clearly. **[*CBSE 2019 (56/4/1)*]**

(*b*) When mercuric iodide is added to an aqueous solution of KI, the freezing point is raised.

(*ii*) 0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1}, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the van't Hoff factor and the dissociation constant of acid.

Ans. (*i*) (*a*) At higher altitudes, partial pressure of oxygen is less than that at ground level, so that oxygen concentration becomes less in blood or tissues. Hence, people suffer from anoxia.

(*b*) Due to the formation of complex $K_2[HgI_4]$, number of particles in the solution decreases and hence the freezing point is raised.

(*ii*) Mass = Density × Volume

$\therefore$ Mass of acetic acid $= 1.06 \text{ g mL}^{-1} \times 0.6 \text{ mL} = 0.636 \text{ g}$

$$\text{Number of moles of acetic acid} = \frac{\text{Mass of acetic acid}}{\text{Molar mass}} = \frac{0.636 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0106 \text{ mol}$$

Mass of water $= 1 \text{ g mL}^{-1} \times 1000 \text{ mL} = 1000 \text{ g}$

$$\text{Molality} = \frac{\text{Number of moles of acetic acid}}{\text{Mass of water in grams}} \times 1000$$

$$= \frac{0.0106}{1000} \times 1000 = 0.0106 \text{ mol kg}^{-1}$$

$$\Delta T_f = K_f \,.\, m$$

$$= 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1}$$

$$= 0.0197 \text{ K}$$

$$\text{van't Hoff Factor } (i) = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}}$$

$$i = \mathbf{1.041} \qquad \ldots(i)$$

If α is the degree of dissociation of acetic acid, then we would have $n(1 - \alpha)$ moles of undissociated acid, $n\alpha$ moles of CH_3COO^- and $n\alpha$ moles of H^+ ions at equilibrium.

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & H^+ & + & CH_3COO^- \\ n \text{ mol} & & 0 & & 0 \\ n(1-\alpha) & & n\alpha \text{ mol} & & n\alpha \text{ mol} \end{array}$$

Thus, total moles of particles $= n - n\alpha + n\alpha + n\alpha = n(1 + \alpha)$

$$i = \frac{\text{Total number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}}$$

$$i = \frac{n(1+\alpha)}{n} = 1 + \alpha \qquad \ldots(ii)$$

From (*i*) and (*ii*), we have

$$1.041 = 1 + \alpha \quad \Rightarrow \quad \alpha = 1.041 - 1 = 0.041$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[CH_3COO^-] = n(1 - \alpha) = 0.0106\,(1 - 0.041) = 0.0106 \times 0.959$$

$$[H^+] = n\alpha = 0.0106 \times 0.041$$

$$[CH_3COO^-] = n\alpha = 0.0106 \times 0.041$$

$$\therefore \quad K_a = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106 \times 0.959}$$

$$= \mathbf{1.86 \times 10^{-5}}$$

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

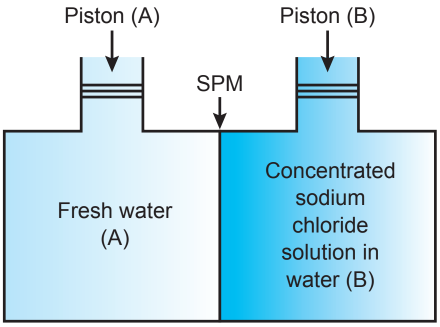
1. **Consider the figure and mark the correct option.**

   (*a*) water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B).

   (*b*) water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B).

   (*c*) water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B).

   (*d*) water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A).



2. **23 g of ethanol is dissolved in 36 g of water. The mole fraction of ethanol is**

   (*a*) 2 (*b*) 0.5

   (*c*) 0.2 (*d*) 0.8

3. **We have three aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order ___________.**

   (*a*) $i_A < i_B < i_C$ (*b*) $i_A > i_B > i_C$

   (*c*) $i_A = i_B = i_C$ (*d*) $i_A < i_B > i_C$

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. (3 × 1 = 3)

4. **Assertion (A) :** The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.

   Reason (R) : Elevation of boiling point is directly proportional to the number of species present in the solution.

5. **Assertion (A) :** If one component of a solution obeys Raoult's law over a certain range of composition, the other component will not obey Henry's law in that range.

   Reason (R) : Raoult's law is a special case of Henry's law.

6. **Assertion (A) :** If more and more solute is added to a solvent, the freezing point of the solution keeps on reducing.

   Reason (R) : Presence of large amount of the solid solute does not allow the solution to freeze.

Answer the following questions:

7. Which one of these has the highest freezing point? **(1)**

(*i*) 1 M glucose (*ii*) 1 M NaCl (*iii*) 1 M $CaCl_2$

8. What are minimum boiling azeotropes? Give one example. **(1)**

9. Explain why

(*i*) A decrease in temperature is observed on mixing ethanol and acetone.

(*ii*) Potassium chloride solution freezes at a lower temperature than water. **(2)**

10. Draw the graph between vapour pressure and temperature and explain the elevation in boiling point of a solvent in solution. **(2)**

11. Differentiate between molarity and molality of a solution. Explain how molarity value of a solution can be converted into its molality. **(2)**

12. CCl_4 and water are immiscible whereas ethanol and water are miscible in all proportions. Correlate this behaviour with molecular structure of these compounds. **(2)**

13. Calculate the boiling point of a 1 M aqueous solution (density 1.04 g mL^{-1}) of potassium chloride (K_b for water = 0.52 K kg mol^{-1}, Atomic masses: K = 39 u, Cl = 35.5 u)

Assume, potassium chloride is completely dissociated in solution. **(3)**

14. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate the osmotic pressure of the solution. (R = 8.314 J K^{-1} mol^{-1}). **(3)**

15. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86 C/m. Assume van't Hoff factor for NaCl is 1.87. (Molar mass of NaCl = 58.5 g). **(3)**

16. (*i*) Calculate the molality of a sulphuric acid solution in which the mole fraction of water is 0.85.

(*ii*) The graphical representation of vapour pressures of two component system as a function of composition is given alongside.

By graphic inspection, answer the following questions:

(*a*) Are the A–B interactions weaker, stronger or of the same magnitude as A–A and B–B?

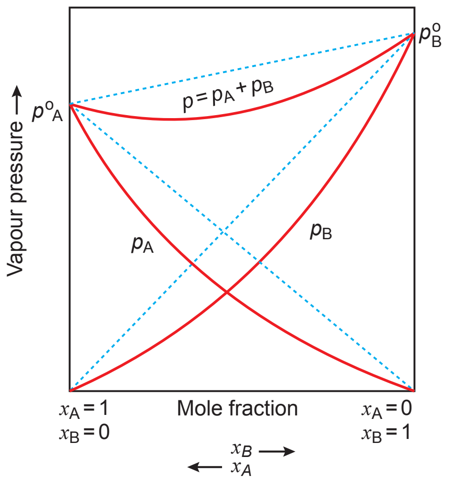
(*b*) Name the type of deviation shown by this system from Raoult's law.

(*c*) Predict the sign of $\Delta_{mix}H$ for this system.

(*d*) Predict the sign of $\Delta_{mix}V$ for this system.

(*e*) Give an example of such a system.

(*f*) What type of azeotrope will this system form, if possible? **(5)**



Answers

1. (*b*) **2.** (*c*) **3.** (*c*) **4.** (*a*) **5.** (*b*)

6. (*c*) **7.** (*i*) **13.** 374.227 K **14.** 7.384 atm **15.** 8.199 g **16.** (*i*) 9.8 m

Chapter–3

Electrochemistry

basic concepts

1. **Electrochemistry:** Electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.
2. **Ohm's Law:** It states that the potential difference (V) across the conductor is directly proportional to the current (I) flowing through it. Mathematically,

$$V \propto I \text{ or } V = IR$$

where R is a constant called resistance of the conductor. Ohm's law is obeyed by both the metallic, as well as electrolytic conductors.

3. **Resistance (R):** It is the property of a substance by which it obstructs the flow of electric current through it. The electrical resistance (R) of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A).

Thus, $R \propto \frac{l}{A}$ or $R = \rho\frac{l}{A}$

where ρ (rho) is a constant of proportionality called specific resistance or resistivity.

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

If l =1 cm and A =1 cm^2 then $R = \rho$.

Thus, resistivity may be defined as the resistance offered by a conductor of 1 cm length with area of cross-section equal to 1 cm^2, *i.e.*, it is the resistance of 1 cm^3 of the conductor.

Units: $\rho = R\frac{A}{l} = \text{ohm}\frac{\text{cm}^2}{\text{cm}} = \text{ohm cm}$

Its SI unit is ohm metre (Ω m).

4. **Conductance (G):** It is the reciprocal of resistance and may be defined as the ease with which the electric current flows through a conductor.

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

Its SI unit is Siemen (S).

$$1 \text{ S} = \text{ohm}^{-1} \text{ (mho)}$$

5. **Conductivity (κ):** It is the reciprocal of resistivity (ρ).

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = G \times \frac{l}{A}$$

If l = 1 cm and A = 1 cm^2, then $\kappa = G$.

Hence, conductivity of an electrolytic solution may be defined as the conductance of a solution of 1 cm length with area of cross-section equal to 1 cm^2.

Alternatively, it may be defined as the conductance of 1 cm^3 of the solution of an electrolyte.

Units: $\kappa = \frac{1}{\rho} = \frac{1}{\text{ohm cm}} = \text{ohm}^{-1}\text{cm}^{-1}(\text{S cm}^{-1})$

The SI unit of conductivity is S m^{-1}.

6. Factors Affecting Metallic Conductance

Electrical conductance through metal is called metallic or electronic conductance and is due to the movement of electrons. It depends on:

(*a*) The nature and structure of metal.

(*b*) The number of valence electrons per atom.

(*c*) Temperature (it decreases with increase in temperature).

7. Factors Affecting Electrolytic Conductance

Electrolyte: An electrolyte is a substance that dissociates in solution to produce ions and hence conduct electricity in dissolved or molten state.

Examples: HCl, NaOH, KCl (Strong electrolytes).
CH_3COOH, NH_4OH (Weak electrolytes).

The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. The following factors govern the flow of electricity through a solution of electrolyte.

(*a*) Nature of electrolyte or interionic attractions: Lesser the solute–solute interactions, greater will be the freedom of movement of ions and higher will be the conductance.

(*b*) Solvation of Ions: Larger the magnitude of solute–solvent interactions, greater is the extent of solvation and lower will be the electrical conductance.

(*c*) The nature of solvent and its viscosity: Larger the solvent–solvent interactions, larger will be the viscosity and more will be the resistance offered by the solvent to flow of ions and hence lesser will be the electrical conductance.

(*d*) Temperature: As the temperature of electrolytic solution rises solute–solute, solute–solvent and solvent–solvent interactions decrease, which results in the increase of electrolytic conductance.

8. Difference between Metallic and Electrolytic Conductance

S.No.	Metallic Conductance	Electrolytic Conductance
(*i*)	Movement of electrons is responsible for conduction.	Movement of ions is responsible for conduction.
(*ii*)	Does not involve transfer of matter.	Matter moves in the form of ions.
(*iii*)	Decreases with increase in temperature as kernels start vibrating which produce hindrance in the flow of electrons.	Increases with increase in temperature due to decrease in interionic attraction or increase in dissociation.

9. Measurement of Conductance: As we know, $\kappa = \frac{1}{R} \times \frac{l}{A}$

The value of κ could be known, if we measure l, A and R. The value of the resistance of the solution between two parallel electrodes is determined by using 'Wheatstone' bridge method (Fig. 3.1).

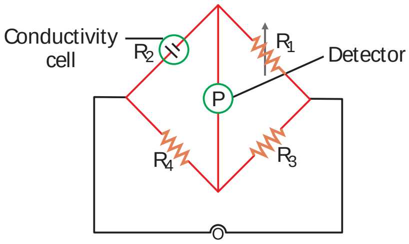


Fig. 3.1: Wheatstone Bridge

It consists of two fixed resistance R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The bridge is balanced when no current passes through the detector. Under these conditions,

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{or} \quad R_2 = \frac{R_1 R_4}{R_3}$$

Knowing the values of R_1, R_3 and R_4 the resistance of the solution, R_2 is determined. The reciprocal of R_2 gives the conductance of the solution.

10. Molar Conductivity (Λ_m): It may be defined as the conducting power of all the ions produced by dissolving one gram mole of an electrolyte placed between two large electrodes at one centimetre apart.

Mathematically,

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{c}$$

where, V is the volume of solution in cm^3 containing 1 gram mole of electrolyte and c is the molar concentration.

Units: $\Lambda_m = \frac{\kappa \times 1000}{c} = \frac{S\ cm^{-1}}{mol\ cm^{-3}}$

$= ohm^{-1}\ cm^2\ mol^{-1}$ or $S\ cm^2\ mol^{-1}$

11. Variation of Conductivity and Molar Conductivity with Concentration:

Conductivity decreases with the decrease in concentration, this is because the number of ions per unit volume that carry the current in the solution decreases on dilution.

Molar conductivity ($\Lambda_m = \kappa \times V$) increases with the decrease in concentration or increase in dilution. This is because the total volume V of solution containing one mole of electrolyte increases with increase in dilution. It has been found that the decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Graphical representation of the variation of Λ_m vs $\sqrt{c}$

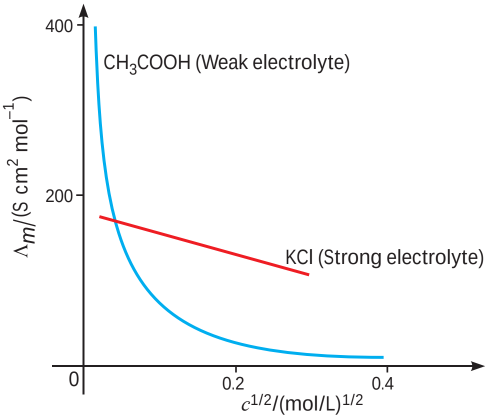


Fig. 3.2: Λ_m vs $\sqrt{c}$ for weak and strong electrolytes

Limiting Molar Conductivity (Λ^o_m): The limiting value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution.

It is possible to determine the molar conductivity at infinite dilution (Λ^o_m) in case of strong electrolyte by extrapolation of curve of Λ_m vs $\sqrt{c}$ (Fig. 3.2). On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve as the curve becomes almost parallel to y-axis when concentration approaches to zero.

The mathematical relationship between Λ_m and Λ^o_m for strong electrolyte was developed by Debye, Huckel and Onsager. In simplified form, the equation can be given as

$$\Lambda_m = \Lambda^o_m - bc^{1/2}$$

where Λ^o_m is the molar conductivity at infinite dilution and b is a constant which depends on the nature of the solvent and temperature.

12. **Kohlrausch's Law:** It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

In general, if an electrolyte on dissociation gives ν_+ cations and ν_- anions then its limiting molar conductivity is given by

$$\Lambda_m^o = \nu_+\lambda_+^o + \nu_-\lambda_-^o$$

Here, λ_+^o and λ_-^o are the limiting molar conductivities of cations and anions, respectively.

Applications of Kohlrausch's Law:

(*a*) **Calculation of molar conductivities of weak electrolyte at infinite dilution:** For example, molar conductivity of acetic acid (weak acid) at infinite dilution can be obtained from the knowledge of molar conductivities at infinite dilution of strong electrolytes like HCl, CH_3COONa and NaCl as illustrated below:

$$\Lambda^o_{m(CH_3COOH)} = \lambda^o_{CH_3COO^-} + \lambda^o_{H^+}$$

$$= [\lambda^o_{CH_3COO^-} + \lambda^o_{Na^+}] + [\lambda^o_{H^+} + \lambda^o_{Cl^-}] - [\lambda^o_{Na^+} + \lambda^o_{Cl^-}]$$

i.e., $$\Lambda^o_{m(CH_3COOH)} = \Lambda^o_{m(CH_3COONa)} + \Lambda^o_{m(HCl)} - \Lambda^o_{m(NaCl)}$$

(*b*) **Determination of degree of dissociation of weak electrolytes:**

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^o}$$

(*c*) **Determination of dissociation constant (*K*) of weak electrolytes:**

$$K = \frac{c\alpha^2}{1-\alpha}$$

$$\text{Also, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^o}$$

$$\therefore \quad K = \frac{c(\Lambda_m^c/\Lambda_m^o)^2}{1-\Lambda_m^c/\Lambda_m^o} = \frac{c(\Lambda_m^c)^2}{\Lambda_m^o(\Lambda_m^o - \Lambda_m^c)}$$

(*d*) **Determination of solubility of sparingly soluble salts:**

$$\Lambda_m^o = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}} \quad \text{or, Solubility} = \frac{\kappa \times 1000}{\Lambda_m^o}$$

13. **Electrochemical Cells:** An electrochemical cell is a device in which chemical energy of the redox reaction is converted into electrical energy. The redox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy.

The simplest electrochemical cell is Daniel cell or Galvanic cell in which a zinc rod is placed in a solution of Zn^{2+} ions (say, $ZnSO_4$) in the left container and a bar of copper metal is immersed in a solution of Cu^{2+} ions (say, $CuSO_4$) in the right container. The two metals which act as electrodes are connected by a metallic wire through a voltmeter. The two solutions are joined by an inverted U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly. This arrangement of U-tube is called salt bridge (Fig. 3.3).

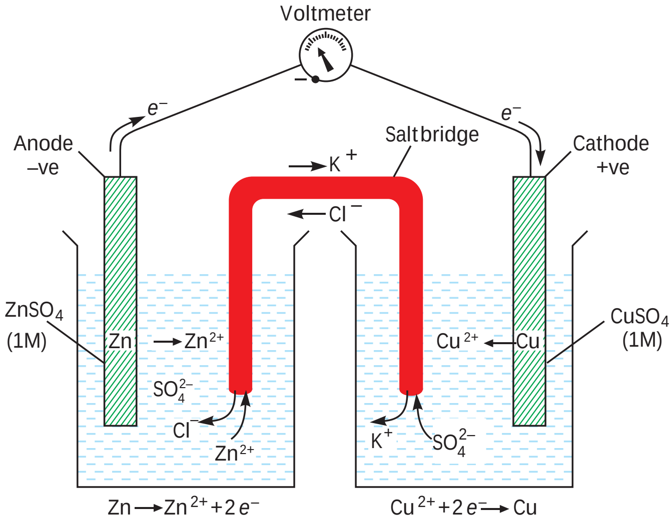


Fig. 3.3: A simple voltaic cell

The overall cell reaction,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

can be split into two half cells. The deflection in the voltmeter indicates the flow of current through the external circuit. The conventional current flows through the outer circuit from copper metal to zinc metal, which implies flow of electrons from zinc to copper bar.

(*a*) At zinc electrode, the metal undergoes oxidation and releases two electrons.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-} \text{ (oxidation)}$$

Because oxidation is taking place, the electrode behaves as anode. These electrons travel through wire and reach the copper metal.

(*b*) $$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s) \text{ (reduction)}$$

The above reaction occurs at the copper electrode. Electronation takes place which is a reduction process and that is why it acts as cathode.

As a result of the two half cell reactions, zinc metal dissolves in anode solution to form Zn^{2+} ions, while the Cu^{2+} ions are discharged at the cathode by accepting two electrons and are deposited at cathode. The electrical neutrality is maintained in two half cells using a salt bridge. The anions of the inert electrolyte in the salt bridge migrate to the anodic chamber and cations to the cathodic chamber.

As a result, as the reaction progresses, copper bar gains weight whereas zinc rod loses weight. As a consequence, the cell continues to function till either zinc metal or copper ions in solution are consumed fully.

Since electrons are released at anode, it acquires negative polarity and cathode becomes positive because it needs electrons for the reduction of +ve ions. This observation is against the usual electrolytic cell where anode is +ve and cathode is –ve.

Salt Bridge and Its Functions

A commonly used form of salt bridge consists of a glass U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly.

The electrolytes that are often used in salt bridge are called inert electrolytes which are supposed:

(*a*) not to interact chemically with either of the solutions present in anodic or cathodic chamber.

(*b*) not to interfere with overall cell reaction.

(*c*) only those electrolytes can be used in a salt bridge in which mobility of ions is almost the same.

Example, KCl, K_2SO_4, etc.

A salt bridge carries out two important functions:

(*a*) It allows only flow of ions through it. Thus, the circuit is completed.

(*b*) It also maintains the electrical neutrality.

14. **Cell Diagram or Representation of an Electrochemical Cell:** The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations: The Daniel cell is represented as follows:

$$Zn(s) \mid Zn^{2+}(c_1) \parallel Cu^{2+}(c_2) \mid Cu(s)$$

(*a*) Anode half cell is written on the left hand side while cathode half cell on right hand side.

(*b*) A single vertical line separates the metal from aqueous solution of its own ions.

$Zn(s) \mid Zn^{2+}(aq)$;	$Cu^{2+}(aq) \mid Cu(s)$
Anodic chamber	Cathodic chamber

(*c*) A double vertical line represents salt bridge which allows the passage of ions through it but prevents the mixing of two solutions.

(*d*) The molar concentration (*c*) is placed in brackets after the formula of the corresponding ion.

(*e*) The value of EMF of the cell is written on the extreme right of the cell. For example,

$$Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu(s) \qquad EMF = +1.1\ V$$

(*f*) If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket, say for example, when a zinc anode is connected to a hydrogen electrode.

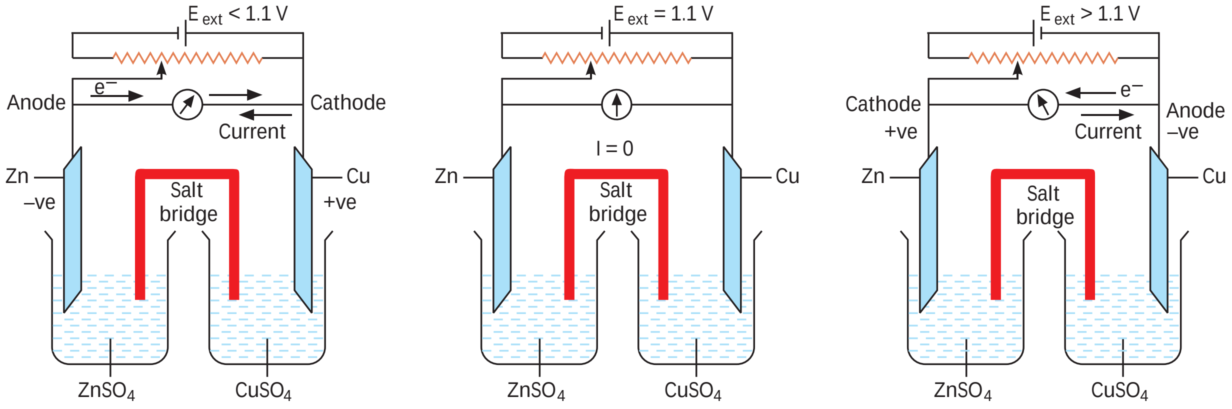
$$Zn(s) \mid Zn^{2+}(c_1) \parallel H^{+}(c_2) \mid H_2\ (Pt)$$

15. Reversibility of Daniel Cell:

(*a*) When external voltage is less than 1.10 V, electrons flow from Zn to Cu but current flows from Cu to Zn, *i.e.*, in opposite direction. Zinc dissolves at anode and copper deposits at cathode [see Fig. 3.4(*a*)]

(*b*) When external voltage applied is less than 1.10 V and is increased slowly, it is observed that the reaction continues to take place till the external voltage attains the value 1.10 V. When this is so, reaction stops altogether and no current flows [see Fig. 3.4(*b*)].

(*c*) If the value of external voltage exceeds the voltage of Daniel cell (1.10 V), the reaction takes place in opposite direction, *i.e.*, the cell functions like an electrolytic cell [see Fig. 3.4(*c*)].



(a) (b) (c)

Fig. 3.4: Functioning of Daniel cell when external voltage E_{ext} opposing the cell potential is applied

16. Electrode Potential: It may be defined as the tendency of a metal, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged.

The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.

$$M(s) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^{-}$$

Or

$$M^{n+}(aq) + ne^{-} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} M(s)$$

Characteristics:

(*a*) Both oxidation and reduction potentials are equal in magnitude but opposite in sign.

(*b*) The reduction potential shows an increase with increasing concentration and decrease with decreasing concentration of ions in a solution.

(*c*) It is not a thermodynamic property, so values of *E* are not additive.

17. Standard Hydrogen Electrode (SHE): It is a reference electrode and its reduction potential is arbitrarily assigned as zero volt at all temperature.

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution having 1M concentration of H^+ ions. Pure hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a temperature of 298 K (Fig. 3.5).

The hydrogen electrode can act both ways—as an anode or as a cathode.

Acting as anode — oxidation takes place,

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

Acting as cathode — reduction takes place,

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

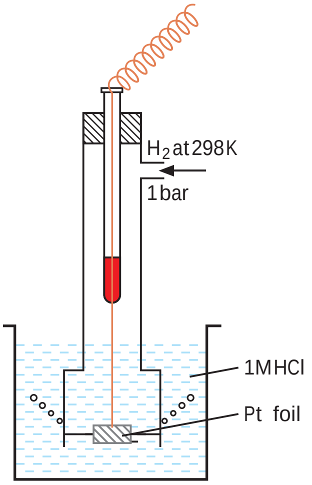


Fig. 3.5: Standard or Normal Hydrogen Electrode

Representation of SHE

$Pt(s) \mid H_2\,(g) \mid H^+\,(aq)\ (c = 1\ M)$

18. **Standard Electrode Potential (E^o):** It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are:

(*a*) 1 M concentration of each ion in the solution.

(*b*) A temperature of 298 K.

(*c*) 1 bar pressure for each gas.

19. **Cell Potential or EMF of a Cell:** The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

$$E_{\text{cell}} = E_{\text{reduction}} - E_{\text{oxidation}} = E_{\text{cathode}} - E_{\text{anode}}$$

Since anode is put on left and cathode on right, therefore it follows

$$E_{\text{cell}} = E_R - E_L$$

For a Daniel cell,

$$E^o_{\text{cell}} = E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn}$$
$$= 0.34V - (-0.76V)$$
$$= 1.10V$$

20. **Nernst Equation:** It relates electrode potential with the concentration of ions.

For an electrode reaction, $M^{n+}\,(aq) + ne^- \longrightarrow M(s)$

Nernst equation can be written as

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

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

where, $E_{M^{n+}/M}$ = Electrode potential

$E^o_{M^{n+}/M}$ = Standard electrode potential

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

T = Temperature in kelvin

n = No. of electrons gained

F = Faraday constant (96500 C mol^{-1})

Substituting the value of R and F, we get

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]},\ \text{at 298 K}$$

or

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} + \frac{0.0591}{n}\log[M^{n+}],\ \text{at 298 K}$$

Thus, the reduction potential increases with the increase in the concentration of ions.

For a general electrochemical reaction of the type:

$$aA + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation can be given as

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

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{2.303}{nF}RT\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Substituting the values of R and F we get

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}, \text{ at } 298 \text{ K}$$

21. Equilibrium Constant from Nernst Equation: For a Daniel cell, at equilibrium

$$E_{\text{cell}} = 0 = E^{\circ}_{\text{cell}} - \frac{2.303RT}{2F}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

or

$$E^{\circ}_{\text{cell}} = \frac{2.303RT}{2F}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

But at equilibrium, $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_c$

$\therefore$

$$E^{\circ}_{\text{cell}} = \frac{2.303RT}{2F}\log K_c$$

$$E^{\circ}_{\text{cell}} = \frac{2.303 \times 8.314 \times 298}{2 \times 96500}\log K_c = \frac{0.0591}{2}\log K_c$$

In general, $E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log K_c$ or, $\log K_c = \frac{n}{0.0591}E^{\circ}_{\text{cell}}$

22. EMF and Gibbs Free Energy: The work done by a reversible galvanic cell is equal to decrease in its free energy.

Mathematically, $\Delta_r G = -nFE_{\text{cell}}$

If concentration of all the reacting species is unity, then,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} \text{ and we get, } \Delta_r G^o = -nFE^{\circ}_{\text{cell}}$$

From $\Delta_r G^o$, we can calculate the equilibrium constant of a reaction,

$$\Delta_r G^o = -RT \ln K_c \quad \text{or} \quad \Delta_r G^o = -2.303\, RT \log K_c$$

23. Electrochemical Series: The arrangement of various standard half-cells in the order of their decreasing standard reduction potential values is known as electrochemical series.

- A negative value of E° means that the redox couple is stronger reducing agent than H^+/H_2. *e.g.*, Mg (– 2.36).
- A positive value of E° means that the redox couple is weaker reducing agent than H^+/H_2. *e.g.*, Br_2 (1.09).

24. Concentration Cells: If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells. In these cells, oxidation takes place on the electrode with lower concentration (c_1) while reduction takes place on the electrode with higher concentration (c_2). For example,

$H_2 \mid H^+(c_1) \parallel H^+(c_2) \mid H_2$; $Cu \mid Cu^{2+}(c_1) \parallel Cu^{2+}(c_2) \mid Cu$

$Zn \mid Zn^{2+}(c_1) \parallel Zn^{2+}(c_2) \mid Zn$

The EMF of concentration cell at 298 K is given by

$$E_{\text{cell}} = \frac{0.0591}{n}\log\frac{c_2}{c_1}, \text{ where } c_2 > c_1$$

25. Electrolysis: The process of decomposition of an electrolyte when electric current is passed through its aqueous solution or fused state is called electrolysis.

The process of electrolysis of a substance is governed by Faraday's laws of electrolysis.

(*a*) Faraday's first law of electrolysis

"The amount of any substance deposited or liberated at the electrode is directly proportional to the quantity of electricity passing through the electrolyte."

If w grams of the substance deposited on passing Q coulombs of electricity, then

$$w \propto Q \quad \text{or} \quad w \propto I \times t \qquad [\because Q = I \times t]$$

or $$w = Z \times I \times t$$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

- **Electrochemical equivalent (Z):** If $I = 1$ ampere and $t = 1$ second, then

  $$w = Z$$

  Thus, the electrochemical equivalence may be defined as the amount of the substance deposited by passing one ampere of current for one second or by passing one coulomb of charge through the electrolyte.
- 1 Faraday = Quantity of electricity carried by 1 mole of electrons.

  (6.023×10^{23} mol^{-1} $\times$ 1.6×10^{-19} C = 96472 C mol^{-1} $\simeq$ 96500 C mol^{-1})
- If n mol of electrons are involved in an electrode reaction, then

  $n \times 96500$ C of charge will deposit = M g of the element

  1 C of charge will deposit $= \dfrac{M}{n \times 96500}$ g of element

  But 1 C of charge deposit mass of element = Z g

  $$\therefore \qquad Z = \frac{M}{n \times 96500}\text{g} = \frac{E}{96500}\text{g}$$

  where E is the equivalent mass of the element and is equal to $\dfrac{\text{Atomic mass}}{\text{Valency}}$ of the element.

  or $$E = 96500 \times Z$$
- **Equivalent mass:** The mass of an element deposited by passing 96500 C of charge.

(b) Faraday's second law of electrolysis

"When same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent masses."

Mathematically, $$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

26. Commercial Cells (Batteries): Batteries are the electrochemical cells used commercially to generate electricity. "Any battery consists of two or more than two galvanic cells connected in series where the chemical energy of the redox reactions is converted into electrical energy." There are mainly two types of batteries:

(a) Primary cells (Batteries): These cells are not chargeable because the electrode reaction occurs only once and after the use over a period of time the cells become dead and cannot be reused.

The most familiar example of this type of cell is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in watches, radios, calculators, etc. It consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and $ZnCl_2$ (Fig. 3.6).

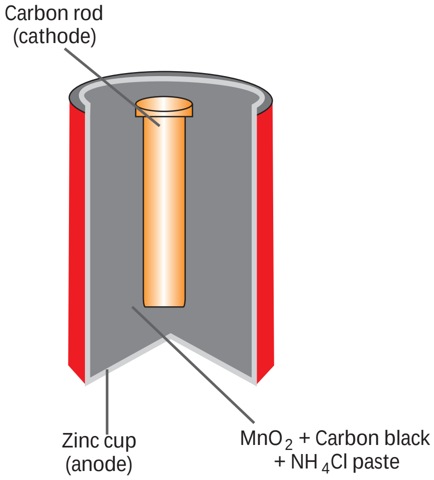


Fig. 3.6: The dry cell

The electrode reactions are:

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

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

The cell has a potential of nearly 1.5 V.

Another type of primary cell is the mercury cell, consisting of zinc–mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:

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

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

The cell potential is approximately 1.35 V and remains constant as the ionic concentration of the solution is not changed during its life.

(*b*) Secondary cells (Batteries)

A secondary battery is rechargeable and can be used again and again. It is recharged by passing current through it from an external source. Most familiar example of secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode.

A 38% solution of H_2SO_4 is used as an electrolyte (Fig. 3.7).

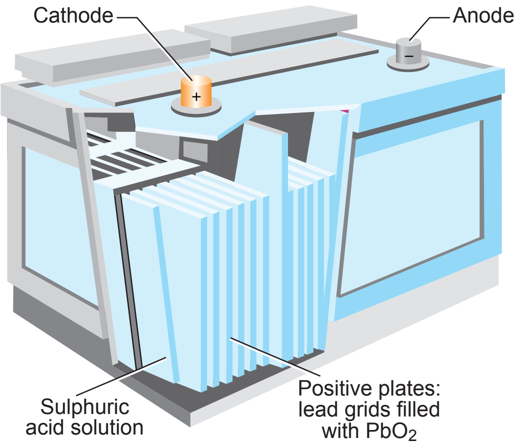


Fig. 3.7: The lead storage battery

The cell reactions when the battery is in use, are:

At anode:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

The overall reaction is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

On recharging the cell, operated like an electrolytic cell; the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

At anode: $PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^-$

At cathode: $PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$

Another important secondary cell is the nickel–cadmium cell which has longer life than the lead storage cell but is costly. Here, the overall reaction during discharge of the battery is

$$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

27. Fuel Cells: Fuel cells are those cells which produce electrical energy directly from the combustion of fuels such as hydrogen, carbon monoxide or methane. The most successful fuel cell, $H_2–O_2$ cell utilises the reaction between hydrogen and oxygen to produce water. Hydrogen and oxygen are bubbled through a porous carbon electrode in the cell into concentrated aqueous sodium hydroxide. Catalysts are incorporated into the electrode (Fig. 3.8). The electrode reactions are

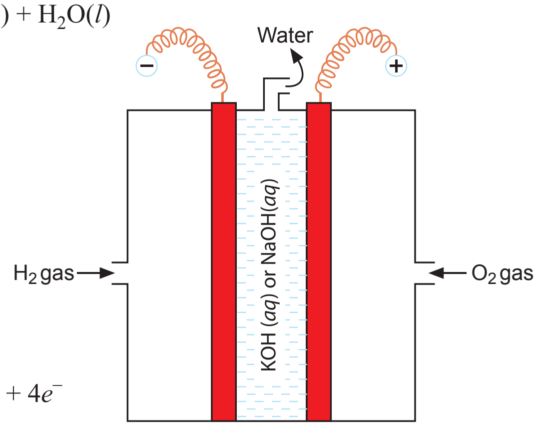


Fig. 3.8: A simple $H_2–O_2$ fuel cell

Anodic reaction: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Cathodic reaction: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Advantages of Fuel Cells:

(*a*) It is a pollution-free device since no harmful products are formed.

(*b*) Its efficiency is about 75% which is considerably higher than conventional cells.

(*c*) These cells are light in weight as compared to electrical generators to produce corresponding quantity of power.

(*d*) It is a continuous source of energy if the supply of gases is maintained.

28. Corrosion: The process of slow eating up of metals by gases and water vapours present in atmosphere due to the formation of certain compounds like oxides, sulphides, carbonates, etc. is called corrosion. Corrosion of iron is known as rusting. Chemically, rust is hydrated ferric oxide, $Fe_2O_3.xH_2O$. Corrosion may be considered as an electrochemical phenomenon. According to electrochemical theory of rusting, the impure iron surface behaves like a small electrochemical cell in the presence of moisture containing oxygen or carbon dioxide. Such a cell is called corrosion cell or corrosion couple. In these miniature corrosion cells, pure iron acts as anode, impure surface area acts as cathode and moisture having dissolved carbon dioxide or oxygen acts as electrolyte.

At anode, oxidation of iron takes place. Thus, Fe enters into the solution as Fe^{2+} ions leaving behind electrons which are pushed into cathodic area.

$$Fe \longrightarrow Fe^{2+} + 2e^-;\ E^o_{Fe^{2+}/Fe} = -0.44\ V \qquad ...(i)$$

At cathode, the electrons are picked up by the H^+ ions which are produced from H_2CO_3 (formed due to dissolution of CO_2 in moisture) or from H_2O.

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

H^+ ions, thus formed, reduces the dissolved oxygen as the net reaction at the cathodic area is

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O;\ E^o_{H^+/O_2/H_2O} = 1.23\ V \qquad ...(ii)$$

The overall reaction of the corrosion cell can be obtained by adding equations (*i*) and (*ii*)

$$Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O;\ E^o_{cell} = 1.67\ V$$

The ferrous ions so formed move through water and come at the surface where these are further oxidised by atmospheric oxygen to ferric ions and form rust which is hydrated ferric oxide (Fig. 3.9).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3.xH_2O}$$

29. Prevention of Corrosion: The metal surface can be protected against corrosion by the following methods:

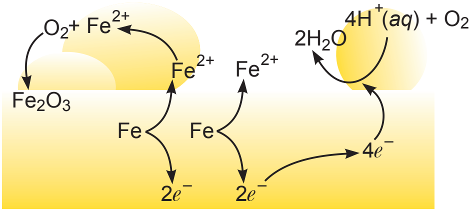


Fig. 3.9: Corrosion

(*a*) **Barrier protection:** A thin film is introduced between iron and atmospheric oxygen, carbon dioxide and moisture. The following methods are adopted for depositing thin film on metal surface:

(*i*) By covering the surface with paint or a thin film of grease.

(*ii*) By electroplating iron with some non-corrosive metals such as nickel, chromium, copper, etc.

(*b*) **Sacrificial protection:** In this method, iron surface is covered with a more electropositive metal than iron which gets oxidised in preference to iron. In such a situation the more electropositive metal loses electrons instead of iron and thus this metal is sacrificed at the cost of iron, hence the name sacrificial protection. Iron is generally coated with zinc and this process is called galvanization.

(*c*) **Electrical protection:** This is also a case of sacrificial protection. This method is used for the protection of underground water pipes or iron tanks. In this method, the exposed surface of iron is protected by connecting it to a block of some active metal such as magnesium, aluminium or zinc (Fig. 3.10). This more electropositive metal acts as anode and lose electrons in preference to iron. The iron surface acts as cathode. This method, therefore, is also called cathodic protection. The electrons released at the anode are accepted by H^+ ions of water at the surface of iron. More electropositive metal is consumed gradually in the process and needs periodical replacement.

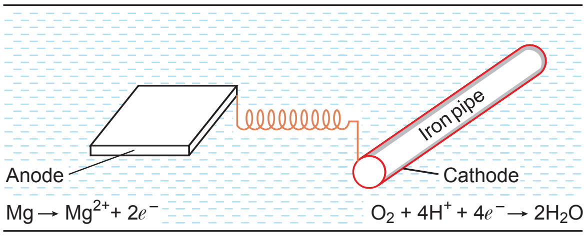


Fig. 3.10: Electric Protection

30. **Products of Electrolysis:** Under the influence of electric current through molten electrolytes or their aqueous solutions, ions move towards oppositely charged electrodes. Many times the electrode products differ. For example, the electrolysis of molten sodium chloride yields sodium metal at the cathode and chlorine gas is liberated at the anode.

$$\underset{\text{(molten state)}}{NaCl(s)} \longrightarrow Na^+ + Cl^-$$

At anode, $Cl^- \longrightarrow Cl + e^-$ Oxidation

$Cl + Cl \longrightarrow Cl_2(g)$

At cathode, $Na^+ + e^- \longrightarrow Na(s)$ Reduction

However, when a concentrated aqueous solution of sodium chloride is electrolysed, H_2 gas at cathode and Cl_2 gas at anode are obtained. This is because water is preferably reduced at cathode.

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

This happens because the standard reduction potential of water is greater than the standard reduction potential of Na^+ ion.

$$Na^+(aq) + e^- \longrightarrow Na(s) \qquad E^o_{cell} = -2.71\text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^o_{cell} = -0.83\text{ V}$$

At anode, however, Cl_2 gas is liberated because of over potential of oxygen. In fact, the remaining solution after electrolysis yields solid NaOH on evaporating. Thus,

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

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

$$2H_2O(l) + 2Cl^-(aq) + 2Na^+(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq) + 2Na^+(aq)$$

(a) Electrolysis of dilute H_2SO_4

During electrolysis of dilute H_2SO_4, the products are $H_2(g)$ at cathode and $O_2(g)$ at anode:

$$H_2SO_4 \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

At anode, $H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \qquad E^o_{cell} = +1.23\text{ V}$

At cathode, $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

If H_2SO_4 is concentrated then the following reaction occurs at anode

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^- \qquad E^o_{cell} = +1.96\text{ V}$$

(b) Electrolysis of aqueous copper sulphate using inert electrodes (Pt)

In this, copper is deposited at cathode and oxygen is liberated at anode.

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

At anode $H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \qquad E^o_{cell} = +1.23\text{ V}$

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^- \qquad E^o_{cell} = +1.96\text{ V}$$

Water, having low E^o, would be preferably oxidised at anode instead of SO_4^{2-} ions.

Cu^{2+} ions have greater reduction potential, copper metal is deposited at the cathode.

At cathode, $$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s), \qquad E^o_{cell} = +0.34\text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq), \; E^o_{cell} = -0.83\text{ V}$$

(*c*) If $CuSO_4$ is electrolysed between two copper electrodes (active electrodes), the Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction occurs

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Thus, copper metal is deposited at cathode. At the anode, copper is converted into Cu^{2+} ions with the following change:

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

Thus, copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This forms the basis of an industrial process in which impure copper is converted into copper of high purity. The impure copper is made as anode that dissolves on passing current and pure copper is deposited at cathode.

(*d*) **Electrolysis of aqueous sodium bromide:** Like aqueous NaCl, the electrode products are Br_2 (*l*) at anode and H_2 (*g*) at cathode.

Conclusions: 1. Cathodic reaction will be one which has higher $E^o_{reduction}$ value.

2. Anodic reaction will be one which has higher $E^o_{oxidation}$ value or lower $E^o_{reduction}$ value.

Important Formulae

1. $R = \rho\left(\frac{l}{A}\right) = \rho \times \text{Cell constant}$

where, R = Resistance

A = Area of cross-section of the electrodes

ρ = Resistivity

2. $\kappa = \frac{1}{R} \times \text{cell constant}$

where, κ = Conductivity or specific conductance

3. $\Lambda_m = \frac{\kappa \times 1000}{M}$

where, Λ_m = Molar conductivity

M = Molarity of the solution.

4. $\Lambda^o_m(A_xB_y) = x\Lambda^o_m(A^{y+}) + y\Lambda^o_m(B^{x-})$

where, Λ^o_m = Molar conductivity at infinite dilution, x and y are the number of cations and anions produced by one formula unit of the electrolyte on complete dissociation.

5. $\alpha = \frac{\Lambda^c_m}{\Lambda^o_m}$

where, α = Degree of dissociation

Λ^c_m = Molar conductivity at a given concentration

6. For a weak binary electrolyte *AB*

$$K = \frac{c\alpha^2}{1-\alpha} = \frac{c(\Lambda^c_m)^2}{\Lambda^o_m(\Lambda^o_m - \Lambda^c_m)}$$

where, K = Dissociation constant

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$
$$= E^{o}_{right} - E^{o}_{left}$$

7. Nernst equations for a general electrode reaction:

$$M^{n+} + ne^{-} \longrightarrow M$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{2.303\ RT}{nF}\log\frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]} \quad \text{at 298 K}$$

8. Nernst equation for a general electrochemical reaction:

$$aA + bB \xrightarrow{ne^{-}} cC + dD$$

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

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \quad \text{at 298 K}$$

9. $\log\ K_c = \frac{n}{0.0591}E^{o}_{cell}$

where, K_c = Equilibrium constant

10. $\Delta_r G^{o} = -\ nFE^{o}_{cell}$

$\Delta_r G^{\circ} = -2.303RT\log K_c$

where, $\Delta_r G^{\circ}$ = Standard Gibbs energy of the reaction

11. $Q = I \times t$

where Q = Quantity of charge in coulombs

I = Current in amperes

t = Time in seconds

12. $m = Z \times I \times t$

where m = Mass of the substance deposited at the electrodes

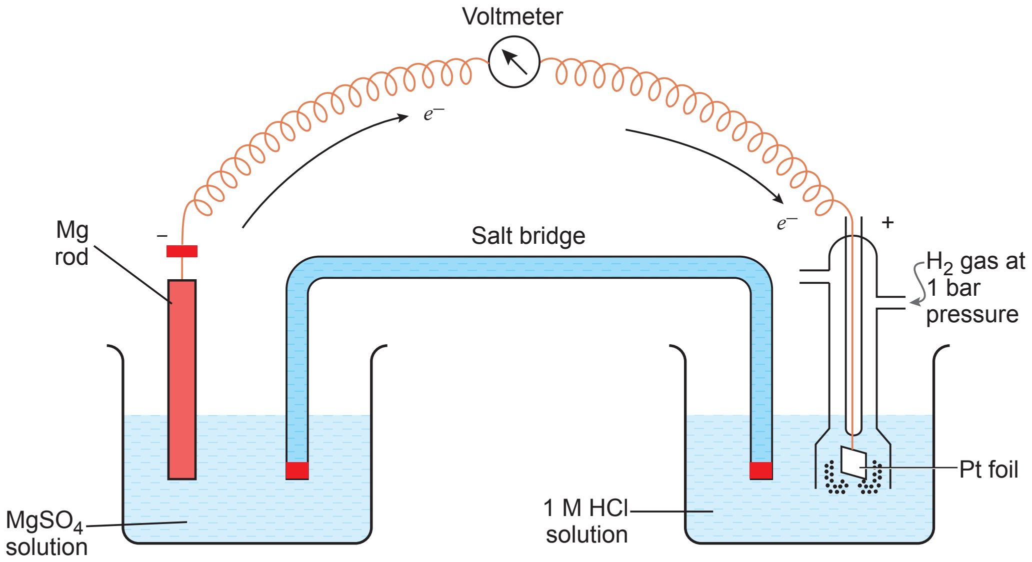
Z = Electrochemical equivalent

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. How would you determine the standard electrode potential of the system Mg^{2+} | Mg?

Ans. Set up an electrochemical cell consisting of Mg | $MgSO_4$ (1 M) as one electrode by dipping a magnesium rod in 1 M $MgSO_4$ solution and standard hydrogen electrode Pt, H_2 (1 atm) | H^{+} (1 M) as the second electrode as shown in given figure.



Measure the EMF of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that electrons flow from magnesium electrode to hydrogen electrode. Thus, the cell may be represented as follows:

$$\text{Mg} \mid \text{Mg}^{2+}\ (1\ \text{M}) \mid\mid \text{H}^{+}\ (1\ \text{M}) \mid \text{H}_2, (1\ \text{atm}), \text{Pt}(s)$$

$$E^{o}_{\text{cell}} = E^{o}_{\text{H}^+/\frac{1}{2}\text{H}_2} - E^{o}_{\text{Mg}^{2+}/\text{Mg}}$$

But $$E^{o}_{\text{H}^+/\frac{1}{2}\text{H}_2} = 0$$

Hence, $$E^{o}_{\text{Mg}^{2+}/\text{Mg}} = -\ E^{o}_{\text{cell}}$$

Q. 2. Can you store copper sulphate solutions in a zinc pot? ***[HOTS]***

Ans. For this we have to check whether the following reaction will take place or not.

$$\text{Zn}(s) + \text{CuSO}_4(aq) \longrightarrow \text{ZnSO}_4(aq) + \text{Cu}(s)$$

$$E^{o}_{\text{cell}} = E^{o}_{\text{Cu}^{2+}/\text{Cu}} - E^{o}_{\text{Zn}^{2+}/\text{Zn}} = 0.34 - (-0.76) = 1.10\ \text{V}$$

As E^{o}_{cell} is positive, the reaction will take place. Therefore, we cannot store copper sulphate in zinc pot.

Q. 3. Consult the table of the standard electrode potential and suggest three substances that can oxidise ferrous ions under suitable conditions.

Ans. Oxidation of ferrous ions means

$$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^{-};\ E^{o}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\ \text{V}$$

Only those substances can oxidise Fe^{2+} to Fe^{3+} which are stronger oxidising agents and have positive reduction potentials greater than 0.77 V so that E_{cell} of the cell reaction is positive. This is for elements lying below $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the electrochemical series, for example, Br_2, Cl_2 and F_2.

Q. 4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10. ***[HOTS]***

Ans. For hydrogen electrode

$$\text{H}^{+} + e^{-} \longrightarrow \frac{1}{2}\text{H}_2$$

$$E_{\text{H}^+/\frac{1}{2}\text{H}_2} = E^{o}_{\text{H}^+/\frac{1}{2}\text{H}_2} - \frac{0.0591}{n}\log\frac{1}{[\text{H}^+]}$$

Here, $n = 1$, $$\log\frac{1}{[\text{H}^+]} = \text{pH} = 10,\ E^{o}_{\text{H}^+/\frac{1}{2}\text{H}_2} = 0$$

∴ $$E_{\text{H}^+/\frac{1}{2}\text{H}_2} = 0 - 0.0591 \times 10 = \mathbf{-\ 0.591\ V}$$

Q. 5. Calculate the emf of the cell in which the following reaction takes place:

$Ni(s) + 2Ag^+(0.002\ M) \longrightarrow Ni^{2+}\ (0.160\ M) + 2Ag(s)$

Given that $E^o_{cell} = 1.05$ V

Ans. From Nernst equation to the given cell reaction

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05\ V - \frac{0.0591}{2} \log \frac{0.160}{(0.002)^2} = 1.05 - \frac{0.0591}{2} \log (4 \times 10^4)$$

$$= 1.05 - \frac{0.0591}{2} (4.6021) = 1.05 - 0.14\ V = \mathbf{0.91\ V}$$

Q. 6. The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$

has $E^o_{cell} = 0.236$ V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans. $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ or $2I^- \longrightarrow I_2 + 2e^-$

Thus, for the given cell reaction, $n = 2$.

$$\Delta_r G^\circ = -nFE^o_{cell} = -2 \times 96500 \times 0.236\ J\ mol^{-1} = -45548\ J\ mol^{-1} = \mathbf{-45.55\ kJ\ mol^{-1}}$$

$$\Delta_r G^\circ = -2.303\ RT \log K_c$$

$$-\log K_c = \frac{\Delta_r G^o}{2.303\ RT} = \frac{-45.55\ kJ\ mol^{-1}}{2.303 \times 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1} \times 298K} = -7.983$$

$\therefore$ K_c = Antilog (7.983) = $\mathbf{9.616 \times 10^7}$

Q. 7. Why does the conductivity of a solution decrease with dilution?

Ans. Conductivity of a solution is the conductance of ions present in a unit volume of the solution. On dilution, the number of ions per unit volume decreases. So, the conductivity also decreases.

Q. 8. Suggest a way to determine the Λ^o_m value of water. ***[HOTS]***

Ans.

$$\Lambda^o_{m(H_2O)} = \lambda^o_{(H^+)} + \lambda^o_{(OH^-)}$$

$$= \lambda^o_{(H^+)} + \lambda^o_{(OH^-)} + \lambda^o_{(Cl^-)} - \lambda^o_{(Cl^-)} + \lambda^o_{(Na^+)} - \lambda^o_{(Na^+)}$$

Rearranging we get

$$\Lambda^o_{m(H_2O)} = [\lambda^o_{(H^+)} + \lambda^o_{(Cl^-)}] + [\lambda^o_{(Na^+)} + \lambda^o_{(OH^-)}] - [\lambda^o_{(Na^+)} + \lambda^o_{(Cl^-)}]$$

$$\Lambda^o_{m(H_2O)} = \Lambda^o_{m(HCl)} + \Lambda^o_{m(NaOH)} - \Lambda^o_{m(NaCl)}$$

Thus, the molar conductivity of water at infinite dilution can be determined from the knowledge of $\Lambda^o_{m(HCl)}$, $\Lambda^o_{m(NaOH)}$ and $\Lambda^o_{m(NaCl)}$.

Q. 9. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant.

Given $\lambda^o(H^+) = 349.6$ S cm^2 mol^{-1} and λ^o $(HCOO^-) = 54.6$ S cm^2 mol^{-1}. ***[HOTS]***

Ans.

$$\Lambda^o_m\ (HCOOH) = \lambda^o_{H^+} + \lambda^o_{HCOO^-} = 349.6\ S\ cm^2\ mol^{-1} + 54.6\ S\ cm^2\ mol^{-1}$$

$$\Lambda^o_m = 404.2\ S\ cm^2\ mol^{-1}$$

$$\Lambda^c_m = 46.1\ S\ cm^2\ mol^{-1}\ (Given)$$

$$\therefore \quad \alpha = \frac{\Lambda^c_m}{\Lambda^0_m} = \frac{46.1}{404.2} = 0.114$$

$$\begin{array}{llll} & \mathrm{HCOOH} \rightleftharpoons & \mathrm{HCOO^-} & + \ \mathrm{H^+} \\ \text{Initial conc.} & c \text{ mol L}^{-1} & 0 & 0 \\ \text{Conc. at equilibrium} & c(1-\alpha) & c\alpha & c\alpha \end{array}$$

$$K = \frac{c\alpha \,.\, c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114} = \mathbf{3.67 \times 10^{-4}}$$

Q. 10. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire? **[*HOTS*]**

Ans. Q (coulomb) = I (ampere) × t (s) = (0.5 ampere) (2 × 60 × 60 s) = 3600 C

A flow of 96500 C is equivalent to the flow of 1 mole of electrons, *i.e.*, 6.02×10^{23} electrons

∴ 3600 C is equivalent to flow of electrons = $\frac{6.02 \times 10^{23}}{96500} \times 3600 = \mathbf{2.246 \times 10^{22}}$ **electrons**

Q. 11. Suggest a list of metals that are extracted electrolytically.

Ans. Na, Ca, Mg and Al.

Q. 12. Consider the reaction:

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

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

Ans. From the given reaction, 1 mole of $Cr_2O_7^{2-}$ ions require

6F = 6 × 96500 C = 579000 C of electricity for reduction to Cr^{3+} ion.

Q. 13. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Ans. During recharging, electrical energy is supplied to the cell from an external source. The reactions are reverse of those that takes place during discharge.

$$\begin{array}{l} \mathrm{PbSO_4}(s) + 2e^- \longrightarrow \mathrm{Pb}(s) + \mathrm{SO_4^{2-}}(aq) \\ \underline{\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{PbO_2}(s) + \mathrm{SO_4^{2-}}(aq) + 4\mathrm{H^+}(aq) + 2e^-} \\ \underline{2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 4\mathrm{H^+}(aq) + 2\mathrm{SO_4^{2-}}(aq)} \end{array}$$

Q. 14. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methyl alcohol and methane.

Q. 15. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Ans. The water layer present on the surface of iron dissolves acidic oxides of air like CO_2 to form acids which dissociate to give H^+ ions.

$$\mathrm{H_2O + CO_2 \longrightarrow H_2CO_3,\ H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}}$$

In the presence of H^+ ions, iron starts losing electrons at some spot to form ferrous ions. Hence, this spot acts as the anode:

$$\mathrm{Fe}(s) \longrightarrow \mathrm{Fe^{2+}}(aq) + 2e^-$$

The electrons thus released move through the metal to reach another spot where H^+ ions and the dissolved oxygen gain these electrons and reduction reaction takes place. Hence, this spot acts as the cathode:

$$\mathrm{O_2}(g) + 4\mathrm{H^+}(aq) + 4e^- \longrightarrow 2\mathrm{H_2O}(l)$$

The overall reaction is given as:

$$2\mathrm{Fe}(s) + \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) \longrightarrow 2\mathrm{Fe^{2+}}(aq) + 2\mathrm{H_2O}(l)$$

Therefore, an electrochemical cell is set up on the surface.

Ferrous ions are further oxidised by the atmospheric oxygen to ferric ions which combine with water molecules to form hydrated ferric oxide, $Fe_2O_3.xH_2O$, which is rust.

NCERT Textbook Exercises

Q. 1. Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn

Ans. Mg, Al, Zn, Fe, Cu.

Q. 2. Given the standard electrode potentials

$K^+ / K = -2.93$ V, $Ag^+ / Ag = 0.80$ V, $Hg^{2+} / Hg = 0.79$ V,

$Mg^{2+} / Mg = -2.37$ V, $Cr^{3+} / Cr = -0.74$ V

Arrange these metals in their increasing order of reducing power. **[*CBSE (AI) 2010*]**

Ans. Lower the reduction potential, more easily it is oxidised and hence greater is the reducing power. Therefore, the increasing order of reducing power is Ag < Hg < Cr < Mg < K.

Q. 3. Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

(*i*) Which of the electrode is negatively charged?

(*ii*) The carriers of the current in the cell.

(*iii*) Individual reaction at each electrode.

Ans. The cell will be represented as:

$$Zn(s) \mid Zn^{2+}(aq) \mid\mid Ag^+(aq) \mid Ag(s)$$

(*i*) Anode (zinc electrode) will be negatively charged.

(*ii*) Electrons and ions.

(*iii*) The reaction occurring

At anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Q. 4. Calculate the standard cell potentials of galvanic cell in which the following reactions take place:

(*i*) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$

(*ii*) $Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Given: $E^o_{Cr^{3+}/Cr} = -0.74$ V, $E^o_{Cd^{2+}/Cd} = -0.40$ V,

$E^o_{Ag^+/Ag} = 0.80$ V, $E^o_{Fe^{3+}/Fe^{2+}} = 0.77$ V

Calculate $\Delta_r G°$ and equilibrium constant of the reactions.

Ans. (*i*) $E°_{cell} = E°_{cathode} - E°_{anode} = -0.40\text{ V} - (-0.74\text{ V}) = \mathbf{+0.34\ V}$

$$\Delta_r G° = -nFE^o_{cell} = -6 \text{ mol} \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$= -196860 \text{ C V mol}^{-1} = -196860 \text{ J mol}^{-1}$$

$$\mathbf{= -196.86\ kJ\ mol^{-1}}$$

$$\Delta_r G° = -2.303\, RT \log K_c$$

$$-196860 = -2.303 \times 8.314 \times 298 \log K_C \quad \text{or} \quad \log K_c = 34.5014$$

$$K_c = \text{Antilog } 34.5014 = \mathbf{3.172 \times 10^{34}}$$

(*ii*)

$$E^o_{cell} = +0.80\text{ V} - 0.77\text{ V} = \mathbf{+\ 0.03\ V}$$

$$\Delta_r G° = -nFE^o_{cell} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V})$$

$$= -2895 \text{ CV mol}^{-1} = -2895 \text{ J mol}^{-1} = \mathbf{-\ 2.895\ kJ\ mol^{-1}}$$

$$\Delta_r G° = -2.303\, RT \log K_C$$

$$-2895 = -2.303 \times 8.314 \times 298 \times \log K_C$$

or $\log K_c = 0.5074$

or $K_c = \text{Antilog } (0.5074) = \mathbf{3.22}$

Q. 5. Write the Nernst equation and emf of the following cells at 298 K:

(*i*) Mg(*s*) | Mg^{2+} (0.001 M) || Cu^{2+} (0.0001 M) | Cu(*s*)

(*ii*) Fe(*s*) | Fe^{2+} (0.001 M) || H^+ (1 M) | $H_2(g)$ (1 bar) | Pt(*s*)

(*iii*) Sn(*s*) | Sn^{2+} (0.050 M) || H^+ (0.020 M) | $H_2(g)$ (1 bar) | Pt(*s*)

(*iv*) Pt(*s*) | Br^- (0.010 M) | $Br_2(l)$ || H^+ (0.030) | $H_2(g)$ (1 bar) | Pt(*s*)

Given, $E^o_{Mg^{2+}/Mg} = -2.37$ V, $E^o_{Cu^{2+}/Cu} = +0.34$ V, $E^o_{Fe^{2+}/Fe} = -0.44$ V, $E^o_{Sn^{2+}/Sn} = -0.14$ V, $E^o_{1/2Br_2/Br^-} = +1.08$ V.

Ans. (*i*) Cell reaction: $Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu; \, n = 2$

Nernst equation: $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$

$\therefore$ $E_{cell} = 0.34 - (-2.37) - \frac{0.0591}{2}\log\frac{10^{-3}}{10^{-4}} = 2.71 - 0.02955 = \mathbf{2.68\ V}$

(*ii*) Cell reaction: $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2; \; n = 2$

Nernst equation: $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[H^+]^2}$

$\therefore$ $E_{cell} = 0 - (-0.44) - \frac{0.0591}{2}\log\frac{10^{-3}}{(1)^2}$

$= 0.44 - \frac{0.0591}{2}\times(-3) = 0.44 + 0.0887 = \mathbf{0.529\ V}$

(*iii*) Cell reaction: $Sn + 2H^+ \longrightarrow Sn^{2+} + H_2; \; n = 2$

Nernst equation: $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Sn^{2+}]}{[H^+]^2}$

$= 0 - (-0.14) - \frac{0.0591}{2}\log\frac{0.05}{(0.02)^2}$

$= 0.14 - \frac{0.0591}{2}\log 125 = 0.14 - \frac{0.0591}{2}(2.0969) = \mathbf{0.078\ V}$

(*iv*) Cell reaction: $2Br^- + 2H^+ \longrightarrow Br_2 + H_2; \, n = 2$

Nernst equation: $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{1}{[Br^-]^2[H^+]^2}$

$\therefore$ $E_{cell} = (0 - 1.08) - \frac{0.0591}{2}\log\frac{1}{(0.01)^2\,(0.03)^2}$

$= -1.08 - \frac{0.0591}{2}\log(1.111\times10^7)$

$= -1.08 - \frac{0.0591}{2}(7.0457)$

$= -1.08 - 0.208$

$= \mathbf{-1.288\ V}$

As E_{cell} is negative, therefore cell reaction will not take place. For the cell to show positive emf cell, representation should be

Pt | H_2O (1 bar) | H^+ (0.03 M) || Br^- (0.01 M) | $Br_2(l)$ | Pt(s)

Q. 6. In the button cells widely used in watches and other devices, the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^\circ$ and E^o for the reaction.

Ans. At anode: $\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2e^-$

At cathode: $\mathrm{Ag_2O + H_2O} + 2e^- \longrightarrow \mathrm{2Ag + 2OH^-}$

$$\mathrm{Zn + Ag_2O + H_2O \longrightarrow Zn^{2+} + 2Ag + 2OH^-}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Zn^{2+}/Zn}}$$

$$E^\circ_{\text{cell}} = 0.34\text{ V} - (-0.76\text{ V}) = \mathbf{1.10\ V}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}\,,\ n = 2$$

$$\Delta G^\circ = -2 \times 96500 \times 1.10$$

$$\boldsymbol{\Delta G^\circ = -2.123 \times 10^5\ \text{J/mol}}$$

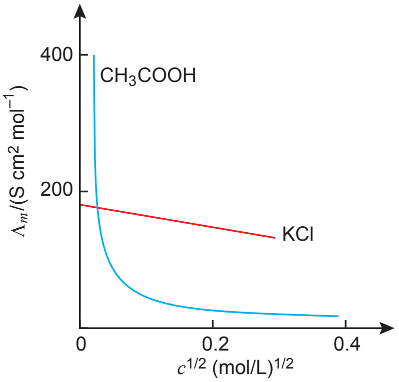
Q. 7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Ans. Refer to Basic Concepts Points 5 and 10 for definition.

Variation of Conductivity and Molar Conductivity with Concentration: Conductivity always decreases with the decrease in concentration both, for weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$G = \dfrac{\kappa A}{l} = \kappa$ (both A and l are unity in their appropriate units in m or cm).

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with the area of cross section A and distance of unit length. Therefore,



Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

$$\Lambda_m = \frac{\kappa A}{l} = \kappa$$

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Molar conductivity increases with the decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Q. 8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} Calculate its molar conductivity.

Ans. $\Lambda_m = \dfrac{\kappa \times 1000}{\text{Molarity}} = \dfrac{0.0248\text{ S cm}^{-1} \times 1000\text{ cm}^3 \times \text{L}^{-1}}{0.20\text{ mol L}^{-1}} = \mathbf{124\ S\ cm^2\ mol^{-1}}$

Q. 9. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10^{-3} S cm^{-1}?

Ans. Conductivity $(\kappa) = \dfrac{1}{\text{Resistance (R)}} \times$ Cell constant

$\kappa = 0.146 \times 10^{-3}\text{ S cm}^{-1},\ R = 1500\ \Omega$

$$0.146 \times 10^{-3}\text{ S cm}^{-1} = \frac{1}{1500\ \Omega} \times \text{Cell constant}$$

$\therefore$ Cell constant $= 0.146 \times 10^{-3}\text{ S cm}^{-1} \times 1500\ \Omega$

$$= 219 \times 10^{-3}\text{ cm}^{-1} = \mathbf{0.219\ cm^{-1}}$$

Q. 10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

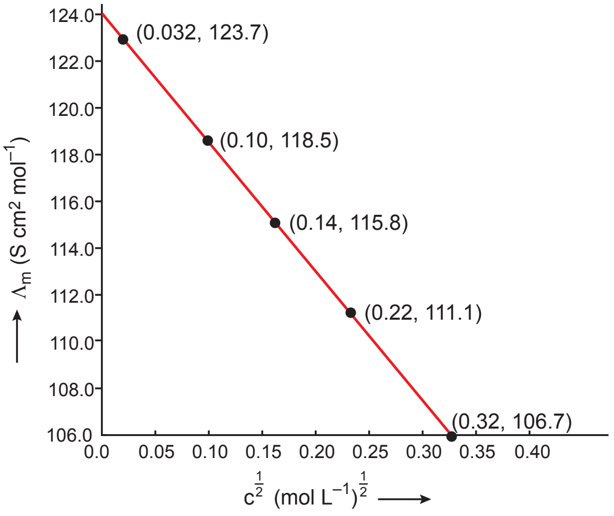
Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa$/S m^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m°.

Ans. $\frac{1\,\text{S cm}^{-1}}{100\,\text{S m}^{-1}} = 1$ (unit conversion factor)

Conc. (M)	κ (S m^{-1})	κ (S cm^{-1})	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}}$ (S cm^2 mol^{-1})	c$^{1/2}$ (M$^{1/2}$)
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = \mathbf{123.7}$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = \mathbf{118.5}$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = \mathbf{115.8}$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = \mathbf{111.1}$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = \mathbf{106.7}$	0.316

Plot between Λ_m and c$^{1/2}$



Λ_m^0 = Intercept on the Λ_m axis = **124.0 S cm^2 mol^{-1}**

Q. 11. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1} Calculate its molar conductivity. If Λ_m^o for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant? ***[CBSE Delhi 2008]***

Ans. $c = 0.00241$ M, $\kappa = 7.896 \times 10^{-5}$ S cm^{-1}, $\Lambda_m^\circ = 390.5$ S cm^2 mol^{-1}

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Substituting the values, we get

$$\Lambda_m = \frac{7.896 \times 10^{-5}\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.00241\ \text{mol L}^{-1}} = \mathbf{32.76\ S\ cm^2\ mol^{-1}}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{32.76}{390.5} = 0.084$$

$$\alpha = 8.4\%$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
Initial concentration	c	0	0
Concentration at equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha\,.\,c\alpha}{c\,(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K = \frac{0.00241(0.084)^2}{(1-0.084)} = \mathbf{1.86 \times 10^{-5}}$$

Q. 12. How much charge is required for the following reduction:

(*i*) 1 mol of Al^{3+} to Al? **(*ii*) 1 mol of Cu^{2+} to Cu?**

(*iii*) 1 mol of MnO_4^- to Mn^{2+}? **[*CBSE 2020 (56/5/1)*]**

Ans. (*i*) $$Al^{3+} + 3e^- \longrightarrow Al$$

∴ Quantity of charge required for reduction of 1 mol of Al^{3+} = 3F

= 3 × 96500 C = **289500 C**

(*ii*) $$Cu^{2+} + 2e^- \longrightarrow Cu$$

∴ Quantity of charge required for reduction of 1 mol of Cu^{2+} = 2F = 2 × 96500 C

= **193000 C**

(*iii*) $$MnO_4^- \longrightarrow Mn^{2+}$$

Oxidation number of Mn changes from +7 to +2.

∴ Quantity of charge required = 5F = 5 × 96500 C = **482500 C**

Q. 13. How much electricity in terms of Faraday is required to produce

(*i*) 20.0 g of Ca from molten $CaCl_2$?

(*ii*) 40.0 g of Al from molten Al_2O_3?

Ans. (*i*) $$Ca^{2+} + 2e^- \longrightarrow Ca$$

As, 40 g of Ca, require electricity = 2 F

∴ 20 g of Ca will require electricity = $\frac{20}{40} \times 2 = \mathbf{1\ F}$

(*ii*) $$Al^{3+} + 3e^- \longrightarrow Al$$

As, 1 mol of Al, *i.e.*, 27 g of Al require electricity = 3 F

∴ 40 g of Al will require electricity = $\frac{3}{27} \times 40 = \mathbf{4.44\ F}$

Q. 14. How much electricity is required in coulomb for the oxidation of

(*i*) 1 mol of H_2O to O_2 **(*ii*) 1 mol of FeO to Fe_2O_3?**

Ans. (*i*) The electrode reaction for 1 mol of H_2O is given as

$$H_2O \longrightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$$

∴ Quantity of electricity required = 2F = 2 × 96500 C = **193000 C**

(*ii*) The electrode reaction is given as

$$2FeO + \frac{1}{2} O_2 \longrightarrow Fe_2O_3$$

i.e., $$2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$$

For the oxidation of 2 moles of FeO, required charge = 2 F

∴ For the oxidation 1 mole of FeO, required charge = 1 F = **96500 C**

Q. 15. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? [*CBSE (F) 2014*]

Ans. Quantity of electricity passed = $I \times t = (5\text{ A}) \times (20 \times 60\text{ s}) = 6000\text{ C}$

The electrode reaction is: $Ni^{2+} + 2e^- \longrightarrow Ni$

2×96500 C deposit Ni = 58.7 g

$\therefore$ 6000 C will deposit Ni = $\dfrac{58.7}{2 \times 96500} \times 6000\text{ g} = \mathbf{1.825\text{ g}}$

Q. 16. Three electrolytic cells A, B and C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively were connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited? [*CBSE Delhi 2008*]

Ans. $Ag^+ + e^- \longrightarrow Ag$

108 g of Ag is deposited by 96500 C

$\therefore$ 1.45 g of Ag will be deposited by $\dfrac{96500}{108} \times 1.45\text{ C} = 1295.6\text{ C}$

$$t = \frac{Q}{I} = \frac{1295.6}{1.50} = \mathbf{863.7\text{ s}}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

2×96500 C deposit Cu = 63.5 g

$\therefore$ Cu deposited by 1295.6 C = $\dfrac{63.5}{2 \times 96500} \times 1295.6 = \mathbf{0.426\text{ g}}$

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

2×96500 C deposit Zn = 65.3 g

$\therefore$ Zn deposited by 1295.6 C = $\dfrac{65.3}{2 \times 96500} \times 1295.6 = \mathbf{0.438\text{ g}}$

Q. 17. Using the standard electrode potentials given below, predict if the reaction between the following is feasible:

(*i*) Fe^{3+} (*aq*) and I^- (*aq*) **(*ii*) Ag^+ (*aq*) and Cu (*s*)**
(*iii*) Fe^{3+} (*aq*) and Br^- (*aq*) **(*iv*) Ag(*s*) and Fe^{3+} (*aq*)**
(*v*) Br_2 (*aq*) and Fe^{2+} (*aq*)

Given standard electrode potentials:

$E^o_{1/2I_2/I^-} = 0.541\text{ V}$, $E^o_{Cu^{2+}/Cu} = +0.34\text{ V}$,

$E^o_{1/2\,Br_2/Br^-} = +1.090\text{ V}$, $E^o_{Ag^+/Ag} = +0.80\text{ V}$, $E^o_{Fe^{3+}/Fe^{2+}} = +0.77\text{ V}$.

Ans. A reaction is feasible if e.m.f. of the cell reaction is positive.

(*i*) $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2$

$\therefore$ $E^o_{cell} = E^o_{Fe^{3+}/Fe^{2+}} - E^o_{1/2\,I_2/I^-}$

$= 0.77\text{ V} - 0.54\text{ V} = \mathbf{0.23\text{ V}}$ **(feasible).**

(*ii*) $Ag^+(aq) + Cu \longrightarrow Ag(s) + Cu^{2+}(aq)$

$E^o_{cell} = E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} = 0.80\text{ V} - 0.34\text{ V} = \mathbf{0.46\text{ V}}$ **(feasible).**

(*iii*) $Fe^{3+}(aq) + Br^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}Br_2$

$E^o_{cell} = 0.77\text{ V} - 1.09\text{ V} = \mathbf{-0.32\text{ V}}$ **(not feasible).**

(*iv*) $Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$,

$E^o_{cell} = 0.77\text{ V} - 0.80\text{ V} = \mathbf{-0.03\text{ V}}$ **(not feasible).**

(*v*) $\frac{1}{2}Br_2(aq) + Fe^{2+}(aq) \longrightarrow Br^- + Fe^{3+}$,

$E^o_{cell} = 1.09\text{ V} - 0.77\text{ V} = \mathbf{0.32\text{ V}}$ **(feasible).**

Q. 18. Predict the products of electrolysis in each of the following

(*i*) An aqueous solution of $AgNO_3$ with silver electrodes.

(*ii*) An aqueous solution of $AgNO_3$ with platinum electrodes.

(*iii*) A dilute solution of H_2SO_4 with platinum electrodes. *[CBSE 2019 (56/3/2)]*

(*iv*) An aqueous solution of $CuCl_2$ with platinum electrodes. *[CBSE 2020 (56/4/3)]*

Ans. (***i***) **Electrolysis of aqueous solution of $AgNO_3$ with silver electrodes:**

$$AgNO_3(s) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

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

At cathode: Since, the reduction potential of Ag^+ (+0.80 V) is greater than that of water, (– 0.83 V), Ag^+ will get reduced preferentially and silver metal will get deposited at the cathode. will be deposited as Ag in preference to H^+ ions.

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

At anode: Following reactions may take place

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

$$NO_3^-(aq) \longrightarrow NO_3 + e^-$$

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

Among these reactions, the reduction potential of silver is minimum. Therefore, the silver anode will itself undergo oxidation to form Ag^+ ions which will pass into the solution.

(***ii***) At cathode: As given in part (*i*).

At anode: Since the reduction potential of water is less than that of NO_3^- ions, water will get preferentially oxidised and oxygen will be evolved.

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

(***iii***) At cathode:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g); \qquad E^o = 0.00\text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq); E^o = -0.83\text{ V}$$

Since, H^+ ions possess a higher reduction potential as compared to that of water, H^+ will get preferentially reduced and H_2 gas is obtained at the cathode.

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

At anode: $H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-; E^o = +1.23\text{ V}$

$$SO_4^{2-}(aq) \longrightarrow SO_4 + 2e^-; \; E^o = 2.0\text{ V}$$

Since, the reduction potential of H_2O is less than that of SO_4^{2-} ions, water will get preferentially oxidised and oxygen will be evolved at the anode.

(***iv***) At cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq); E^o = -0.83\text{ V}$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); E^o = +0.34\text{ V}$$

As E^o for Cu^{2+} is greater than H_2O. So, copper metal is deposited at the anode.

At anode: $H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-; E^o = +1.23\text{ V}$

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-(aq); E^o = +1.36\text{ V}$$

Since E^o value of H_2O is less than Cl^-, water will get preferentially oxidised at anode and O_2 gas will be evolved.

Multiple Choice Questions [1mark]

Choose and write the correct option(s) in the following questions.

1. **An electrochemical cell can behave like an electrolytic cell when ____________.** *[NCERT Exemplar; CBSE 2020 (56/4/2)]*

   (*a*) $E_{cell} = 0$ (*b*) $E_{cell} > E_{ext}$

   (*c*) $E_{ext} > E_{cell}$ (*d*) $E_{cell} = E_{ext}$

2. **The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called ________________.** *[NCERT Exemplar]*

   (*a*) Cell potential (*b*) Cell emf

   (*c*) Potential difference (*d*) Cell voltage

3. **A hypothetical electrochemical cell is shown below:**

   $A \mid A^+(xM) \parallel B^+(yM) \mid B$

   The emf measured is +0.20 V. The cell reaction is

   (*a*) $A + B^+ \longrightarrow A^+ + B$ (*b*) The cell reaction cannot be predicted.

   (*c*) $A^+ + e^- \longrightarrow A$, $B^+ + e^- \longrightarrow B$ (*d*) $A^+ + B \longrightarrow A + B^+$

4. **Which cell will measure standard electrode potential of copper electrode?** *[NCERT Exemplar]*

   (*a*) $Pt(s) \mid H_2 \text{ (g, 0.1 bar)} \mid H^+\text{(aq., 1 M)} \parallel Cu^{2+}\text{ (aq., 1M)} \mid Cu$

   (*b*) $Pt(s) \mid H_2 \text{ (g, 1 bar)} \mid H^+\text{(aq., 1 M)} \parallel Cu^{2+}\text{ (aq., 2M)} \mid Cu$

   (*c*) $Pt(s) \mid H_2 \text{ (g, 1 bar)} \mid H^+\text{(aq., 1 M)} \parallel Cu^{2+}\text{ (aq., 1M)} \mid Cu$

   (*d*) $Pt(s) \mid H_2 \text{ (g, 1 bar)} \mid H^+\text{(aq., 0.1 M)} \parallel Cu^{2+}\text{ (aq., 1M)} \mid Cu$

5. **The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that ______________.** *[NCERT Exemplar]*

   (*a*) this redox couple is a stronger reducing agent than the H^+/H_2 couple.

   (*b*) this redox couple is a stronger oxidising agent than H^+/H_2.

   (*c*) Cu can displace H_2 from acid.

   (*d*) Cu cannot displace H_2 from acid.

6. **Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is – 0.74 V. The two couple in their standard states are connected to make cell. The cell potential will be:**

   (*a*) +1.19 V (*b*) 0.89 V

   (*c*) +0.18 V (*d*) +1.83 V

7. **Which of the following statement is not correct about an inert electrode in a cell?** *[NCERT Exemplar]*

   (*a*) It does not participate in the cell reaction.

   (*b*) It provides surface either for oxidation or for reduction reaction.

   (*c*) It provides surface for conduction of electrons.

   (*d*) It provides surface for redox reaction.

8. **Using the data given below find out the strongest reducing agent.** *[NCERT Exemplar]*

   $E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\text{ V}$ $E^o_{Cl_2/Cl^-} = 1.36\text{ V}$

   $E^o_{MnO_4^-/Mn^{2+}} = 1.51\text{ V}$ $E^o_{Cr^{3+}/Cr} = -0.74\text{ V}$

   (*a*) Cl^- (*b*) Cr (*c*) Cr^{3+} (*d*) Mn^{2+}

9. **Using the data given in Q. 8 find out in which option the order of reducing power is correct.** *[NCERT Exemplar]*

   (*a*) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$ (*b*) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$

   (*c*) $Cr^{3+} < Cl^- < Cr_2O_7^{2-} < MnO_4^-$ (*d*) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$

10. **Use the data given in Q. 8 find out the most stable oxidised species.** *[NCERT Exemplar]*

    (*a*) Cr^{3+} (*b*) MnO_4^- (*c*) $Cr_2O_7^{2-}$ (*d*) Mn^{2+}

11. The electrode potential data are given below

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}, \qquad E^o = +0.77\ V$$
$$Al^{3+} + 3e^- \longrightarrow Al, \qquad E^o = -1.66\ V$$
$$Br_2 + 2e^- \longrightarrow 2Br^-, \qquad E^o = +1.80\ V$$

Based on the data, the reducing power of Fe^{2+}, Al, Br^- will increase in the order.

(*a*) $Br^- < Fe^{2+} < Al$ (*b*) $Fe^{2+} < Al < Br^-$ (*c*) $Al < Br^- < Fe^{2+}$ (*d*) $Al < Fe^{2+} < Br^-$

12. Which one of the following is always true about the spontaneous cell reaction in a galvanic cell?

(*a*) $E^o_{cell} > 0, \Delta G^o < 0, Q > K_c$ (*b*) $E^o_{cell} < 0, \Delta G^o < 0, Q < K_c$

(*c*) $E^o_{cell} > 0, \Delta G^o > 0, Q > K_c$ (*d*) $E^o_{cell} > 0, \Delta G^o < 0, Q < K_c$

13. The standard emf of a galvanic cell involving 3 moles of electrons in a redox reaction is 0.59 V. The equilibrium constant for the reaction of the cell is:

(*a*) 10^{10} (*b*) 10^{20} (*c*) 10^{30} (*d*) 10^{15}

14. The SI unit of conductivity is

(*a*) Sm^{-1} (*b*) Scm^{-1} (*c*) Sm (*d*) Scm

15. Which of the statements about solutions of electrolytes is not correct? [*NCERT Exemplar*]

(*a*) Conductivity of solution depends upon size of ions.

(*b*) Conductivity depends upon viscosity of solution.

(*c*) Conductivity does not depend upon solvation of ions present in solution.

(*d*) Conductivity of solution increases with temperature.

16. On increasing temperature,

(*a*) ionic conductance increases and electronic conductance decreases.

(*b*) ionic conductance decreases and electronic conductance increases.

(*c*) both ionic and electronic conductance increase.

(*d*) both ionic and electronic conductance decrease.

17. $\Lambda^o_{m(NH_4OH)}$ is equal to ______________. [*NCERT Exemplar*]

(*a*) $\Lambda^0_{m(NH_4OH)} + \Lambda^0_{m(NH_4Cl)} - \Lambda^0_{m(HCl)}$ (*b*) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaCl)}$

(*c*) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{m(NaOH)}$ (*d*) $\Lambda^0_{m(NaOH)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{m(NH_4Cl)}$

18. Charge carried by 1 mole of electrons is

(*a*) 6.023×10^{23} coulomb (*b*) 9.65×10^4 coulomb

(*c*) 1.6×10^{-19} coulomb (*d*) 6.28×10^{19} coulomb

19. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is ______________. [*NCERT Exemplar*]

(*a*) 1F (*b*) 6F (*c*) 3F (*d*) 2F

20. In the electrolysis of aqueous sodium chloride solution, which of the following half cell reaction will occur at anode? [*NCERT Exemplar*]

(*a*) $Na^+(aq) + e^- \longrightarrow Na(s); \qquad E^o_{cell} = -2.71\ V$

(*b*) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-; \qquad E^o_{cell} = 1.23\ V$

(*c*) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g); \qquad E^o_{cell} = 0.00\ V$

(*d*) $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-; \qquad E^o_{cell} = 1.36\ V$

21. E^o_{cell} for some half cell reactions are given below. On the basis of these mark the correct answer.

(*i*) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g) \qquad E^o_{cell} = 0.00\ V$

(*ii*) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^o_{cell} = 1.23\ V$

(*iii*) $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-; \qquad E^o_{cell} = 1.96\ V$ [*NCERT Exemplar*] (*a*) In dilute sulphuric acid solution, hydrogen will be reduced at cathode.

(*b*) In concentrated sulphuric acid solution, water will be oxidised at anode.

(*c*) In dilute sulphuric acid solution, water will be oxidised at anode.

(*d*) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate at anode.

22. The electrolyte used in the mercury cell is

(*a*) paste of NH_4Cl and $ZnCl_2$ (*b*) paste of HgO and carbon

(*c*) paste of KOH and ZnO (*d*) paste of PbO and H_2SO_4

23. A device that converts energy of combustion of fuels like hydrogen and methane directly into electrical energy is known as:

(*a*) dynamo (*b*) Ni-Cd cell (*c*) fuel cell (*d*) electrolytic cell

24. Which metal is used as electrode which do not participate in the reaction but provides surface for conduction of electrons?

(*a*) Cu (*b*) Pt (*c*) Zn (*d*) Fe

Answers

1. (*c*) **2.** (*b*) **3.** (*a*) **4.** (*c*) **5.** (*b*), (*d*) **6.** (*b*) **7.** (*d*) **8.** (*b*) **9.** (*b*) **10.** (*a*)
11. (*a*) **12.** (*d*) **13.** (*c*) **14.** (*a*) **15.** (*c*) **16.** (*a*) **17.** (*b*) **18.** (*b*) **19.** (*c*) **20.** (*b*)
21. (*a*), (*c*) **22.** (*c*) **23.** (*c*) **24.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***

(b) ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***

(c) ***Assertion (A) is correct, but Reason (R) is incorrect statement.***

(d) ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. Assertion (*A*) : E_{cell} should have a positive value for the cell to function.
Reason (*R*) : $E_{cathode} < E_{anode}$

2. Assertion (*A*) : Mercury cell does not give steady potential.
Reason (*R*) : In the cell reaction, ions are not involved in solution.

3. Assertion (*A*) : Cu is less reactive than hydrogen.
Reason (*R*) : $E^{o}_{Cu^{2+}/Cu}$ is negative.

4. Assertion (*A*) : Copper sulphate cannot be stored in zinc vessel.
Reason (*R*) : Zinc is less reactive than copper.

5. Assertion (*A*) : $E_{Ag^{+}/Ag}$ increases with increase in concentration of Ag^{+} ions.
Reason (*R*) : $E_{Ag^{+}/Ag}$ has a positive value.

6. Assertion (*A*) : Current stops flowing when $E_{cell} = 0$.
Reason (*R*) : Equilibrium of the cell reaction is attained.

7. Assertion (*A*) : For measuring resistance of an ionic solution an AC source is used.
Reason (*R*) : Concentration of ionic solution will change if DC source is used.

8. Assertion (*A*) : Conductivity of all electrolytes decreases on dilution.
Reason (*R*) : On dilution number of ions per unit volume decreases.

9. Assertion (*A*) : Conductivity decreases for weak electrolyte and increases for strong electrolyte with decrease in concentration.
Reason (*R*) : On dilution, the number of ions per unit volume that carry the current decreases.

10. **Assertion (*A*)** : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason (*R*) : For weak electrolytes degree of dissociation increases with dilution of solution.

11. **Assertion (*A*)** : Electrolysis of NaCl solution gives chlorine at anode instead of O_2.
Reason (*R*) : Formation of oxygen at anode requires overvoltage.

12. **Assertion (*A*)** : The following reaction takes place at cathode during the electrolysis of aqueous sodium chloride:

$$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-$$

Reason (*R*) : The reaction with lower value of E^o is preferred at cathode.

Answers

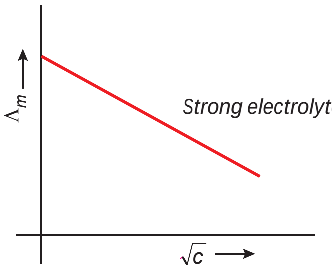
1. (*c*) **2.** (*d*) **3.** (*c*) **4.** (*c*) **5.** (*b*) **6.** (*a*) **7.** (*a*) **8.** (*a*) **9.** (*d*) **10.** (*a*)
11. (*a*) **12.** (*c*)

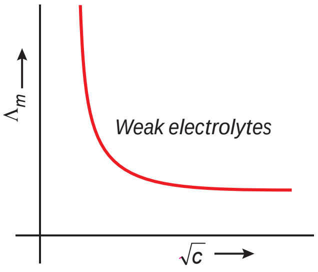
Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The conductivity or specific conductivity of an electrolytic solution varies with the concentration of the solutions of different electrolytes. For comparing the conductances of the solutions of different electrolytes, it is essential that the solutions should have equal volumes and they must contain definite amount of the electrolytes which give ions carrying the same total charge. The conducting power of an electrolytic solution can be expressed in terms of equivalent conductance and molar conductance. The equivalent conductance of a solution does not vary linearly with concentration and it is related with specific conductance. The effect of equivalent conductance can be studied by plotting values against the square root of the concentration. Following two figures show the behaviour of strong and weak electrolytes with change of concentration.





1. **Write the relationship between specific conductivity and equivalent conductivity?**

Ans. $\Lambda = \kappa \times \dfrac{1000}{N}$

2. **What is the effect of decreasing concentration on the molar conductivity of a weak electrolyte?**

Ans. The molar conductivity of a weak electrolyte increases with decrease in concentration.

3. **Write the mathematical expression for Kohlrausch's law in terms of equivalent conductivities.**

Ans. $\Lambda^o_{eq} = \lambda^o_+ + \lambda^o_-$

4. **What is meant by limiting molar conductivity?**

Ans. The molar conductivity of a solution at infinite dilution is called limiting molar conductivity.

5. **Which equation gives the relationship between equivalent or molar conductivity and concentration of a strong electrolyte?**

Ans. Debye-Huckel Onsager equation

$$\Lambda = \Lambda^o - A\sqrt{c}$$

PASSAGE–2

Redox reactions play an important role in chemistry. Whenever a redox reaction takes place directly in a single beaker, chemical energy in the form of heat is produced. By suitable means, it is possible to bring about the redox reactions indirectly so as to convert the chemical energy into electrical energy. A device used to convert the chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell. If a redox reaction is allowed to take place in such a way that oxidation half reaction takes place in one beaker and the reduction half reaction in another beaker, the electrons given out by the former will be taken by the latter and the current will flow. The two portions of the cell are called half cells. The values of standard redox potential (E^o) of two half cell reactions decides in which way the reaction will proceed. A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidised. For example, In Daniel cell, zinc goes into solution and copper gets deposited.

1. Formulate the galvanic cell in which the following reaction takes place:

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

Ans. The cell is represented as

$$Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

2. Is it safe to stir $AgNO_3$ solution with a copper spoon? Why or why not?

Given: $E^o_{Ag^+/Ag} = 0.80$ volt and $E^o_{Cu^{2+}/Cu} = 0.34$ volt

Ans. No, it is not safe to stir $AgNO_3$ solution with copper, because copper is more reactive than Ag and can displace Ag from $AgNO_3$ solution.

3. Two half cell reactions of an electrochemical cell are given below:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l), \quad E^o = +1.51\text{ V}$$

$$Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-, \quad E^o = +0.15\text{ V}$$

Construct the redox reaction from the two half cell reactions and predict if this reaction favours formation of reactants or products shown in the equation.

Ans. The redox reaction will be

$$2MnO_4^-(aq) + 16H^+(aq) + 5Sn^{2+}(aq) \longrightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$

$E^o_{Cell} = E^o_{Cathode} - E^o_{Anode} = 1.51\text{ V} - 0.15\text{ V} = 0.36\text{ V}$, *i.e.*, it will be positive.

Hence, reaction will favour formation of products.

4. State the factors that influence the value of cell potential of the following cell:

$$Mg(s) \mid Mg^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

Ans. The factors that influence the value of cell potential are concentration of Mg^{2+} and Ag^+ ions in the solution and temperature.

5. Can E^o_{cell} or $\Delta_r G^o$ for cell reaction ever be equal to zero?

Ans. No, E^o_{cell} or $\Delta_r G^o$ for cell reaction can never be zero.

$$\Delta G^o = -nFE^o$$

E^o is never zero hence ΔG^o will also be not equal to zero.

Very Short Answer Questions [1 mark]

Q. 1. What would happen if no salt bridge were used in an electrochemical cell (like Zn–Cu cell)?

Ans. The metal ions (Zn^{2+}) formed by the loss of electrons will accumulate in one electrode and the negative ions (SO_4^{2-}) will accumulate in the other. Thus, the solutions will develop charges and the current will stop flowing. Moreover, the inner circuit will not be completed.

Q. 2. Why does a galvanic cell become dead after some time?

Ans. As the reaction proceeds, concentration of ions in anodic half keeps on increasing while in the cathodic half it keeps on decreasing. Hence, their electrode potentials also keeps on changing until they become equal and then e.m.f. of the cell becomes zero.

Q. 3. Consider a cell given below:

$$\mathbf{Cu \mid Cu^{2+} \parallel Cl^- \mid Cl_2, Pt}$$ *[NCERT Exemplar]*

Write the reactions that occur at anode and cathode.

Ans. Anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode: $Cl_2 + 2e^- \longrightarrow 2Cl^-$

Q. 4. Depict the galvanic cell in which the cell reaction is $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$. *[NCERT Exemplar] [HOTS]*

Ans. $Cu \mid Cu^{2+}(\text{conc.}) \mid\mid Ag^+(\text{conc.}) \mid Ag$

Q. 5. What is the reference electrode in determining the standard electrode potential?

Ans. Normal hydrogen electrode (NHE).

Q. 6. Why is it not possible to measure the single electrode potential?

Ans. Oxidation or reduction cannot take place alone. Moreover, electrode potential is a relative tendency and can be measured with respect to a reference electrode only.

Q. 7. Define electrochemical series.

Ans. The arrangement of elements in the increasing or decreasing order of their standard reduction potential is called electrochemical series.

Q. 8. Write Nernst equation for single electrode potential.

Ans. For the electrode reaction $M^{n+} + ne^- \longrightarrow M$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{[M]}{[M^{n+}]} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

Q. 9. Write Nernst equation for the general cell reaction $aA + bB \xrightarrow{ne^-} xX + yY$.

Ans. If n moles of electrons are transferred, Nernst equation is $E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln\frac{[X]^x[Y]^y}{[A]^a[B]^b}$.

Q. 10. Write Nernst equation for the reaction

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$

Ans. $E_{cell} = E^o_{cell} - \frac{RT}{6F}\ln\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} \qquad (\because n = 6)$

Q. 11. How can the reduction potential of an electrode be increased?

Ans. $M^{n+} + ne^- \longrightarrow M,$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]} = E^o_{M^{n+}/M} + \frac{RT}{nF}\ln[M^{n+}]$$

Thus, electrode potential can be increased by increasing the metal ion concentration.

Q. 12. What flows in the internal circuit of a galvanic cell?

Ans. Ions.

Q. 13. What does the negative value of E^o_{cell} indicate?

Ans. Negative E^o_{cell} value means $\Delta_r G^o$ will be +ve, and the cell will not work.

Q. 14. Why is alternating current used for measuring resistance of an electrolytic solution? *[NCERT Exemplar]*

Ans. Alternating current is used to prevent electrolysis so that concentration of ions in the solution remains constant.

Q. 15. What is meant by cell constant?

Ans. Cell constant is the ratio of distance (l) between electrodes and area of cross-section (A). It is denoted by $\frac{l}{A}$. Its unit is cm^{-1}.

Q. 16. Define specific conductance or conductivity.

Ans. Specific conductance is defined as conductance of electrolyte when distance between electrodes is 1 cm and area of cross section is 1 cm^2.

Q. 17. What is the effect of temperature on ionic conductance? *[CBSE 2019 (56/3/2)]*

Ans. The ionic conductance increases with increase in temperature because the degree of dissociation increases with increase in temperature.

Q. 18. Write the mathematical expression for Kohlrausch's law.

Ans. $\Lambda_m^o = v_c\Lambda_c^o + v_a\Lambda_a^o$, where ν_c and ν_a are the number of cations and anions respectively in one formula unit of the compound.

Q. 19. Why on dilution the Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually? *[NCERT Exemplar]*

Ans. In the case of CH_3COOH, which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.

$$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$$

Q. 20. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn? *[CBSE Patna 2015]*

Ans. $Zn^{2+} + 2e^- \longrightarrow Zn$

Quantity of charge required for the reduction of one mole of Zn^{2+} = 2F = 2 × 96500 C = 193000 C

Q. 21. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed? *[NCERT Exemplar] [HOTS]*

Ans. The pH of the solution will increase as NaOH is formed in the electrolytic cell.

Q. 22. Value of standard electrode potential for the oxidation of Cl– ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water? *[NCERT Exemplar]*

Ans. On electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential hence Cl^- is oxidised instead of water.

Q. 23. What is primary cell? Give an example. *[CBSE Delhi 2008]*

Ans. A primary cell is one in which the redox reaction occurs only once and the cell becomes dead after some time and cannot be used again, *e.g.*, dry cell.

Q. 24. Why does a dry cell become dead after a long time even if it has not been used?

Ans. Even though not in use, a dry cell becomes dead after some time because the acidic NH_4Cl corrodes the zinc container.

Q. 25. What is the role of $ZnCl_2$ in a dry cell?

Ans. $ZnCl_2$ combines with the NH_3 produced to form the complex salt $[Zn(NH_3)_2 Cl_2]$ otherwise the pressure developed due to NH_3 would crack the seal of the cell.

Q. 26. Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why? *[NCERT Exemplar]*

Ans. Ions are not involved in the overall cell reaction of mercury cells.

Q. 27. Write the name of the electrolyte used in (*i*) fuel cell (*ii*) mercury cell.

Ans. (*i*) Concentrated aqueous KOH solution.

(*ii*) Moist mercuric oxide (HgO) mixed with KOH.

Q. 28. What is the overall electrochemical reaction taking place in rusting?

Ans. $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

Q. 29. Write the chemical formula of rust.

Ans. $Fe_2O_3 . xH_2O$

Q. 30. What is galvanization?

Ans. The process of coating zinc over iron is called galvanization.

Q. 31. What is cathodic protection?

Ans. A process in which a metal is connected with a more reactive metal which acts as anode and the metal to be protected acts as a cathode is known as cathodic protection.

Q. 32. Which type of a metal can be used in cathodic protection of iron against rusting?

Ans. A metal which is more electropositive than iron such as Al, Zn, Mg can be used in cathodic protection of iron against rusting.

Q. 33. Using the E^o values of X and Y, predict which is better for coating the surface of iron to prevent rust and why?

Given: $[E^o_{(Fe^{2+}/Fe)} = -0.44\ V]$, $[E^o_{(X^{2+}/X)} = -2.36\ V]$, $[E^o_{(Y^{2+}/Y)} = -0.14\ V]$ ***[CBSE 2019 (56/4/3)]***

Ans. X, as its standard reduction potential is less than Y. Therefore, it will undergo oxidation more easily than Y.

Q. 34. Three iron sheets have been coated separately with three metals *A*, *B* and *C* whose standard electrode potentials are given below.

Metal	***A***	***B***	***C***	**Iron**
E^o	**– 0.46 V**	**– 0.66 V**	**– 0.20 V**	**– 0.44 V**

Identify in which case rusting will take place faster when coating is damaged. ***[HOTS]***

Ans. As iron (– 0.44 V) has lower standard reduction potential than C (– 0.20 V) only and therefore when coating is broken, rusting will take place faster.

Short Answer Questions–I [2 marks]

Q. 1. At what pH of HCl solution will hydrogen gas electrode show electrode potential of –0.118 V? H_2 gas is passed at 298 K and 1 atm pressure.

Ans. $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation,

$$E_{H^+/\frac{1}{2}H_2} = E^o_{H^+/\frac{1}{2}H_2} - \frac{0.059}{n}\log\frac{1}{[H^+]}$$

$$-0.118 = 0 - \frac{0.059}{1}\log\frac{1}{[H^+]}$$

$$-0.118 = 0.059 \log [H^+]$$

or $$-0.118 = -0.059\ pH$$

$$pH = \mathbf{2}$$

Q. 2. Calculate $\Delta_r G^o$ and log K_c for the following reaction: ***[CBSE 2019 (56/4/1)]***

$$Cd^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cd(s)$$

Given: $E^o_{Cd^{2+}/Cd} = -0.403\ V$, $E^o_{Zn^{2+}/Zn} = -0.763\ V$

Ans. $Cd^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cd(s)$

Here,
$$\begin{aligned} E^o_{cell} &= E^o_{cathode} - E^o_{anode} \\ &= E^o_{Cd^{2+}/Cd} - E^o_{Zn^{2+}/Zn} \\ &= -0.403\ V - (-0.763\ V) \\ &= 0.360\ V \end{aligned}$$

$$E^o_{cell} = 0.360\ V;\ n = 2$$

$$\begin{aligned} \Delta_r G^o &= -nFE^o_{cell} \\ &= -2 \times 96500\ mol^{-1} \times 0.36\ V \\ &= 69480\ CV\ mol^{-1} \\ &= 69480\ J\ mol^{-1} \\ &= \mathbf{69.48\ kJ\ mol^{-1}} \end{aligned}$$

$$\log K_c = \frac{n}{0.059} E^o_{cell}$$

$$= \frac{2}{0.059} \times 0.36$$

$$\log K_c = \mathbf{12.20}$$

Q. 3. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity. **[*CBSE Delhi 2013*]**

Ans. $\wedge_m = \frac{\kappa \times 1000}{C} = \frac{0.025 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}} = \mathbf{125 \text{ S cm}^2 \text{ mol}^{-1}}$

Q. 4. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution. **[*CBSE (AI) 2012*]**

Ans. $\wedge_m = \frac{\kappa \times 1000}{M}$

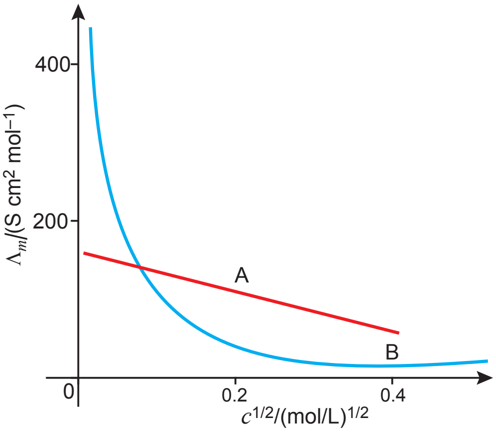
$$\kappa = \frac{\wedge_m \times M}{1000}$$

$$\kappa = \frac{138.95 \text{ S cm}^2 \text{mol}^{-1} \times 1.5 \text{ mol L}^{-1}}{1000 \text{ cm}^3 \text{ L}^{-1}} = \mathbf{0.208455 \text{ cm}^{-1}}$$

Q. 5. The following curve is obtained when molar conductivity (Λ_m) is plotted against the square root of concentration, $c^{1/2}$ for two electrolytes A and B.

(*i*) How do you account for the increase in the molar conductivity of the electrolyte A on dilution?

(*ii*) As seen from the graph, the value of limiting molar conductivity (Λ^o_m) for electrolyte B cannot be obtained graphically. How can this value be obtained? **[*CBSE Sample Paper 2016*]**



Ans. (*i*) As seen from the graph, electrolyte 'A' is a strong electrolyte which is ionised almost completely in solutions. For strong electrolyte 'A', the number of ions does not increase appreciably on dilution and only mobility of ions increases due to decrease in interionic attraction. Therefore, molar conductivity increases a little as shown in graph by a straight line.

(*ii*) Limiting molar conductivity (Λ^o_m) for weak electrolyte 'B' can be obtained by using Kohlrausch law of independent migration of ions which says that limiting molar conductivity of an electrolyte is equal to the sum of the individual contribution of the cation and anion of the electrolyte.

Q. 6. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? **[*CBSE (AI) 2014*]**

Ans. Kohlrausch law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of cation and anion of the electrolyte.

In general, if an electrolyte on dissociation gives ν_+ cations and ν_- anions then its limiting molar conductivity is given by

$$\Lambda^o_m = \nu_+ \lambda^o_+ + \nu_- \lambda^o_-$$

where λ^o_+ and λ^o_- are the limiting molar conductivities of cations and anions respectively.

Conductivity of a solution decreases with dilution. This is due to the fact that the number of ions per unit volume that carry the current in a solution decreases with dilution.

Q. 7. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}. Given $\lambda^o_{(H^+)}$ = 349.6 S cm^2 mol^{-1} and $\lambda^o_{(CH_3COO^-)}$ = 40.9 S cm^2 mol^{-1} [*CBSE Delhi 2017*]

Ans. $\Lambda^o_{(CH_3COOH)} = \lambda^o_{(CH_3COO^-)} + \lambda^o_{(H^+)}$

$= (40.9 + 349.6)$ S cm^2 mol^{-1}

$= 390.5$ S cm^2 mol^{-1}

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{39.05 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1$$

$\Rightarrow \quad \alpha = \mathbf{10\%}$

Q. 8. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of $CuSO_4$.
(Molar mass of Cu = 63.5 g mol^{-1}, 1 F = 96500 C mol^{-1}) [*CBSE Allahabad 2015*]

Ans. $Cu^{2+} + 2e^- \longrightarrow Cu$

63.5 g of copper is deposited by 2 × 96500 C.

$\therefore$ 1.27 g of copper will be deposited by $\dfrac{2 \times 96500 \times 1.27}{63.5}$ C = 3860 C

$I = 2$ A, $Q = 3860$ C

$$\therefore\ t = \frac{Q}{I} = \frac{3860}{2} = \mathbf{1930\ s}$$

Q. 9. How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours? [*CBSE (AI) 2011*]

Ans. Mass of mercury produced at the cathode,

$$m = Z \times I \times t = \frac{M \times I \times t}{n \times F}$$

$$m = \frac{\text{M g mol}^{-1} \times 2\text{A} \times 3 \times 60 \times 60 \text{ s}}{2 \times 96500 \text{ C mol}^{-1}}$$

$$= 0.1119 \times \text{M g} = 0.119 \times \text{M g}$$

No. of moles of mercury produced $= \dfrac{0.119 \times \text{M g}}{\text{M g mol}^{-1}} = \mathbf{0.119\ mol}$

Q. 10. When a current of 0.75 A is passed through a $CuSO_4$ solution for 25 min, 0.369 g of copper is deposited at the cathode. Calculate the atomic mass of copper.

Ans. $W = Z \times I \times t$

$$0.369 = \frac{M}{2 \times 96500} \times 0.75 \times 25 \times 60 \qquad (M = \text{molar mass of copper})$$

M = **63.3 g/mol**

Q. 11. How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 milliampere?

Ans. $Q = I \times t$

Here, $I = \dfrac{300}{1000} = 0.3$ A; $t = 60$ s; Q = 0.3 A × 60 s = 18 C

$2Cl^- \longrightarrow Cl_2 + 2e^-$

2 × 96500 C deposit Cl_2 = 1 mol

$\therefore$ 18 C will deposit $Cl_2 = \dfrac{1 \text{ mol} \times 18 \text{ C} \times 6.022 \times 10^{23}}{2 \times 96500 \text{ C}}$ molecules

$= \mathbf{5.616 \times 10^{19}}$ **molecules**

Q. 12 Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation:

$$CrO_3(aq) + 6H^+ + 6e^- \longrightarrow Cr(s) + 3H_2O$$

Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of Cr = 52 g mol^{-1}, 1 F = 96500 C mol^{-1}]

Ans. 6 × 96500 C deposit Cr = 52 g

$\therefore$ 24,000 C will deposit Cr = $\dfrac{52\text{ g}}{6 \times 96500\text{ C}} \times 24,000\text{ C} = \mathbf{2.155\ g}$

52 g of Cr is deposited by 6 × 96500 C.

$\therefore$ 1.5 g of Cr require = $\dfrac{6 \times 96500\text{ C}}{52\text{ g}} \times 1.5\text{ g} = 16701.9\text{ C}$

$$Q = I \times t \qquad \Longrightarrow \qquad t = \frac{Q}{I}$$

$\therefore$ Time for which the current is passed = $\dfrac{16701.9\text{ C}}{12.5\text{ A}} = \mathbf{1336.15\ s}$

Q. 13. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E^o values to justify your answer.

Cathode : $Na^+(aq) + e^- \longrightarrow Na(s)$ $\quad E^o = -2.71$ V

$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$ $\quad E^o = 0.00$ V

Anode : $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$ $\quad E^o = +1.36$ V

$2H_2O(aq) \longrightarrow O_2(g) + 4H^+ + 4e^-$ $\quad E^o = +1.23$ V **[*CBSE 2019 (56/5/2)*]**

Ans. $H_2(g)$ is produced due to greater E^o value of H^+ ion and $Cl_2(g)$ is produced due to over-potential of oxygen.

Q. 14. Define the following terms:

(*i*) Molar conductivity (Λ_m) **(*ii*) Secondary batteries** **[*CBSE (AI) 2014*]**

Ans. (*i*) Molar conductivity, Λ_m of a solution at a dilution V is defined as the conductance of all the ions produced from one gram mole of the electrolyte dissolved in $V\ cm^3$ of the solution when the electrodes are one centimetre apart and the area of the electrodes is so large that the whole of the solution is contained between them.

$$\Lambda_m = \kappa \times V \quad or \quad \Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

where, κ is the conductivity and V is the volume of the solution containing 1 mole of the electrolyte.

(*ii*) Secondary batteries are those batteries which can be recharged by passing electric current through them and hence can be used over again *e.g.,* lead storage battery.

Q. 15. For the given cells:

Lead storage cell, Mercury cell, Fuel cell and Dry cell

Answer the following:

(*i*) Which cell is used in hearing aids?

(*ii*) Which cell was used in Apollo space programme? **[*CBSE 2020 (56/3/1)*]**

(*iii*) Which cell is used in automobiles and inverters?

(*iv*) Which cell does not have long life? **[*CBSE Delhi 2016; South 2016*]**

Ans. (*i*) Mercury cell (*ii*) Fuel cell

(*iii*) Lead storage cell (*iv*) Dry cell

Q. 16. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. **[*CBSE (AI) 2017*]**

Ans. Mercury cell

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

At cathode: $HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

$$\overline{Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)}$$

Q. 17. Write electrode reactions taking place in (*i*) Ni–Cd cell, (*ii*) Lead Acid Accumulator.

Ans. (*i*)

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^- \quad \text{(at anode)}$$

$$NiO_2(s) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq) \quad \text{(at cathode)}$$

(*ii*)

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^- \quad \text{(at anode)}$$

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l) \quad \text{(at cathode)}$$

Q. 18. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. ***[CBSE Delhi 2011]***

Ans. According to electrochemical theory of rusting, the impure iron surface behaves like small electrochemical cell in the presence of water containing dissolved oxygen or carbon dioxide. In this cell pure iron acts as anode and impure iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below.

At anode: $Fe \longrightarrow Fe^{2+} + 2e^-; \quad E^o_{Fe^{2+}/Fe} = -0.44\ V$

At cathode: $2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O; \quad E^o_{H^+/O_2/H_2O} = 1.23\ V$

Overall reaction: $Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O; \quad E^o_{cell} = 1.67\ V$

The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which comes out in the form of hydrated ferric oxide (rust).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.\,xH_2O \text{ (Rust)}$$

Short Answer Questions–II [3 marks]

Q. 1. One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. The other half-cell consists of a zinc electrode in a 0.10 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver ions in the solution.

(Given: $E^o_{Zn^{2+}/Zn} = -0.763$ V, $E^o_{Ag^+/Ag} = +0.80$ V) ***[CBSE (F) 2010]***

Ans. Electrochemical cell

$Zn(s)\,|\,Zn^{2+}\,(0.10\ M)\,||\,Ag^+\,(conc.)\,|\,Ag(s)$

$$E^o_{cell} = E^o_R - E^o_L = E^o_{Ag^+/Ag} - E^o_{Zn^{2+}/Zn}$$

$$= 0.80\ V - (-0.763)V = 1.563\ V$$

We know that,

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$1.48 = 1.563 - \frac{0.0591}{2}\log\frac{[0.10]}{[Ag^+]^2}$$

$$\log\frac{[0.10]}{[Ag^+]^2} = \frac{0.083}{0.02955} = 2.8087$$

Or

$$\frac{[0.10]}{[Ag^+]^2} = \text{antilog } 2.8087 = 643.7$$

$$[Ag^+]^2 = \frac{0.10}{643.7} = 1.553 \times 10^{-4}$$

$$[Ag^+] = \mathbf{1.247 \times 10^{-2}\ M}$$

Q. 2. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ($E^o_{Zn^{2+}/Zn}$ = – 0.76 V).

Ans. The electrode reaction written as reduction reaction is

$$Zn^{2+} + 2e^- \longrightarrow Zn\ (n = 2)$$

Applying Nernst equation, we get

$$E_{Zn^{2+}/Zn} = E^o_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$$[Zn^{2+}] = \frac{95}{100} \times 0.1\ M = 0.095\ M$$

$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095}$$

$$= -0.76 - 0.02955\ (\log 1000 - \log 95)$$

$$= -0.76 - 0.02955\ (3 - 1.9777) = -0.76 - 0.03021 = \mathbf{-0.79021\ V}$$

Q. 3. A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1 molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

(*i*) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

(*ii*) Calculate the cell potential, *E*, at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.

[$E^o_{Ni^{2+}/Ni}$ = – 0.25 V; $E^o_{Ag^+/Ag}$ = 0.80 V, log 10^{-1} = – 1] ***[CBSE (F) 2012]***

Ans. (*i*) **At anode:** $Ni \longrightarrow Ni^{2+} + 2e^-$

At cathode: $[Ag^+ + e^- \longrightarrow Ag] \times 2$

Cell reaction: $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Ag^+/Ag} - E^o_{Ni^{2+}/Ni}$$

$$= 0.80\ V - (-0.25\ V)$$

$$E^o_{cell} = \mathbf{1.05\ V}$$

(*ii*)
$$E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

Here, $n = 2$, $E^o_{cell} = 1.05$ V, $[Ni^{2+}] = 0.1$ M, $[Ag^+] = 1.0$ M

$$E_{cell} = 1.05\ V - \frac{0.059}{2} \log \frac{(0.1)}{(1)^2}$$

$$E_{cell} = 1.05V - 0.0295 \log 10^{-1}$$

$$= 1.05 + 0.0295\ V = \mathbf{1.0795\ V}$$

Q. 4. The emf of a cell corresponding to the reaction.

$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(0.1\ M) + H_2\ (g, 1\ atm)$ is 0.28 volt at 25°C.

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^o_{Zn^{2+}/Zn}$ = – 0.76 V, $E^o_{H^+/H_2}$ = 0 V ***[HOTS]***

Ans. Half-cell reactions:

At anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

Cell reaction: $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$= \left(E^{\circ}_{\text{H}^+/\text{H}_2} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}\right) - \frac{0.0591}{2}\log\frac{0.1}{[\text{H}^+]^2}$$

$$= [0 - (-0.76)] - 0.02955\,[\log 10^{-1} - 2\log(\text{H}^+)]$$

$$0.28 = 0.76 - 0.02955\,(-1 + 2\,\text{pH}) \qquad [\because\ \text{pH} = -\log(\text{H}^+)]$$

$$2\,\text{pH} - 1 = 16.244$$

$$\text{pH} = \mathbf{8.62}$$

Q. 5. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction

$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2$ is 960 kJ ($F = 96{,}500$ C mol^{-1}). ***[HOTS]***

Ans. $Al_2O_3(2Al^{3+} + 3O^{2-}) \longrightarrow 2Al + \frac{3}{2}O_2,\ n = 6e^-$

$\therefore \qquad \frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,\ n = \frac{2}{3} \times 6e^- = 4e^-$

$$\Delta_r G = 960 \times 1000 = 960000\ \text{J}$$

Now, $\qquad \Delta_r G = -nFE_{\text{cell}}$

$$\Rightarrow \qquad E_{\text{cell}} = -\frac{\Delta_r G}{nF} = \frac{-960000}{4 \times 96500} = \mathbf{-\,2.487\ V}$$

$\therefore$ Minimum potential difference needed to reduce Al_2O_3 is **– 2.487 V**.

Q. 6. Calculate $\Delta_r G^{\circ}$ and log K_c for the following reaction at 298 K:

$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s)$

Given: $E^{\circ}_{\text{cell}} = 0.30$ V ***[CBSE (F) 2016]***

Ans.

$$\begin{array}{lll}
Cr(s) & \longrightarrow & Cr^{3+}(aq) + 3e^-]\times 2 \\
Fe^{2+}(aq) + 2e^- & \longrightarrow & Fe(s) \qquad]\times 3 \\
\hline
2Cr(s) + 3Fe^{2+}(aq) & \longrightarrow & 2Cr^{3+}(aq) + 3Fe(s),\quad n = 6 \\
\hline
\end{array}$$

Here, $n = 6$, $E^{\circ}_{\text{cell}} = 0.30$ V

Substituting the values in the expression, $\log K_c = \frac{n}{0.059}E^{\circ}_{\text{cell}}$, we get

$$\log K_c = \frac{6}{0.059} \times 0.30$$

or $\qquad \log K_c = 30.5084$

$$K_c = \text{Antilog}\ (30.5084)$$

or $\qquad K_c = \mathbf{3.224 \times 10^{30}}$

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

$$= -6 \times 96500 \times 0.30$$

$$= -173700\ \text{J mol}^{-1}$$

$$\Delta G^{\circ} = \mathbf{-\,173.7\ kJ\ mol^{-1}}$$

Q. 7. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. [*CBSE (AI) 2012*]

Ans. $A = \pi r^2 = 3.14 \times \left(\frac{1}{2}\text{cm}\right)^2 = 0.785\ \text{cm}^2;\ l = 50\ \text{cm}$

$$\text{Resistivity, } \rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3\,\text{ohm} \times 0.785\ \text{cm}^2}{50\ \text{cm}} = \mathbf{87.135\ ohm\ cm}$$

$$\text{Conductivity, } \kappa = \frac{1}{\rho} = \frac{1}{87.135\ \text{ohm cm}} = \mathbf{0.01148\ S\ cm^{-1}}$$

$$\text{Molar Conductivity, } \Lambda_m = \frac{\kappa \times 1000}{\text{M}}$$

$$= \frac{0.01148\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.05\ \text{mol L}^{-1}}$$

$$= \mathbf{229.6\ S\ cm^2\ mol^{-1}}$$

Q. 8. From the following molar conductivities at infinite dilution, calculate Λ^o_m for NH_4OH.

Λ^o_m for $Ba(OH)_2 = 457.6\ \Omega^{-1}\ cm^2\ mol^{-1}$

Λ^o_m for $BaCl_2 = 240.6\ \Omega^{-1}\ cm^2\ mol^{-1}$

Λ^o_m for $NH_4Cl = 129.8\ \Omega^{-1}\ cm^2\ mol^{-1}$

Ans. $\Lambda^o_{m(NH_4OH)} = \lambda^o_{NH_4^+} + \lambda^o_{OH^-}$

$$= (\lambda^o_{NH_4^+} + \lambda^o_{Cl^-}) + \frac{1}{2}(\lambda^o_{Ba^{2+}} + 2\lambda^o_{OH^-}) - \frac{1}{2}(\lambda^o_{Ba^{2+}} + 2\lambda^o_{Cl^-})$$

$$= \Lambda^o_{m(NH_4Cl)} + \frac{1}{2}[\Lambda^o_{m(Ba(OH)_2)}] - \frac{1}{2}[\Lambda^o_{m(BaCl_2)}]$$

$$= 129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} \times 240.6$$

$$= \mathbf{238.3\ ohm^{-1}\,cm^2\,mol^{-1}}$$

Q. 9. Conductivity of 2.5×10^{-4} M methanoic acid is $5.25 \times 10^{-5}\ S\ cm^{-1}$. Calculate its molar conductivity and degree of dissociation.

Given: $\lambda^o(H^+) = 349.5\ S\ cm^2\ mol^{-1}$ and $\lambda^o(HCOO^-) = 50.5\ S\ cm^2\ mol^{-1}$. [*CBSE Allahabad 2015*]

Ans.

$$\Lambda^c_m = \frac{\kappa \times 1000}{M}$$

$$\Lambda^c_m = \frac{5.25 \times 10^{-5}\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{2.5 \times 10^{-4}\ \text{mol L}^{-1}}$$

$$\Lambda^c_m = \mathbf{210\ S\ cm^2\ mol^{-1}}$$

$$\Lambda^o_m\,(\text{HCOOH}) = \Lambda^o_{HCOO^-} + \Lambda^o_{H^+}$$

$$= 50.5\ \text{S cm}^2\ \text{mol}^{-1} + 349.5\ \text{S cm}^2\ \text{mol}^{-1}$$

$$= 400\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{210\ \text{S cm}^2\ \text{mol}^{-1}}{400\ \text{S cm}^2\ \text{mol}^{-1}} = 0.525$$

or $\alpha = \mathbf{52.5\%}$

Q. 10. ***(i)*** **A current of 1.50 A was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The weight of Ag deposited was 1.50 g. How long did the current flow?**

(ii) **Write the reactions taking place at the anode and cathode in the above cell.**

(iii) **Give reactions taking place at the two electrodes if these are made up of Ag.**

Ans. (*i*) $Ag^+ + e^- \longrightarrow Ag$

Quantity of charge required to deposit 108 g of silver = 96500 C

$\therefore$ Quantity of charge required to deposit 1.50 g of silver = $\frac{96500}{108} \times 1.50 = 1340.28$ C

$$t = \frac{Q}{I}$$

$\therefore$ Time taken = $\frac{1340.28}{1.50}$ = **893.52 s**

(*ii*) Inert electrodes

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

Cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

(*iii*) Ag electrodes

Anode: $Ag(s) \longrightarrow Ag^+(aq) + e^-$

Cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Q. 11. (*i*) **Calculate $\Delta_r G°$ for the reaction**

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$

Given: $E^o_{cell} = +2.71$ V, 1 F = 95600 C mol^{-1}

(*ii*) **Name the type of cell which was used in Apollo space programme for providing electrical power.** [*CBSE (AI) 2014*]

Ans. (*i*) $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$

$$\Delta_r G° = -nFE^o_{cell}$$

Here, $n = 2$, $F = 96500$ C mol^{-1} and $E^o_{cell} = 2.71$ V

$$\therefore \quad \Delta_r G° = -2 \times 96500 \text{ C mol}^{-1} \times 2.71 \text{ V}$$
$$= -523030 \text{ J mol}^{-1}$$
$$= \mathbf{-523.03 \text{ kJ mol}^{-1}}$$

(*ii*) $H_2—O_2$ fuel cell

Long Answer Questions [5 marks]

Q. 1. **The electrochemical cell given alongside converts the chemical energy released during the redox reaction**

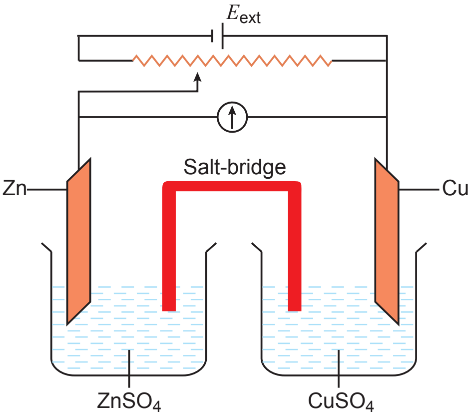
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

to electrical energy. It gives an electrical potential of 1.1 V when concentration Zn^{2+} and Cu^{2+} ions is unity. State the direction of flow of current and also specify whether zinc and copper are deposited or dissolved at their respective electrodes when:

(*i*) **an external opposite potential of less than 1.1 V is applied.**

(*ii*) **an external potential of 1.1 V is applied.**

(*iii*) **an external potential of greater than 1.1 V is applied.** [*HOTS*]



Ans. (*i*) Reaction continues to take place.

Electrons flow from Zn electrode to copper electrode, hence current flows from Cu to Zn. Zn dissolves and copper deposits at their respective electrodes.

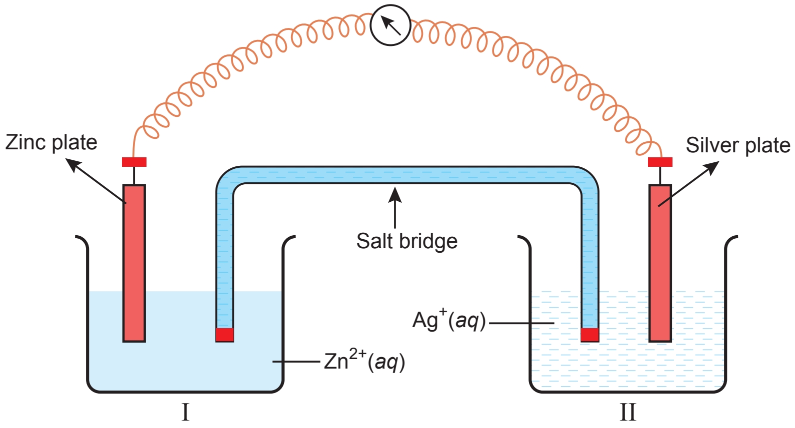
(*ii*) The reaction stops and no current flows.

A state of equilibrium is achieved and no change is observed at zinc and copper electrodes.

(*iii*) Reaction takes place in opposite directions.

Electrons flow from copper electrode to zinc electrode and hence current flows from Zn to Cu. Zinc deposits and copper dissolves at their respective electrodes. The cell functions as an electrolytic cell.

Q. 2. Consider the figure given below and answer the questions (*i*) to (*vi*):



(*i*) Write the direction of electron flow.

(*ii*) Is silver plate the anode or cathode?

(*iii*) What will happen if salt bridge is removed?

(*iv*) When will the cell stop functioning?

(*v*) How will concentration of Zn^{2+} ions and Ag^{+} ions be affected when the cell functions?

(*vi*) How will the concentration of Zn^{2+} ions and Ag^{+} ions be affected after the cell becomes 'dead'? **[*NCERT Exemplar*] [*HOTS*]**

Ans. (*i*) Electrons move from Zn to Ag.

(*ii*) Ag is the cathode.

(*iii*) Cell will stop functioning.

(*iv*) When $E_{cell} = 0$.

(*v*) Concentration of Zn^{2+} ions will increase and concentration of Ag^{+} ions will decrease.

(*vi*) When $E_{cell} = 0$, equilibrium is reached and concentration of Zn^{2+} ions and Ag^{+} ions will not change.

Q. 3. Calculate e.m.f and ΔG for the following cell at 298 K:

$$Mg(s) \mid Mg^{2+}\ (0.01\ M) \mid\mid Ag^{+}\ (0.0001\ M) \mid Ag(s)$$

Given: [$E^{o}_{Mg^{2+}/Mg} = -2.37$ V, $E^{o}_{Ag^{+}/Ag} = +0.80$ V] **[*CBSE Guwahati 2015*]**

Ans. At anode : $Mg \longrightarrow Mg^{2+} + 2e^{-}$

At cathode: $[Ag^{+} + e^{-} \longrightarrow Ag] \times 2$

$$Mg + 2Ag^{+} \longrightarrow Mg^{2+} + 2Ag; \quad n = 2$$

$$\begin{aligned} E^{o}_{cell} &= E^{o}_{cathode} - E^{o}_{anode} \\ &= E^{o}_{Ag^{+}/Ag} - E^{o}_{Mg^{2+}/Mg} \\ &= 0.80\ V - (-2.37\ V) \\ &= 3.17\ V \end{aligned}$$

Substituting $E^o_{cell} = 3.17$ V, $n = 2$, $[Mg^{2+}] = 1 \times 10^{-2}$ M, $[Ag^+] = 1 \times 10^{-4}$ M in Nernst equation for above cell reaction,

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log\frac{[Mg^{2+}]}{[Ag^+]^2}, \text{ we get}$$

$$E_{cell} = 3.17 - \frac{0.059}{2}\log\frac{10^{-2}}{(10^{-4})^2}$$

$$E_{cell} = 3.17 - 0.0295 \log 10^6$$

$$E_{cell} = 3.17 - 0.177 \text{ V}$$

$$E_{cell} = 2.993 \text{ V}$$

$$E_{cell} = \mathbf{2.993\ V}$$

Substituting $n = 2$, $F = 96500$ C mol^{-1}, $E_{cell} = 2.993$ V in the expression, $\Delta G = -nFE_{cell}$ we get

$$\Delta G = -2 \times 96500 \text{ C mol}^{-1} \times 2.993 \text{ V}$$

$$\Delta G = -577649 \text{ J mol}^{-1}$$

$$= \mathbf{-577.649\ kJ\ mol^{-1}}$$

Q. 4. (*i*) Calculate the standard free energy change for the following reaction at 25°C.

$$\mathbf{Au(s) + Ca^{2+}(1\ M) \longrightarrow Au^{3+}(1\ M) + Ca(s)}$$

$$\mathbf{E^o_{Au^{3+}/Au} = +1.50\ V,\quad E^o_{Ca^{2+}/Ca} = -2.87\ V}$$

Predict whether the reaction will be spontaneous or not at 25°C. Which of the above two half cells will act as an oxidising agent and which one will be a reducing agent?

(*ii*) Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for half reaction: **[*HOTS*]**

$$\mathbf{Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-} \text{ is } -0.71V}$$

and for $$\mathbf{Al^{3+} + 3e^- \longrightarrow 2Al(s) \text{ is } -1.66V}$$

Ans. (*i*)

$$E^o_{cell} = E^o_{Ca^{2+}/Ca} - E^o_{Au^{3+}/Au}$$

$$= (-2.87 \text{ V}) - (1.50 \text{ V})$$

$$= -4.37 \text{ V}$$

$$\Delta_r G^o_{cell} = -nFE^o_{cell}$$

$$= -6 \times 96500 \times (-4.37 \text{ V})$$

$$= \mathbf{+2530.230\ kJ/mol}$$

Since $\Delta_r G^o$ is positive, therefore, reaction is non-spontaneous.

Au^{3+}/Au half cell will be an oxidising agent while Ca^{2+}/Ca half cell will be a reducing agent.

(*ii*) E^o_{cell} for reaction of tarnished silver ware with aluminium pan is

(– 0.71 V) – (– 1.66 V) *i.e.*, **+ 0.95 V**

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as E^o_{cell} is positive.

Q. 5. (*i*) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K:

$$\mathbf{Sn(s) \mid Sn^{2+}(0.004\ M) \parallel H^+(0.020\ M) \mid H_2(g)\ (1\ bar) \mid Pt(s)}$$

(Given : $E^o_{Sn^{2+}/Sn} = -0.14$ V)

(*ii*) Give reasons:

(*a*) On the basis of E^o values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(*b*) Conductivity of CH_3COOH decreases on dilution.

Ans. (*i*) At anode: $\mathrm{Sn} \longrightarrow \mathrm{Sn}^{2+} + 2e^-$

At cathode: $\mathrm{H}^+ + e^- \longrightarrow \frac{1}{2}\mathrm{H}_2 \;] \times 2$

Cell reaction: $\mathrm{Sn} + 2\mathrm{H}^+ \longrightarrow \mathrm{Sn}^{2+} + \mathrm{H}_2$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{H^+/H_2}} - E^\circ_{\mathrm{Sn^{2+}/Sn}} = 0.00\text{ V} - (-0.14\text{ V}) = 0.14\text{ V}$

$[\mathrm{Sn}^{2+}] = 4 \times 10^{-3}$ M; $[\mathrm{H}^+] = 2 \times 10^{-2}$ M; $n = 2$

Substituting these values in the Nernst equation for above cell reaction

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log\frac{[\mathrm{Sn}^{2+}]}{[\mathrm{H}^+]^2}, \text{ we get}$$

$$E_{\text{cell}} = 0.14 - \frac{0.059}{2}\log\frac{4 \times 10^{-3}}{(2 \times 10^{-2})^2}$$

or $E_{\text{cell}} = 0.14 - 0.0295 \log 10$

$E_{\text{cell}} = 0.1400 - 0.0295 = \mathbf{0.1105\ V}$

(*ii*) (*a*) Due to the oxygen overpotential, liberation of chlorine gas is preferred.

(*b*) As number of ions per unit volume that carry the current in the solution decreases on dilution and therefore conductivity of CH_3COOH decreases on dilution.

Q. 6. (*i*) Represent the cell in which the following reaction takes place:

$$\mathbf{2Al(\mathit{s}) + 3Ni^{2+}(0.1\ M) \longrightarrow 2Al^{3+}(0.01\ M) + 3Ni(\mathit{s})}$$

Calculate the emf if $E^\circ_{\text{cell}} = 1.41$ V.

(*ii*) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ°_m) for weak electrolyte? **[*CBSE 2019 (56/2/2)*]**

Ans. (*i*) $2\mathrm{Al}(s) + 3\mathrm{Ni}^{2+}(0.1\text{ M}) \longrightarrow 2\mathrm{Al}^{3+}(0.01\text{ M}) + 3\mathrm{Ni}(s), n = 6$

Cell representation: $\mathrm{Al}(s)\,|\,\mathrm{Al}^{3+}(0.01\text{ M})\,||\,\mathrm{Ni}^{2+}(0.1\text{ M})\,|\,\mathrm{Ni}(s)$

Here, $n = 6$, $E^\circ_{\text{cell}} = 1.41$ V, $[\mathrm{Ni}^{2+}] = 0.1$ M, $[\mathrm{Al}^{3+}] = 1 \times 10^{-2}$ M

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Ni}^{2+}]^3}, \text{ we get}$$

$$E_{\text{cell}} = 1.41 - \frac{0.0591}{6}\log\frac{(10^{-2})^2}{(0.1)^3}$$

$$= 1.41 - 0.00985 \log 10^{-1}$$

$$= 1.41 + 0.00985 = 1.41985\text{ V}$$

$E_{\text{cell}} = \mathbf{1.42\ V}$

(*ii*) With increase in concentration, the greater interionic attraction retard the motion of the ions and therefore, the molar conductivity falls for both with increasing concentration. The limiting molar conductivity (Λ°_m) for weak electrolyte can be calculated by using Kohlrausch's law.

Q. 7. At 291 K, the molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 S cm^2 mol^{-1} respectively. If the molar conductivity of a centinormal solution of NH_4OH is 9.33 S cm^2 mol^{-1}, what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation constant of NH_4OH. **[*HOTS*]**

Ans. Here, we are given:

Λ°_m for $NH_4Cl = 129.8$ S cm^2 mol^{-1}

Λ°_m for NaOH $= 217.4$ S cm^2 mol^{-1}

Λ°_m for NaCl $= 108.9$ S cm^2 mol^{-1}

By Kohlrausch's law,

$$\Lambda^{\circ}_{m} \text{ for } NH_4OH = \lambda^{\circ}_{NH_4^+} + \lambda^{\circ}_{OH^-}$$

$$= \Lambda^{o}_{m}(NH_4Cl) + \Lambda^{o}_{m}(NaOH) - \Lambda^{o}_{m}(NaCl)$$

$$= [129.8 + 217.4 - 108.9] \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 238.3 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^{c}_{m} = 9.33 \text{ S cm}^2 \text{ mol}^{-1} \text{ (Given)}$$

$$\therefore \quad \text{Degree of dissociation } (\alpha) = \frac{\Lambda^{c}_{m}}{\Lambda^{o}_{m}} = \frac{9.33}{238.3} = 0.0392$$

or Percentage dissociation = 0.0392 × 100 = **3.92%**

Calculation of dissociation constant

	NH_4OH	$\rightleftharpoons$	NH_4^+	+	OH^-
Initial conc.	c		0		0
Equilibrium conc.	$c - c\alpha$ $= c(1 - \alpha)$		$c\alpha$		$c\alpha$

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Substituting, $c = 0.01$ N $= 0.01$ M, and $\alpha = 0.0392$, we get

We get, $$K = \frac{(0.01)\,(0.0392)^2}{1 - 0.0392}$$

$$= \frac{10^{-2} \times (3.92 \times 10^{-2})^2}{0.9608}$$

$$= \mathbf{1.599 \times 10^{-5}}$$

Q. 8. (*i*) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.

(*ii*) Calculate Λ°_{m} for acetic acid.

Given that Λ°_{m} (HCl) = 426 S cm^2 mol^{-1}, Λ°_{m} (NaCl) = 126 S cm^2 mol^{-1}

Λ°_{m} (CH_3COONa) = 91 S cm^2 mol^{-1} ***[CBSE Delhi 2010]***

Ans. (*i*) For definition refer to Basic Concepts Point 12.

Expression for the molar conductivity of acetic acid: $\Lambda^{\circ}_{m}(CH_3COOH) = \Lambda^{\circ}_{CH_3COO^-} + \Lambda^{\circ}_{H^+}$

(*ii*) $$\Lambda^{\circ}_{m}(CH_3COOH) = \Lambda^{\circ}_{CH_3COO^-} + \Lambda^{\circ}_{H^+}$$

$$= \Lambda^{\circ}_{CH_3COO^-} + \Lambda^{\circ}_{Na^+} + \Lambda^{\circ}_{H^+} + \Lambda^{\circ}_{Cl^-} - (\Lambda^{\circ}_{Na^+} + \Lambda^{\circ}_{Cl^-})$$

$$= \Lambda^{\circ}_{m(CH_3COONa)} + \Lambda^{\circ}_{m(HCl)} - \Lambda^{\circ}_{m(NaCl)}$$

$$= (91 + 426 - 126) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= \mathbf{391 \text{ S cm}^2 \text{ mol}^{-1}}$$

Q. 9. (*i*) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(*ii*) Calculate the potential for half-cell containing 0.10M $K_2Cr_2O_7$ (*aq*), 0.20 M Cr^{3+}(*aq*) and 1.0 × 10^{-4} M H^+(*aq*). The half cell reaction is

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

and the standard electrode potential is given as E° = 1.33V. ***[CBSE (AI) 2011]***

Ans. (*i*) Refer to Basic Concepts Point 26(*b*).

(*ii*) For half cell reaction

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

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

Here, $E^o = 1.33$ V, $n = 6$, $[Cr^{3+}] = 0.2$ M

$[Cr_2O_7^{2-}] = 0.1$ M, $[H^+] = 1 \times 10^{-4}$ M

Substituting these values in the given expression, we get

$$E_{cell} = 1.33\text{ V}- \frac{0.0591}{6}\log\frac{(0.20)^2}{(0.1)(10^{-4})^{14}}$$

$$= 1.33\text{ V} - \frac{0.0591}{6}\log(4 \times 10^{55})$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[\log 4 + \log 10^{55}]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[2\log 2 + 55\log 10]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[2 \times 0.3010 + 55]$$

$$= 1.33\text{ V} - 0.548\text{ V} = \mathbf{0.782\ V}$$

Q. 10. (*i*) Define the following terms: **[*CBSE (AI) 2014*]**

(*a*) Limiting molar conductivity

(*b*) Fuel cell

(*ii*) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Ans. (*i*) (*a*) The limiting value of molar conductivity when concentration approaches to zero is called limiting molar conductivity.

(*b*) A fuel cell is a device which converts energy produced during the combustion of fuels like hydrogen, methane, methyl alcohol etc. directly into electrical energy. One such successful fuel cell is hydrogen-oxygen fuel cell.

(*ii*) For 0.1 mol L^{-1} KCl solution,

Conductivity, $\kappa = 1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, Resistance, $R = 100\ \Omega$

Cell constant = Conductivity × resistance

$$= 1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1} \times 100\ \Omega = 1.29\ cm^{-1}$$

For 0.02 mol L^{-1} solution,

Resistance = 520 Ω, Cell constant = 1.29 cm^{-1}

$$\text{Conductivity, } \kappa = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{129\ cm^{-1}}{520\ \Omega} = \mathbf{0.00248\ \Omega^{-1}\ cm^{-1}}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\text{Conductivity }(\kappa) \times 1000\ cm^3\ L^{-1}}{\text{Molarity}}$$

$$= \frac{0.00248\ \Omega^{-1}\ cm^{-1} \times 1000\ cm^3\ L^{-1}}{0.02\ mol\ L^{-1}}$$

$$= \mathbf{124\ \Omega^{-1}\ cm^2\ mol^{-1}}$$

Q. 11. (*i*) **State two advantages of H_2—O_2 fuel cell over ordinary cell.** [*CBSE 2020 (56/1/1)*]

(*ii*) **Silver is electrodeposited on a metallic vessel of total surface area 500 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.**

[Given: Density of silver = 10.5 g cm^{-3}, Atomic mass of silver = 108 amu, F = 96,500 C mol^{-1}]

Ans. (*i*) **Advantages of fuel cell:**

(*a*) It is a pollution-free device since no harmful products are formed.

(*b*) Its efficiency is about 75% which is considerably higher than conventional cells.

(*c*) It is a continuous source of energy if the supply of gases is maintained. (*Any Two*)

(*ii*)

$$m = Z\,I\,t = \frac{108}{96500} \times 0.5 \times 2 \times 3600 = 4.029 \text{ g}$$

$$d = \frac{m}{V} \quad \Rightarrow \quad V = \frac{m}{d}$$

$$V = \frac{4.029 \text{ g}}{10.5 \text{ g cm}^{-3}} = 0.3837 \text{ cm}^3$$

Let the thickness of silver deposited be x cm.

$$\therefore \quad V = A \times x \quad \text{or} \quad x = \frac{V}{A}$$

$$x = \frac{0.3837}{500} = \mathbf{7.67 \times 10^{-4} \text{ cm.}}$$

Q. 12. (*i*) **Calculate E°_{cell} for the following reaction at 298 K:**

$$2Al(s) + 3Cu^{2+}(0.01\text{ M}) \longrightarrow 2Al^{3+}(0.01\text{ M}) + 3Cu(s)$$

Given: E_{cell} = 1.98 V

(*ii*) **Using the E° values of A and B, predict which is better for coating the surface of iron [$E^{\circ}_{Fe^{2+}/Fe}$ = –0.44 V] to prevent corrosion and why?**

Given: [$E^{\circ}_{A^{2+}/A}$ = – 2.37 V, $E^{\circ}_{B^{2+}/B}$ = – 0.14 V] [*CBSE Central 2016*]

Ans. (*i*)

$$\begin{array}{l} [Al(s) \longrightarrow Al^{3+}(aq) + 3e^-] \times 2 \\ [Cu^{2+} + 2e^- \longrightarrow Cu] \times 3 \\ \hline 2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu, \quad n = 6 \end{array}$$

Here, $n = 6$, $E_{cell} = 1.98$ V, $[Al^{3+}] = 1 \times 10^{-2}$ M, $[Cu^{2+}] = 1 \times 10^{-2}$ M

Substituting these values in the Nernst equation for above electrochemical change,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} \quad \text{we get}$$

$$1.98 = E^{\circ}_{cell} - \frac{0.059}{6} \log \frac{(10^{-2})^2}{(10^{-2})^3}$$

$$1.98 = E^{\circ}_{cell} - \frac{0.059}{6} \log 10^2$$

$$E^{\circ}_{cell} = 1.98 + \frac{0.059}{6} \times 2 \log 10$$

$$= 1.98 + 0.0197 = \mathbf{1.9997 \text{ V}}$$

(*ii*) A, as its standard reduction potential is less than B, therefore, it will undergo oxidation more easily than B.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. **While charging the lead storage battery ______________.**

   (*a*) $PbSO_4$ anode is reduced to Pb. (*b*) $PbSO_4$ cathode is reduced to Pb.

   (*c*) $PbSO_4$ cathode is oxidised to Pb. (*d*) $PbSO_4$ anode is oxidised to PbO_2.

2. **When 0.1 mole of MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is**

   (*a*) 96500 C (*b*) 9650 C

   (*c*) 96.50 C (*d*) 2 × 96500 C

3. **Which of the following statement is correct?**

   (*a*) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.

   (*b*) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.

   (*c*) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.

   (*d*) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. **Assertion (*A*)** : Rusting of iron is quicker in saline water than in ordinary water.

   Reason (*R*) : Salt water helps in flow of current in the miniature cell developed on the iron surface.

5. **Assertion (*A*)** : An electrochemical cell can be set up only if the redox reaction is spontaneous.

   Reason (*R*) : A reaction is spontaneous if free energy change is negative.

6. **Assertion (*A*)** : If $\lambda^o_{Na^+}$ and $\lambda^o_{Cl^-}$ are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation: $\lambda^o_{NaCl} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}$

   Reason (*R*) : This is according to Kohlrausch law of independent migration of ions.

Answer the following questions:

7. What does the negative sign in the expression $E^o_{Zn^{2+}/Zn} = -0.76\text{ V}$ mean? **(1)**

8. What is the value of K_c, when $E^o = 0$ V? **(1)**

9. (*i*) For a weak electrolyte, molar conductance in dilute solution increases sharply as its concentration in solution is decreased. Give reason.

   (*ii*) Write overall cell reaction for lead storage battery when the battery is being charged. **(2)**

10. Two half-reactions of an electrochemical cell are given below:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l); \quad E^o = +1.51\text{ V}$$

$$Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-, \quad E^o = +0.51\text{ V}$$

Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured. **(2)**

11. Determine the values of equilibrium constant (K_c) and $\Delta G°$ for the following reaction:

$$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(s) + 2Ag(s), E^o = 1.05\text{ V}$$

(1 F = 96500 C mol^{-1}) **(2)**

12. Account for the following:

(*i*) Alkaline medium inhibits the rusting of iron.

(*ii*) Iron does not rust even if the zinc coating is broken in a galvanized iron pipe. **(2)**

13. A voltaic cell is set up at 25°C with the following half cells:

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)

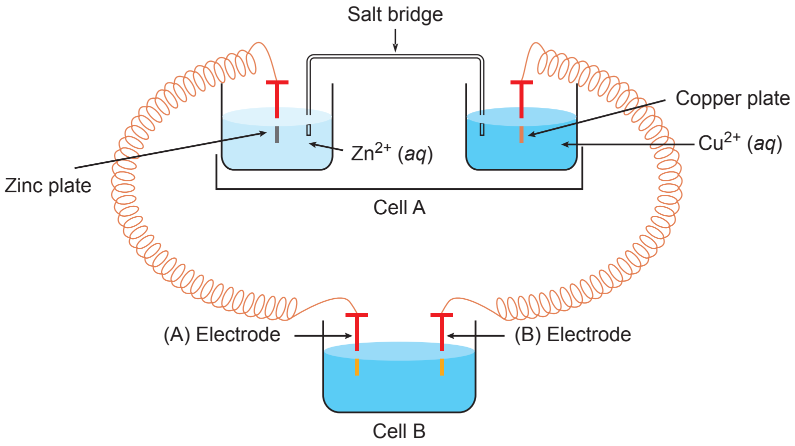
Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$E^o_{Ni^{2+}/Ni} = -0.25$ V; $E^o_{Al^{3+}/Al} = -1.66$ V ($\log 8 \times 10^{-6} = -5.097$) **(3)**

14. The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ^o_m for acetic acid is 390.5 S cm^2 mol^{-1}. **(3)**

15. Give three point of differences between electrochemical cell and electrolytic cell. **(3)**

16. Consider the figure given below and answer the following questions.



(*i*) Cell 'A' has E_{cell} = 2 V and Cell 'B' has E_{cell} = 1.1 V. Which of the two cells 'A' or 'B' will act as an electrolytic cell? Which electrode reactions will occurs in this cell?

(*ii*) In cell 'A' has E_{cell} = 0.5 V and cell 'B' has E_{cell} = 1.1 V then what will be the reactions at anode and cathode? **(5)**

Answers

1. (*a*) **2.** (*b*) **3.** (*c*) **4.** (*a*) **5.** (*b*) **6.** (*a*) **10.** 0.3105 V

11. 3.92×10^{39}; –202.65 kJ **13.** 1.4602 V **14.** 1.77×10^{-5} mol L^{-1}

Chapter–4

Chemical Kinetics

basic concepts

1. **Chemical Kinetics:** It is the branch of physical chemistry which deals with the study of the rate of chemical reaction and the mechanism by which the reaction occurs.
2. **Rate of Reaction:** It may be defined as the change in concentration of a reactant or product in unit time.

   For a general reaction, interval of $R \longrightarrow P$, the rate of reaction may be expressed as

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration of } R}{\text{Time taken}}$$

$$= \frac{\text{Increase in concentration of } P}{\text{Time taken}}$$

$$\text{Rate of reaction} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

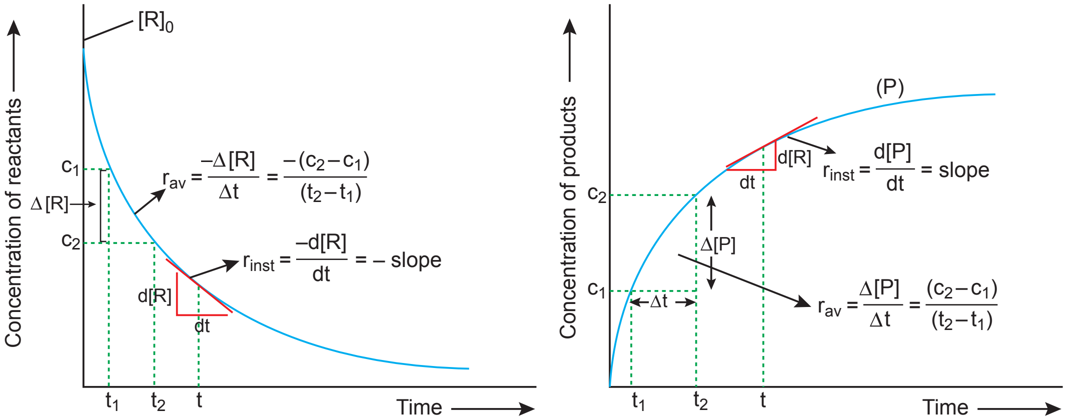
   The negative sign in the rate expression indicates the decrease in the concentration of the reactant and gives a positive value of the rate.

   Units of rate are mol L^{-1} s^{-1} or atm s^{-1} (in gaseous reactions).

   The above expression of rate gives us the average rate of reaction.
3. **Instantaneous Rate of Reaction:** It is the rate of reaction at a particular moment of time and measured as a very small concentration change over a very small interval of time.

   Mathematically, Instantaneous rate = (Average rate) $\Delta t \to 0$

   For a general reaction, $R \longrightarrow P$



(a) (b)

Fig. 4.1: Instantaneous and average rate of reaction

$$\text{Instantaneous rate} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate can be determined graphically by drawing a tangent at time t on either side of the curve for concentration of A or B vs time and calculating its slope.

Thus,
$$r_{inst} = \frac{-d[R]}{dt} = -\text{ slope (for } R)$$
$$r_{inst} = \frac{+d[P]}{dt} = \text{slope (for } P)$$

4. **General Expression for Rate of Reaction:** For a general reaction,
$$aA + bB \longrightarrow cC + dD$$
$$r_{av} = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$
$$r_{inst} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

5. **Factors Affecting the Rate of a Chemical Reaction:**

Rate of a reaction is influenced by following factors:

(*a*) **Nature of reactants:** It has been observed that ionic substances react more rapidly than the substances with covalent bond. This is because ions are immediately available in aqueous solution on dissociation hence, react rapidly but covalent molecules consume part of energy in breaking of bonds.

(*b*) **Concentration of reactants:** Rate of a reaction is directly proportional to the concentration of reactants.

(*c*) **Temperature:** Rate of a reaction increases with the increase in temperature.

(*d*) **Presence of catalyst:** In presence of catalyst, the rate of reaction generally increases and the equilibrium state is attained quickly in reversible reactions.

(*e*) **Surface area of the reactants:** The smaller the particle size, greater the surface area and faster is the reaction.

(*f*) **Radiations:** There are many reactions which either do not take place at all or are quite slow in the dark but take place at a considerable speed when exposed to sunlight or ultraviolet radiations, such reactions are called **photochemical reactions**. Examples are photosynthesis of carbohydrates, photography, etc.

6. **Rate Law:** It is an experimentally determined expression which relates the rate of reaction with concentration of reactants.

For a hypothetical reaction,
$$A + B \longrightarrow \text{Products}$$
$$\text{Rate} \propto [A]^m [B]^n$$
or
$$\text{Rate} = k[A]^m [B]^n$$

where k is a constant called specific rate of reaction or rate constant.

If
$$[A] = [B] = 1 \text{ mol L}^{-1} \text{ then}$$
$$\text{Rate} = k$$

Thus, rate constant may be defined as the rate of reaction when the concentration of each reactant in the reaction is unity.

7. **Order of Reaction:** It may be defined as the sum of powers of the concentration of the reactants in the rate law expression.

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

For a hypothetical reaction,
$$aA + bB + cC \longrightarrow \text{Products}$$

Let rate $= k[A]^m [B]^n [C]^p$

where, m = order of reaction with respect to A

n = order of reaction with respect to B

p = order of reaction with respect to C

Overall order of reaction $= m + n + p$

Units of rate constant:

For an *n*th order reaction, $A \longrightarrow \text{Product}$

$$\text{Rate} = k[A]^n$$

or
$$k = \frac{\text{Rate}}{[A]^n} = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

$$= (\text{concentration})^{1-n}\ \text{time}^{-1}$$

On considering S.I. unit of concentration as mol L^{-1} and time as seconds, the unit of $k = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$

(*a*) Examples of zero order reactions

(*i*) Some enzyme catalysed reactions and reactions which occur on metal surfaces.

(*ii*) Decomposition of gaseous ammonia on a hot platinum surface.

$$2NH_3(g) \xrightarrow[\text{Pt Catalyst}]{1130K} N_2(g) + 3H_2(g)$$

(*iii*) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

(*iv*) $2HI(g) \xrightarrow{\text{gold}} H_2(g) + I_2(g)$

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

(*b*) Examples of 1st order reactions

(*i*) All radioactive disintegrations are of the first order.

(*ii*) Decomposition of sulphuryl chloride.

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

Unit of $k = s^{-1}$. Therefore, change in unit concentration does not alter the value of k.

(*c*) Examples of 2nd order reactions

(*i*) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(*ii*) $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

Unit of k = litre mol^{-1} second^{-1}

(*d*) Examples of 3rd order reactions

(*i*) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(*ii*) $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$

Unit of k = litre^2 mol^{-2} second^{-1}

8. **(*a*) Elementary reaction:** A reaction which take place in one step is called an **elementary reaction**. When a sequence of elementary reactions gives the products, the reaction is called **complex reaction**.

(*b*) Molecularity: The number of reacting species (molecules, atoms, ions) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.

Reactions are classified as unimolecular, bimolecular and trimolecular for molecularity 1, 2 and 3 respectively.

Examples:

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Unimolecular reaction)

$2HI(g) \longrightarrow H_2(g) + I_2(g)$ (Bimolecular reaction)

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ (Trimolecular reaction)

The probability of more than three molecules colliding simultaneously is rare. Therefore, molecularity of a reaction does not extend beyond three. Molecularity can be defined only for an elementary reaction and has no meaning for a complex reaction.

(*c*) Intermediates: The species which are produced in one step and consumed in another are called intermediates.

(*d*) **Mechanism of reaction:** A series of elementary reactions proposed to account for the overall reaction is called mechanism of reaction. The overall rate of the reaction is controlled by the slowest step in a reaction and is called the **rate determining step**.

Consider the reaction, $2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$

The rate equation for this reaction is found to be

$$\text{Rate} = -\frac{1}{2}\frac{d}{dt}[H_2O_2] = k[H_2O_2]\,[I^-]$$

Evidences suggest that this reaction takes place in two steps as follows:

Step I. $H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$ (Intermediate)

Step II. $H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O_2$

The first step, being slow, is the rate determining step. Thus, the rate of formation of intermediate, IO^- will determine the rate of reaction.

9. **Pseudo First Order Reaction:** A reaction which is not truly of first order but under certain conditions becomes reaction of the first order is called a pseudo first order reaction. For example, the inversion of cane sugar is a bimolecular reaction but it is a first order reaction as concentration of H_2O is quite large and does not change appreciably.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]$$

10. **Zero Order Reactions:** In such reactions, the rate remains constant throughout the course of reaction, *i.e.*, the rate does not change with the change in concentration of reactants.

$$\text{Rate} = k\,[\text{Reactant}]^0 \quad \text{or} \quad \text{Rate} = k$$

Zero order reactions generally occur in a heterogeneous system, wherein the reactant is absorbed on the surface of a solid catalyst (here it is converted into product). The fraction of the surface of the catalyst covered by the reactant is proportional to its concentration at low values and the rate of reaction is of the first order. However, after certain concentration limit of the reactant, the surface of the catalyst is fully covered. As the concentration of the reactant further increases, no change in it takes place. Thus, rate becomes independent of concentration and the order of reaction becomes zero.

Integrated rate law for zero order reaction:

Consider a general zero order reaction

$$R \longrightarrow P$$

As it is a reaction of zero order

$$\therefore \quad \frac{-d[R]}{dt} = k[R]^0 = k \quad \Rightarrow \quad -d[R] = kdt$$

$$-\int dt[R] = k\int dt$$

$$-[R] = kt + C \qquad \ldots(i)$$

where C is constant of integration.

When $t = 0$, $[R] = [R]_0$

$$C = -[R]_0$$

Substituting the value of C in equation (*i*), we get

$$-[R] = kt - [R]_0$$

$$kt = [R]_0 - [R]$$

$$t = \frac{1}{k}\{[R]_0 - [R]\} \qquad \ldots(ii)$$

or

$$k = \frac{1}{t}\{[R]_0 - [R]\}$$

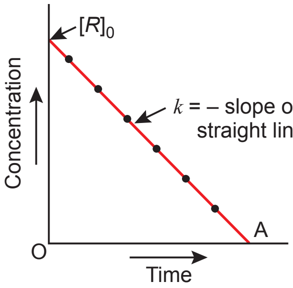


Fig. 4.2: Variation of concentration with time for a zero order reaction

Half-life of a reaction: It is the time in which the concentration of a reactant is reduced to half of its original value.

Half-life period of a zero order reaction:

When $[R] = \frac{[R]_0}{2}, t = t_{1/2}$

Substituting these values in equation (*ii*), we get

$$\therefore \qquad t_{1/2} = \frac{1}{k}\left\{[R]_0 - \frac{[R]_0}{2}\right\}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

$$t_{1/2} \propto [R]_0$$

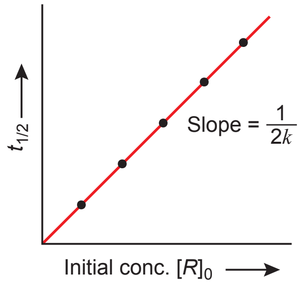


Fig. 4.3: Plot of $t_{1/2}$ versus initial concentration $[R]_0$ for a zero order reaction

11. First Order Reactions: In this class of reactions, the rate of reaction is directly proportional to the first power of the concentration of reacting substance.

$$\text{Rate} = k[\text{Reactant}]^1$$

Integrated rate law for 1st order reaction:

Consider the general first order reaction

$$R \longrightarrow P$$

As the reaction follows first order kinetics,

$$\therefore \qquad \frac{-d[R]}{dt} \propto [R]$$

$$\frac{-d[R]}{dt} = k[R] \qquad \Rightarrow \qquad \frac{-d[R]}{[R]} = k[dt]$$

Integrating both sides, we get

$$-\ln[R] = kt + C \qquad \ldots(i)$$

where C is constant of integration

When $t = 0$, $[R] = [R]_0$

$$-\ln[R]_0 = 0 + C$$

Substituting the value of C in (*i*), we get

$$-\ln[R] = kt - \ln[R]_0$$

$$\ln[R] = -kt + \ln[R]_0$$

$$kt = \ln\frac{[R]_0}{[R]} = 2.303\log\frac{[R]_0}{[R]}$$

$$\log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

$$\boxed{t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}}$$

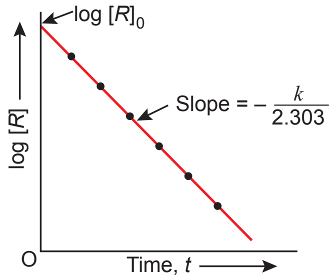


Fig. 4.4: Plot of log $[R]$ versus t

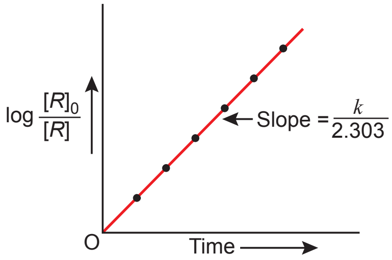


Fig. 4.5: Plot of log $[R]_0/[R]$ versus time (t)

where $[R]_0$ is initial concentration and $[R]$ is the final concentration.

Half-life period for a first order reaction

When $\quad t = t_{1/2}, \quad [R] = \frac{[R]_0}{2}$

$$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303}{k}\times 0.3010 \qquad \text{or} \qquad t_{1/2} = \frac{0.693}{k}$$

Since no concentration term is involved, therefore, $t_{1/2}$ for a first order reaction is independent of initial concentration.

12. **Integrated Rate Equation for a Gaseous System:** Consider a typical first order gas phase reaction.

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

Let P_i be the initial pressure of A and P_t the total pressure at time 't' and P_A, P_B and P_C be the partial pressures of A, B and C respectively at time t.

$$\text{Total pressure, } P_t = P_A + P_B + P_C \text{ (pressure units)}$$

If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

	$A(g) \longrightarrow$	$B(g)$ +	$C(g)$
At $t = 0$	P_i atm	0 atm	0 atm
At time $= t$	$(P_i - x)$ atm	x atm	x atm

$$P_t = (P_i - x) + x + x = P_i + x \quad or \quad x = P_t - P_i$$

$$P_A = P_i - x = P_i - (P_t - P_i) = 2P_i - P_t$$

$$k = \frac{2.303}{t} \log \frac{P_i}{P_A} = \frac{2.303}{t} \log \frac{P_i}{(2P_i - P_t)}$$

13. **Determination of Order of Reaction:**

There are many methods available for the determination of order of reaction.

(*a*) Graphical method (*b*) Initial rate method (*c*) Integrated rate law method

(*a*) Graphical method: This method is applicable to those reactions wherein only one reactant is involved.

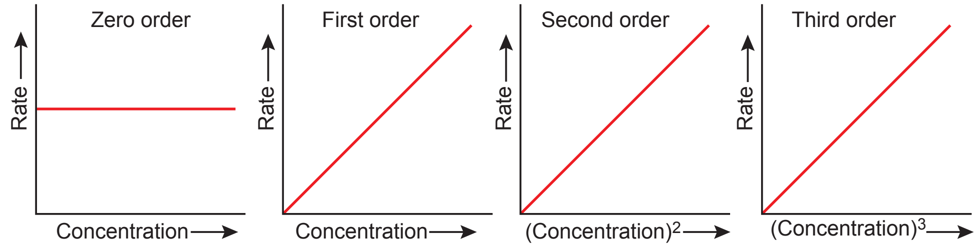


Fig. 4.6

(*b*) Initial rate method: This method is used to determine the order of reaction in such cases where more than one reactant is involved. It involves determination of order of reaction with respect to each reactant separately. For this, order of a particular reactant is determined. A series of experiment are carried out in which the concentration of that particular reactant is changed whereas the concentration of other reactants are kept constant. In each experiment, the rate is determined from the plot of concentration vs time. Similarly, concentration of another reactant is varied keeping the concentration of rest of the reactant constant and initial rate is determined. The data obtained are then compared to see how the initial rate depends on the initial concentration of each reactant. Thus, on the basis of the results the form of rate law is determined.

(*c*) Integrated rate law method: There are integrated rate law equations which are very convenient to understand the variation in concentration with time, for different order of reactions. After studying the concentrations at various intervals of time, the data are put in all the integrated rate law equations one by one. The expression which gives a constant value of the rate constant decides the order of the reaction.

Zero order equation; $k = \dfrac{[R]_0 - [R]}{t}$,

First order equation; $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$

14. **Temperature Dependence of Rate of a Reaction:**

(*a*) Temperature coefficient: It is defined as the ratio of rate constants of the reaction at two temperatures differing by 10°.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } (T + 10)^\circ}{\text{Rate constant at } T^\circ}$$

For most of the reactions, temperature coefficient lies between 2 and 3.

(*b*) **Collision frequency (*z*):** It is defined as total number of collisions per unit volume per unit time.

(*c*) **Effective collisions:** Collisions which lead to the formation of product molecules are called effective collisions.

Rate of reaction = $f \times z$, where z is the collision frequency and f is the fraction of collisions, which are effective.

(*d*) **Threshold energy:** The minimum energy that the reacting molecules must possess in order to undergo effective collisions to form the product is called threshold energy.

(*e*) **Activated complex:** The arrangement of atoms corresponding the energy maxima (threshold energy) during the course of a reaction is called activated complex or transition state. The activated complex has partial reactant character and partial product character.

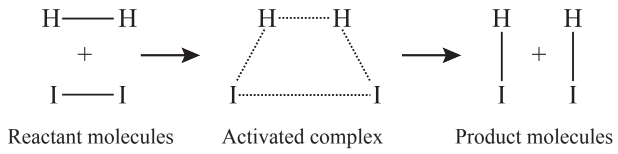


Fig. 4.7: Formation of activated complex from H_2 and I_2 during HI formation

Characteristics of an activated complex

(*i*) The potential energy of the activated complex is maximum.

(*ii*) The activated complex has a transient existence and breaks up at a definite rate to form the products.

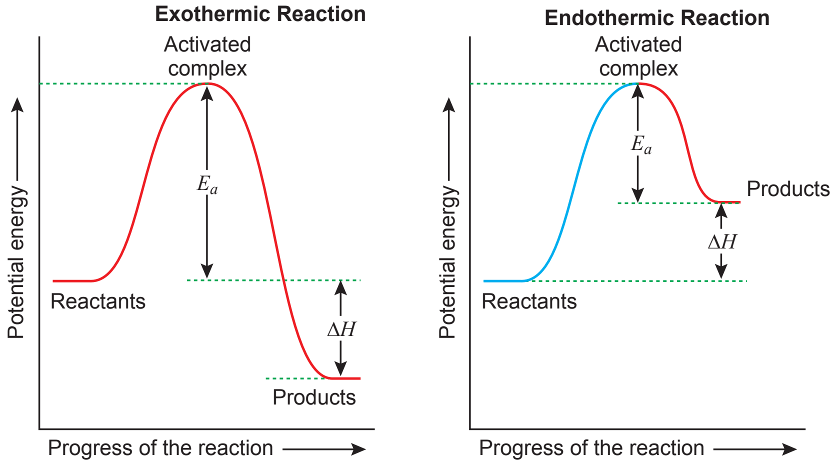


Fig. 4.8: Concept of Activation Energy

(*f*) **Activation energy:** The energy required to form activated complex is called activation energy. It is the difference between the threshold energy and the average energy possessed by the reacting molecules.

Activation energy (E_a) = Threshold energy – Average energy possessed by reacting molecules

$$\text{Reactants} \xrightarrow{\text{Activation energy}} \text{Activated complex} \xrightarrow{\text{Energy}} \text{Products}$$

For fast reactions, activation energies are low whereas for slow reactions activation energies are high.

(*g*) **Arrhenius equation:** It relates rate constant with temperature in the following way:

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

where A is constant called frequency factor, E_a is the energy of activation.

$$\ln k = \ln A - \frac{E_a}{RT}$$

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

A plot of log k vs. $1/T$ is a straight line whose slope is $-\dfrac{E_a}{2.303\,R}$ and intercept is log A.

If k_1 and k_2 are the rate constants at two temperatures T_1 and T_2, then

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \qquad ...(i)$$

$$\log k_2 = \log A - \frac{E_a}{2.303\,\mathrm{RT}_2} \qquad ...(ii)$$

Subtracting (*i*) from (*ii*), we get,

$$\log k_2 - \log k_1 = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

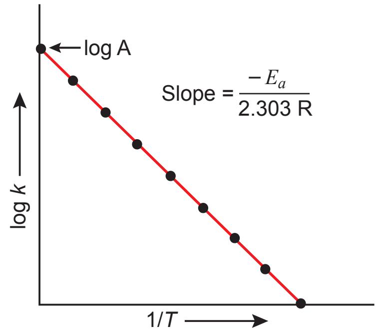


Fig. 4.9: log k vs 1/T

(*h*) Effect of temperature on rate of reaction:

Increasing the temperature of a reaction mixture increases the fraction of molecules, which collide with energies greater than E_a. It is clear from the diagram alongside that with 10° rise in temperature, the area showing the fraction of molecules having energy equal to or greater than activation energy gets almost double leading to almost doubling of the rate of reaction.

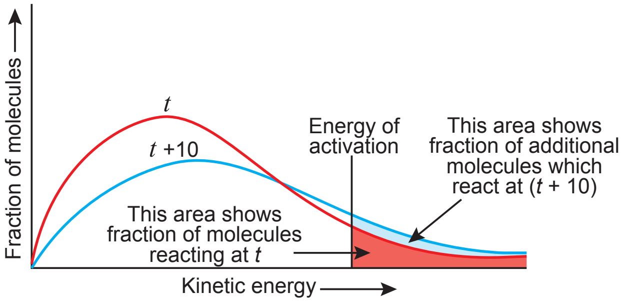


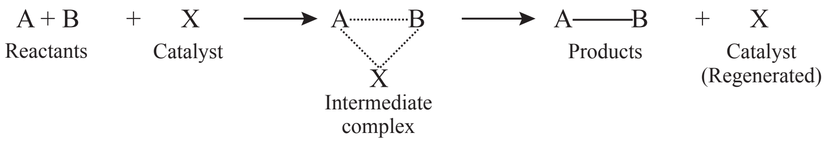
Fig. 4.10: Distribution curve showing temperature dependence of rate of a reaction

15. Catalyst: A catalyst is a substance which alters the rate of reaction without itself undergoing any chemical change at the end of the reaction.

For example, catalyst MnO_2 increases the rate of decomposition of potassium chlorate to a great extent.

$$2KClO_3 \xrightarrow[\text{Heat}]{MnO_2} 2KCl + 3O_2$$

According to intermediate complex theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.



It is believed that the catalyst provides an alternate pathway by reducing the activation energy between reactants and products hence lowering the potential energy barrier as shown in Fig. 4.11.

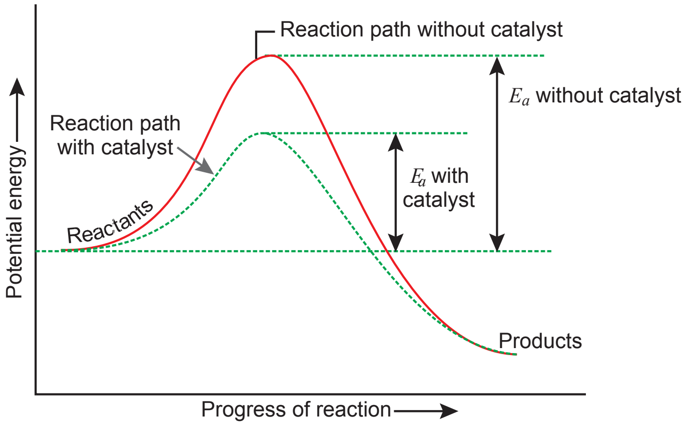


Fig. 4.11: Effect of catalyst on activation energy

It is clear from the Arrhenius equation $(k = Ae^{-E_a/RT})$ that lower the value of activation energy faster will be the rate of reaction.

For example, SO_2 is oxidised to SO_3 in the presence of nitric oxide as catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3$$

$$\underset{\text{Reactant}}{O_2(g)} + \underset{\text{Catalyst}}{2NO(g)} \longrightarrow \underset{\text{Intermediate}}{2NO_2(g)}$$

$$\underset{\text{Intermediate}}{NO_2(g)} + \underset{\text{Reactant}}{SO_2(g)} \longrightarrow \underset{\text{Product}}{SO_3(g)} + \underset{\text{Catalyst}}{NO(g)}$$

Characteristics of a catalyst

(*i*) It can only catalyse the spontaneous reaction but not the non-spontaneous reaction.

(*ii*) It does not change the equilibrium constant, but only helps in attaining equilibrium faster.

(*iii*) It can catalyse both forward and backward reactions to the same extent to maintain the equilibrium state in case of reversible reaction.

(*iv*) It does not alter the free energy change (ΔG) of a reaction.

(*v*) A small amount of the catalyst can catalyse a large amount of reactions.

16. Collision Theory of Chemical Reactions:

(*i*) Only effective collisions bring about a chemical reaction. The collisions in which molecules collide with sufficient kinetic energy (threshold energy) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

(*ii*) In collision theory, activation energy and proper orientation of the molecules together determine the criteria of an effective collision and hence the rate of chemical reaction.

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Where, Z_{AB} = The collision frequency of reactants A and B

P = Probability factor or steric factor

(It take into accounts the fact that in a collision, molecules must be properly oriented)

$e^{-Ea/RT}$ = Fraction of molecules with energies equal to or greater than E_a.

Important Formulae

1. Integrated Rate Equations

(*i*) For a zero order reaction:

$$t = \frac{[R]_0 - [R]}{k} \quad \text{and} \quad t_{1/2} = \frac{[R]_0}{2k}$$

(*ii*) For a first order reaction:

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \quad \text{and} \quad t_{1/2} = \frac{0.693}{k}$$

Amount of the substance left after n half lives of Ist order reaction = $\frac{[R]_0}{2^n}$.

2. Arrhenius Equation

(*i*) $k = A\,e^{-E_a/RT}$

where k = Rate constant, A = Arrhenius factor or frequency factor, E_a = Activation energy, R = Gas constant, T = Temperature in Kelvin

(*ii*) $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

where k_1 = Rate constant at T_1 and k_2 = Rate constant at T_2

(*iii*) $E_a = -2.303 \times R \times \text{slope}\left(\text{in a plot of } \log k \text{ } vs \text{ } \frac{1}{T}\right)$

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. For the reaction $R \rightarrow P$ the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Ans. The average rate $= -\dfrac{\Delta[R]}{\Delta t} = -\dfrac{[R_2]-[R_1]}{t_2-t_1}$

$$= -\frac{0.02\text{ M} - 0.030\text{ M}}{25\text{ min}} = -\frac{-0.01\text{ M}}{25\text{ min}} = 4 \times 10^{-4}\text{ M min}^{-1}$$

or $$= \frac{0.01\text{ M}}{25 \times 60\text{ s}} = \mathbf{6.66 \times 10^{-6}\ M\ s^{-1}}.$$

Q. 2. In a reaction 2A → Products, concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Rate of reaction = Rate of disappearance of A

$$= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{(0.4-0.5)\text{ mol L}^{-1}}{10\text{ min}} = \mathbf{0.005\ mol\ L^{-1}\ min^{-1}}$$

Q. 3. For a reaction, A + B → Product, the rate law is given by $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

Ans. Order of reaction $= \dfrac{1}{2} + 2 = \mathbf{\dfrac{5}{2}}$.

Q. 4. The conversion of molecule X to Y follows second order kinetics. If concentration of X is increased to three times, how will it affect the rate of formation of Y?

Ans. Rate $= k[X]^2$

$r_1 = k[X]^2$ ...(*i*)

$r_2 = k[3X]^2$ ...(*ii*)

Dividing (*ii*) by (*i*), $\dfrac{r_2}{r_1} = \dfrac{9k[X]^2}{k[X]^2}$

$r_2 = 9r_1$

Thus, rate of formation of Y will increase by **nine times**.

Q. 5. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 3 g?

Ans. Given $[R]_0 = 5$ g, $[R] = 3$g, $k = 1.15 \times 10^{-3}\text{ s}^{-1}$. As the reaction is of first order,

$$\therefore \quad t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{1.15 \times 10^{-3}\text{ s}^{-1}}\log\frac{5\text{ g}}{3\text{ g}} = 2.00 \times 10^3 (\log 1.667)\text{ s}$$

$$= 2.0 \times 10^3 \times 0.2219\text{ s} = 443.8\text{ s} = \mathbf{444\ s}$$

Q. 6. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans. For a first order reaction, $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{60\text{ min}} = \mathbf{1.155 \times 10^{-2}\ min^{-1}}$

Q. 7. What will be the effect of temperature on rate constant?

Ans. The rate constant of a reaction is nearly doubled with rise in temperature by 10°. The exact dependence of the rate constant on temperature is given by Arrhenius equation, $k = Ae^{-E_a/RT}$ where A is called frequency factor and E_a is the activation energy of the reaction.

Q. 8. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a.

Ans.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$E_a = 2.303\,R \log \frac{k_2}{k_1}\left[\frac{T_1 T_2}{T_2 - T_1}\right]$$

$$= (2.303)\,(8.314\text{ J K}^{-1}\text{ mol}^{-1})\left(\log \frac{2}{1}\right)\times\left(\frac{298\text{ K}\times 308\text{ K}}{308\text{ K} - 298\text{ K}}\right)$$

$$= 52898\text{ J mol}^{-1} = \mathbf{52.9\text{ kJ mol}^{-1}}$$

Q. 9. The activation energy for reaction, $2HI(g) \longrightarrow H_2(g) + I_2(g)$, is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

Ans. Fraction of molecules having energy equal to or greater than activation energy,

$$x = \frac{n}{N} = e^{-E_a/RT}$$

$$\therefore \qquad \ln x = -\frac{E_a}{RT} \quad \text{or} \quad \log x = -\frac{E_a}{2.303\,RT}$$

or

$$\log x = -\frac{209.5\times 10^3\text{ J mol}^{-1}}{2.303\times 8.314\text{ J K}^{-1}\text{ mol}^{-1}\times 581\text{ K}} = -18.8323$$

$$x = \text{Antilog }(-18.8323)$$

$$= \text{Antilog }(\overline{19}.1677) = \mathbf{1.471\times 10^{-19}}$$

NCERT Textbook Exercises

Q. 1. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants:

(*a*) $3NO(g) \longrightarrow N_2O(g) + NO_2(g)$ rate = $k[NO]^2$

(*b*) $H_2O_2(aq) + 3I^-(aq) + 2H^+ \longrightarrow 2H_2O(l) + I_3^-(aq)$ rate = $k[H_2O_2][I^-]$

(*c*) $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$ rate = $k[CH_3CHO]^{3/2}$

(*d*) $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$ rate = $k[C_2H_5Cl]$

Ans. (*a*) Rate = $k[NO]^2$, Order of reaction w.r.t. reactant NO = 2, Order of reaction = 2

Unit of *k*: $k = \dfrac{\text{Rate}}{[NO]^2} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1}\text{s}^{-1}$

(*b*) Rate $= k[H_2O_2][I^-]$, Order of reaction w.r.t. reactant H_2O_2 = 1, Order of reaction w.r.t. reactant I^- = 1,

Order of reaction = 1 + 1 = 2.

Unit of *k*: $k = \dfrac{\text{Rate}}{[H_2O_2][I^-]} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})\,(\text{mol L}^{-1})} = \text{L mol}^{-1}\text{ s}^{-1}$

(*c*) Rate = $k[CH_3CHO]^{3/2}$, Order of reaction w.r.t. reactant $CH_3CHO = \dfrac{3}{2}$, Order of reaction $= \dfrac{3}{2}$

Unit of *k*: $k = \dfrac{\text{Rate}}{[CH_3CHO]^{3/2}} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{3/2}} = \text{mol}^{-1/2}\text{L}^{1/2}\text{s}^{-1}$

(*d*) Rate = $k[C_2H_5Cl]$, Order of reaction w.r.t. reactant $C_2H_5Cl = 1$, Order of reaction = 1.

Unit of *k*: $k = \dfrac{\text{Rate}}{[C_2H_5Cl]} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}$

Q. 2. For the reaction $2A + B \rightarrow A_2B$, the rate $= k\,[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}. Calculate the initial rate of the reaction when $[A] = 0.1$ mol L^{-1} and $[B] = 0.2$ mol L^{-1}. Calculate the rate of reaction after $[A]$ is reduced to 0.06 mol L^{-1}.

Ans.

$$\text{Initial rate} = k\,[A][B]^2 = (2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1})\ (0.1\ \text{mol L}^{-1})\ (0.2\ \text{mol L}^{-1})^2$$
$$= \mathbf{8 \times 10^{-9}\ mol\ L^{-1}\ s^{-1}}$$

When $[A]$ is reduced from 0.10 mol L^{-1} to 0.06 mol L^{-1}, *i.e.*, 0.04 mol L^{-1} of A has reacted,

$$B \text{ reacted} = \frac{1}{2} \times 0.04\ \text{mol L}^{-1} = 0.02\ \text{mol L}^{-1}$$

Now
$$[B] = 0.2 - 0.02 = 0.18\ \text{mol L}^{-1}$$
$$\text{Rate} = (2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1})\ (0.06\ \text{mol L}^{-1})\ (0.18\ \text{mol L}^{-1})^2$$
$$= \mathbf{3.89 \times 10^{-9}\ mol\ L^{-1}\ s^{-1}}$$

Q. 3. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}?

Ans.

$$2NH_3 \longrightarrow N_2 + 3H_2$$
$$\text{Rate} = -\frac{1}{2}\frac{d\,[NH_3]}{dt} = \frac{d\,[N_2]}{dt} = \frac{1}{3}\frac{d\,[H_2]}{dt}$$

For zero order reaction, rate $= k$

$$\therefore \quad -\frac{1}{2}\frac{d\,[NH_3]}{dt} = \frac{d\,[N_2]}{dt} = \frac{1}{3}\frac{d\,[H_2]}{dt}$$
$$= 2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$\text{Rate of production of } N_2 = \frac{d\,[N_2]}{dt} = \mathbf{2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

$$\text{Rate of production of } H_2 = \frac{d\,[H_2]}{dt}$$
$$= 3 \times (2.5 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}) = \mathbf{7.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

Q. 4. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

$$\text{Rate} = k\,[CH_3OCH_3]^{3/2}.$$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, *i.e.,*

$$\text{Rate} = k[P_{CH_3OCH_3}]^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

Ans. In terms of pressure, unit of rate = bar min^{-1}

$$\text{Unit of } k = \frac{\text{Rate}}{[P_{CH_3OCH_3}]^{3/2}} = \frac{\text{bar min}^{-1}}{(\text{bar})^{3/2}} = \mathbf{bar^{-1/2}\ min^{-1}}$$

Q. 5. Mention the factors that affects the rate of a chemical reaction.

Ans. Refer to Basic Concepts Point 5.

Q. 6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (*i*) doubled (*ii*) reduced to half?

Ans.

$$\text{Rate} = k\,[A]^2 = ka^2$$

If $[A] = 2a$, $\quad \text{Rate} = k\,[2a]^2 = 4ka^2 =$ **4 times of the initial rate**

If $[A] = \frac{1}{2}a$, $\quad \text{Rate} = k\left(\frac{a}{2}\right)^2 = \frac{1}{4}ka^2 = \mathbf{\frac{1}{4}}$ **times of the initial rate**

Q. 7. What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

Ans. The rate constant of a reaction increases with increase in temperature and becomes nearly double for every 10°C rise of temperature. The effect can be represented quantitatively by Arrhenius equation,

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

where E_a is the activation energy of the reaction and A is the frequency factor.

Q. 8. In a pseudo first order hydrolysis of an ester in water, the following results were obtained:

t/s	**0**	**30**	**60**	**90**
[A]/mol L^{-1}	**0.55**	**0.31**	**0.17**	**0.085**

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

Ans. Average rate of reaction between the interval 30–60 s.

$$= -\frac{C_2 - C_1}{t_2 - t_1}$$

$$= -\frac{(0.17 - 0.31)}{60 - 30} = \frac{0.14}{30}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$= \mathbf{4.67 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}}$$

Q. 9. A reaction is first order in *A* and second order in *B*.

(*i*) Write the differential rate equation.

(*ii*) How is the rate affected on increasing the concentration of *B* three times?

(*iii*) How is the rate affected when concentration of both *A* and *B* are doubled?

Ans. (*i*) Rate $= \dfrac{-d[R]}{dt} = k[A][B]^2$

(*ii*) If the concentration of *B* is tripled, then

Rate $= k[A][3B]^2 = 9k[A][B]^2$, *i.e.*, the rate of reaction becomes 9 times.

(*iii*) If the concentration of both *A* and *B* are doubled, then

Rate $= k[2A][2B]^2 = 8k[A][B]^2$, *i.e.*, the rate of reaction becomes 8 times.

Q. 10. In a reaction between *A* and *B*, the initial rate of reaction (r_0) was measured for different initial concentrations of *A* and *B* as given below:

A/mol L^{-1}	**0.20**	**0.20**	**0.40**
B/mol L^{-1}	**0.30**	**0.10**	**0.05**
r_0/mol L^{-1} s^{-1}	**5.07×10^{-5}**	**5.07×10^{-5}**	**1.43×10^{-4}**

What is the order of reaction with respect to *A* and *B*?

Ans. Let the rate law be $r_0 = k[A]^m\,[B]^n$

$$(r_0)_1 = 5.07 \times 10^{-5} = k\,(0.20)^m\,(0.30)^n \quad ...(i)$$

$$(r_0)_2 = 5.07 \times 10^{-5} = k\,(0.20)^m\,(0.10)^n \quad ...(ii)$$

$$(r_0)_3 = 1.43 \times 10^{-4} = k\,(0.40)^m\,(0.05)^n \quad ...(iii)$$

Dividing (*i*) by (*ii*), $\dfrac{(r_0)_1}{(r_0)_2} = \dfrac{5.07\times10^{-5}}{5.07\times10^{-5}} = \dfrac{k(0.20)^m(0.30)^n}{k(0.20)^m(0.10)^n}$

$$1 = 3^n \ \text{ or } 3^0 = 3^n \quad \Rightarrow \quad n = 0$$

Dividing (*iii*) by (*ii*), $\dfrac{(r_0)_3}{(r_0)_2} = \dfrac{1.43\times10^{-4}}{5.07\times10^{-5}} = \dfrac{k(0.40)^m(0.05)^n}{k(0.20)^m(0.10)^n}$

$$2.821 = 2^m \times (1/2)^0$$

$$\Rightarrow \quad \log 2.821 = m \log 2$$

$$\Rightarrow \quad m = \frac{\log 2.821}{\log 2} = 1.496 = 1.5$$

Thus, order of reaction w.r.t. A = **1.5** and order of reaction w.r.t. B = **0**.

Q. 11. The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \longrightarrow C + D$$

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Ans. Suppose order of reaction w.r.t. reactant A is m and with respect to B is n. Then the rate law will be

$$\text{Rate} = k\,[A]^m\,[B]^n$$

Substituting the values of experiments I to IV, we have

$$(\text{Rate})_{\text{expt } I} = 6.0 \times 10^{-3} = k\,(0.1)^m\,(0.1)^n \qquad ...(i)$$

$$(\text{Rate})_{\text{expt } II} = 7.2 \times 10^{-2} = k\,(0.3)^m\,(0.2)^n \qquad ...(ii)$$

$$(\text{Rate})_{\text{expt } III} = 2.88 \times 10^{-1} = k\,(0.3)^m\,(0.4)^n \qquad ...(iii)$$

$$(\text{Rate})_{\text{expt } IV} = 2.4 \times 10^{-2} = k\,(0.4)^m\,(0.1)^n \qquad ...(iv)$$

$$\therefore \quad \frac{(\text{Rate})_{\text{expt } I}}{(\text{Rate})_{\text{expt } IV}} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k\,(0.1)^m\,(0.1)^n}{k\,(0.4)^m (0.1)^n}$$

$$\text{or} \quad \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m, \quad m = 1$$

$$\frac{(\text{Rate})_{\text{expt } II}}{(\text{Rate})_{\text{expt } III}} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k\,(0.3)^m\,(0.2)^n}{k\,(0.3)^m (0.4)^n}$$

$$\text{or} \quad \frac{1}{4} = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n$$

$$\text{or} \quad \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n \quad \text{or} \quad n = 2$$

∴ Rate law expression is given by

$$\textbf{Rate} = \boldsymbol{k\,[A]\,[B]^2}$$

Order of reaction w.r.t. A = **1**;

Order of reaction w.r.t. B = **2**.

Overall order of reaction = 1 + 2 = **3**

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{6.0 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}}{(0.1\ \text{mol L}^{-1})\,(0.1\ \text{mol L}^{-1})^2}$$

$$= \mathbf{6.0\ mol^{-2}\ L^{2}\ min^{-1}}$$

Q. 12. The reaction between *A* and *B* is first order with respect to *A* and zero order with respect to *B*. Fill in the blanks in the following table:

Experiment	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	—	0.2	4.0×10^{-2}
III	0.4	0.4	—
IV	—	0.2	2.0×10^{-2}

[CBSE 2019 (56/5/2)]

Ans. The rate expression for the reaction is given as

$$\text{Rate} = k\,[A]^1\,[B]^0 = k[A]$$

For experiment I, Rate = 2.0×10^{-2} mol L^{-1} min^{-1} = k (0.1 M) or k = **0.2 min^{-1}**

For experiment II, Rate = 4.0×10^{-2} mol L^{-1} min^{-1} = (0.2 min^{-1}) [A] or [A] = **0.2 mol L^{-1}**

For experiment III, Rate = (0.2 min^{-1}) (0.4 mol L^{-1}) = **0.08 mol L^{-1} min^{-1}**

For experiment IV, Rate = 2.0×10^{-2} mol L^{-1} min^{-1} = 0.2 min^{-1} [A] or [A] = **0.1 mol L^{-1}**

Q. 13. Calculate the half-life of a first order reaction from their rate constants given below:

(i) **200 s^{-1}** ***(ii)*** **2 min^{-1}**

(iii) **4 $years^{-1}$**

Ans. Half-life period of a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

$$(i)\quad t_{1/2} = \frac{0.693}{200\ s^{-1}} = 0.346 \times 10^{-2}\,s = \mathbf{3.46 \times 10^{-3}\,s}$$

$$(ii)\quad t_{1/2} = \frac{0.693}{2\ min^{-1}} = 0.346\ min = \mathbf{3.46 \times 10^{-1}\,min}$$

$$(iii)\quad t_{1/2} = \frac{0.693}{4\ year^{-1}} = 0.173\ year = \mathbf{1.73 \times 10^{-1}\,year}$$

Q. 14. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Ans. Radioactive decay follows first order kinetics.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}\ year^{-1} = 1.21 \times 10^{-4}\ year^{-1}$$

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{(1.21\times10^{-4}\ year^{-1})}\log\frac{100}{80}$$

$$= \frac{2.303}{1.21\times10^{-4}\ year^{-1}} \times 0.09691$$

= **1845 years (approx.)**

Q. 15. The experimental data for the decomposition of N_2O_5

$$[2N_2O_5 \longrightarrow 4NO_2 + O_2]$$

in gas phase at 318 K are given below:

t (s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^5 \times [N_2O_5]$/mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) **Plot [N_2O_5] against *t*.**

(ii) **Find the half-life period for the reaction.**

(iii) **Draw a graph between log [N_2O_5] and *t*.**

(iv) **What is rate law?**

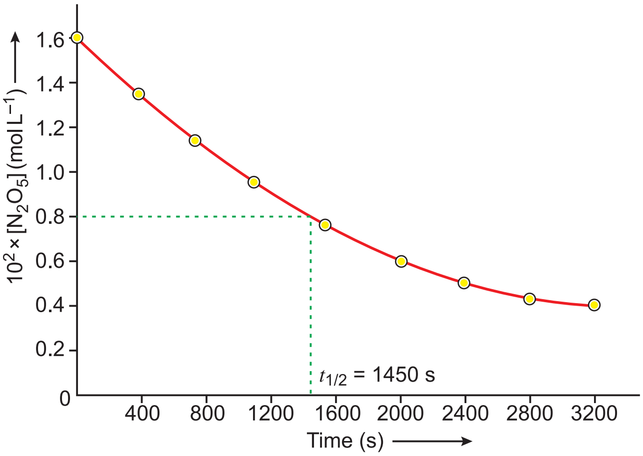
(*v*) Calculate the rate constant.

(*vi*) Calculate the half-life period from *k* and compare it with (*ii*).

Ans.

t (*s*)	0	400	800	1200	1600	2000	2400	2800	3200
$10^5 \times [N_2O_5]$/mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35
log $[N_2O_5]$	– 1.79	– 1.87	– 1.94	– 2.03	– 2.11	– 2.19	– 2.28	– 2.37	– 2.46

(*i*) Plot of $[N_2O_5]$ versus time

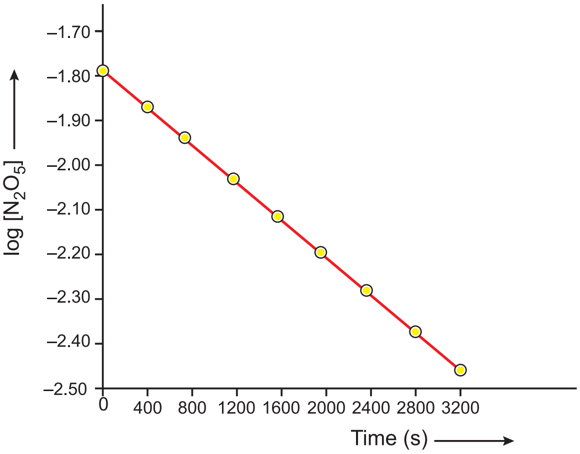


(*ii*) Initial concentration of $[N_2O_5] = 1.63 \times 10^2$ M

Half of the concentration = 0.815×10^2 M

Time corresponding to this concentration = 1450 s. Hence, $t_{1/2}$ = **1450 s**.

(*iii*) Plot of log $[N_2O_5]$ versus time



(*iv*) As plot of log $[N_2O_5]$ vs time is a straight line, hence it is a reaction of first order.

∴ Rate law is,

$$\text{Rate} = k\,[N_2O_5]$$

(*v*) Slope of the line $= -\dfrac{k}{2.303}$ ...(*i*)

$$\text{Slope} = \frac{-2.46-(-1.79)}{3200-0} = -\frac{0.67}{3200} \qquad \text{...(ii)}$$

From equation (*i*) and (*ii*), we get

$$-\frac{k}{2.303} = \frac{-0.67}{3200} \quad \text{or} \quad k = \frac{0.67 \times 2.303}{3200}$$

or $k = \mathbf{4.82 \times 10^{-4}\ s^{-1}}$

(*vi*) $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}\,\text{s}^{-1}} = \mathbf{1438\ s}$$

The two values are almost same within limits of possible error.

Q. 16. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

Ans. $$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad \text{as} \quad [R] = \frac{[R]_0}{16}$$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{\frac{[R]_0}{16}} = \frac{2.303}{60} \times 4 \log 2$$

$$= \frac{2.303}{60} \times 4 \times 0.3010 = \mathbf{4.62 \times 10^{-2}\ s}$$

Q. 17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 µg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

Ans. As radioactive disintegration follows first order kinetics,

$\therefore$ Decay constant of ^{90}Sr, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2}\ \text{y}^{-1}$

To calculate the amount left after 10 years:

$[R]_0 = 1$ µg, $t = 10$ years, $k = 2.466 \times 10^{-2}\ \text{y}^{-1}$, $[R] = ?$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$$

or $\log [R] = -0.1071$

or $[R] = \text{Antilog}\ \bar{1}.8929 = \mathbf{0.7814\ µg}$

To calculate the amount left after 60 years:

$$2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{[R]}$$

or $\log [R] = -0.6425$

or $[R] = \text{Antilog}\ \bar{1}.3575 = \mathbf{0.2278\ µg}$

Q. 18. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction. **[*CBSE 2019 (56/5/2)*]**

Ans. For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

When the reaction is 99% completed, $[R] = [R]_0 - 0.99\,[R]_0 = 0.01\,[R]_0$

When the reaction is 90% completed, $[R] = [R]_0 - 0.9[R]_0 = 0.1[R]_0$

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303}{k} \log \frac{[R]_0}{0.01[R]_0}}{\frac{2.303}{k} \log \frac{[R]_0}{0.1[R]_0}} = \frac{\log 10^2}{\log 10} = \frac{2 \log 10}{\log 10} = 2$$

Hence, $t_{99\%} = 2t_{90\%}$

Q. 19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans. For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

When $t = 40$ minutes, $\dfrac{[R]_0}{[R]} = \dfrac{100}{100-30} = \dfrac{10}{7}$

$$k = \frac{2.303}{40}\log\frac{10}{7}$$

$$k = \frac{2.303}{40}\log 1.428 = \frac{2.303}{40} \times 0.1547$$

$$k = 8.91 \times 10^{-3}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.91\times 10^{-3}}$$

$$t_{1/2} = \mathbf{77.78\ min}$$

Q. 20. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained:

***t* (s)**	**0**	**360**	**720**
***P* (mm of Hg)**	**35.0**	**54.0**	**63.0**

Calculate the rate constant.

Ans. $(CH_3)_2CHN{=}NCH(CH_3)_2(g) \longrightarrow N_2(g) + C_6H_{14}(g)$

Initial pressure P_0 $\quad 0 \quad 0$

After time t $\quad P_0 - p \quad p \quad p$

Total pressure after time t $(P_t) = (P_0 - p) + p + p = P_0 + p$ *or* $p = P_t - P_0$

$a \propto P_0$ and $(a - x) \propto P_0 - p$ or substituting the value of p,

$a - x \propto P_0 - (P_t - P_0)$, *i.e.*, $(a - x) \propto 2P_0 - P_t$

For a first order reaction

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

$$= \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

When $t = 360$ s $\quad k = \dfrac{2.303}{360\text{s}}\log\dfrac{35.0}{2\times 35.0 - 54.0} = \dfrac{2.303}{360\text{ s}}\log\dfrac{35}{16}$

$$= \frac{2.303}{360\text{ s}}(0.3400) = 2.175 \times 10^{-3}\ \text{s}^{-1}$$

When $t = 720$ s, $\quad k = \dfrac{2.303}{720\text{ s}}\log\dfrac{35.0}{2\times 35.0 - 63.0} = \dfrac{2.303}{720\text{ s}}\log 5$

$$= \frac{2.303}{720\text{ s}}(0.6990) = 2.235 \times 10^{-3}\ \text{s}^{-1}$$

Average value of $k = \dfrac{2.175 + 2.235}{2} \times 10^{-3}\ \text{s}^{-1} = \mathbf{2.20 \times 10^{-3}\ s^{-1}}$

Q. 21. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	**Time/s**	**Total pressure/atm**
1	0	0.5
2	100	0.6

Calculate the rate of reaction when total pressure is 0.65 atm.

Ans. $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

$$k = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

When $t = 100$ s, $$k = \frac{2.303}{100\text{ s}} \log \frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100\text{ s}} \log (1.25)$$

$$= \frac{2.303}{100\text{ s}} (0.0969) = \mathbf{2.2316 \times 10^{-3}\ s^{-1}}$$

When $P_t = 0.65$ atm, *i.e.*, $P_0 + p = 0.65$ atm

$$\therefore \quad p = 0.65 - P_0 = 0.65 - 0.50 = 0.15 \text{ atm}$$

Pressure of SO_2Cl_2 at time t ($p_{SO_2Cl_2}$) $= P_0 - p = 0.50 - 0.15$ atm $= 0.35$ atm

$$\therefore \quad \text{Rate} = k \times p_{SO_2Cl_2} = (2.2316 \times 10^{-3}\ s^{-1})\ (0.35 \text{ atm})$$

$$= \mathbf{7.8 \times 10^{-4}\ atm\ s^{-1}}$$

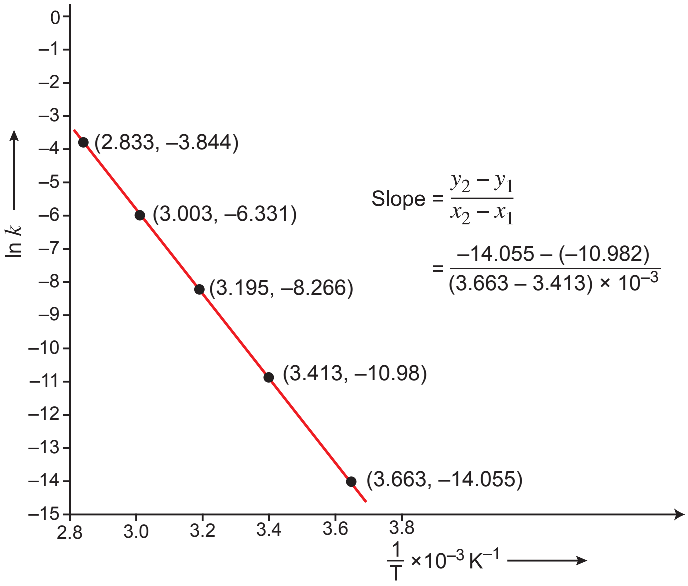
Q. 22. The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

T°C	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between ln *k* and 1/*T* and calculate the values of *A* and E_a. Predict the rate constant at 30°C and 50°C.

Ans. To draw the graph of ln *k* versus $\frac{1}{T}$, we can re-write the given data as follows:

***T* (K)**	273	293	313	333	353
$1/T$ (K^{-1})	0.003663	0.003413	0.00319	0.003003	0.002833
ln *k*	– 14.055	– 10.982	– 8.266	– 6.331	– 3.844



Graph of ln k vs 1/T

From the graph, we find that

$$\text{Slope} = \frac{-E_a}{R} = \frac{-(-3.073)}{0.25 \times 10^{-3}}$$

$$\therefore \quad \text{Activation energy, } E_a = \frac{3.073}{0.25 \times 10^{-3}} \times 8.314 = 102195.7 \text{ J mol}^{-1} = \mathbf{102.20\ kJ/mol}$$

We know that $$\ln k = \ln A - \frac{E_a}{RT}$$

or $$\ln A = \left(\frac{E_a}{R}\right)\frac{1}{T} + \ln k$$

At $T = 273$ K, $\ln k = -14.055$

$$\therefore \quad \ln A = \frac{102.20}{8.314 \times 10^{-3} \times 273} - 14.055 = 30.973$$

Frequency factor, $A = 2.83 \times 10^{13}$

The value of rate constant at two different temperatures can be determined as follows:

T	$1/T$	Value of ln k (from graph)	Value of k
303	0.003300	-9.7	$6.13 \times 10^{-5}\ s^{-1}$
323	0.003096	-6.3	$1.84 \times 10^{-3}\ s^{-1}$

Q. 23. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}\ s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor?

Ans. Given, $k = 2.418 \times 10^{-5}\ s^{-1}$, $E_a = 179.9\ \text{kJ mol}^{-1}$, $T = 546$ K.

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

or $$\log A = \log k + \frac{E_a}{2.303\,RT}$$

$$\log A = \log(2.418 \times 10^{-5}\ s^{-1}) + \frac{179.9\ \text{kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1} \times 546\ \text{K}}$$

$$= (-5 + 0.3834)\ s^{-1} + 17.2081$$

$$= 12.5915\ s^{-1}$$

or $$A = \text{Antilog}\ (12.5915)\ s^{-1}$$

$$= \mathbf{3.904 \times 10^{12}\ s^{-1}}$$

Q. 24. Consider a certain reaction $A \longrightarrow$ Products with $k = 2.0 \times 10^{-2}\ s^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

Ans. The units of k show that the reaction is of first order. Hence, $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$

$\therefore$ $$2.0 \times 10^{-2}\ s^{-1} = \frac{2.303}{100\ s} \log \frac{1.0\ \text{mol L}^{-1}}{[A]} \quad \text{or } \log [A] = -0.8684$$

$\therefore$ $$[A] = \text{Antilog}\ (-0.8684) = \text{Antilog}\ (\bar{1}.1316) = \mathbf{0.1354\ mol\ L^{-1}}$$

Q. 25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2} = 3.00$ hours. What fraction of sample of sucrose remains after 8 hours?

Ans. Since sucrose decomposes according to first order rate law,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

As $t_{1/2} = 3.0$ hours,

$\therefore$ $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3h} = 0.231\ h^{-1}$$

$$0.231\ h^{-1} = \frac{2.303}{8h} \log \frac{[R]_0}{[R]}$$

or $$\log \frac{[R]_0}{[R]} = 0.8024$$

or $$\frac{[R]_0}{[R]} = \text{Antilog}\ (0.8024) = 6.345$$

or $$\frac{[R]}{[R]_0} = \frac{1}{6.345} = \mathbf{0.158}$$

Q. 26. The decomposition of hydrocarbon follows the equation: $k = (4.5 \times 10^{11}\ s^{-1})\ e^{-(28000\ K)/T}$. Calculate E_a.

Ans. From Arrhenius equation, $k = A\, e^{-E_a/RT}$

$\therefore$ $$-\frac{E_a}{RT} = -\frac{28000\ K}{T}$$

or $$E_a = 28000\ \text{K} \times R = 28000\ \text{K} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= \mathbf{232.79\ kJ\ mol^{-1}}$$

Q. 27. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes.

Ans. Given, $\log k = 14.34 - \dfrac{1.25 \times 10^4}{T}$

Comparing with the equation, $\log k = \log A - \dfrac{E_a}{2.303\, RT}$, we get

$$\frac{E_a}{2.303\, R} = 1.25 \times 10^4$$

or $$E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$$

$$= 23.934 \times 10^4 \text{ J mol}^{-1}$$

$$E_a = \mathbf{239.34 \text{ kJ mol}^{-1}}$$

Given, $t_{1/2} = 256 \text{ min} = 256 \times 60 \text{ s}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60} = 4.5 \times 10^{-5} \text{ s}^{-1}$$

Substituting the value of k in given equation, we get

$$\log (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\log 4.51 + \log 10^{-5} = 14.34 - \frac{1.25 \times 10^4}{T}$$

or $$\log 4.51 - 5 \log 10 = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$0.6542 - 5 = 14.34 - \frac{1.25 \times 10^4}{T} \quad \text{or} \quad \frac{1.25 \times 10^4}{T} = 18.6858$$

or $$T = \frac{1.25 \times 10^4}{18.6858} = \mathbf{669 \text{ K (approx.)}}$$

Q. 28. The decomposition of A into product has value of k as 4.5×10^3 s^{-1} at 10°C and energy of activation is 60 kJ mol^{-1}. At what temperature would k be 1.5×10^4 s^{-1}?

Ans. $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$, $T_1 = 10 + 273 \text{ K} = 283 \text{ K}$; $k_2 = 1.5 \times 10^4 \text{ s}^{-1}$, $T_2 = ?$, $E_a = 60 \text{ kJ mol}^{-1}$

From Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}}\left(\frac{T_2 - 283}{283 T_2}\right)$$

or $$\log 3.333 = 3133.63\left(\frac{T_2 - 283}{283 T_2}\right) \quad \text{or} \quad \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283 T_2}$$

or $$0.0472\, T_2 = T_2 - 283$$

or $$0.9528\, T_2 = 283$$

or $$T_2 = \frac{283}{0.9528} = 297 \text{ K} = 297 - 273\text{°C} = \mathbf{24\text{°C}}$$

Q. 29. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4×10^{10} s^{-1}, calculate k at 318 K and E_a.

Ans. $$k_1 = \frac{2.303}{t_1} \log \frac{[R]_0}{[R]_0 - 0.10\,[R]_0} = \frac{2.303}{t_1} \log \frac{100}{90}$$

$$= \frac{2.303}{t_1}(0.0458) = \frac{0.1055}{t_1} \quad \text{or} \quad t_1 = \frac{0.1055}{k_{298\text{K}}}$$

$$k_2 = \frac{2.303}{t_2}\log\frac{[R]_0}{[R]_0 - 0.25\,[R]_0} = \frac{2.303}{t_2}\log\frac{100}{75}$$

$$= \frac{2.303}{t_2}(0.125) = \frac{0.2879}{t_2} \quad \text{or} \quad t_2 = \frac{0.2879}{k_{308\text{K}}}$$

But $t_1 = t_2$. Hence, $\frac{0.1055}{k_1} = \frac{0.2879}{k_2}$ or $\frac{k_2}{k_1} = 2.7289$

Now, from Arrhenius equation, $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$

$$\therefore \quad \log(2.7289) = \frac{E_a}{2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}} \times \frac{(308 - 298)\ \text{K}}{298\ \text{K} \times 308\ \text{K}}$$

$$0.4360 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$$

or $\quad E_a = \mathbf{76.623\ kJ\ mol^{-1}}$

Calculation of k at 318 K:

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

$$= \log(4 \times 10^{10}) - \frac{76.623\ \text{kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3}\ \text{kJ K}^{-1}\text{mol}^{-1} \times 318\ \text{K}}$$

$$= 10.6021 - 12.5843 = -1.9822$$

or $\quad k = \text{Antilog}(-1.9822) = \text{Antilog}(\bar{2}.0178)$

$$= \mathbf{1.042 \times 10^{-2}\ s^{-1}}$$

Q. 30. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

[CBSE 2019 (56/4/1)]

Ans. $\quad k_2 = 4k_1 \quad \Rightarrow \quad \frac{k_2}{k_1} = 4$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\Rightarrow \quad \log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{313 - 293}{293 \times 313}\right)$$

$$2 \times \log 2 = \frac{E_a}{19.147}\left(\frac{20}{91709}\right)$$

$$E_a = \frac{2 \times 0.3010 \times 19.147 \times 91709}{20} = \mathbf{52.85\ kJ/mol}$$

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. In the reaction,

$$\mathbf{BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \longrightarrow 3Br_2(l) + 3H_2O(l)}$$

The rate of appearance of bromine is related to rate of disappearance of bromide ion as

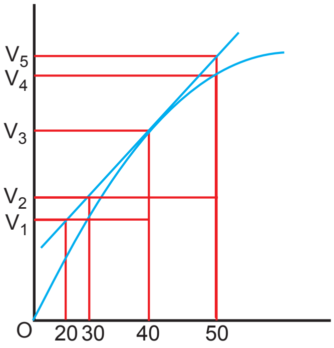
(*a*) $\frac{d[\text{Br}_2]}{dt} = \frac{-5}{3}\frac{d[\text{Br}^-]}{dt}$

(*b*) $\frac{d[\text{Br}_2]}{dt} = \frac{5}{3}\frac{d[\text{Br}^-]}{dt}$

(*c*) $\frac{d[\text{Br}_2]}{dt} = \frac{3}{5}\frac{d[\text{Br}^-]}{dt}$

(*d*) $\frac{d[\text{Br}_2]}{dt} = \frac{-3}{5}\frac{d[\text{Br}^-]}{dt}$

2. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in figure. On the basis of this mark the correct option. [*NCERT Exemplar*]



(*a*) Average rate upto 40 seconds is $\dfrac{V_3 - V_2}{40}$

(*b*) Average rate upto 40 seconds is $\dfrac{V_3 - V_2}{40 - 30}$

(*c*) Average rate upto 40 seconds is $\dfrac{V_3}{40}$

(*d*) Average rate upto 40 seconds is $\dfrac{V_3 - V_1}{40 - 20}$

3. Consider the graph given in the above question. Which of the following options does not show instantaneous rate of reaction at 40th second? [*NCERT Exemplar*]

(*a*) $\dfrac{V_5 - V_2}{50 - 30}$ (*b*) $\dfrac{V_4 - V_2}{50 - 30}$ (*c*) $\dfrac{V_3 - V_2}{40 - 30}$ (*d*) $\dfrac{V_3 - V_1}{40 - 20}$

4. The rate constant of reaction is 2.0×10^{-6} mol^{-2} L^{2} s^{-1}. The order of the reaction is

(*a*) 0 (*b*) 2 (*c*) 1 (*d*) 3

5. The rate of a gaseous reaction is given by the expression, rate = $k[A]\,[B]$. If the volume of the reaction vessel is suddenly reduced to 1/4 of the initial volume, the reaction rate related to original rate will be

(*a*) 1/16 (*b*) $\dfrac{1}{8}$ (*c*) 8 (*d*) 16

6. Which of the following is not correct about order of a reaction? [*NCERT Exemplar*]

(*a*) The order of a reaction can be a fractional number.

(*b*) Order of a reaction is experimentally determined quantity.

(*c*) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.

(*d*) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

7. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction? [*NCERT Exemplar*]

(*a*) Order is same as molecularity. (*b*) Order is less than the molecularity.

(*c*) Order is greater than the molecularity. (*d*) Molecularity can never be zero.

8. For the reaction,

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

The experimental data suggests,

$$\text{Rate} = k[H_2][Br_2]^{\frac{1}{2}}$$

The molecularity and order for the reaction is

(*a*) 2 and 2 (*b*) 2 and $1\frac{1}{2}$ (*c*) $1\frac{1}{2}$ and 2 (*d*) $1\frac{1}{2}$ and $1\frac{1}{2}$

9. The unit of rate constant of a zero order reaction is

(*a*) litre second^{-1} (*b*) litre mole^{-1} second^{-1} (*c*) mole litre^{-1} second^{-1} (*d*) mole second^{-1}

10. Rate law cannot be determined from balanced chemical equation if ________. [*NCERT Exemplar*]

(*a*) reverse reaction is involved (*b*) it is an elementary reaction

(*c*) it is a sequence of elementary reactions (*d*) any of the reactants is in excess

11. In the reaction, A $\longrightarrow$ B, the rate of reaction increases two times on increasing the concentration of A four times, the order of reaction is

(*a*) 2 (*b*) 0 (*c*) $\dfrac{1}{2}$ (*d*) 3

12. Which of the following is a zero order reaction?

(*a*) Decomposition of N_2O_5 (*b*) Decomposition of NH_3

(*c*) Decomposition of N_2O (*d*) Radioactive decay of unstable nuclei

13. Diazonium salt decomposes as

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

at 0° C. The evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore it is

(*a*) a first order reaction

(*b*) a second order reaction

(*c*) independent of the initial concentration of the salt

(*d*) a zero order reaction

14. In the graph plotted between ln [*R*] and *t* for a first order reaction, the intercept on *y*-axis is

(*a*) $-k$ (*b*) $[R]_0$ (*c*) $\ln [R]_0$ (*d*) $k/2.303$

15. If 75% of the first-order reaction was completed in 32 minutes, 50% of the same reaction would be completed in:

(*a*) 8 min (*b*) 4 min (*c*) 16 min (*d*) 24 min

16. The half life of a first order reaction is 69.35 sec. The value of rate constant of the reaction is

(*a*) 1.0 s^{-1} (*b*) 0.1 s^{-1} (*c*) 0.01 s^{-1} (*d*) 0.001 s^{-1}

17. Consider a first order gas phase decomposition reaction given below: [*NCERT Exemplar*]

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

The initial pressure of the system before decomposition of A was p_i. After lapse of time '*t*', total pressure of the system increased by *x* units and became 'p_t'. The rate constant *k* for the reaction is given as ____________.

(*a*) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{p_i - x}$ (*b*) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i - p_t}$

(*c*) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i + p_t}$ (*d*) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{p_i + x}$

18. The activation energy of a reaction is zero. The rate of the reaction

(*a*) increases with increase of temperature (*b*) decreases with decrease of temperature

(*c*) decreases with increase of temperature (*d*) is nearly independent of temperature

19. The activation energy of a reaction can be determined from the slope of which of the following graphs?

(*a*) $\ln k \text{ vs } \dfrac{1}{T}$ (*b*) $\dfrac{T}{\ln k} \text{ vs } \dfrac{1}{T}$

(*c*) $\ln k$ vs T (*d*) $\dfrac{\ln k}{T} \text{ vs } T$

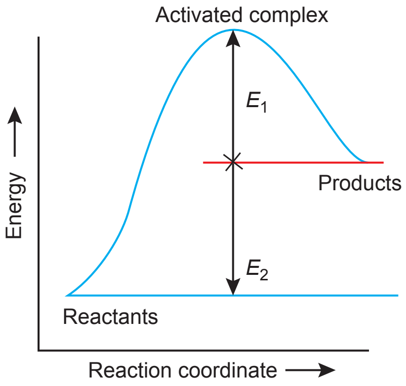
20. Consider figure and mark the correct option. [*NCERT Exemplar*]

(*a*) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

(*b*) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.

(*c*) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.

(*d*) Activation energy of backward reaction is E_1 and product is more stable than reactant.



21. The role of a catalyst is to change ________________. [*NCERT Exemplar*]

(*a*) gibbs energy of reaction
(*b*) enthalpy of reaction
(*c*) activation energy of reaction
(*d*) equilibrium constant

22. In the presence of a catalyst, the heat evolved or absorbed during the reaction ________________. [*NCERT Exemplar*]

(*a*) increases
(*b*) decreases
(*c*) remains unchanged
(*d*) may increase or decrease

Answers

1. (*d*) **2.** (*c*) **3.** (*b*) **4.** (*d*) **5.** (*d*) **6.** (*c*) **7.** (*a*), (*d*) **8.** (*b*) **9.** (*c*) **10.** (*a,c,d*)
11. (*c*) **12.** (*b*) **13.** (*a*) **14.** (*c*) **15.** (*c*) **16.** (*c*) **17.** (*b*) **18.** (*d*) **19.** (*a*) **20.** (*a*)
21. (*c*) **22.** (*c*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***
(*b*) ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***
(*c*) ***Assertion (A) is correct, but Reason (R) is incorrect statement.***
(*d*) ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. Assertion (*A*) : Instantaneous rate is used to predict the rate of a reaction at a particular moment of time.
Reason (*R*) : Average rate is constant for the time interval for which it is calculated.

2. Assertion (*A*) : For the reaction, $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$, rate = $k[CHCl_3]\,[Cl_2]^{1/2}$
Reason (*R*) : Rate law for any reaction can be predicted with the help of a balanced chemical equation.

3. Assertion (*A*) : The rate of the reaction is the rate of change of concentration of a reaction or a product.
Reason (*R*) : Rate of reaction remains constant during the course of reaction.

4. Assertion (*A*) : Order of the reaction can be zero or fractional.
Reason (*R*) : We cannot determine order from balanced chemical equation.

5. Assertion (*A*) : Order and molecularity are same.
Reason (*R*) : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

6. Assertion (*A*) : For the reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2;$$

Rate = $k[N_2O_5]$.

Reason (*R*) : Rate of decomposition of N_2O_5 is determined by slow step.

7. Assertion (*A*) : The inversion of cane sugar,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

is a pseudo first order reaction.

Reason (*R*) : H_2O in this reaction is present in very less amount as compared to $C_{12}H_{22}O_{11}$.

8. Assertion (*A*) : For each ten degree rise of temperature the specific rate constant is nearly doubled.
Reason (*R*) : Energy-wise distribution of molecules in a gas is an experimental function of temperature.

9. Assertion (*A*) : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
Reason (*R*) : Lower the activation energy, faster is the reaction.

10. Assertion (*A*) : Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

Reason (*R*) : Reactant molecules undergo chemical change irrespective of their orientation during collision.

11. Assertion (*A*) : The enthalpy of reaction remains constant in the presence of a catalyst.

Reason (*R*) : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

12. Assertion (*A*) : All collision of reactant molecules lead to product formation.

Reason (*R*) : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Answers

1. (*b*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*d*) **6.** (*b*) **7.** (*c*) **8.** (*b*) **9.** (*c*) **10.** (*c*)
11. (*a*) **12.** (*d*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The rate of a chemical reaction is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Rate of the reaction depends upon the nature of reactants, concentration of reactants, temperature, presence of catalyst, surface area of the reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

1. Express the rate of the following reaction in terms of different reactants and products.

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$$

Ans. Rate of reaction $= -\frac{1}{4}\frac{d[NH_3]}{dt}$

$$= -\frac{1}{5}\frac{d[O_2]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{1}{6}\frac{d[H_2O]}{dt}$$

2. Why do pieces of wood burn faster than a log of wood of the same mass?

Ans. Pieces of wood have larger surface area than the log of wood of the same mass. Greater the surface area, faster is the reaction.

3. Why does the rate of any reaction generally decrease during the course of the reaction?

Ans. The rate of reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate of reaction decreases.

4. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of the molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

5. The kinetics of the reaction

$$mA + nB + pC \longrightarrow m'X + n'Y + p'Z$$

obey the rate expression $dx/dt = k[A]^m[B]^n$

Calculate total order and molecularity of the reaction.

Ans. The total order of reaction = $m + n$

The molecularity of the reaction = $m + n + p$

PASSAGE–2

Temperature has a marked effect on the rate of reaction. For most of the reactions,the rate of reaction becomes nearly double for every 10 degree rise in temperature. The effect of temperature is usually expressed in terms of temperature coefficient. The quantitative dependence of reaction rate on temperature was first explained by Swante Arrhenius. Arrhenius proposed a simple equation known as Arrhenius equation

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

This equation provides a relationship between the rate constant (k) of a reaction and the temperature of the system. A is the Arrhenius factor or pre-exponential factor, E_a is the activation energy and R is the gas constant.

1. Define 'activation energy' of a reaction. ***[CBSE (AI) 2011]***

Ans. The energy required to form the intermediate called activated complex is known as activation energy.

Activation energy = Threshold energy – Average energy of the reactants

2. How does a catalyst affect the rate of a reaction? Explain with respect to the Arrhenius equation.

Ans. A catalyst decreases the activation energy. According to Arrhenius equation, lower the activation energy, greater will be the rate constant and thus the rate of reaction increases.

3. Can a reaction have zero activation energy? Justify.

Ans. No, $E_a \neq 0$.

If $E_a = 0$, then according to Arrhenius equation,

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

$$k = Ae^0 = \text{A},$$

i.e., Rate constant = Collision frequency

This means every collision results into a chemical reaction which cannot be true.

4. The plot of log k vs X is linear with slope = – E_a/2.303R. What is X?

Ans. $1/T$

5. What is the fraction of molecules having energy greater than activation energy, E_a?

Ans. $e^{-Ea/RT}$ at temperature T.

Very Short Answer Questions [1 mark]

Q. 1. For the assumed reaction $X_2 + 3Y_2 \longrightarrow 2XY_3$, write the rate of equation in terms of rate of disappearance of Y_2. ***[HOTS]***

Ans.

$$\text{Rate} = -\frac{d[X_2]}{dt} = -\frac{1}{3}\frac{d[Y_2]}{dt} = +\frac{1}{2}\frac{d[XY_3]}{dt}$$

$$\text{Rate of disappearance of } Y_2 = -\frac{d[\text{Y}_2]}{dt} = -3\frac{d[\text{X}_2]}{dt} = +\frac{3}{2}\frac{d[\text{XY}_3]}{dt}$$

Q. 2. Why does the rate of a reaction increase with rise in temperature? ***[NCERT Exemplar]***

Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.*, the activation energy), which leads to faster rate.

Q. 3. Define 'order of a reaction'. ***[CBSE 2019 (56/2/1)]***

Ans. Order of a reaction may be defined as the sum of the powers of the concentration terms of the reactants in the rate law expression.

Q. 4. Identify the order of reaction from the following unit for its rate constant:
L mol^{-1}s^{-1} [*CBSE (F) 2010*]

Ans. Second order.

Q. 5. For the reaction $A \longrightarrow B$, the rate of reaction becomes three times when the concentration of A is increased by nine times. What is the order of reaction? [*HOTS*]

Ans. Let, $r = k\,[A]^n$ …(*i*)

Given, $3r = k\,[9A]^n$ …(*ii*)

Dividing equation (*ii*) by (*i*), we get

$$\frac{3r}{r} = \frac{k[9A]^n}{k[A]^n} = \frac{9^n k[A]^n}{k[A]^n}$$

$$3 = 9^n \quad \text{or} \quad 3^1 = 3^{2n}$$

$$\Rightarrow \quad 2n = 1 \quad \text{or} \quad n = \frac{1}{2}$$

$$\therefore \quad \text{Rate, } r = k[A]^{1/2}$$

$$\text{Order of reaction} = \mathbf{\frac{1}{2}}$$

Q. 6. For which type of reactions, order and molecularity have the same value? [*NCERT Exemplar*]

Ans. If the reaction is an elementary reaction, order is same as molecularity.

Q. 7. Why is the probability of reaction with molecularity higher than three very rare? [*NCERT Exemplar*]

Ans. The probability of more than three molecules colliding simultaneously is very small. Hence, possibility of molecularity being three is very low.

Q. 8. For a reaction, $A + B \longrightarrow$ Products, the rate law is Rate = $k[A][B]^{3/2}$. Can the reaction be an elementary reaction? Explain. [*HOTS*]

Ans. During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with respect to B would have been 1, but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not an elementary reaction.

Q. 9. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction? [*HOTS*]

Ans. As $t_{75\%} = 2t_{50\%}$

Therefore, it is a first order reaction.

Q. 10. What is the effect of adding a catalyst on

(*i*) Activation energy (E_a), and

(*ii*) Gibbs energy (ΔG) of a reaction? [*CBSE Delhi 2017; (AI) 2017*]

Ans. (*i*) Decreases

(*ii*) No effect

Q. 11. Define threshold energy of a reaction.

Ans. Threshold energy is the minimum energy which must be possessed by reacting molecules in order to undergo effective collision which leads to formation of product molecules.

Q. 12. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example. [*NCERT Exemplar*]

Ans. Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.

Q. 13. In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why? [*CBSE Delhi 2013*]

Ans. This is due to improper orientation of the colliding molecules at the time of collision.

Short Answer Questions–I [2 marks]

Q. 1. For the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ the rate of formation of $NO_2(g)$ is 2.8×10^{-3} Ms^{-1}. Calculate the rate of disappearance of $N_2O_5(g)$. *[CBSE 2018]*

Ans. $$\text{Rate} = \frac{-1}{2}\frac{\Delta(N_2O_5)}{\Delta t} = +\frac{1}{4}\frac{\Delta(NO_2)}{\Delta t} = +\frac{\Delta(O_2)}{\Delta t}$$

$$\text{Rate of disappearance of } N_2O_5 = -\frac{\Delta(N_2O_5)}{\Delta t} = \frac{1}{2}\frac{\Delta(NO_2)}{\Delta t}$$

$$= \frac{1}{2} \times 2.8 \times 10^{-3}\ Ms^{-1} = \mathbf{1.4 \times 10^{-3}\ Ms^{-1}}$$

Q. 2. The rate law for the reaction: Ester + H^+ $\longrightarrow$ Acid + Alcohol is:

$$\frac{dx}{dt} = k\,[\text{Ester}]\,[H^+]^0$$

What would be the effect on the rate if (*i*) concentration of the ester is doubled? (*ii*) concentration of H^+ is doubled?

Ans. (*i*) The rate of reaction will be doubled. (*ii*) No effect on rate.

Q. 3. Differentiate between rate of reaction and reaction rate constant.

Ans.

S. No.	Rate of Reaction	Reaction Rate Constant
(*i*)	Rate of reaction is the change in concentration of a reactant or product in a unit interval of time.	It is the rate of reaction when the molar concentration of each of the reactants is unity.
(*ii*)	The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time.	The rate constant does not depend upon the concentrations of the reactants.
(*iii*)	Its units are always mol litre^{-1} time^{-1}.	Its units depend upon the order of reaction.

Q. 4. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction? *[CBSE (AI) 2011]*

Ans. Consider the reaction $nR \longrightarrow$ Products

As the reaction is of second order

$$\therefore \quad \text{Rate, } r = k\,[R]^2 \qquad \text{...}(i)$$

If the concentration of the reactant reduced to half, then

$$\text{Rate, } r' = k\left[\frac{R}{2}\right]^2 \qquad \text{...}(ii)$$

Dividing equation (*ii*) by (*i*), we get

$$\frac{r'}{r} = \frac{k\,[R]^2}{4k\,[R]^2} = \frac{1}{4}$$

$$r' = \frac{1}{4}r\text{, i.e., rate of reaction becomes } \frac{1}{4^{th}} \text{ of the initial rate.}$$

The unit of rate constant is **mol^{-1} L s^{-1}**.

Q. 5. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are: *[CBSE (AI) 2011]*

(*i*) L^{-1} mol s^{-1} (*ii*) L mol^{-1} s^{-1}.

Ans. An experimentally determined expression which relates the rate of reaction with the concentration of reactants is called rate law while the rate of reaction when concentration of each reactant is unity in a rate law expression is called rate constant.

(*i*) Comparing power of mole in L^{-1} mol s^{-1} and $(\text{mol } L^{-1})^{1-n}\ s^{-1}$,

We get

$$1 = 1 - n \quad \Rightarrow \quad n = 0 \text{ i.e., zero order reaction}$$

(*ii*) Again comparing power of mole in L $mol^{-1}s^{-1}$ and $(\text{mol } L^{-1})^{1-n} s^{-1}$, we get

$$-1 = 1 - n \quad \Rightarrow \quad n = 2, \text{ i.e., second order reaction}$$

Q. 6. Calculate the overall order of a reaction which has the rate expression,

(*i*) Rate = $k[A]^{1/2}[B]^{3/2}$ (*ii*) Rate = $k[A]^{3/2}[B]^{-1}$

Ans. (*i*) Order = $\frac{1}{2}+\frac{3}{2}=2$, *i.e.*, second order.

(*ii*) Order = $\frac{3}{2}+(-1)=\frac{1}{2}$, *i.e.*, half order.

Q. 7. Write two differences between 'order of reaction' and 'molecularity of reaction'.[*CBSE Delhi 2014*]

Ans. Differences between order and molecularity of reaction:

S.No.	Order	Molecularity
(*i*)	It is the sum of the powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously so as to result into a chemical reaction.
(*ii*)	It is determined experimentally.	It is a theoretical concept.
(*iii*)	It can be zero or a fraction.	It cannot be zero or a fraction.
(*iv*)	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning.

(*Any two*)

Q. 8. For a reaction: $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

Rate = k

(*i*) Write the order and molecularity of this reaction.

(*ii*) Write the unit of k. [*CBSE South 2016*]

Ans. (*i*) Zero order, bimolecular

(*ii*) mol L^{-1} s^{-1}

Q. 9. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions? [*NCERT Exemplar*]

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

Q. 10. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.

$$2H_2O_2 \xrightarrow{OH^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below:

Step-I $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ **(slow)**

Step-II $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ **(fast)**

(*i*) Write the rate law expression and determine the order of reaction w.r.t. H_2O_2.

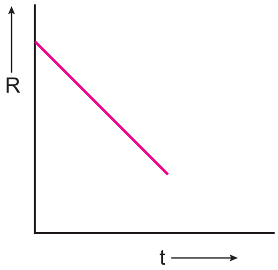
(*ii*) What is the molecularity of each individual step?

Ans. (*i*) Rate = $k\,[H_2O_2]^1\,[I^-]^1$

Order of reaction w.r.t $H_2O_2 = 1$

(*ii*) Molecularity of step I = 2 and step II = 2.

Q. 11. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs. time (t) plot is given alongside.



(*i*) Predict the order of the reaction.

(*ii*) What is the slope of the curve? [*CBSE (AI) 2014*]

Ans. (*i*) Order of the reaction is zero.

(*ii*) Slope = $\frac{d[R]}{dt}=-k$

Q. 12. The rate constant for a reaction of zero order in *A* is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of *A* to fall from 0.10 M to 0.075 M?

Ans. $k = 0.0030 \text{ mol } L^{-1}s^{-1}$, $[R]_0 = 0.10$ M, $[R] = 0.075$ M

We know that

$$[R] = -kt + [R]_0$$

$$0.075 = -0.0030t + 0.10$$

$$\Rightarrow \quad 3t = 100 - 75 \quad \Rightarrow \quad t = \mathbf{8.33 \text{ seconds}}$$

Q. 13. Define the following terms:

(*i*) Pseudo first order reaction

(*ii*) Half life period of reaction ($t_{1/2}$) [*CBSE Delhi 2014*]

Ans. (*i*) A reaction which is not truely of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, *e.g.*, acid hydrolysis of ethyl acetate.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate $\propto [CH_3COOC_2H_5]$ as H_2O is in excess.

(*ii*) The half life ($t_{1/2}$) of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration $[R]_0$.

For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$, *i.e.*, independent of $[R]_0$.

For a zero order reaction, $t_{1/2} = \dfrac{[R]_0}{2k}$, *i.e.*, $t_{1/2} \propto [R]_0$.

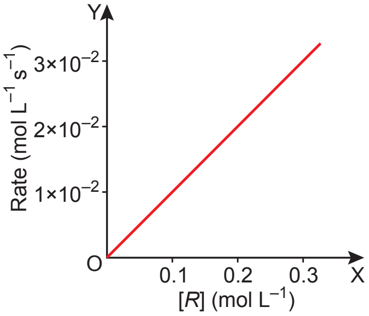
Q. 14. For a reaction: $A + H_2O \longrightarrow B$, Rate $\propto [A]$.

What is its (*i*) molecularity (*ii*) order of reaction?

Ans. (*i*) Pseudo unimolecular

(*ii*) Order = 1.

Q. 15. The rate for the reaction $R \longrightarrow P$ is rate $= k[R]$. It has been shown graphically alongside. What is rate constant for the reaction?



Ans. From the graph

Case I: Rate $= k[A]$

$$1 \times 10^{-2} \text{ mol } L^{-1} \text{ s}^{-1} = k\,(0.1 \text{ mol } L^{-1})$$

$$\therefore \quad k = \frac{1\times10^{-2} \text{ mol } L^{-1} \text{ s}^{-1}}{0.1 \text{ mol } L^{-1}} = 0.1 \text{ s}^{-1}$$

Case II:

$$3 \times 10^{-2} \text{ mol } L^{-1}s^{-1} = k\,(0.3 \text{ mol } L^{-1})$$

$$k = \frac{3\times10^{-2} \text{ mol } L^{-1} \text{ s}^{-1}}{0.3 \text{ mol } L^{-1}} = 0.1 \text{ s}^{-1}$$

Hence, $\boldsymbol{k = 0.1 \text{ s}^{-1}}$

Q. 16. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to $\frac{1}{10}$th of its initial value? [*CBSE (F) 2013*]

Ans.

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \quad \text{as} \quad [R] = \frac{[R]_0}{10}$$

$$\therefore \quad t = \frac{2.303}{k}\log\frac{[R]_0}{\frac{[R]_0}{10}} = \frac{2.303}{60}\times\log 10 = \frac{2.303}{60}\times 1 = \mathbf{3.838\times10^{-2}\,s}$$

Q. 17. (*i*) For a reaction $A + B \longrightarrow P$, the rate law is given by,

$$r = k[A]^{1/2}[B]^2.$$

What is the order of this reaction?

(*ii*) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half life of the reaction. *[CBSE (AI) 2013]*

Ans. (*i*) Order of reaction $= \frac{1}{2} + 2 = \mathbf{\frac{5}{2}}$

(*ii*) Radioactive decay follows first order kinetics.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}}\ \text{s} = \mathbf{1.26 \times 10^{13}\ s}$$

Q. 18. 87.5% of the substance disintegrated in 45 minutes (first order reaction). What is its half-life?

Ans. $\left(\frac{1}{2}\right)^n = \frac{12.5}{100}$ because 87.5% has disintegrated, amount left is 12.5%.

$$\left(\frac{1}{2}\right)^n = \left(\frac{1}{8}\right) \quad \Rightarrow \quad \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^3$$

Number of half lives = 3

$$t_{1/2} = \frac{45}{3} = \mathbf{15\ minutes}$$

Q. 19. After 24 hrs, only 0.125 gm out of the initial quantity of 1 gm of a radioactive isotope remains behind. What is its half life period? *[CBSE Sample Paper 2017]*

Ans. Here, $[R]_0 = 1$ g, $[R] = 0.125$ g, $t = 24$ h

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{24}\log\frac{1}{0.125} \quad \Rightarrow \quad k = \frac{2.303}{24}\log 8$$

$$k = \frac{2.303}{24} \times 0.9031 \quad \Rightarrow \quad k = 0.0866\ \text{h}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} \quad \Rightarrow \quad t_{1/2} = \frac{0.693}{0.0866\ \text{h}^{-1}} \text{ or } t_{1/2} = \mathbf{8\ h}$$

Q. 20. Show that in a first order reaction, time required for completion of 99.9% is 10 times that of half-life ($t_{1/2}$) of the reaction. *[CBSE (F) 2016]*

Ans. $t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\frac{2.303}{k}\log\frac{100}{100-99.9}}{\frac{2.303}{k}\log\frac{100}{100-50}} = \frac{\log\frac{100}{0.1}}{\log\frac{100}{50}} = \frac{\log 10^3}{\log 2} = \frac{3\log 10}{0.3010}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{30}{3.01} \simeq 10$$

$$t_{99.9\%} = 10t_{50\%}$$

Q. 21. Rate constant k for first order reaction has been found to be $2.54 \times 10^{-3}\ s^{-1}$. Calculate its three-fourth life. *[CBSE Sample Paper 2013]*

Ans.

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \qquad ...(i)$$

$$k = 2.54 \times 10^{-3}\ \text{s}^{-1};\ [R] = \frac{[R]_0}{4}$$

Substituting these values in equation (*i*), we get

$$t_{3/4} = \frac{2.303}{2.54\times10^{-3}}\log\frac{[R]_0}{\frac{[R]_0}{4}} = 0.9066\times10^{3}\log 4$$

$$t_{3/4} = 0.9066 \times 10^{3} \times 0.6021 \text{ s}$$

$$= \mathbf{5.46 \times 10^{2}\ s}$$

Q. 22. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/second^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010) **[*HOTS*]**

Ans. $$k = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

Here, $P_0 = 0.4$ atm, $t = 100$ s, $P_t = 0.7$ atm

$$\therefore \quad k = \frac{2.303}{100}\log\frac{0.4}{2\times0.4-0.7}$$

$$= \frac{2.303}{100}\log\frac{0.4}{0.1} = \frac{2.303}{100}\log 4$$

$$= \frac{2.303}{100}\times0.6021$$

$$k = \mathbf{1.386 \times 10^{-2}\ s^{-1}}$$

Q. 23. (*i*) Explain why H_2 and O_2 do not react at room temperature.

(*ii*) Write the rate equation for the reaction $A_2 + 3B_2 \longrightarrow 2C$, if the overall order of the reaction is zero. **[*CBSE (AI) 2017*]**

Ans. (*i*) Due to high activation energy for the reaction.

(*ii*) Rate = $k[A_2]^0[B_2]^0$ or Rate = k

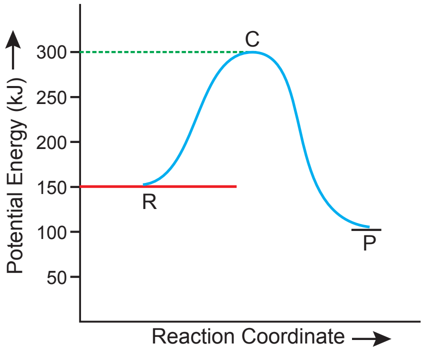
Q. 24. Answer the following questions on the basis of the given plot of potential energy vs reaction coordinate:

(*i*) What is the threshold energy for the reaction?

(*ii*) What is the activation energy for forward reaction?

(*iii*) What is the activation energy for backward reaction?

(*iv*) What is enthalpy change for the forward reaction?



Ans. (*i*) Threshold energy for the reaction = 300 kJ mol^{-1}

(*ii*) Activation energy for the forward reaction = 300 – 150
= 150 kJ mol^{-1}

(*iii*) Activation energy for the backward reaction = 300 – 100
= 200 kJ mol^{-1}

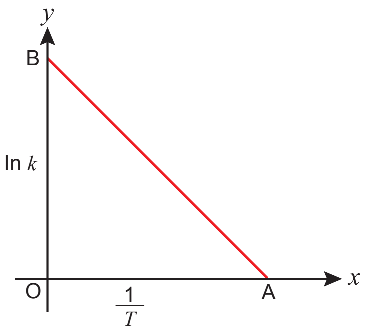
(*iv*) Enthalpy change for the forward reaction $\Delta_r H = 100 - 150$
= – 50 kJ mol^{-1}

Q. 25. **A graph between ln k and $\frac{1}{T}$ for a reaction is given. Here k is rate constant and T is temperature in kelvin. If $OA = a$ and $OB = b$, answer the following:**

(*i*) What is the activation energy (E_a) of the reaction?

(*ii*) What is the frequency factor (A) for the reaction?

[*HOTS*]



Ans. According to Arrhenius equation, $\ln k = -\frac{E_a}{RT} + \ln A$

(*i*) Slope $= -\frac{OB}{OA} = -\frac{b}{a} = -\frac{E_a}{R}$ or $E_a = \frac{b}{a} R$

(*ii*) Intercept on y-axis $= OB = b = \ln A$ or $A = e^b$

Short Answer Questions–II [3 marks]

Q. 1. **$A + 2B \longrightarrow 3C + 2D$. The rate of disappearance of B is 1×10^{-2} mol L^{-1} s^{-1}. What will be (*i*) Rate of the reaction (*ii*) Rate of change in concentration of A and C?**

Ans. (*i*) As $\frac{-d[B]}{dt} = 1 \times 10^{-2}$ mol L^{-1} s^{-1}

$$\therefore \quad \text{Rate} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{2} \times 1 \times 10^{-2} = \mathbf{0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$$

(*ii*)
$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt}$$

Rate of change in concentration of A

$$= -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$
$$= \mathbf{0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$$

Rate of change in concentration of C

$$= +\frac{d[C]}{dt} = -\frac{3}{2}\frac{d[B]}{dt} = \frac{3}{2} \times 1 \times 10^{-2}$$
$$= \mathbf{1.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$$

Q. 2. **The rate of reaction, $2NO + Cl_2 \longrightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes eight times when concentration of both NO and Cl_2 are doubled. Deduce the order of the reaction.** **[*HOTS*]**

Ans. Let

$$r = k[NO]^x [Cl_2]^y \quad \ldots(i)$$
$$2r = k[NO]^x [2Cl_2]^y \quad \ldots(ii)$$
$$8r = k[2NO]^x [2Cl_2]^y \quad \ldots(iii)$$

Dividing (*iii*) by (*ii*), we get

$$\frac{8r}{2r} = \frac{k[2NO]^x [2Cl_2]^y}{k[NO]^x [2Cl_2]^y}$$
$$2^2 = [2]^x$$
$$x = 2$$

Putting the value of x in (*i*) and (*ii*), we get

$$r = k[NO]^2 [Cl_2]^y$$
$$2r = k[NO]^2 [2Cl_2]^y$$
$$\frac{2r}{r} = \frac{[2Cl_2]^y}{[Cl_2]^y}$$

$$2 = [2]^y$$
$$y = 1$$
$$\text{Rate} = k\,[NO]^2\,[Cl_2]^1$$

Overall order of reaction = $x + y = 2 + 1 =$ **3**

Q. 3. Following reaction takes place in one step:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

How will the rate of the above reaction change if the volume of the reaction vessel is reduced to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume? **[*HOTS*]**

Ans. $$\text{Rate} = k\,[NO]^2\,[O_2]$$

Let initially, moles of NO = a, moles of $O_2 = b$, volume of the vessel = V. Then

$$[NO] = \frac{a}{V}\,M,\ [O_2] = \frac{b}{V}\,M$$

$$\therefore \qquad \text{Rate } (r_1) = k\left(\frac{a}{V}\right)^2\left(\frac{b}{V}\right) = k\frac{a^2 b}{V^3} \qquad \ldots(i)$$

Now, new volume = $\frac{V}{3}$

$\therefore$ New concentrations:
$$[NO] = \frac{a}{V/3} = \frac{3a}{V}$$
$$[O_2] = \frac{b}{V/3} = \frac{3b}{V}$$

$$\therefore \qquad \text{New rate } (r_2) = k\left(\frac{3a}{V}\right)^2\left(\frac{3b}{V}\right) = \frac{27ka^2 b}{V^3} \qquad \ldots(ii)$$

$$\therefore \qquad \frac{r_2}{r_1} = 27 \qquad \text{or} \qquad r_2 = 27r_1,$$ *i.e.*, rate becomes **27 times**.

Thus, there is no effect on the order of reaction.

Q. 4. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide. **[*HOTS*]**

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

The rate law for this reaction is:

$$\text{Rate} = k\,[NO]^2\,[O_2]$$

Propose a mechanism for the reaction.

Ans. The probable proposed mechanism may be,

$$NO + O_2 \longrightarrow NO_3 \text{ (fast)} \qquad \text{Step I}$$
$$NO_3 + NO \xrightarrow{k_1} NO_2 + NO_2 \text{ (slow)} \qquad \text{Step II}$$

Since slowest reaction is the rate determining step, therefore

$$\text{Rate} = k_1\,[NO_3]\,[NO]$$
$$K = \frac{[NO_3]}{[NO][O_2]}$$
$$[NO_3] = K\,[NO]\,[O_2]$$
$$\text{Rate} = k_1K\,[NO]\,[O_2]\,[NO] = K'[NO]^2\,[O_2], \text{ where } K' = k_1.K$$

Q. 5. The reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5}. Suppose in a case $[N_2] = 0.80$ mol L^{-1} and $[O_2] = 0.20$ mol L^{-1} before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K.

[*CBSE (AI) 2012*] [*HOTS*]

Ans.

	N_2	+	O_2	$\longrightarrow$	$2NO$
Initial conc. in mol L^{-1}	0.8		0.2		0
Change in conc. in mol L^{-1}	$-x$		$-x$		$+2x$
Equilibrium conc. in mol L^{-1}	$0.8-x$		$0.2-x$		$2x$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} \qquad \therefore \quad 1\times10^{-5} = \frac{(2x)^2}{(0.8-x)\,(0.2-x)}$$

As $x << 0.2$, therefore $0.8 - x \approx 0.8$ and $0.2 - x \approx 0.2$

$$\therefore \qquad 1 \times 10^{-5} = \frac{4x^2}{0.16} \qquad \Rightarrow \qquad 4x^2 = 16 \times 10^{-7}$$

$$x = 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

Thus at equilibrium,

$$[NO] = 2x = 2 \times 6.324 \times 10^{-4} = \mathbf{12.648 \times 10^{-4} \text{ mol L}^{-1}}$$

$$[N_2] = 0.8 - 6.324 \times 10^{-4} \text{ mol L}^{-1} = \mathbf{0.799 \text{ mol L}^{-1}}$$

$$[O_2] = 0.2 - 6.324 \times 10^{-4} \text{ mol L}^{-1} = \mathbf{0.199 \text{ mol L}^{-1}}$$

Q. 6. Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction? ***[CBSE 2019 (56/3/2), 2020 (56/5/1)]***

Ans.
- The sum of powers of the concentration of the reactants in the rate law expression is known as order of that reaction.

  Consider the general reaction,

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

  Let

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

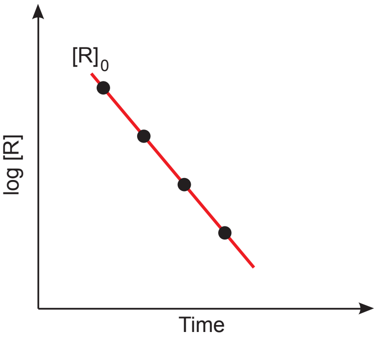
  where x and y represent the order w.r.t. t. The reactants A and B respectively. Overall order of reaction $= x + y$.
- Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions.

  For a complex reaction molecularity has no meaning and order is given by the slowest step. Molecularity of the slowest step is same as the order of the overall reaction.

Q. 7. Observe the graph in diagram and answer the following questions.

(*i*) If slope is equal to -2.0×10^{-6} sec^{-1}, what will be the value of rate constant?

(*ii*) How does the half-life of zero order reaction relate to its rate constant? ***[CBSE Sample Paper 2017]***



Ans. (*i*) $\text{Slope} = -\dfrac{k}{2.303}$ or $k = -2.303 \times \text{Slope}$

$$\therefore \qquad k = -2.303 \times (-2.0 \times 10^{-6} \text{ s}^{-1})$$

$$k = \mathbf{4.606 \times 10^{-6} \text{ s}^{-1}}$$

(*ii*) For a zero order reaction

$$t = \frac{[R]_0 - [R]}{k}$$

$$\text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore \qquad t_{1/2} = \frac{[R]_0 - \dfrac{[R]_0}{2}}{k} \qquad \text{or} \qquad t_{1/2} = \frac{[R]_0}{2k}$$

Q. 8. A solution of H_2O_2 when titrated against $KMnO_4$ solution at different intervals of time gave the following results:

Time (minutes)	**0**	**10**	**20**
Volume of $KMnO_4$ (mL)	**23.8**	**14.7**	**9.1**

Show that decomposition of H_2O_2 is first order reaction.

Ans. (*i*) $k = \dfrac{2.303}{10} \log \dfrac{23.8}{14.7} = \dfrac{2.303}{10} \times 0.2093 = \mathbf{0.048 \text{ min}^{-1}}$

(*ii*) $k = \dfrac{2.303}{20} \log \dfrac{23.8}{9.1} = \dfrac{2.303}{20} \times 0.4176 = \mathbf{0.048 \text{ min}^{-1}}$

Since the value of k comes out to be constant in both the cases, therefore the reaction is of first order.

Q. 9. Define half-life of a reaction. Write the expression of half-life for *[CBSE (F) 2014]*

(*i*) zero order reaction and **(*ii*) first order reaction.**

Ans. The half life ($t_{1/2}$) of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

(*i*) $t_{1/2}$ for a zero order reaction $= \dfrac{[R]_0}{2k}$ where $[R]_0$ = initial concentration, k = rate constant

(*ii*) $t_{1/2}$ for a first order reaction $= \dfrac{0.693}{k}$

Q. 10. A first order reaction is 50% complete in 25 minutes. Calculate the time for 80% completion of the reaction. *[CBSE 2019 (56/3/2)]*

Ans. $t_{1/2} = \dfrac{0.693}{k} \quad \Rightarrow \quad k = \dfrac{0.693}{t_{1/2}}$

$$k = \frac{0.693}{25 \text{ min}} = 2.772 \times 10^{-2} \text{ min}$$

$$[R] = [R]_0 - 80\% \text{ of } [R]_0 \text{ or } [R] = [R]_0 - \frac{80 \times [R]_0}{100} \text{ or } [R] = 0.2[R]_0$$

Substituting the value of k and $[R]$ in the expression

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}, \text{ we get}$$

$$t = \frac{2.303}{2.772 \times 10^{-2}} \times \log \frac{[R]_0}{0.2[R]_0}$$

$$t = \frac{2.303}{2.772 \times 10^{-2}} \log 5$$

$$t = \frac{2.303 \times 0.699}{2.772 \times 10^{-2}} \text{ or } t = \mathbf{58.07 \text{ min}}$$

Q. 11. Following data are obtained for the reaction:

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(*i*) Show that it follows first order reaction.

(*ii*) Calculate the half-life.

(Given log 2 = 0.3010, log 4 = 0.6021) *[CBSE Delhi 2017]*

Ans. (*i*) At 300 s,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303}{300} \log 2$$

$$k = \frac{2.303}{300} \times 0.3010 = 2.31 \times 10^{-3} \text{ s}^{-1}$$

At 600 s

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303}{600} \log 4$$

$$k = \frac{2.303}{600} \times 0.6021 = 2.31 \times 10^{-3} \text{ s}^{-1}$$

k is constant and is equal to $2.31 \times 10^{-3}\ \text{s}^{-1}$ when we use first order equation. Hence, it follows first order reaction.

(*ii*) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{2.31\times10^{-3}\,\text{s}^{-1}} = \mathbf{300\ s}$

Q. 12. $^{238}_{92}U$ changes to $^{206}_{92}Pb$ by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb had accumulated due to decay of ^{238}U, find out the age of the ore. (Half-life of $^{238}U = 4.5 \times 10^9$ years) **[*HOTS*]**

Ans. $[A]_0$ = Initial amount of ^{238}U = amount of ^{238}U left at time t + amount of ^{238}U decayed

$$[A]_0 = 1.0 + \text{amount of } ^{238}\text{U decayed}$$

Now, amount of ^{238}U decayed $= \dfrac{0.1\times 238}{206}\ \text{g} = 0.1155\ \text{g}$

$\therefore \qquad [A]_0 = 1.0\ \text{g} + 0.1155\ \text{g} = 1.1155\ \text{g}$

Determination of k: $\qquad k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{4.5\times10^9} = 0.154 \times 10^{-9}\ \text{year}^{-1}$

Determination of time: $\qquad t = \dfrac{2.303}{k}\log\dfrac{[A]_0}{[A]}$

Substituting the values of $[A]_0 = 1.1155$ g and $k = 0.154 \times 10^{-9}\ \text{year}^{-1}$

$$t = \frac{2.303}{0.154\times10^{-9}}\log\frac{1.1155}{1}$$
$$= 0.7099 \times 10^9\ \text{year}$$
$$= \mathbf{7.099 \times 10^8\ year}$$

Q. 13. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at a constant volume:

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

S. No.	Time/s	Total Pressure/atm
1.	0	0.5
2.	100	0.512

Calculate the rate constant. **[*HOTS*]**

Ans. Let the pressure of $N_2O_5(g)$ decrease by $2x$ atm. As two moles of N_2O_5 decompose to give two moles of $N_2O_4(g)$ and one mole of $O_2(g)$, the pressure of $N_2O_4(g)$ increases by $2x$ atm and that of $O_2(g)$ increases by x atm.

	$2N_2O_5(g)$ $\longrightarrow$	$2N_2O_4(g)$ +	$O_2(g)$
At $t = 0$	0.5 atm	0 atm	0 atm
At time t	$(0.5 - 2x)$ atm	$2x$ atm	x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$
$$= (0.5 - 2x) + 2x + x = 0.5 + x$$
$$x = p_t - 0.5$$
$$p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm,

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476\ \text{atm}$$

Thus, $\qquad k = \dfrac{2.303}{t}\log\dfrac{p_i}{p_A}$

$$= \frac{2.303}{100\ \text{s}}\log\frac{0.5\ \text{atm}}{0.476\ \text{atm}}$$
$$= \frac{2.303}{100\ \text{s}}\times 0.02136 = \mathbf{4.92 \times 10^{-4}\ s^{-1}}$$

Q. 14. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T}\,\text{K}$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.

(Given: $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$) **[*CBSE Delhi 2016*]**

Ans. Comparing the equation, $\log k = 14.2 - \frac{1.0 \times 10^4}{T}$ K with the equation, $\log k = \log A - \frac{E_a}{2.303\,RT}$, we get

$$\frac{E_a}{2.303\,RT} = \frac{1.0 \times 10^4 K}{T} \quad \text{or} \quad E_a = 1.0 \times 10^4\ \text{K} \times 2.303 \times R$$

$$E_a = 1.0 \times 10^4\ \text{K} \times 2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$= 19.1471 \times 10^4\ \text{J mol}^{-1} = \mathbf{191.47\ kJ\ mol^{-1}}$$

For a first order reaction, $t_{1/2} = \frac{0.693}{k}$ or $k = \frac{0.693}{t_{1/2}}$

$$\therefore \qquad k = \frac{0.693}{200\ \text{min}} = \mathbf{3.465 \times 10^{-3}\ min^{-1}}$$

Q. 15. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a).

(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021) **[*CBSE Patna 2015*]**

Ans. Substituting $k_1 = 2\times10^{-2}$, $k_2 = 4\times10^{-2}$, $T_1 = 300$ K, $T_2 = 310$ K, $R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$ in the expression

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\times R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$

$$\log\frac{4\times10^{-2}}{2\times10^{-2}} = \frac{E_a}{2.303\times 8.314}\left(\frac{310-300}{300\times310}\right)$$

$$\log 2 = \frac{E_a}{19.147}\times\frac{10}{300\times310}$$

$$E_a = 0.3010 \times 19.147 \times 300 \times 31 = 53598\ \text{J mol}^{-1}$$

$$E_a = \mathbf{53.598\ kJ\ mol^{-1}}$$

Q. 16. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $k = 1.6 \times 10^6\ \text{s}^{-1}$ at 280 K? [$R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$]

Ans. Given $T_1 = 280$ K, $k_1 = 1.6 \times 10^6\ \text{s}^{-1}$, $k_2 = ?$, $E_a = 0$, $T_2 = 300$ K.

By Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

As, $E_a = 0$

$$\therefore \qquad \log\frac{k_2}{k_1} = 0$$

$$\text{or} \qquad \frac{k_2}{k_1} = 1 \qquad \text{or} \qquad k_2 = k_1$$

Thus, the rate constant at 300 K is $\mathbf{1.6 \times 10^6\ s^{-1}}$.

Q. 17. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

[$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$; log 4 = 0.602] **[*HOTS*]**

Ans. For a first order reaction, $k = \frac{0.693}{t_{1/2}}$

$T_1 = 300$ K, $\qquad k_1 = \frac{0.693}{20} = 3.456 \times 10^{-2}\ \text{min}^{-1}$

$T_2 = 350$ K, $\qquad k_2 = \dfrac{0.693}{5} = 1.386 \times 10^{-1}\ \text{min}^{-1}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log \frac{1.386 \times 10^{-1}}{3.465 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{350 - 300}{350 \times 300}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{50}{350 \times 300}\right)$$

$$0.602 = \frac{E_a}{19.147}\left(\frac{50}{350 \times 300}\right)$$

$$E_a = \frac{0.602 \times 19.147 \times 350 \times 300}{50}$$

$$= 24205.63 \text{ J mol}^{-1}$$

$$= \mathbf{24.206\ kJ\ mol^{-1}}$$

Q. 18. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. [*CBSE 2018*]

(Given: log 2 = 0.3010, log 4 = 0.6021, $R = 8.314$ J K^{-1} mol^{-1})

Ans. For a first order reaction, $k = \dfrac{0.693}{t_{1/2}}$

So, $k_1 = \dfrac{0.693}{40}\ \text{min}^{-1}$ and $k_2 = \dfrac{0.693}{20}\ \text{min}^{-1}$

$$\frac{k_2}{k_1} = \frac{0.693\ \text{min}^{-1}/20}{0.693\ \text{min}^{-1}/40} = 2$$

Here, $T_1 = 300$ K, $T_2 = 320$ K and $R = 8.314$ J K^{-1} mol^{-1}

Substituting these values in the expression

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314\ \text{JK}^{-1}\text{mol}^{-1}}\left(\frac{320\ \text{K} - 300\ \text{K}}{300\ \text{K} \times 320\ \text{K}}\right)$$

$$0.3010 = \frac{E_a \times 20}{19.147\ \text{J mol}^{-1} \times 300 \times 320}$$

or $$E_a = \frac{0.3010 \times 19.147 \times 300 \times 320\ \text{J mol}^{-1}}{20} = 27663.58 \text{ J mol}^{-1}$$

$$E_a = \mathbf{27.66\ kJ\ mol^{-1}}$$

Long Answer Questions [5 marks]

Q. 1. For the reaction,

$$2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g),$$

the following data were collected. All the measurements were taken at 263 K:

Experiment	Initial [NO] (M)	Initial [Cl_2] (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(*i*) Write the expression for rate law.

(*ii*) Calculate the value of rate constant and specify its units.

(*iii*) What is the initial rate of disappearance of Cl_2 in experiment 4? [*CBSE Delhi 2012*]

Ans. Suppose order w.r.t. NO is m and order w.r.t. Cl_2 is n. Then the rate will be

$$\text{Rate} = k\,[\text{NO}]^m\,[\text{Cl}_2]^n$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$0.60 = k(0.15)^m\,(0.15)^n \qquad ...(i)$$

$$1.20 = k(0.15)^m\,(0.30)^n \qquad ...(ii)$$

$$2.40 = k(0.30)^m\,(0.15)^n \qquad ...(iii)$$

Dividing equation (*iii*) by (*i*), we get

$$\frac{2.40}{0.60} = \frac{k\,(0.30)^m\,(0.15)^n}{k\,(0.15)^m(0.15)^n}$$

$$4 = 2^m \text{ or } 2^2 = 2^m \text{ or } m = 2$$

Dividing equation (*ii*) by (*i*), we get

$$\frac{1.20}{0.60} = \frac{k\,(0.15)^m\,(0.30)^n}{k\,(0.15)^m(0.15)^n}$$

$$2 = 2^n \text{ or } n = 1$$

(*i*) Rate law expression is, Rate $= k[\text{NO}]^2\,[\text{Cl}_2]$

(*ii*) $0.60 \text{ mol L}^{-1} \text{ min}^{-1} = k(0.15 \text{ mol L}^{-1})^2\,(0.15 \text{ mol L}^{-1})$

$$k = \mathbf{177.78\ mol^{-2}\ L^2\ min^{-1}}$$

(*iii*) Rate $= 177.78 \text{ mol}^{-2}\text{ L}^2\text{ min}^{-1} \times (0.25 \text{ mol L}^{-1})^2\,(0.25 \text{ mol L}^{-1})$

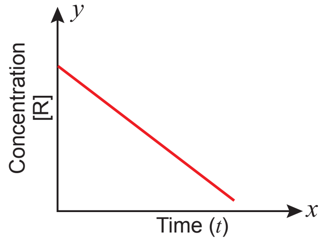
$$= \mathbf{2.778\ mol\ L^{-1}\ min^{-1}}$$

Q. 2. Consider the reaction $R \xrightarrow{k} P$. The change in concentration of R with time is shown in the following plot: [*CBSE 2019 (56/4/1)*]

(*i*) Predict the order of the reaction.

(*ii*) Derive the expression for the time required for the completion of the reaction.

(*iii*) What does the slope of the above line indicate?



Ans. (*i*) The reaction $R \longrightarrow P$ is a zero order reaction.

(*ii*) For the reaction $R \xrightarrow{k} P$

$$\text{rate} = \frac{-d[R]}{dt} = k$$

$$d[R] = -k\,dt$$

Integrating both sides,

$$[R] = -kt + C, \qquad \text{where } C = \text{constant of integration} \qquad ...(i)$$

At $t = 0$, $[R] = [R]_0$

Substituting this in equation (*i*)

$$C = [R]_0$$

Substituting the value of C in equation (*i*)

$$[R] = -kt + [R]_0 \qquad ...(ii)$$

$$kt = [R]_0 - [R]$$

$$\Rightarrow \qquad t = \frac{[R]_0 - [R]}{k}$$

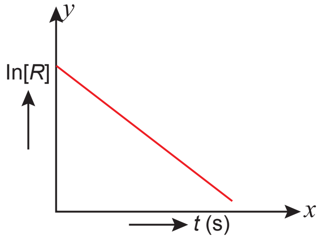
On completion of reactions, $[R] = 0$

$$\therefore \qquad t = \frac{[R]_0}{k}$$

(*iii*) From equation (*ii*), we have slope of curve

$$\text{Slope} = \frac{d[R]}{dt} = -k$$

Q. 3. For a certain chemical reaction variation in the concentration ln [R] vs. time plot is given alongside. **[*HOTS*]**



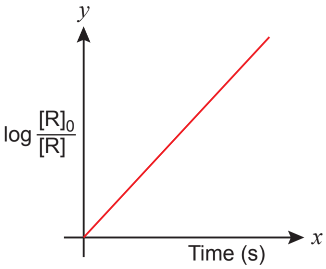
For this reaction

- **(*i*) what is the order of the reaction?**
- **(*ii*) what are the units of rate constant k?**
- **(*iii*) give the relationship between k and $t_{1/2}$ (half-life period).**
- **(*iv*) what is the slope of the curve?**
- **(*v*) draw the plot log $[R]_0/[R]$ vs time t(s).**

Ans. (*i*) First order (*ii*) time^{-1} (s^{-1})

(*iii*) $k = \dfrac{0.693}{t_{1/2}}$ (*iv*) slope = – k (rate constant)

(*v*)



Q. 4. Nitrogen pentoxide decomposes according to equation:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

This first order reaction was allowed to proceed at 40°C and the data below were collected:

$[N_2O_5]$ (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

- **(*i*) Calculate the rate constant. Include units with your answer.**
- **(*ii*) What will be the concentration of N_2O_5 after 100 minutes?**
- **(*iii*) Calculate the initial rate of reaction.** **[*CBSE Delhi 2011*]**

Ans. (*i*) When t = 20 min, $[R] = 0.289$ mol L^{-1}

Also, $[R]_0 = 0.400$ mol L^{-1}

For a first order reaction

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$\therefore \quad k = \frac{2.303}{20}\log\frac{0.400}{0.289} \Rightarrow k = \frac{2.303}{20}\log\frac{4.00}{2.89}$$

$$\Rightarrow \quad k = \frac{2.303}{20}[\log 4.00 - \log 2.89] \Rightarrow k = \frac{2.303}{20}[0.6021 - 0.4609]$$

$$\Rightarrow \quad k = \frac{2.303}{20}\times 0.1412 \Rightarrow k = 2.303 \times 0.00706 = 0.016259 \text{ min}^{-1}$$

$$\Rightarrow \quad \mathbf{k = 1.6259 \times 10^{-2}\ min^{-1}}$$

(*ii*)
$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

Here, $[R]_0 = 0.400$ mol^{-1}, t = 100 min, $k = 1.626 \times 10^{-2}$ min^{-1}

$$100 = \frac{2.303}{1.626\times 10^{-2}}\log\frac{0.400}{[R]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]} \quad \Rightarrow \quad 0.7060 = \log \frac{0.4}{[R]}$$

$$\text{Antilog } (0.7060) = \frac{0.4}{[R]}$$

$$5.082 = \frac{0.4}{[R]} \quad \Rightarrow \quad [R] = \frac{0.4}{5.082} = \mathbf{0.0787\ M}$$

(*iii*) Initial rate, *i.e.*, rate of reaction when $t = 0$

When, $t = 0.00$ min, $[R] = 0.400$ mol L^{-1}

Also, $k = 1.626 \times 10^{-2}$ min^{-1}

$\therefore$ Initial rate $= k\,[R]$

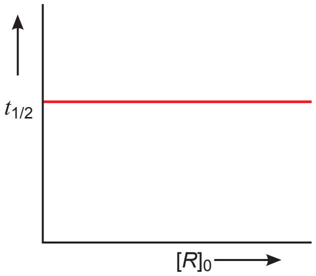
$= 1.626 \times 10^{-2}$ min$^{-1} \times 0.400$ mol L^{-1}

$= \mathbf{6.504 \times 10^{-3}}$ **mol L^{-1} min^{-1}**

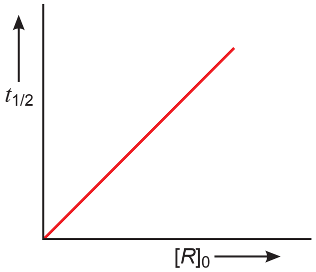
Q. 5. **(*i*) A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.** **[*CBSE (F) 2017*]**

(*ii*) Predict the order of the reaction in the given plots: **[*CBSE 2019 (56/2/1)*]**

(*a*)



(*b*)



where $[R]_0$ is the concentration of reactant.

(Given: log 2 = 0.3010, log 4 = 0.6021)

Ans. (*i*) For a first order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

$$\therefore \quad \frac{t_{3/4}}{t_{1/2}} = \frac{\dfrac{2.303}{k} \log \dfrac{100}{25}}{\dfrac{2.303}{k} \log \dfrac{100}{50}} = \frac{\log 4}{\log 2} = \frac{0.6021}{0.3010}$$

$$\frac{40 \text{ min}}{t_{1/2}} = 2 \qquad \text{or} \qquad t_{1/2} = \mathbf{20\ min.}$$

(*ii*) (*a*) First order (*b*) Zero order

Q. 6. **For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:**

t/s	**0**	**30**	**60**
[CH_3COOCH_3]/mol L^{-1}	**0.60**	**0.30**	**0.15**

(*i*) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(*ii*) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(Given log 2 = 0.3010, log 4 = 0.6021) **[*CBSE Delhi 2015*]**

Ans. (*i*) $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$ …(*i*)

Substituting $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.30$ mol L^{-1} and $t = 30$ s in equation (*i*), we get

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$k = \frac{2.303}{30} \log 2 = \frac{2.303}{30} \times 0.3010$$

$$k = 0.0231 \text{ s}^{-1}$$

Again substituting, $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.15$ mol L^{-1} and $t = 60$ in equation (*i*), we get

$$k = \frac{2.303}{60}\log\frac{0.60}{0.15}$$

$$k = \frac{2.303}{60}\times\log 4 = \frac{2.303}{60}\times 0.6021$$

$$k = 0.0231\ s^{-1}$$

As the value of k is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.

(*ii*) Average rate $= -\dfrac{\Delta[CH_3COOCH_3]}{\Delta t} = \dfrac{-[0.15-0.30]}{60-30} = \dfrac{0.15}{30}$

Average rate = **0.005 mol L^{-1} s^{-1}**

Q. 7. (*i*) Write the rate law for a first order reaction. Justify the statement that half life for a first order reaction is independent of the initial concentration of the reactant.

(*ii*) The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C?

Ans. (*i*) Consider the first order reaction,

$$R \longrightarrow P$$

For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

$$\text{Rate} = \frac{-d[R]}{dt} = k[R]$$

For a first order reaction,

$t = \dfrac{2.303}{k}\log\dfrac{[R]_0}{[R]}$, where $[R]_0$ = initial concentration, $[R]$ = concentration at time t.

At $t_{1/2}$, $[R] = [R]_0/2$

So, the above equation becomes

$$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2}$$

$$t_{1/2} = \frac{2.303}{k}\log 2 \quad \text{or} \quad t_{1/2} = \frac{2.303}{k}\times 0.3010$$

$$t_{1/2} = \frac{0.693}{k}$$

This shows that half life of a first order reaction is independent of the initial concentration of the reactant.

(*ii*) According to Arrhenius equation,

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

For uncatalysed reaction,

$$\log k_1 = \log A - \frac{E_{a_1}}{2.303\ RT} \quad ...(i)$$

For catalysed reaction,

$$\log k_2 = \log A - \frac{E_{a_2}}{2.303\ RT} \quad ...(ii)$$

A is equal for both reactions.

Subtracting equation (*i*) from equation (*ii*),

$$\log\frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{2.303\ RT} = \frac{(75.2-50.14)\text{ kJ mol}^{-1}}{2.303\times 8.314\text{ JK}^{-1}\text{ mol}^{-1}\times 298\text{ K}} = 4.39$$

$$\frac{k_2}{k_1} = \text{antilog}\,(4.39) = \mathbf{2.45\times 10^4}$$

Rate of reaction increases by **2.45×10^4 times.**

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

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

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be ________________.

(*a*) the same (*b*) doubled
(*c*) quadrupled (*d*) halved

2. Which of the following expressions is correct for the rate of reaction given below?

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

(*a*) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (*b*) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

(*c*) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (*d*) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

3. Which of the following statement is not correct for the catalyst?

(*a*) It catalyses the forward and backward reaction to the same extent.
(*b*) It alters ΔG of the reaction.
(*c*) It is a substance that does not change the equilibrium constant of a reaction.
(*d*) It provides an alternate mechanism by reducing activation energy between reactants and products.

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. Assertion (*A*) : Many of photochemical changes have positive sign of ΔG, yet they are spontaneous.

Reason (*R*) : The activation energy in photochemical reactions is provided by light energy.

5. Assertion (*A*) : In a reversible endothermic reaction, E_{act} of the forward reaction is higher than that of the backward reaction.

Reason (*R*) : The threshold energy of the forward reaction is more than that of the backward reaction.

6. Assertion (*A*) : The order of the reaction

$$2NO(g) + 2H_2(g) \longrightarrow 2H_2O(g) + N_2(g) \text{ is } 3.$$

Reason (*R*) : Order of reaction with respect to a given reactant is the power of the reactant's concentration in the rate equation.

Answer the following questions:

7. State a condition under which a bimolecular reaction is kinetically first order. **(1)**

8. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example. **(1)**

9. A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$. **(2)**

10. For a zero order reaction will the molecularity be equal to zero? Explain. **(2)**

11. (*i*) The conversion of the molecule X to Y follows second order kinetics. If the concentration X is increased to three times, how will it affect the rate of formation of Y?

(*ii*) The specific reaction rate of a reaction is 6.2×10^{-3} mol L^{-1} s^{-1}. What is the order of reaction? **(2)**

12. Derive an expression to calculate time required for completion of zero order reaction. **(2)**

13. The rate constant for the decomposition of ethyl iodide

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

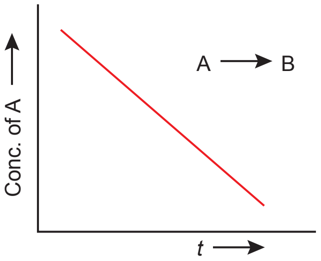
at 600 K is 1.60×10^{-5} s^{-1}. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700 K. **(3)**

14. For a general reaction A $\longrightarrow$ B, plot of concentration of A vs time is given in figure. Answer the following questions on the basis of this graph.

(*i*) What is the order of the reaction?

(*ii*) What is the slope of the curve?

(*iii*) What are the units of rate constant? **(3)**



15. The following data were obtained for the reaction:

$$A + 2B \longrightarrow C$$

Experiment	[A]/M	[B]/M	Initial rate of formation of C/M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(*i*) Find the order of reaction with respect to A and B.

(*ii*) Write the rate law and overall order of reaction.

(*iii*) Calculate the rate constant (k). **(3)**

16. (*i*) For an elementary reaction

$$2A + B \longrightarrow 3C$$

the rate of appearance of C at time '*t*' is 1.3×10^{-4} mol L^{-1} s^{-1}.

Calculate at this time

(*a*) rate of the reaction.

(*b*) rate of disappearance of A.

(*ii*) The decomposition of $N_2O_5(g)$ is a first order reaction with a rate constant of 5×10^{-4} s^{-1} at 45°C, *i.e.*, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$. If initial concentration of N_2O_5 is 0.25 M, calculate its concentration after 2 min. Also, calculate half-life for decomposition of $N_2O_5(g)$. **(5)**

Answers

1. (*a*) **2.** (*c*) **3.** (*b*) **4.** (*b*) **5.** (*c*) **6.** (*a*) **9.** 77.78 min **13.** 6.36×10^{-3} s^{-1}
15. (*iii*) 6.0 L^2 mol^{-1} min^{-1} **16.** (*i*) (*a*) 0.43×10^{-4} mol L^{-1} s^{-1}, (*b*) 0.86×10^{-4} mol L^{-1} s^{-1} (*ii*) 0.235 M, 1386 s

Chapter–5

Surface Chemistry

basic concepts

The chemistry which deals with the boundary separating two bulk phases is termed as **surface chemistry**. The boundary is also called surface or interface. Solid–solid, solid–liquid interfaces are known. As gases are completely miscible they do not form any interfaces. Interface is only a few molecules thick but its area is dependent on the particle size of the bulk phases. Important applications of surface chemistry are: corrosion, electrode processes, adsorption, heterogeneous catalysis.

1. **Adsorption:** The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid leading to a higher concentration on the surface in comparison to the bulk is called adsorption. Examples are: (*i*) water vapours on silica gel, (*ii*) H_2, O_2, NH_3 on activated charcoal.
   - ➡ **Adsorbate:** The substance accumulating at the surface of the solid during adsorption is called adsorbate.
   - ➡ **Adsorbent:** The surface on which adsorption occurs is called adsorbent.
   - ➡ **Desorption:** The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.
2. **Absorption:** It is the phenomenon in which a substance is uniformly distributed throughout the bulk, *i.e.*, it is the penetration of the substance through the surface into the bulk of the solid. **Example:** water vapours are absorbed by anhydrous $CaCl_2$.
3. **Sorption:** Sometimes the adsorbate dissolves into adsorbent. Initially, the adsorbate appears on the surface of adsorbent and later passes into the body of adsorbent. Thus, adsorption changes into absorption. Such side by side occurrence of absorption and adsorption, is called sorption.
4. **Types of Adsorption:** There are mainly two types of adsorption:
   - ➡ **Physical adsorption:** If the force of attraction between the adsorbate and adsorbent are van der Waals' forces, then the adsorption is called physical adsorption or physisorption.
   - ➡ **Chemical adsorption:** If the force of attraction between the particles of adsorbate and adsorbent are almost of the same strength as the chemical bond, the adsorption is called chemical adsorption or chemisorption.
5. **Enthalpy or Heat of Adsorption:** It may be defined as the enthalpy change when one mole of an adsorbate is adsorbed at the surface of adsorbent. It is low in case of physical adsorption and high in case of chemisorption.
6. **Adsorption Isotherm:** When extent of adsorption x/m (where x is the amount of adsorbate, m is mass of adsorbent) is plotted against pressure at a constant temperature, curve thus obtained is known as adsorption isotherm.
   - ➡ **Adsorption Isobar:** A plot of extent of adsorption (x/m) vs. temperature at constant pressure is called adsorption isobar.

➡ **Adsorption Isostere:** The straight line, showing variation of pressure (p) with temperature (T) for a given quantity of adsorption is called adsorption isostere.

7. Freundlich Adsorption Isotherm: It gives the relationship between magnitude of adsorption $\left(\frac{x}{m}\right)$ and pressure at a constant temperature (Fig. 5.1). It can be expressed as

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

where x is the amount of gas adsorbed by m grams of adsorbent at a pressure p, k and n are constants.

Taking logarithm of equation (i)

$$\log \frac{x}{m} = \frac{1}{n} \log p + \log k$$

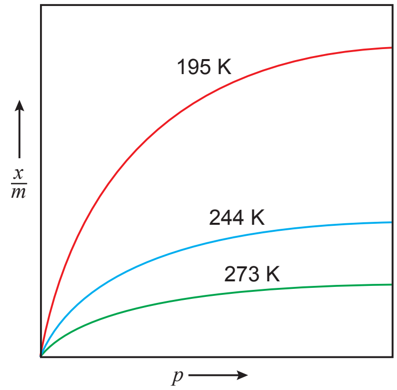


Fig. 5.1: Adsorption isotherm

A plot of $\log \frac{x}{m}$ vs $\log p$ is a straight line (Fig. 5.2). The slope of straight line gives the value of $\frac{1}{n}$ and intercept is $\log k$. This isotherm explains the behaviour of adsorption approximately. $\frac{1}{n}$ can have any value between 0 and 1.

(i) When $\frac{1}{n} = 0, \frac{x}{m} = k$, which shows that adsorption is independent of pressure.

(ii) When $\frac{1}{n} = 1, \frac{x}{m} = kp, \frac{x}{m} \propto p$, adsorption varies directly as pressure.

Both the above observations have been verified.

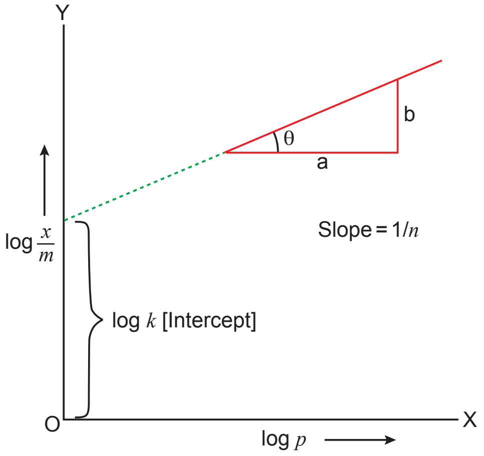


Fig. 5.2: Freundlich isotherm

The experimental isotherm always seems to approach saturation at high pressure. It cannot be explained by Freundlich isotherm. Thus, Freundlich isotherm fails at high pressure.

➡ **Adsorption from Solution**

Freundlich adsorption isotherm between $\frac{x}{m}$ (mass of solute adsorbed per gram of the adsorbent) and the equilibrium concentration C is given by the expression

$$\frac{x}{m} = kC^{1/n}$$

$\log \frac{x}{m} = \frac{1}{n} \log C + \log k$. Plot of $\log \frac{x}{m}$ vs $\log C$ is a straight line.

➡ **Saturation Pressure:** The pressure beyond which adsorption becomes independent of pressure is called saturation pressure.

8. Applications of Adsorption:

(i) Gas masks: Activated charcoal or mixture of adsorbents is used in gas masks so that all toxic gases are preferably adsorbed and the air for breathing is purified.

(ii) Production of high vacuum: The remaining traces of air can be adsorbed by activated charcoal from a vessel evacuated by a vacuum pump to give high vacuum.

(*iii*) **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. For example, use of finely divided iron in the manufacture of ammonia and finely divided nickel in the hydrogenation of vegetable oil.

(*iv*) **Removal of colouring matter from solutions:** Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(*v*) **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(*vi*) **In curing diseases:** A number of drugs are used to kill germs by getting adsorbed on them.

(*vii*) **Adsorption indicators:** Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. In precipitation titration, the indicator is adsorbed at the endpoint producing a characteristic colour on the precipitate.

(*viii*) **Chromatographic analysis:** It is based on the phenomenon of adsorption and finds a number of application in analytical and industrial fields.

(*ix*) **Separation of inert gases:** A mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures. This is due to the difference in degree of adsorption of gases by charcoal.

9. **Catalyst:** A catalyst is a substance which influences the speed of a chemical reaction without itself undergoing any chemical change at the end of the reaction and the phenomenon is known as catalysis.

Catalysis is of two types:

(*a*) Heterogeneous catalysis

(*b*) Homogeneous catalysis

(*a*) **Heterogeneous catalysis:** When the catalyst is in a different phase from that of reactants, the phenomenon is known as heterogeneous catalysis.

Examples: (*i*) Oxidation of ammonia to nitric oxide.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt\,(s)} 4NO(g) + 6H_2O(g)$$

(*ii*) Contact process for the manufacture of sulphuric acid.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5\,(s)} 2SO_3(g)$$

(*iii*) Hydrogenation of unsaturated organic compounds.

$$H_2C{=}CH_2(g) + H_2(g) \xrightarrow{Ni\,(s)} H_3C{-}CH_3(g)$$

$$\text{Vegetable oil}(l) + H_2(g) \xrightarrow{Ni\,(s)} \text{Vegetable ghee}(s)$$

Adsorption Theory of Heterogeneous Catalysis:

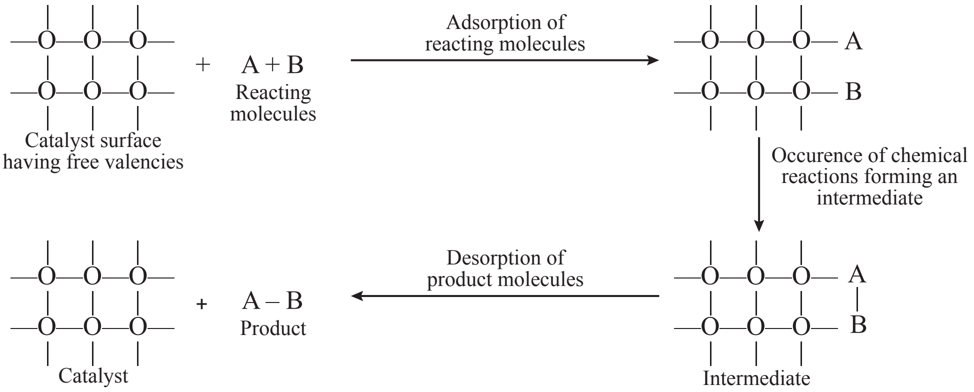


Fig. 5.3: Adsorption of reacting molecules, formation of intermediate and desorption of products

Modern theory has five steps:

- Diffusion of reactants on the surface of catalyst.

- Adsorption of reactant molecules on the surface of catalyst.
- Chemical reaction takes place on the surface of heated catalyst through formation of intermediates.
- Desorption of product molecules from the surface of catalyst.
- Diffusion of products away from the surface of catalyst (Fig. 5.3).

(*b*) **Homogeneous catalysis:** When the catalyst is present in the same phase as that of reactants, the phenomenon is known as homogeneous catalysis.

Examples:

(*i*) Oxidation of SO_2 into SO_3 in the presence of nitric oxide (NO)

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(*ii*) Inversion of sugarcane

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

(*iii*) Hydrolysis of ester

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{H_2SO_4(l)} CH_3COOH(aq) + C_2H_5OH(aq)$$

10. Characteristics of Catalytic Reactions

(*i*) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(*ii*) A small quantity of catalyst is generally needed to produce almost unlimited reactions.

(*iii*) A catalyst cannot, in general, initiate a reaction.

(*iv*) A catalyst is more effective when it is finely divided.

(*v*) A catalyst is specific in its action.

(*vi*) Change of temperature changes the rate of a catalytic reaction as it would do for the same reaction without a catalyst.

(*vii*) A catalyst does not alter the final position of equilibrium, although it decreases the time required to establish it.

11. Important Features of Solid Catalyst

Activity of a catalyst: The ability of a catalyst to increase the rate of a reaction is called activity of a catalyst. For example, a mixture of hydrogen and oxygen does not react at all under normal conditions. However, in the presence of platinum as a catalyst they react with explosive violence.

$$H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{Pt} H_2O(l) \qquad \text{(explosion and very fast reaction takes place)}$$

Selectivity of a catalyst: It is the ability of a catalyst to direct a reaction to yield a particular product. For example, both dehydrogenation and dehydration of ethanol are possible. But, in presence of a suitable catalyst, only one reaction is made to occur.

$$CH_3CH_2OH \xrightarrow[573K]{Cu} CH_3CHO + H_2 \qquad \text{(dehydrogenation)}$$

$$CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O \qquad \text{(dehydration)}$$

12. Catalytic Promoters:

A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter of a catalyst. In fact, a promoter is a catalyst for a catalyst. For example, molybdenum acts as a promoter for iron catalyst in the manufacture of ammonia by Haber's process.

$$N_2(g) + 3H_2(g) \underset{Mo(s)}{\overset{Fe(s)}{\rightleftharpoons}} 2NH_3(g)$$

13. **Shape-Selective Catalysis:** The catalytic reaction which depends upon the pore structure of the catalyst and the size of the reactant and product molecules is known as shape-selective catalysis. Zeolites exhibit shape-selective catalysis because of their honeycomb-like structures.

➡ **Zeolites or Shape-Selective Catalysts:** Zeolites are microporous aluminosilicate having the general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y].mH_2O$ where n is the charge on the metal ion M^{n+}. They have honeycomb-like structures. Before being used they are heated in vacuum so that water of hydration is lost. As a result they become porous. The pore size is in the range of 260-740 pm. The catalytic reactions taking place in zeolites depends upon the size and shape of reactant and product molecules as well as the pores and cavities of zeolites, that is why zeolites are called shape-selective catalysts. Zeolites have found usage as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst is ZSM-5. It converts alcohols directly into gasoline by dehydration.

14. **Enzyme Catalysis:** Enzymes are complex nitrogenous organic compounds produced in living cells of plants and animals. Chemically, enzymes are globular proteins with high molar mass ranging from 15,000 to 1,000,000 g mol^{-1}. They are also called biocatalyst as they catalyse a large number of chemical reactions that occur in the bodies of plants and animals to maintain their life process.

Characteristics:

(*i*) Enzymes form a colloidal solution in water and hence they are very active catalysts.

(*ii*) Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.

(*iii*) They are highly specific in nature, *i.e.*, one catalyst cannot catalyse more than one reaction.

(*iv*) They are highly specific to temperature. The optimum temperature of their activity is 35°C to 40°C. They are deactivated at higher temperatures.

(*v*) Their activity is increased in the presence of certain substances, known as co-enzymes.

(*vi*) A small quantity of enzyme catalyst is sufficient for a large change.

(*vii*) The enzyme activity can be reduced by the presence of certain compounds known as inhibitors. The use of many drugs is based on their action as enzyme inhibitors in the body.

Examples:

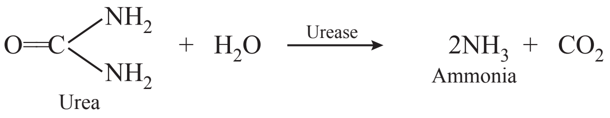
(*i*) $$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(*ii*) $$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

(*iii*) $$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

(*iv*) $$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

(*v*)



$$\underset{\text{Urea}}{O{=}C(NH_2)_2} + H_2O \xrightarrow{\text{Urease}} \underset{\text{Ammonia}}{2NH_3} + CO_2$$

(*vi*) In stomach, enzyme pepsin converts proteins into peptides, whereas in intestines, pancreatic trypsin converts proteins into amino acids by hydrolysis. These amino acids are absorbed by blood and are used in the building of tissues.

(*vii*) Ptyalin enzyme present in human saliva converts starch into glucose.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Mechanism of Enzyme Catalysed Reaction

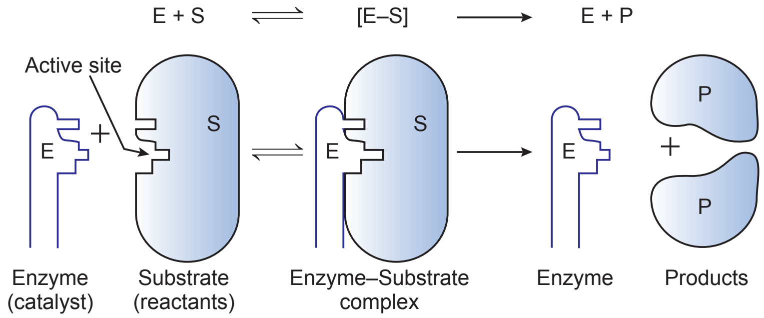


Fig. 5.4: Mechanism of enzyme catalysed reaction

The enzyme catalysed reactions may be considered to proceed in two steps (Fig. 5.4).

(*i*) Binding of enzyme to substrate to form an activated complex.

$$E + S \longrightarrow ES^*$$

(*ii*) Decomposition of the activated complex to form the product.

$$ES^* \longrightarrow E + P$$

15. Catalysis in Industry

Table 5.1: Some Industrial Catalytic Process

	Process	Catalyst
(*i*)	Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773 K temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
(*ii*)	Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(g) + O_2(g) \longrightarrow 4HNO_3(aq)$	Platinised asbestos; temperature 573 K.
(*iii*)	Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7(l)}$ $H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673-723 K.

16. Colloidal Solution: A colloidal solution is a heterogeneous system in which a definite substance is distributed in the form of very small particles (diameter between 10^{-4} and 10^{-7} cm) as dispersed phase in another substance called the dispersion medium.

Dispersed phase + Dispersion medium = Dispersed system (Colloidal solution)

Examples: glue, ink, smoke, etc.

Dispersed phase: The phase of colloid particles is called dispersed phase. This is like a solute in the solution (homogeneous mixtures).

Dispersion medium: The medium in which dispersed particles are dispersed is called dispersion medium. This is like a solvent in true solutions (particle size less than 10^{-9} m). If water being the medium, colloids are called hydrosols.

Crystalloids: The substances whose aqueous solutions can pass the semipermeable membrane are called crystalloids.

17. Classification of Colloids Based on Physical State of Dispersed Phase and Dispersion Medium

Table 5.2: Different Types of Colloidal Systems

Dispersed Phase	Dispersion Medium	Type of Colloid	Examples
Gas	Gas	No colloidal solution	—
Gas	Liquid	Foam	Froth, whipped cream, soap lather
Gas	Solid	Solid sol	Pumice stone, foam rubber
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide spray
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Solid	Gel	Cheese, butter, jellies
Solid	Gas	Aerosol	Smoke, dust
Solid	Liquid	Sol	Paints, cell fluids, gold sol, $Fe(OH)_3$ sol, etc.
Solid	Solid	Solid sol	Some coloured glasses, gems and precious stones

Sols are called hydrosols, benzosols and alcosols according to their dispersion medium water, benzene and alcohol, respectively.

18. Classification Based on the Nature of Interaction between Dispersed Phase and Dispersion Medium

(*i*) **Lyophobic sols:** Particles of dispersed phase have no affinity for dispersion medium, rather they hate dispersion medium. They are not easily prepared and need stabilizing agents for their preservation. They are irreversible. **Examples:** sols of gold, silver, $Fe(OH)_3$, As_2O_3, etc. They are also called extrinsic colloids.

(*ii*) **Lyophilic sols:** Particles of dispersed phase have great affinity for the dispersion medium. They are self-stabilized because of strong attractive forces operating between the suspended particles and the dispersion medium. They are reversible in nature. **Examples:** gums, gelatin, starch, albumin, etc. They are also known as intrinsic colloids.

19. Classification Based on Type of Particles of the Dispersed Phase

(*i*) **Macromolecular colloids:** Macromolecules in suitable solvents form solution, where size of the macromolecules may fall within the colloidal range. The system showing such characteristics are called macromolecular colloids. The colloids are quite stable and in many respect they resemble true solutions. **Examples** of naturally occurring macromolecules are starch, cellulose, proteins and those of man-made macromolecules are nylon, polythene, polystyrene, synthetic rubber, etc.

(*ii*) **Multimolecular colloids:** A large number of atoms or smaller molecules (diameter < 1 nm) of a substance on dissolution aggregate together to form species having size in the colloidal range. Such species are called multimolecular colloids. **Examples:** a sulphur sol consist of particles containing thousands of S_8 sulphur molecules, a platinum or gold sol may have particles of various sizes having many atoms.

(*iii*) **Associated colloids (micelles):** There are certain substances which at low concentrations behave like normal strong electrolytes but at higher concentration behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and aggregated particles are called micelles. **Examples:** soaps and detergents.

20. Surface Active Agents: Those substances which tend to concentrate on the surface of solutions and therefore, lower the surface tension are called surface active agents, *e.g.*, soaps and detergents.

➡ **Critical Micelle Concentration (CMC):** It is the lowest concentration of the surfactant (soap solution) at which micelle formation takes place.

- **Kraft temperature:** Formation of micelles takes place only above a particular temperature called Kraft temperature.

21. Preparation of Colloidal Solutions

1. **Dispersion method:** In this method bigger suspension particles (greater than 10^{-4} cm) are broken down into smaller particles of colloidal size (10^{-4} to 10^{-7} cm).
   (*i*) **Mechanical dispersion:** A colloidal mill is used. Useful in manufacturing dye stuffs, printing inks, paints, varnishes and dental creams.

   (*ii*) **Electrodispersion:** An arc is produced between rods of metals immersed in water containing KOH, surrounded by ice-cold water. KOH is added to stabilise the sol. Ag, Au, Pt, Cu sols are prepared in this manner. The method is known as Bredig's arc method.

   (*iii*) **Dispersion by third substance (Peptization):** The process of passing a precipitate into a colloidal solution by adding an electrolyte is called peptization. In this process, dispersion medium (liquid) breaks up the precipitate into a colloidal state. Cellulose nitrate is peptised by organic solvents such as ethyl alcohol. The commercial name of the product is collodion. **Example:** fresh precipitate of $Fe(OH)_3$ gets easily dispersed into the colloidal solution of $Fe(OH)_3$ by adding $FeCl_3$ solution.

2. **Condensation methods:** In this case we start with molecular-sized particles of the substance and then build them to particles of colloidal dimensions. The different methods are:

   (*a*) By chemical reaction:

   (*i*) **Double decomposition:** Sulphides of metal are usually prepared by this method.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3(sol) + 3H_2O$$

   (*ii*) **Hydrolysis:** A red sol of $Fe(OH)_3$ is obtained by adding some ferric chloride to a beaker of boiling water.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3(sol) + 3HCl$$

   (*iii*) **Reduction:** Colloidal gold, known as purple of cassius is prepared by reducing auric chloride by stannous chloride.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 2Au(sol) + 3SnCl_4$$

   (*iv*) **Oxidation:** Colloidal solutions of non-metals like sulphur, selenium and iodine may be obtained by oxidation.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S(sol)$$

   (*b*) By exchange of solvent, *i.e.*, by lowering of solubility: A substance is dissolved in a solvent and the solution is poured into another solvent in which it is less soluble. For example, sulphur sol is formed by pouring its solution in CS_2 into water.

   (*c*) By excessive cooling: A colloidal solution of ice in an organic solvent like chloroform or ether can be prepared by excessive cooling of water in these solvents.

   (*d*) By cathodic reduction: When lead salts are electrolysed, a sol of lead is obtained at cathode.

22. Purification of Colloidal Solutions:

(*a*) Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. In this process, a bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing. The molecules and ions diffuse through membrane into the water outside and pure colloidal solution is left behind [Fig. 5.5(*a*)]. The dialysis can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. This process is called **electrodialysis** [Fig. 5.5(*b*)].

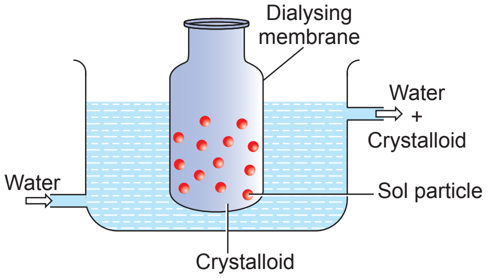


Fig. 5.5(a): Dialysis

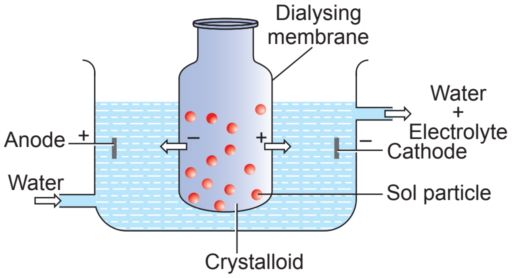


Fig. 5.5(b): Electrodialysis

(*b*) **Ultrafiltration:** Ultrafiltration is a process of separating the colloidal particles from the solvent and soluble solute particles present in the colloidal solution by specially prepared filters which are permeable to all substances except the colloidal particles. An ultra-filter paper may be prepared by soaking the filter paper in a collodion solution (a 4% solution of nitrocellulose in a mixture of alcohol and ether), hardening by formaldehyde and then finally drying it. Other filter media commonly used are unglazed porcelain and finely sintered glass. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied.

23. Properties of Colloids:

(*a*) **Brownian movement:** When a colloidal solution is viewed under a powerful microscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This zig-zag motion of colloidal particles in the dispersion medium is called Brownian movement after the name of its discoverer Robert Brown.

This motion is independent of the nature of the colloidal particles. It is more rapid when the size of the particles is small and solution is less viscous. Brownian movement is believed to be due to unequal bombardment of colloidal particles by the molecules of the dispersion medium. Since with increase of particle size the chances of unequal bombardment decreases, the Brownian movement too disappears.

(*b*) **Tyndall effect:** When a strong converging beam of light is passed through a colloidal solution placed in a dark room, the path of beam gets illuminated with a bluish light when viewed at right angles to the direction of the passage of light. This phenomenon is known as Tyndall effect (Fig. 5.6). The Tyndall effect is due to scattering of light by colloidal particles.

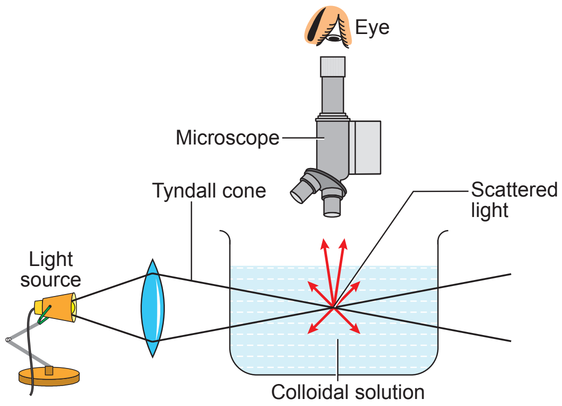


Fig. 5.6: Tyndall Effect

Tyndall effect is observed only when the following two conditions are satisfied:

(*i*) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(*ii*) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Tyndall effect is used to distinguish between a colloidal and true solution.

(*c*) **Colour:** The colour of colloidal solution depends on the wavelengths of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of the colloidal solution also changes with manner in which the observer receives the light. For example, a mixture of milk and water appears red when viewed by the transmitted light and blue when viewed by the reflected light.

(*d*) **Charge on colloidal particles :** A list of some common sols with the nature of the charge on their particle is given in the table below:

S.No.	Positively Charged Sols	Negatively Charged Sols
(*i*)	Hydrated metallic oxides, *e.g.*, $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.	Metal particles, *e.g.*, gold, silver, copper sols.
(*ii*)	Basic dyes like methylene blue sol.	Acidic dyes like eosin, Congo red sols.
(*iii*)	Haemoglobin.	Sols of starch, gum, gelation, clay, charcoal, etc.
(*iv*)	Oxides, *e.g.*, TiO_2 sol.	Metallic sulphides, *e.g.*, As_2S_3, Sb_2S_3, CdS sols.

- **Origin of charge:** There have been number of views regarding the origin of charge on colloidal particles such as:
  - (*i*) Due to friction between colloidal particles and molecules of dispersion medium.
  - (*ii*) Dissociation of molecules followed by aggregation of ions.
  - (*iii*) Due to electron capture during electrodispersion of metals.
  - (*iv*) Due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer.

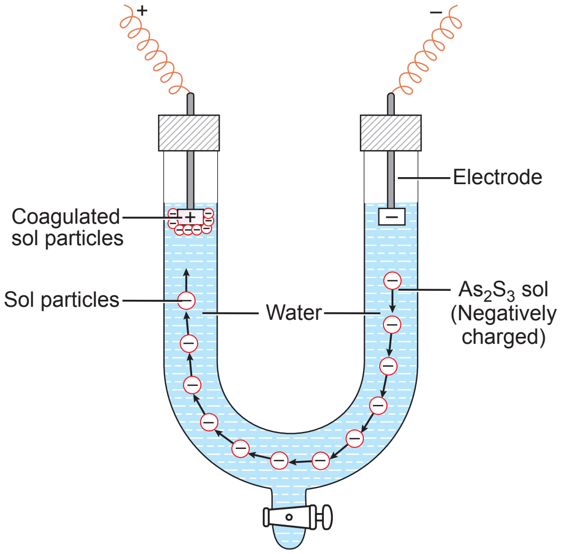


Fig. 5.7: Electrophoresis

Preferential adsorption of ions is the most accepted view. According to this view the charge on colloidal particles is due to preferential adsorption of ions present in the dispersion medium. The ions preferred by colloidal particles are those which are common with their own lattice. A few examples are given below:

(*i*) If silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged sol results. However, when silver iodide is formed by adding potassium iodide to silver nitrate solution, positively charged sol results due to adsorption of Ag^+ ions from dispersion medium.

$$AgI + \underset{\substack{\text{(Dispersion}\\ \text{medium)}}}{I^-} \longrightarrow \underset{\text{Negative Sol}}{AgI : I^-}$$

$$AgI + \underset{\substack{\text{(Dispersion}\\ \text{medium)}}}{Ag^+} \longrightarrow \underset{\text{Positive Sol}}{AgI : Ag^+}$$

(*ii*) When ferric chloride is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions. However, if ferric chloride is added to NaOH a negatively charged sol is obtained due to adsorption of OH^- ions.

$$FeCl_3 + H_2O \longrightarrow \underset{\text{Positively charged sol}}{Fe_2O_3 . xH_2O : Fe^{3+}}$$

$$FeCl_3 + NaOH \longrightarrow \underset{\text{Negatively charged sol}}{Fe_2O_3 . xH_2O : OH^-}$$

Helmholtz electro-kinetic electrical double layer: When positive or negative ions of the electrolytes are adsorbed on the surface of colloidal particles, it forms a fixed layer. It attracts the counter-ions from the dispersion medium to form a second layer which is mobile and is called diffused layer. The combination of the two layers of opposite charges around the colloidal particle thus formed is called Helmholtz electrical double layer.

Electro-kinetic potential or zeta potential: The potential difference between the fixed layer and the diffused layer of opposite charges is called electro-kinetic potential or zeta potential.

(*e*) **Electrophoresis:** The movement of colloidal particles towards oppositely charged electrode in an electric field is called electrophoresis (Fig. 5.7). If the movement of colloidal particles takes place towards the cathode, the phenomenon is called cataphoresis.

(*f*) **Electroosmosis:** When electrophoresis, *i.e.*, movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in the electric field. This phenomenon is known as electroosmosis.

(*g*) **Stability of a sol:** The stability of the lyophobic sols is due to the presence of similar charge on colloidal particles. Lyophilic sols are more stable than lyophobic sols as the stability of lyophilic sol is due to two factors. These are same charges and solvation of the colloidal particles.

(*h*) **Coagulation:** The process of aggregation of colloidal particles into an insoluble precipitate by the addition of suitable electrolyte is called coagulation.

- **Hardy and Schulze rules:**
  (*i*) The ions carrying charge opposite to that of sol particles are effective in bringing about the coagulation of sol.
  (*ii*) Coagulating power of the electrolyte is directly proportional to the fourth power of the valency of the ions causing coagulation.
- **Coagulating value:** The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value.

  The smaller the quantity needed, the higher will be the coagulating power of an ion.
- **Coagulation of lyophobic sol is done by**
  (*i*) addition of electrolytes.
  (*ii*) electrophoresis.
  (*iii*) boiling.
  (*iv*) mixing two oppositely charged sols.
  (*v*) persistent dialysis.
- **Coagulation of lyophilic sol is done by**
  (*i*) adding an electrolyte.
  (*ii*) adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

- **Gold number:** The number of milligrams of protective colloids which must be added to 10 mL of given gold sol so that it is just prevented from coagulation by addition of 1 mL of 10% NaCl solution. The smaller the gold number, the higher is the protecting power of lyophilic colloids.

24. **Emulsions:** Emulsions are colloidal systems in which both the dispersed phase and dispersion medium are liquids. There are two types of emulsions:

    (*i*) **Oil in water (O/W) type emulsions:** In such emulsions, oil is the dispersed phase and water is the dispersion medium, *e.g.*, milk, vanishing cream.

    (*ii*) **Water in oil (W/O) type emulsions:** In such emulsions, water is the dispersed phase and oil is the dispersion medium, *e.g.*, butter, cod liver oil.

    ➡ **Emulsifiers:** These are the substances which help in stabilising emulsions. The emulsifier forms a film around every drop of the dispersed phase and hence, prevents drops from coming together. The emulsifiers for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. and for W/O emulsions are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

    ➡ **Demulsification:** The process of decomposing an emulsion into its constituent liquids is called demulsification. It is carried out by centrifugation, freezing, boiling or chemical methods which destroy the emulsifying agents.

25. **Colloids Around Us**

    (*i*) **Blue colour of the sky:** Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

    (*ii*) **Clouds:** Clouds are aerosols having small droplets of water suspended in air.

    (*iii*) **Blood:** Blood is colloidal solution of an albuminoid and the stoppage of bleeding on applying ferric chloride solution is due to coagulation of blood forming a clot.

    (*iv*) **Food articles:** Milk, butter, ice-creams, fruit juices, etc. are of colloidal nature.

    (*v*) **Formation of delta:** River water is colloidal solution of clay. Sea water contains a number of electrolytes. As soon as the river water comes in contact with the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

26. **Application of Colloids:**

    (*i*) **Medicines:** Most of the pharmaceutical preparation are colloidal in nature. For example, colloidal antimony is used in curing Kala-azar, argyrol used as an eye lotion is silver sol protected by gelatin, milk of magnesia is an emulsion used for stomach trouble, colloidal gold and calcium are used for intra-muscular injection.

    (*ii*) **Industrial products:** Paints, ink, rubber, synthetic plastics, graphite lubricants, cement, etc. are all colloidal solutions.

    (*iii*) **Tanning:** When a hide, which contain positively charged particles is soaked in tannin, which has negatively charged particles, mutual coagulation takes place. It results in the hardening of leather. This process is known as tanning.

    (*iv*) **Purification of drinking water:** The water from river contains negatively charged clay particles. On addition of alum which yields trivalent Al^{3+} ions in solution, the negative charge on clay particles is neutralised and consequently, they precipitate out and settle down at the bottom. The clear water is left at the top and can be decanted off.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Write any two characteristics of chemisorption.

Ans. (*i*) Chemisorption is highly specific and it will occur only if there is some possibility of bonding between adsorbent and adsorbate.

(*ii*) As chemisorption involves compound formation therefore it is usually irreversible in nature.

Q. 2. Why does physisorption decrease with increase of temperature?

Ans. Physisorption is an exothermic process:

$$\underset{\text{(Adsorbent)}}{\text{Solid}} + \underset{\text{(Adsorbate)}}{\text{Gas}} \longrightarrow \underset{\text{(Gas adsorbed on solid)}}{\text{Gas/Solid}} + \text{Heat}$$

According to Le Chatelier's principle, if we increase the temperature, equilibrium will shift in the backward direction, *i.e.*, gas is released from the adsorbed surface.

Q. 3. Why are powdered substances more effective adsorbent than their crystalline forms?

Ans. Powdered substances have greater surface area as compared to their crystalline forms. Greater the surface area, greater is the adsorption.

Q. 4. In Haber's process hydrogen is obtained by reacting methane with steam in presence of NiO as catalyst. This process is known as steam reforming. Why is it necessary to remove CO when ammonia is obtained by Haber's process?

Ans. CO acts as catalytic poison and must be removed.

Q. 5. Why is the ester hydrolysis slow in the beginning and becomes faster after some time?

Ans. The ester hydrolysis takes place as follows:

$$\underset{\text{Ester}}{\text{RCOOR'}} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Acid}}{\text{RCOOH}} + \underset{\text{Alcohol}}{\text{R'OH}}$$

The acid produced in the reaction acts as catalyst (autocatalyst) for the reaction. Hence, the reaction becomes faster after sometime.

Q. 6. What is the role of desorption in the process of catalysis?

Ans. The reaction products formed on the catalyst surface get detached from the surface as a result of desorption, thereby making the surface available again for more reaction.

Q. 7. What modification can you suggest in the Hardy-Schulze law?

Ans. This law does not take into account the size of the ion. The smaller the size of anion, greater will be its polarising power. Thus, the law can be modified in terms of polarising power of the flocculating ion. The modified law states that, the greater the polarising power of the flocculating ion, the greater is its power to cause precipitation.

Q. 8. Why is it essential to wash the precipitate with water before estimating it quantitatively?

Ans. Some amount of the electrolytes mixed to form the precipitate remains adsorbed on the surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolytes (or any other impurities) before estimating it quantitatively.

NCERT Textbook Exercises

Q. 1. Distinguish between the meaning of the term adsorption and absorption. Give one example of each.

Ans.

S.No.	Adsorption	Absorption
(*i*)	It is a surface phenomenon. Adsorbate molecules are held at the surface of adsorbent.	Absorption occurs in the bulk of absorbing substance.
(*ii*)	The concentration of the adsorbate at the adsorbent surface is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
(*iii*)	Initially, rate of adsorption is rapid. It decreases slowly till equilibrium is attained. **Example:** Water vapours on silica gel.	Absorption occurs with uniform rate. **Example:** Water vapours are absorbed by anhydrous $CaCl_2$.

Q. 2. What is the difference between physisorption and chemisorption? *[CBSE 2019 (56/5/2)]*

OR

Give three points of differences between physisorption and chemisorption. *[CBSE 2020 (56/1/1)]*

OR

Write two differences between physisorption and chemisorption. *[CBSE 2020 (56/3/1)]*

Ans.

S.No.	Physisorption	Chemisorption
(*i*)	It arises because of van der Waals' forces.	It is caused by chemical bond formation.
(*ii*)	It is not specific in nature.	It is highly specific in nature.
(*iii*)	It is reversible in nature.	It is irreversible.
(*iv*)	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
(*v*)	Enthalpy of adsorption is low (20-40 kJ mol^{-1}) in this case.	Enthalpy of adsorption is high (80-240 kJ mol^{-1}) in this case.
(*vi*)	Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
(*vii*)	No appreciable activation energy is needed.	High activation energy is sometimes needed.
(*viii*)	It results into multimolecular layers on adsorbent surface under high pressure.	It results into unimolecular layer.

Q. 3. Give reason why a finely divided substance is more effective as an adsorbent. *[CBSE (F) 2013; 2019 (56/4/2)]*

Ans. Powdered substances have greater surface area as compared to their crystalline forms. Greater the surface area, greater is the adsorption.

Q. 4. What are the factors, which influence the adsorption of a gas on a solid?

Ans. The extent of adsorption of a gas on a solid surface depends on following factors:

(*i*) The nature of gas

(*ii*) Surface area of adsorbent

(*iii*) Pressure

(*iv*) Temperature

(*v*) Activation of adsorbent.

Q. 5. What is an adsorption isotherm? Describe Freundlich adsorption isotherm.

Ans. Refer to Basic Concepts Points 6 and 7.

Q. 6. What do you understand by activation of adsorbent? How is it achieved?

Ans. Activation of adsorbent means, increasing the adsorbing power of an adsorbent. This can be done by increasing the surface area of the adsorbent which can be achieved in any of the following ways:

(*i*) By removing the gases adsorbed, *i.e.*, wood charcoal can be activated by heating it between 650 K and 1330 K in vacuum or super-heated steam.

(*ii*) By breaking the adsorbent into small pieces.

(*iii*) By making the surface of adsorbent rough.

Q. 7. What role does adsorption play in heterogeneous catalysis? *[CBSE 2020 (56/5/1)]*

Ans. In heterogeneous catalysis, generally the reactants are gaseous whereas the catalyst is a solid. The reactant molecules are adsorbed on the surface of the solid catalyst by physical adsorption or chemical adsorption. As a result, the concentration of the reactant molecules on the surface increases and hence the rate of reaction increases. Alternatively, one of the reactant molecules undergoes fragmentation on the surface of the solid catalyst producing active species which react faster. The product molecules in either case have no affinity for the solid catalyst and are desorbed, making the surface free for fresh adsorption. This theory is called adsorption theory.

Q. 8. Why is adsorption always exothermic?

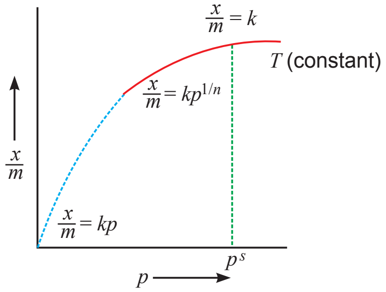
Ans. As the adsorption progresses, the residual forces at the surface decreases resulting in the decrease of surface energy which appears as heat.

Q. 9. How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?

Ans. Refer to Basic Concepts Point 17.

Q. 10. Discuss the effect of pressure and temperature on the adsorption of gases on solids.

Ans. **Effect of pressure on adsorption:** At constant temperature, the extent of adsorption of a gas (*x/m*) on a solid increases with pressure. A graph between *x/m* and the pressure *p* of a gas at constant temperature is called adsorption isotherm.



(*i*) At lower range of pressure, *x/m* is directly proportional to the applied pressure.

$$\frac{x}{m} \propto p^1 \quad \text{or} \quad \frac{x}{m} \propto kp$$

(*ii*) At high pressure range, the extent of adsorption of a gas (*x/m*) is independent of the applied pressure, *i.e.*,

$$\frac{x}{m} \propto p^0 \quad \text{or} \quad \frac{x}{m} = k$$

(*iii*) At intermediate pressure range, the value of *x/m* is proportional to a fractional power of pressure, *i.e.*,

$$\frac{x}{m} \propto p^{1/n} \quad \text{or} \quad \frac{x}{m} = kp^{1/n} \qquad \ldots(i)$$

where 1/*n* is a fraction. Its value may be between 0 and 1.

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p \qquad \ldots(ii)$$

Effect of temperature on adsorption: Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic and hence adsorption decreases with increasing temperature. However, for an endothermic adsorption process, adsorption increases with increase in temperature.

Q. 11. What are lyophilic and lyophobic sols? Give one example of each type. Why is hydrophobic sol easily coagulated?

Ans. For first and second part refer to Basic Concepts Point 18.

The stability of hydrophobic sol is only due to the presence of charge on the colloidal particles. If charge is removed, by addition of suitable electrolytes, the particles will come nearer to each other to form aggregate, *i.e.*, they will coagulate and settle down. The stability of hydrophilic sol is due to charge as well as solvation of the colloidal particles. Both the factors have to be removed to bring about their coagulation.

Q. 12. What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids? **[*CBSE Delhi 2010*]**

Ans. **Multimolecular colloids:** In this type of colloids, colloidal particles are aggregates of atoms or molecules each having size less than 1 nm, *e.g.*, sulphur sol, gold sol. Multimolecular colloids are generally lyophobic in nature.

Macromolecular colloids: In this type of colloids, colloidal particles are themselves large molecules of colloidal dimensions, *e.g.*, starch, proteins, polythene, etc. Macromolecular colloids are generally lyophilic in nature.

Associated colloids: There are certain substances which at low concentrations behave as normal electrolyte, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. Such colloids are known as associated colloids, *e.g.*, soaps and detergents.

Q. 13. What are enzymes? Write in brief the mechanism of enzyme catalysis.

Ans. Refer to Basic Concepts Points 14.

Q. 14. How are colloids classified on the basis of

(*i*) physical states of components,

(*ii*) nature of dispersed phase, and

(*iii*) interaction between dispersed phase and dispersion medium.

Ans. (*i*) Refer to Basic Concepts Point 17.

(*ii*) Refer to Basic Concepts Point 19.

(*iii*) Refer to Basic Concepts Point 18.

Q. 15. Explain what is observed when

(*i*) when a beam of light is passed through a colloidal solution.

(*ii*) an electrolyte, NaCl is added to hydrated ferric oxide sol.

(*iii*) electric current is passed through a colloidal sol. **[*CBSE (AI) 2011*]**

Ans. (*i*) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

(*ii*) The positively charged colloidal particles of $Fe(OH)_3$ get coagulated by the oppositely charged Cl^- ions provided by NaCl.

(*iii*) On passing direct current, colloidal particles move towards the oppositely charged electrode where they lose their charge and get coagulated.

Q. 16. What are emulsions? What are their different types? Give example of each type. **[*CBSE (AI) 2014*]**

Ans. Refer to Basic Concepts Point 24.

Q. 17. How do emulsifiers stabilise emulsions? Name two emulsifiers.

Ans. The emulsifier forms a film around every drop of the dispersed phase and hence, prevents drops from coming together. The emulsifiers for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. and for W/O emulsions are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

Q. 18. Action of soap is due to emulsification and micelle formation. Comment.

Ans. The cleansing action of soap such as sodium stearate is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats.

Q. 19. Give four examples of heterogeneous catalysis.

Ans. A catalyst in different phase than that of the reactants in a reaction is called heterogeneous catalyst and this phenomenon is called heterogeneous catalysis. In heterogeneous catalysis, catalyst is generally a solid and reactants are usually gases (or sometimes liquids).

Some important industrial reactions which are heterogeneous catalytic reactions are given below:

(*i*) Synthesis of ammonia from nitrogen and hydrogen in the presence of iron as a catalyst.

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

(*ii*) Manufacture of sulphur trioxide (SO_3) by the oxidation of sulphur dioxide (SO_2) in the presence of vanadium pentoxide (V_2O_5) as a catalyst.

$$SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{V_2O_5\,(s)} \underset{\text{(Contact Process)}}{SO_3(g)}$$

(*iii*) Dehydration of ethanol by alumina (Al_2O_3).

$$\underset{\text{Ethanol}}{C_2H_5OH(l)} \xrightarrow{Al_2O_3\,(s)} \underset{\text{Ethene}}{C_2H_4(g)} + H_2O\,(l)$$

(*iv*) Reduction of nitrobenzene in the presence of nickel catalyst.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2(l)} + 3H_2 \xrightarrow{\text{Ni }(s)} \underset{\text{Aniline}}{C_6H_5NH_2(l)} + 2H_2O(l)$$

Q. 20. What do you mean by activity and selectivity of catalysts?

Ans. **Activity of catalyst:** The ability of a catalyst to increase the rate of a reaction is called its activity. For example, a mixture of hydrogen and oxygen does not react at all, however, in the presence of platinum as a catalyst the mixture reacts with explosive violence to form water.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Selectivity of catalyst: It is the ability of a catalyst to direct a reaction to yield a particular product. For example, both dehydrogenation and dehydration of ethanol are possible. But in presence of a suitable catalyst only one reaction is made to occur.

$$CH_3CH_2OH \xrightarrow[573\text{ K}]{Cu} CH_3CHO + H_2 \qquad \text{(dehydrogenation)}$$

$$CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O \qquad \text{(dehydration)}$$

Q. 21. Describe some features of catalysis by zeolites.

Ans. Features of catalysis by zeolites:

(*i*) Zeolites are hydrated alumino-silicates which have a three-dimensional network structure containing water molecules in their pores.

(*ii*) To use them as catalysts, they are heated so that water of hydration present in the pores is lost and the pores become vacant.

(*iii*) The size of the pores varies from 260 to 740 pm. Thus, only those molecules can be adsorbed in these pores and catalysed whose size is small enough to enter these pores. Hence, they act as molecular sieves or shape-selective catalysts.

An important catalyst used in petroleum industry is ZSM-5 (Zeolite sieve of molecular porosity 5). It converts alcohols into petrol by dehydrating them to form a mixture of hydrocarbons.

$$\text{Alcohol} \xrightarrow[\text{Dehydration}]{\text{ZSM}-5} \text{Hydrocarbons}$$

Q. 22. What is shape-selective catalysis? *[CBSE Delhi 2010, 2011, 2012; 2020 (56/3/1)]*

Ans. Shape-selective catalysis is chemical reaction in which the rate depends on the pore size of the catalyst, and also on the shape and size of the reactant and product molecules. A shape-selective catalyst has a variety of active sites of different shape and size. Zeolite acts as a shape-selective catalyst. In the crystal of a zeolite, the pore size usually varies from 260 pm to 740 pm. If the reactant molecules are too large they cannot fit into pores of zeolite and no reaction takes place. On the other hand, if the reactant molecules are too small, they would just slip through the pores in the catalyst without any interactions. ZSM-5 is used as shape-selective catalyst to produce gasoline of high octane number from methanol.

$$x\,CH_3OH \xrightarrow[\text{Catalyst}]{\text{ZSM}-5} \underset{\text{Gasoline}}{(CH_2)_x} + xH_2O$$

where x varies from 5 to 10. ZSM-5 stands for zeolite sieve of molecular porosity-5.

Q. 23. Explain the following terms:

(*i*) Electrophoresis **(*ii*) Coagulation**

(*iii*) Dialysis **(*iv*) Tyndall effect**

Ans. (*i*) Refer to Basic Concepts Point 23 (*e*).

(*ii*) Refer to Basic Concepts Point 23 (*h*).

(*iii*) Refer to Basic Concepts Points 22 (*a*).

(*iv*) Refer to Basic Concepts Points 23 (*b*).

Q. 24. Give four uses of emulsions.

Ans. Four uses of emulsions are:

(*i*) The concentration of sulphide ore by froth floatation process is based on emulsification.

(*ii*) Cleansing action of soap and detergents is due to the formation of an emulsion between dirt and soap solution.

(*iii*) Milk is an emulsion of fat in water.

(*iv*) Cosmetics, lotions, creams, hair dyes, shampoos and many drugs, and ointments are emulsions. In form of emulsions, these are more effective.

Q. 25. What are micelles? Give an example of a miceller system.

Ans. The particles of colloidal size formed due to aggregation of several units of soap molecules (surfactants) in a dispersion medium are called 'micelles'. A concentrated solution of soap in water is a miceller system. Such substances are also called associated colloids. In other words, miceller system (or associated colloid) behaves as a true solution in low concentration form and as a colloid in high concentration form. The micelles revert to individual ions on dilution.

Q. 26. Explain the following terms with suitable examples (*i*) Alcosol (*ii*) Aerosol and (*iii*) Hydrosol.

Ans. (*i*) **Alcosol:** It is a colloidal dispersion having alcohol as the dispersion medium, *e.g*., collodion.

(*ii*) **Aerosol:** It is a colloidal dispersion of a solid or liquid in a gas, *e.g*., smoke, fog.

(*iii*) **Hydrosol:** It is a colloidal sol of a solid in water as the dispersion medium *e.g.*, starch sol.

Q. 27. Comment on the statement that "Colloid is not a substance but state of a substance." [*HOTS*]

Ans. The given statement is true. This is because the same substance may exist as a colloid under certain conditions and as a crystalloid under some other conditions. For example, NaCl in water behaves as a crystalloid while in benzene, it behaves as a colloid. It is the size of the particles which matters, *i.e*., the state in which the substance exists. If the size of the particles lies in the range of 1 nm to 1000 nm, it is in the colloidal state.

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. At the equilibrium position in the process of adsorption ______________. [*NCERT Exemplar*]

(*a*) $\Delta H > 0$ (*b*) $\Delta H = T\Delta S$

(*c*) $\Delta H > T\Delta S$ (*d*) $\Delta H < T\Delta S$

2. Which of the following is true in respect of adsorption?

(*a*) $\Delta G < 0, \Delta S < 0, \Delta H > 0$ (*b*) $\Delta G < 0, \Delta S > 0, \Delta H < 0$

(*c*) $\Delta G < 0, \Delta S < 0, \Delta H < 0$ (*d*) $\Delta G > 0, \Delta S > 0, \Delta H < 0$

3. The term 'sorption' stands for ______________. [*NCERT Exemplar*]

(*a*) absorption (*b*) absorption

(*c*) both absorption and adsorption (*d*) desorption

4. Which of the following is not a favorable condition for physical adsorption? [*NCERT Exemplar*]

(*a*) High pressure (*b*) Negative ΔH

(*c*) Higher critical temperature of adsorbate (*d*) High temperature

5. Extent of physisorption of a gas increases with ______________. [*NCERT Exemplar*]

(*a*) increase in temperature (*b*) decrease in temperature

(*c*) decrease in surface area of adsorbent (*d*) decrease in strength of van der Waals forces

6. Physical adsorption of a gaseous species may change to chemical adsorption with ___________. [*NCERT Exemplar*]

(*a*) decrease in temperature (*b*) increase in temperature

(*c*) increase in surface area of adsorbent (*d*) decrease in surface area of adsorbent

7. Extent of adsorption of adsorbate from solution phase increase with ______________. [*NCERT Exemplar*]

(*a*) increase in amount of adsorbate in solution (*b*) decrease in surface area of adsorbent

(*c*) increase in temperature of solution (*d*) decrease in amount of adsorbate in solution

8. Which of the following relation is correct?

(*i*) $\frac{x}{m}$ = Constant at high pressure

(*ii*) $\frac{x}{m}$ = Constant × $p^{1/n}$ (at intermediate pressure)

(*iii*) $\frac{x}{m}$ = Constant × p^{n} (at lower pressure)

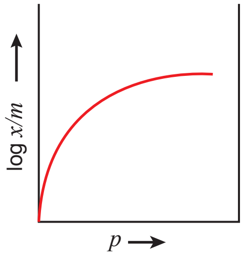
(*a*) All correct
(*b*) All wrong
(*c*) (*i*) and (*ii*) are correct
(*d*) (*iii*) is correct

9. In Freundich isotherm, the intercept on *y*-axis is denoted by

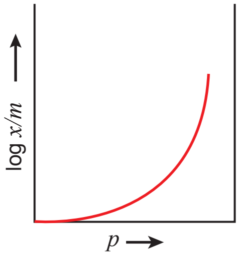
(*a*) $\log \frac{1}{k}$
(*b*) $\log k$
(*c*) $\frac{1}{n}$
(*d*) n

10. Which of the following curves is in accordance with Freundlich adsorption isotherm? [*NCERT Exemplar*]

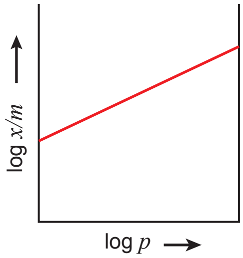
(*a*)



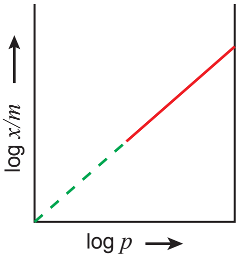
(*b*)



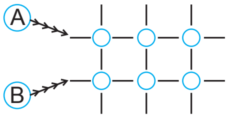
(*c*)



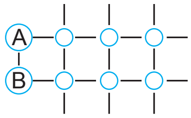
(*d*)



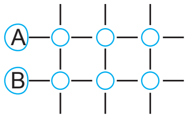
11. Arrange the following diagrams in correct sequence of steps involved in the mechanism of catalysis, in accordance with modern adsorption theory. [*NCERT Exemplar*]



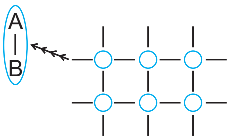
(*i*)



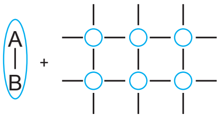
(*ii*)



(*iii*)



(*iv*)



(*v*)

(*a*) (*i*) → (*ii*) → (*iii*) → (*iv*) → (*v*)
(*b*) (*i*) → (*iii*) → (*ii*) → (*iv*) → (*v*)
(*c*) (*i*) → (*iii*) → (*ii*) → (*v*) → (*iv*)
(*d*) (*i*) → (*ii*) → (*iii*) → (*v*) → (*iv*)

12. Which of the following statements are correct about solid catalyst? *[NCERT Exemplar]*

(*a*) Same reactants may give different product by using different catalysts.
(*b*) Catalyst does not change ΔH of reaction.
(*c*) Catalyst is required in large quantities to catalyse reactions.
(*d*) Catalytic activity of a solid catalyst does not depend upon the strength of chemisorption.

13. The enzyme pepsin present in stomach converts

(*a*) proteins into amino acids (*b*) cane sugar into glucose
(*c*) proteins into peptides (*d*) maltose into glucose

14. The rate of an enzyme catalysed reaction is maximum under pH range of

(*a*) 0–7 (*b*) 5–7 (*c*) 7–14 (*d*) 7–10

15. A colloidal system having a solid substance as a dispersed phase and a liquid as a dispersion medium is classified as _______________. *[NCERT Exemplar]*

(*a*) solid sol (*b*) gel (*c*) emulsion (*d*) sol

16. Which of the following options are correct? *[NCERT Exemplar]*

(*a*) Micelle formation by soap in aqueous solution is possible at all temperatures.
(*b*) Micelle formation by soap in aqueous solution occurs above a particular concentration.
(*c*) On dilution of soap solution micelles may revert to individual ions.
(*d*) Soap solution behaves as a normal strong electrolyte at all concentrations.

17. Freshly prepared precipitate sometimes gets converted to colloidal solution by _____________. *[NCERT Exemplar]*

(*a*) coagulation (*b*) electrolysis (*c*) diffusion (*d*) peptisation

18. The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same concentration because of colloidal particles _____________. *[NCERT Exemplar]*

(*a*) exhibit enormous surface area (*b*) remains suspended in the dispersion medium
(*c*) form lyophilic colloids (*d*) are comparatively less in number.

19. Which property of colloidal solution is independent of charge on the colloidal particles?

(*a*) Electro-osmosis (*b*) Tyndall effect
(*c*) Coagulation (*d*) Electrophoresis

20. Which of the following process is responsible for the formation of delta at a place where rivers meet the sea? *[NCERT Exemplar]*

(*a*) Emulsification (*b*) Colloid formation
(*c*) Coagulation (*d*) Peptisation

21. Which of the following electrolytes will have maximum coagulating value for AgI/Ag$^+$ sol? *[NCERT Exemplar]*

(*a*) Na_2S (*b*) Na_3PO_4 (*c*) Na_2SO_4 (*d*) NaCl

22. Method by which lyophobic sol can be protected. *[NCERT Exemplar]*

(*a*) By addition of oppositely charged sol. (*b*) By addition of an electrolyte.
(*c*) By addition of lyophilic sol. (*d*) By boiling.

23. The emulsifying agent present in milk which makes it stable is:

(*a*) maltose (*b*) casein
(*c*) lactose (*d*) Lactobacilli

Answers

1. (*b*) **2.** (*c*) **3.** (*c*) **4.** (*d*) **5.** (*b*) **6.** (*b*) **7.** (*a*) **8.** (*c*) **9.** (*b*) **10.** (*c*)
11. (*b*) **12.** (*a, b*) **13.** (*c*) **14.** (*b*) **15.** (*d*) **16.** (*b, c*) **17.** (*d*) **18.** (*d*) **19.** (*b*) **20.** (*c*)
21. (*b*) **22.** (*c*) **23.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- (*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- (*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- (*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*
- (*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion** (*A*) : Adsorption decreases with increasing temperature.
Reason (*R*) : Adsorption is generally temperature dependent.

2. **Assertion** (*A*) : The enthalpy of physisorption is quite high.
Reason (*R*) : In physisorption, the molecules are adsorbed to the surface with van der Waal's forces.

3. **Assertion** (*A*) : In chemisorption, all gases are absorbed on all solids.
Reason (*R*) : Chemisorption takes place at elevated temperature.

4. **Assertion** (*A*) : The relation $\frac{x}{m} = k.p^{1/n}$ is known as Freundlich adsorption isotherm, where x is the mass of gas adsorbed by m grams of adsorbate, p is the equilibrium pressure, k and n are constants for given system and temperature.
Reason (*R*) : When several substances have same value of $\frac{1}{n}$, the lines by which their adsorption isotherms can be represented will meet at a point.

5. **Assertion** (*A*) : Detergents with low CMC are more economical to use.
Reason (*R*) : Cleansing action of detergents involves the formation of micelles. These are formed when the concentration of detergents becomes equal to CMC.

6. **Assertion** (*A*) : An ordinary filter paper impregnated with collodion solution stops the flow of colloidal particles.
Reason (*R*) : Pore size of the filter paper becomes more than the size of colloidal particle.

7. **Assertion** (*A*) : Colloidal solutions show colligative properties.
Reason (*R*) : Colloidal particles are large in size.

8. **Assertion** (*A*) : Colloidal solutions do not show brownian motion.
Reason (*R*) : Brownian motion is responsible for stability of sols.

9. **Assertion** (*A*) : Colloidal sols scatter light while true solutions do not.
Reason (*R*) : The particles in the colloidal sol move much slower than that of the true solution.

10. **Assertion** (*A*) : Coagulation power of Al^{3+} is more than Na^{+}.
Reason (*R*) : Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy Schulze rule).

11. **Assertion** (*A*) : Precipitation of the sol can be done by mixing two oppositely charged sols.
Reason (*R*) : The greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

12. **Assertion** (*A*) : Milk is an example of water in oil emulsion.
Reason (*R*) : Emulsion contains liquid dispersed in liquid.

13. **Assertion** (*A*) : Aqueous addition of raw sugar when passed over beds of animals charcoal becomes colourless.
Reason (*R*) : The colouring substances get adsorbed by the charcoal.

Answers

1. (*b*) **2.** (*d*) **3.** (*d*) **4.** (*c*) **5.** (*a*) **6.** (*c*) **7.** (*b*) **8.** (*d*) **9.** (*b*) **10.** (*a*)
11. (*b*) **12.** (*d*) **13.** (*a*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phase by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phase that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent. Adsorption of gases by solids depends on nature and surface area of the adsorbent, nature of the gas being adsorbed, temperature, pressure and activation of the solid adsorbent. When a gas is held on surface of a solid by van der Waals forces, it is called as physical adsorption while if a gas is held on the surface of a solid by chemical bond, it is called as chemical adsorption.

1. How do the size of particles of adsorbent influence the extent of adsorption of a gas on a solid?

Ans. Smaller the size of the particles of the adsorbent, greater is the surface area and greater is the adsorption.

2. Why is physical adsorption multilayered?

Ans. Physical adsorption involves van der Waals forces, so any number of layers may be formed one over the other on the surface of the adsorbent.

3. Which has a higher enthalpy of adsorption, physisorption or chemisorption? **[*CBSE (AI) 2013*]**

Ans. Chemisorption due to the involvement of chemical bond formation.

4. How does an increase in temperature affect both physical as well as chemical adsorption?

Ans. With increase in temperature, physical adsorption decreases while chemical adsorption first increases and then decreases.

5. What is the importance of having clean surface in surface studies?

Ans. Clean surface eases the adsorption of adsorbate on the adsorbent.

PASSAGE–2

A colloidal solution is a heterogeneous system in which a definite substance is distributed in the form of very small particles or dispersed phase in another substance called the dispersion medium. If water being the medium, colloids are called hydrosols. Colloids are of two types on the basis of nature of interaction between dispersed phase and dispersion medium: Lyophobic sols and Lyophilic sols. In Lyophobic sols, particles of dispersed phase have no affinity for dispersion medium rather they hate dispersion medium. They are not easily prepared and need stabilizing agents for their preservation. They are irreversible. They are also called extrinsic colloids while in Lyophilic sols, particles of dispersed phase have great affinity for the dispersion medium. They are self-stabilized because of strong attractive forces operating between the suspended particles and the dispersion medium. They are reversible in nature. They are also known as intrinsic colloids.

1. Write the main reason for the stability of colloidal sols. **[*CBSE Delhi 2016; 2019 (56/4/3)*]**

Ans. All the particles of colloidal sol carry the same charge so they keep on repelling each and other and do not aggregate together to form bigger particles.

2. Write the dispersed phase and dispersion medium of smoke. **[*CBSE Guwahati 2015*]**

Ans. Dispersed phase—Solid; Dispersion medium—Gas.

3. What type of colloid is formed when a liquid is dispersed in a solid? Give an example. **[*CBSE (AI) 2017; 2019 (56/2/2)*]**

Ans. Gel, *e.g.*, cheese, jellies

4. In what way is a sol different from a gel?

Ans. Colloidal system in which solid is dispersed in liquid is called sol and that in which liquid is dispersed in solid is called gel.

5. Hydrophobic sol is easily coagulated. Give reason.

Ans. Hydrophobic sol are unstable because they do not undergo hydration. Hence, they are easily coagulated by addition of a small amount of electrolyte, by heating or by shaking.

Very Short Answer Questions [1 mark]

Q. 1. What is sorption?

Ans. Sorption is the process in which adsorption and absorption take place simultaneously, *e.g.*, dyeing of cotton fibres by azo dyes.

Q. 2. What is 'occlusion'?

Ans. The adsorption of gases on the surface of metals is called occlusion.

Q. 3. Define desorption. *[CBSE Delhi 2011]*

Ans. The process of removal of an adsorbed substance from a surface on which it is adsorbed is called desorption.

Q. 4. What is physical adsorption?

Ans. If the adsorbate is held on an adsorbent surface by weak van der Waals' forces, the adsorption is called physical adsorption.

Q. 5. What type of forces are responsible for the occurrence of physisorption? *[CBSE (F) 2014]*

Ans. van der Waals' forces.

Q. 6. What is meant by chemical adsorption?

Ans. If the adsorbate is held on the surface of the adsorbent as a result of chemical reaction forming surface compounds, it is called chemical adsorption.

Q. 7. What is the effect of temperature on chemisorption? *[CBSE (AI) 2014]*

Ans. Chemisorption initially increases then decreases with rise in temperature. The initial increase is due to the fact that heat supplied acts as activation energy. The decrease afterwards is due to the exothermic nature of adsorption equilibrium.

Q. 8. Write one similarity between physisorption and chemisorption. *[CBSE Delhi 2017]*

Ans. Both increase with increase in surface area.

Q. 9. Adsorption of a gas on the surface of solid is generally accompanied by a decrease in entropy still it is a spontaneous process. Why? *[HOTS]*

Ans. According to the equation

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

For a process to be spontaneous, ΔG should be negative. Even though ΔS is negative here, ΔG is negative because reaction is highly exothermic, *i.e.*, ΔH is negative.

Q. 10. Which will be adsorbed more readily on the surface of charcoal and why: NH_3 or CO_2? *[HOTS]*

Ans. NH_3 has higher critical temperature than CO_2, *i.e.*, NH_3 is more liquefiable than CO_2. Hence, NH_3 has greater intermolecular forces of attraction and hence will be adsorbed more readily.

Q. 11. How is adsorption of a gas related to its critical temperature?

Ans. Higher is the critical temperature of a gas, greater is the ease of liquefication, *i.e.*, greater are the van der Waals' forces of attraction and hence greater is the adsorption.

Q. 12. How does a catalyst work?

Ans. Catalysts provide an alternate path involving lower activation energy for the reactants.

Q. 13. What is the role of desorption in the process of catalysis? *[CBSE (F) 2017]*

Ans. Desorption makes the surface available again for fresh adsorption of reactant molecules.

Q. 14. Why is desorption important for a substance to act as good catalyst? *[NCERT Exemplar]*

Ans. After the completion of reaction between adsorbed reactants, the process of desorption is important to remove products and further create space for the other reactant molecules to approach the surface and react.

Q. 15. CO(*g*) and H_2(*g*) react to give different products in the presence of different catalysts. Which ability of the catalyst is shown by these reactions? [*CBSE 2018*]

Ans. Selectivity of the catalyst is shown by these reactions.

Q. 16. Define colloidal solution.

Ans. A colloidal solution is a state in which the particle size lies between 1 nm and 1000 nm. It appears to be homogeneous but actually it is heterogeneous.

Q. 17. What is collodion? [*NCERT Exemplar*]

Ans. It is a 4% solution of nitrocellulose in a mixture of alcohol and ether.

Q. 18. Why are some medicines more effective in the colloidal form? [*NCERT Exemplar*]

Ans. Medicines are more effective in the colloidal form because of large surface area and are easily assimilated in this form.

Q. 19. Write the dispersed phase and dispersion medium of butter. [*CBSE Patna 2015*]

Ans. Dispersed phase : Liquid

Dispersion medium : Solid

Q. 20. Give one example each of sol and gel. [*CBSE Delhi 2014*]

Ans. Sol: Paints, cell fluids

Gel: Butter, cheese

Q. 21. What is common in aquasols and solid aerosols? How do they differ?

Ans. Aquasol and solid aerosol both have solid as the dispersed phase. They differ in dispersion medium. Aquasols have water as the dispersion medium while aerosols have gas as the dispersion medium.

Q. 22. What are lyophobic colloids? Give one example for them. [*CBSE (AI) 2011*]

Ans. Lyophobic sols are those sols in which the particles of the dispersed phase have little affinity for the particles of the dispersion medium, *e.g.*, sols of metal and their sulphides and hydroxides.

Q. 23. Give one example each of lyophobic sol and lyophilic sol. [*CBSE Delhi 2014*]

Ans. Lyophobic sol — Gold sol, As_2S_3 sol

Lyophilic sol — Sol of starch, sol of gum

Q. 24. What is Kraft temperature? [*CBSE 2020 (56/3/1)*]

Ans. Kraft temperature is the minimum temperature above which the formation of micelles takes place.

Q. 25. How will you prepare arsenic sulphide sol in the lab?

Ans. $$As_2O_3 + 3H_2S \longrightarrow \underset{\text{(Yellow sol)}}{As_2S_3} + 3H_2O$$

Q. 26. What is the principle of dialysis?

Ans. Dialysis is based on the principle that ions can pass through semipermeable membrane whereas colloidal particles cannot pass through it.

Q. 27. What happens when dialysis is prolonged? [*NCERT Exemplar*]

Ans. Due to excessive dialysis, traces of electrolyte which stabilises the colloids is removed completely, making the colloid unstable. As a result, coagulation takes place.

Q. 28. What happens when an electric field is applied to a colloidal dispersion? [*NCERT Exemplar*]

Ans. The colloidal particles move towards the oppositely charged electrode and get neutralised and coagulated there.

Q. 29. What is electrodialysis?

Ans. It is a process by which colloidal solutions containing ionic impurities are purified. The colloidal solution containing ionic impurities is placed in a bag of parchment paper in distilled water in electric field. The ions come out through parchment paper and the sol is purified.

Q. 30. Define ultrafiltration.

Ans. In this process, colloidal solutions are purified by carrying out filtration through special types of graded filters called ultra-filters. Filter paper allows the passage of electrolyte but does not allow the passage of colloidal particles.

Q. 31. Why do colloidal solutions exhibit Tyndall effect?

Ans. Colloidal solutions exhibit Tyndall effect because the size of the colloidal particles (1 nm–1000 nm) is such that they can scatter light.

Q. 32. What causes Brownian movement in a colloidal solution? *[NCERT Exemplar]*

Ans. Unbalanced bombardment of the particles of dispersed phase by molecules of dispersion medium causes Brownian motion. This stabilizes the sol.

Q. 33. What is the main cause of charge on a colloidal solution?

Ans. The charge on the colloidal particles is due to adsorption of common ions of the electrolyte on the surface of the colloidal particles, *e.g.*, Fe^{3+} from $FeCl_3$ on the surface of $Fe(OH)_3$ particles.

Q. 34. Give one example of positively charged sol and one example of negatively charged sol.

Ans. $Fe(OH)_3$ is a positively charged sol whereas As_2S_3 is a negatively charged colloid.

Q. 35. What causes electrophoresis?

Ans. Electrophoresis is due to charge on colloidal particles, the charged particles move towards one of the electrodes in electric field.

Q. 36. What is the type of charge on AgI colloidal sol formed when $AgNO_3$ solution is added to KI solution? *[CBSE Bhubaneshwar 2015]*

Ans. Negatively charged sol, AgI/I^- is formed when $AgNO_3$ solution is added to KI solution.

Q. 37. Why is ferric chloride preferred over potassium chloride in case of a cut leading to bleeding? *[CBSE 2019 (56/4/1)]*

Ans. Fe^{3+} ion has greater coagulating power than K^+ ion as ferric ion has higher charge.

Q. 38. Which of the following is most effective electrolyte in the coagulation of AgI/Ag^+ sol?

K_2SO_4, $MgCl_2$, $K_4[Fe(CN)_6]$ *[CBSE Sample Paper 2014]*

Ans. $K_4[Fe(CN)_6]$

Q. 39. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason. *[CBSE Delhi 2015]*

Ans. $BaCl_2$, Ba^{2+} ion has greater coagulating power than K^+ ion as Ba^{2+} ion has higher charge.

Q. 40. How can a lyophilic sol be coagulated?

Ans. This can be done (*i*) by adding an electrolyte, (*ii*) by adding a suitable solvent.

Q. 41. Give one example each of 'oil in water' and 'water in oil' emulsion. *[CBSE Delhi 2014]*

Ans. Oil in water emulsion: milk, vanishing cream.

Water in oil emulsion: Butter, cold cream, cod liver oil.

Q. 42. How will you distinguish between dispersed phase and dispersion medium in an emulsion? *[NCERT Exemplar]*

Ans. On adding dispersion medium, emulsions can be diluted to any extent. The dispersed phase forms a separate layer if added in excess.

Q. 43. Write two differences between sols and emulsions.

Ans. (*i*) Sols are dispersions of solids in liquids while emulsions are dispersions of liquids in liquids.

(*ii*) Sols are quite stable whereas emulsions are less stable.

Q. 44. How do emulsifying agents stabilise the emulsion? *[NCERT Exemplar]*

Ans. The emulsifying agent forms an interfacial layer between suspended particles and the dispersion medium thereby stabilising the emulsion.

Q. 45. A delta is formed at the meeting point of sea water and river water. Why? *[CBSE Allahabad 2015]*

Ans. River water is a colloidal solution of clay and sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in the sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

Q. 46. It is possible to cause artificial rain by spraying silver iodide on the clouds. Comment. *[NCERT Exemplar] [HOTS]*

Ans. Yes. Clouds are colloidal in nature and carry charge. Spray of silver iodide, an electrolyte, results in coagulation leading to rain.

Short Answer Questions–I [2 marks]

Q. 1. Write the differences between physisorption and chemisorption with respect to the following:

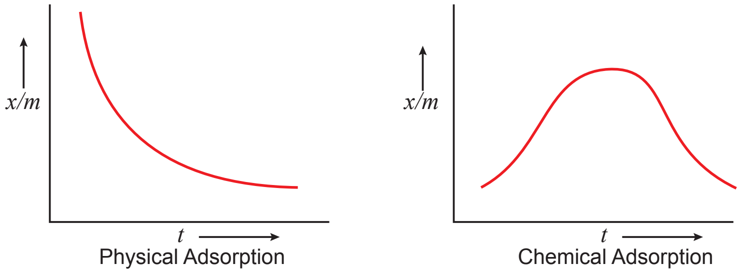
(*i*) Specificity **(*ii*) Temperature dependence**

(*iii*) Reversibility and **(*iv*) Enthalpy change** **[*CBSE Delhi 2013*]**

Ans.

	Physisorption	Chemisorption
(*i*) Specificity	It is not specific in nature.	It is highly specific in nature.
(*ii*) Temperature dependence	Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
(*iii*) Reversibility	It is reversible in nature.	It is irreversible.
(*iv*) Enthalpy change	Enthalpy of adsorption is low (20–40 kJ/mol) in this case.	Enthalpy of adsorption is high (80-240 kJ/mol) in this case.

Q. 2. Physical and chemical adsorption respond differently with a rise in temperature. What is this difference and why is it so?



Ans. Adsorption isobar for physical adsorption shows that the extent of adsorption decreases with the increase in temperature. The adsorption isobar of chemical adsorption shows that the extent of adsorption first increases and then decreases with the increase in temperature. The initial unexpected increase in the extent of adsorption with temperature is due to the fact that the heat supplied acts as activation energy required for chemical adsorption which is much more than that of physical adsorption.

Q. 3. Give an example where physisorption changes to chemisorption with rise in temperature. Explain the reason for change.

Ans. The process of physisorption, for example that of H_2 on finely divided nickel, involves weak van der Waals' forces. With increase in temperature, hydrogen molecules dissociate into hydrogen atoms which are held on the surface by chemisorption.

Q. 4. How are the following colloidal solutions prepared?

(*i*) Sulphur in water (*ii*) Gold in water **[*CBSE Delhi 2013*]**

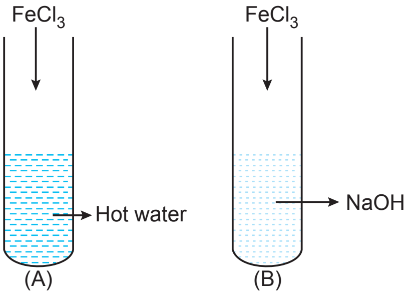
Ans. (*i*) Sulphur sol is prepared by the oxidation of H_2S with SO_2.

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

(*ii*) Gold sol is prepared by the reduction of $AuCl_3$ with formaldehyde.

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

Q. 5. A colloidal solution of ferric oxide is prepared by two different methods as shown below. **[*HOTS*]**



(*i*) What is the charge on colloidal particles in two test tubes (A) and (B)?

(*ii*) Give reasons for the origin of charge.

Ans. (*i*) Colloidal particles of test tube (A) are positively charged whereas colloidal particles of test tube (B) are negatively charged.

(*ii*) In test tube (A), Fe^{3+} is adsorbed on the precipitate $Fe_2O_3.xH_2O$ [or $Fe_2O_3.xH_2O/Fe^{3+}$ is formed].

In test tube (B), OH^- ion is adsorbed on the precipitate $Fe_2O_3.xH_2O$ [or $Fe_2O_3.xH_2O/OH^-$ is formed].

Q. 6. What is meant by coagulation of a colloidal solution? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out. [*CBSE Delhi 2012*]

Ans. The process of settling of colloidal particles through induced aggregation by the addition of some suitable electrolyte is known as coagulation. Three methods by which coagulation of lyophobic sols can be carried out are:

(*i*) **Electrophoresis:** During electrophoresis the colloidal particles move towards oppositely charged electrodes, get discharged and coagulated.

(*ii*) **Boiling:** On boiling a sol, the adsorbed layer is disturbed due to increased collision with the molecules of dispersion medium. This reduces the charge on the particles which ultimately settle down in the form of a precipitate.

(*iii*) **Addition of Electrolytes:** When excess of an electrolyte is added to a colloidal solution, the colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation.

Short Answer Questions–II [3 marks]

Q. 1. Define adsorption with an example. Why is adsorption exothermic in nature? Write the types of adsorption based on the nature of forces between adsorbate and adsorbent. [*CBSE Ajmer 2015*]

Ans. The accumulation of the molecular species at the surface rather than in the bulk of a solid or liquid is known as adsorption. For example, water vapour are adsorbed by silica gel.

When a gas is adsorbed on the surface of a solid its entropy decreases, *i.e.*, ΔS becomes –ve. Since adsorption is a spontaneous process, therefore, ΔG $(= \Delta H - T\Delta S)$ must be negative. As $- T\Delta S$ is +ve, ΔG can be negative only if ΔH has sufficiently high –ve value. Hence, adsorption is exothermic in nature.

There are two types of adsorption based on the nature of forces between adsorbate and adsorbent.

(*i*) Physical adsorption, when accumulation of gas on the surface of a solid occurs due to weak van der Waal forces.

(*ii*) Chemical adsorption, when the gas molecules or atoms are held to the surface of solid by chemical bonds.

Q. 2. Give reasons for the following: [*CBSE Sample Paper 2013*]

(*i*) Rough surface of catalyst is more effective than smooth surface.

(*ii*) Smoke passed through charged plates before allowing it to come out of chimneys in factories.

(*iii*) Ne gets easily adsorbed over charcoal than He.

Ans. (*i*) Rough surface of a catalyst provides more surface area for adsorption.

(*ii*) Smoke is passed through charged plates so that unburnt charged carbon particles get settled between the charged plate leaving behind air free from pollutants.

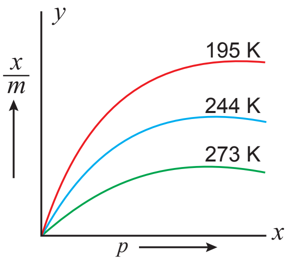
(*iii*) Ne has higher critical temperature, *i.e.*, stronger van der Waals forces therefore easily adsorbed.

Q. 3. Consider the adsorption isotherms given alongside and interpret the variation in the extent of adsorption (x/m) when

(*i*) (*a*) temperature increases at constant pressure.

(*b*) pressure increases at constant temperature.

(*ii*) Name the catalyst and the promoter used in Haber's process for manufacture of ammonia. [*HOTS*]



Ans. (*i*) (*a*) At constant pressure, extent of adsorption $\left(\frac{x}{m}\right)$ decreases with increase in temperature as adsorption is an exothermic process.

(*b*) At constant temperature, first adsorption $\left(\frac{x}{m}\right)$ increases with increase in pressure up to a particular pressure and then it remains constant.

At low pressure, $\frac{x}{m} = kp$

At intermediate range of pressure, $\frac{x}{m} = kp^{1/n} \quad (n > 1)$

At high pressure, $\frac{x}{m} = k$ (independent of pressure)

(*ii*) Finely divided iron is used as a catalyst and molybdenum is used as promoter.

Q. 4. Explain how the phenomenon of adsorption finds application in each of the following processes:

(*i*) Production of vacuum **(*ii*) Heterogeneous catalysis**

(*iii*) Froth Floatation process **[*CBSE Delhi 2011; (F) 2011*]**

Ans. (*i*) **Production of Vacuum:** Adsorption can be successfully applied to create conditions of high vacuum. For this, a bulb of charcoal cooled in liquid air, is connected to vessel which has already been exhausted as far as possible by vacuum pump. The remaining traces of air inspite of low pressure are adsorbed by the charcoal almost completely.

(*ii*) **Heterogeneous Catalysis:** There are many gaseous reactions of industrial importance involving solid catalyst. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process using V_2O_5 catalyst and use of finely divided nickel in the hydrogenation of vegetable oils are the excellent examples. The gaseous reactants are adsorbed on the surface of the solid catalyst. As a result, the concentration of the reactants increases on the surface of the catalyst and hence the rate of reaction increases.

(*iii*) **Froth Floatation Process:** In froth floatation process, the powdered ore is mixed with water. It is then mixed with pine oil (a frother). The oil particles are adsorbed on the surface of ore particles. Now a stream of air is blown through the mixture from below when froth is formed at the water surface. The ore particles stick to the bubbles of the air rises to surface along with the foam while the gangue particles which are wetted by water settle at the bottom. The foam is separated out and is collected and in the course, the ore particles also settle down.

Q. 5. Write one difference in each of the following:

(*i*) Lyophobic sol and Lyophilic sol **(*ii*) Solution and Colloid**

(*iii*) Homogeneous catalysis and Heterogeneous catalysis **[*CBSE Delhi 2017*]**

Ans.

(*i*)	**Lyophobic Sol**	**Lyophilic Sol**
	• Solvent hating • Irreversible in nature	• Solvent loving • Reversible in nature (*Any one*)
(*ii*)	**Solution**	**Colloid**
	• Homogeneous mixture • Does not show Tyndall effect	• Heterogeneous mixture • Shows Tyndall effect (*Any one*)
(*iii*)	**Homogeneous catalysis**	**Heterogeneous catalysis**
	• Reactants and catalyst are in same phase. • $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$ (*Any one*)	• Reactants and catalyst are not in same phase. • $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$ (*Any one*)

Q. 6. Explain the cleansing action of soap. Why do soaps not work in hard water? **[*CBSE (AI) 2012*]**

Ans. The cleansing action of soap such as sodium stearate is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats.

Hard water contains calcium and magnesium salts. In hard water, soap gets precipitated as calcium and magnesium soap which being insoluble stick to the clothes as gummy mass. Therefore, soaps do not work in hard water.

Q. 7. What type of colloidal sols are formed in the following:

(*i*) Sulphur vapours are passed through cold water.

(*ii*) White of an egg is mixed with water.

(*iii*) Soap solution.

Ans. (*i*) Multimolecular because sulphur molecules associate together to form multimolecular colloids.

(*ii*) Macromolecular because protein molecules present in the white of the egg are macromolecules soluble in water.

(*iii*) Associated because $RCOO^-$ ions associate together to form micelles.

Q. 8. (*i*) Write the dispersed phase and dispersion medium of milk. ***[CBSE 2019 (56/2/2)]***

(*ii*) Write one similarity between physisorption and chemisorption.

(*iii*) Write the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$. ***[CBSE (AI) 2017]***

Ans. (*i*) Both the dispersed phase and dispersion medium of milk are liquid.

(*ii*) Both the physisorption and chemisorption increase with increase in surface area.

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

The $Fe(OH)_3$ molecules formed as result of hydrolysis of $FeCl_3$ aggregate leading to the formation of sol.

Q. 9. Define the following terms:

(*i*) Brownian movement

(*ii*) Peptization ***[CBSE 2020 (56/3/1)]***

(*iii*) Multimolecular colloids ***[CBSE Patna 2015]***

Ans. **(*i*) Brownian movement:** The motion of the colloidal particles in a zig-zag path due to unbalanced bombardment by the particles of dispersion medium is called Brownian movement.

(*ii*) Peptization: The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of suitable electrolyte is called peptization. During peptization, the precipitate absorbs one of the ions of the electrolyte on its surface. This causes development of positive or negative charge on precipitates, which ultimately break up into particles of colloidal dimension.

(*iii*) Multimolecular colloids: A large number of atoms or smaller molecules (diameter < 1 nm) of a substance on dissolution aggregate together to form species having size in the colloidal range. Such species are called multimolecular colloids. **Examples:** a sulphur sol consist of particles containing thousands of S_8 sulphur molecules, a platinum or gold sol may have particles of various sizes having many atoms.

Q. 10. Define the following terms giving one suitable example for each:

(*i*) Electrophoresis

(*ii*) Micelles

(*iii*) Peptization ***[CBSE (F) 2012]***

Ans. (*i*) The movement of colloidal particles towards oppositely charged electrodes in an electric field is called electrophoresis.

(*ii*) There are some substances such as soap which at low concentration behave as normal electrolytes, but at higher concentration exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are known as micelles or associated colloids.

(*iii*) The process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte is called peptization.

Q. 11. Define the following terms:

(*i*) Homogeneous catalysis

(*ii*) Coagulation

(*iii*) Macromolecular colloids **[*CBSE Chennai 2015*]**

Ans. (*i*) In a catalysis process if the catalyst and the reactants are in the same phase (liquid or gas), the process is said to be homogeneous catalysis. For example, oxidation of SO_2 to SO_3 with O_2 in the presence of NO as a catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(*ii*) The process of settling of colloidal particles forming a precipitate is called coagulation.

(*iii*) Macromolecules in a suitable solvent form solutions in which the size of the macromolecules may be in colloidal range. Such colloids are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many respect, *e.g.*, starch dispersed in water.

Q. 12. (*i*) Differentiate between adsorption and absorption.

(*ii*) Out of $MgCl_2$ and $AlCl_3$, which one is more effective in causing coagulation of negatively charged sol and why?

(*iii*) Out of sulphur sol and proteins, which one forms multimolecular colloids? [*CBSE Delhi 2016*]

Ans. (*i*)

S.No.	Adsorption	Absorption
(*i*)	It is a surface phenomenon. Adsorbate molecules are held at the surface of adsorbent.	Absorption occurs in the bulk of absorbing substance.
(*ii*)	The concentration of the adsorbate at the adsorbent surface is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
(*iii*)	Initially, rate of adsorption is rapid. It decreases slowly till equilibrium is attained. **Example:** Water vapours on silica gel.	Absorption occurs with uniform rate. **Example:** Water vapours are absorbed by anhydrous $CaCl_2$.

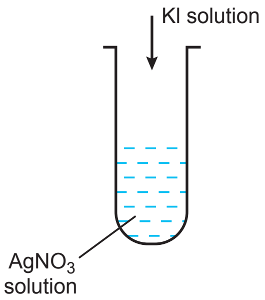
(*ii*) $AlCl_3$ is more effective in causing coagulation of negatively charged sol as Al^{3+} ion has greater positive charge than Mg^{2+} ion.

(*iii*) Sulphur sol.

Q. 13. (*i*) Write the dispersed phase and dispersion medium of dust.

(*ii*) Why is physisorption reversible whereas chemisorption is irreversible?

(*iii*) A colloidal sol is prepared by the method given in the figure. What is the charge on AgI colloidal particles formed in the test tube? How is the sol represented? [*CBSE 2019 (56/2/1)*]



Ans. (*i*) Dust is aerosol in which dispersed phase is solid whereas the dispersion medium is gas.

(*ii*) Physisorption is caused by weak van der Waal's forces therefore it is reversible whereas chemisorption is caused by chemical bond formation therefore it is irreversible.

(*iii*)
- Positive charge
- AgI/Ag^+

Q. 14. (*i*) Out of silica gel and anhydrous $CaCl_2$, which will adsorb the water vapours?

(*ii*) Out of H_2SO_4 and H_3PO_4, which one is more effective in causing coagulation of positively charged sol? Give reason.

(*iii*) Out of sulphur sol and proteins, which one forms macromolecular colloids? [*CBSE South 2016*]

Ans. (*i*) Silica gel

(*ii*) H_3PO_4, as PO_4^{3-} ion has greater negative charge than SO_4^{2-}.

(*iii*) Proteins.

Q. 15. SnO_2 forms a positively charged colloidal sol in acidic medium and a negatively charged sol in the basic medium. Why? Explain. ***[HOTS]***

Ans. SnO_2 is amphoteric in nature. It reacts with acids such as HCl, to form $SnCl_4$ in the solution. The common Sn^{4+} ions are adsorbed on the surface of SnO_2 particles to give a positively charged colloidal sol.

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

$$SnO_2 + Sn^{4+} \longrightarrow \underset{\text{Positively charged sol}}{(SnO_2):Sn^{4+}}$$

Similarly, with base like NaOH, it forms sodium stannate (Na_2SnO_3). The stannate ions get adsorbed on the surface of SnO_2 to give negatively charged colloidal sol.

$$SnO_2 + 2NaOH \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + H_2O$$

$$SnO_2 + SnO_3^{2-} \longrightarrow \underset{\text{Negatively charged sol}}{(SnO_2):SnO_3^{2-}}$$

Q. 16. Explain what is observed when ***[CBSE Sample Paper 2015]***

(*i*) silver nitrate solution is added to potassium iodide solution.

(*ii*) the size of the finest gold sol particles increases in the gold sol.

(*iii*) two oppositely charged sols are mixed in almost equal proportions.

Ans. (*i*) If silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results.

$$AgI + \underset{\text{(From dispersion medium)}}{I^-} \longrightarrow \underset{\text{Negatively charged Sol}}{AgI / I^-}$$

(*ii*) The colour of the colloidal solution depends on the wavelength of the light scattered by the colloidal particles which in turn depends on size and nature of the colloidal particle. Finest gold sol is red in colour, as the size of the particle increases, it appears purple, then blue and finally golden.

(*iii*) Two oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated. Such type of coagulation is called mutual coagulation.

Q. 17. Answer the following questions: ***[CBSE Sample Paper 2016]***

(*i*) What happens when a freshly precipitated $Fe(OH)_3$ is shaken with a little amount of dilute solution of $FeCl_3$?

(*ii*) Why are lyophilic colloidal sols more stable than lyophobic colloidal sols?

(*iii*) What form Freundlich adsorption equation will take at high pressure?

Ans. (*i*) It is converted into colloidal state by preferential adsorption of Fe^{3+} ions.

$$Fe(OH)_3 + FeCl_3 \longrightarrow \underset{\text{Reddish brown coloured colloid}}{[Fe(OH)_3]\,Fe^{3+}} + 3Cl^-$$

(*ii*) This is because the stability of lyophobic sol is only due to the presence of charge on the colloidal particles. On the other hand, the stability of lyophilic sol is due to charge on the colloidal particles as well as solvation of colloidal particles.

(*iii*) Freundlich Adsorption Isotherm, $\frac{x}{m} = kp^{1/n}$

At high pressure (beyond saturation pressure), $\frac{1}{n} = 0$ and $\frac{x}{m}$ = constant *i.e.*, the adsorption is independent of pressure. So, $\frac{x}{m} = kp^0$ or $\frac{x}{m} = k$.

Q. 18. (*i*) What are micelles? How do they differ from ordinary colloidal particles? Give two examples of micelle forming substances.

(*ii*) State Hardy–Schulze rule.

Ans. (*i*) There are some substances which at low concentration behave as normal electrolyte but at higher concentrations exhibit colloidal behaviour due to formation of aggregated particles. The aggregated particles thus formed are called micelles. Surface active agents such as soaps and detergents are the example of micelle forming substances.

The formation of micelles takes place only above a particular temperature called Kraft temperature and above a particular concentration called critical micelle concentration (CMC). On dilution, these colloids revert back to individual ions.

(*ii*) **Hardy–Schulze rule:** Refer to Basic Concepts Point 23(*h*).

Q. 19. Classify colloids where the dispersion medium is water. State their characteristics and write an example of each of these classes. [*CBSE (AI) 2011; (F) 2012*]

Ans. These are of two types:

(*i*) Hydrophilic

Stability: More stable as the stability is due to charge and water envelope surrounding the sol particles.

Nature: Reversible

Examples: Starch, gum, etc.

(*ii*) Hydrophobic

Stability: Less stable as the stability is due to charge only.

Nature: Irreversible

Examples: Metal hydroxide like $Fe(OH)_3$ and metal sulphide like As_2S_3.

Q. 20. Explain the following observations:

(*i*) Sun looks red at the time of setting.

(*ii*) Cottrell's smoke precipitator is fitted at the mouth of the chimney used in factories.

(*iii*) Physical adsorption is multilayered while chemical adsorption is monolayered. [*HOTS*]

Ans. (*i*) At the time of setting, the sun is at horizon. The light emitted by the sun has to travel a relatively longer distance through the atmosphere. As a result, blue part of light is scattered away by the particulate in the atmosphere causing red part to be visible.

(*ii*) Cottrell's smoke precipitator, neutralises the charge on unburnt carbon particles, coming out of chimney and they get precipitated and settle down at the floor of the chamber.

(*iii*) Physical adsorption involves van der Waals' forces, so any number of layers may be formed one over the other on the surface of the adsorbent. Chemical adsorption takes place as a result of the reaction between adsorbent and adsorbate. When the surface of adsorbent is covered with one layer, no further reaction can take place.

Q. 21. (*i*) Why does leather get hardened after tanning? [*CBSE 2019 (56/4/1)*]

(*ii*) On the basis of Hardy-Schulze rule explain why the coagulating power of phosphate is higher than chloride.

(*iii*) Do the vital functions of the body such as digestion get affected during fever? Explain your answer. [*CBSE Sample Paper 2017*]

Ans. (*i*) Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather.

(*ii*) Greater the valency of flocculating ion added, greater is its power to cause coagulation. Thus, for the coagulation of a positively charged sol PO_4^{3-} ion has higher coagulating power than Cl^- ion.

(*iii*) The optimum temperature for enzymatic activity is 298-310 K. On either side of this range enzyme activity decreases, that is why vital function of the body such as digestion get affected during fever.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. **Which of the following is an example of absorption?**
   (*a*) Water on silica gel (*b*) Water on calcium chloride
   (*c*) Hydrogen on finely divided nickel (*d*) Oxygen on metal surface

2. **On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal?**

Gas	CO_2	SO_2	CH_4	H_2
Critical temp./K	304	630	190	33

   (*a*) CO_2 (*b*) SO_2
   (*c*) CH_4 (*d*) H_2

3. **In which of the following reactions heterogenous catalysis is involved?**

(I) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(II) $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

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

(IV) $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$

   (*a*) (II), (III) (*b*) (II), (III), (IV)
   (*c*) (I), (II), (III) (*d*) (IV)

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. (3 × 1 = 3)

4. **Assertion (*A*)** : If a finely divided mixture of clay and charcoal is shaken with water and benzene, the clay will remain in water layer and charcoal will concentrate at the interface between the two liquids.

   Reason (*R*) : In the adsorption of acetic acid from aqueous solution by charcoal it is assumed that a multimolecular layer of adsorbed substance is formed.

5. **Assertion (*A*)** : For the coagulation of sols carrying positive charge, PO_4^{3-} ions are more efficient than SO_4^{2-} or Cl^- ions.

   Reason (*R*) : This follows Hardy-Schulze rule.

6. **Assertion (*A*)** : Colloidal solution is electrically neutral.

   Reason (*R*) : Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles.

Answer the following questions:

7. What is the role of diffusion in heterogenous catalysis? **(1)**

8. What happens when gelatin is added to gold sol? **(1)**

9. (*i*) How does BF_3 act as a catalyst in industrial process?
   (*ii*) Give an example of shape-selective catalysis. **(2)**

10. Give reasons:
    (*i*) Physisorption decreases with increase of temperature.
    (*ii*) Gelatin which is a peptide is added in ice-creams. **(2)**

11. How does a solid catalyst enhance the rate of combination of gaseous molecules? **(2)**

12. Give an example of
    (*i*) Heterogeneous catalysis
    (*ii*) Shape selective catalyst **(2)**

13. Give reason for the following observations:
    (*i*) Colloidal gold is used for intermuscular injection.
    (*ii*) Peptizing agent is added to convert precipitate into colloidal solution.
    (*iii*) Finely divided substance is more effective as an adsorbent. **(3)**

14. Differentiate between the following pairs:
    (*i*) Macromolecular colloids and multimolecular colloids
    (*ii*) Peptization and coagulation
    (*iii*) Electrophoresis and electrodialysis **(3)**

15. What are enzymes? Give mechanism of enzyme catalysis. **(3)**

16. What is heterogeneous catalysis? Explain modern adsorption theory of heterogeneous catalysis. **(5)**

Answers

1. (*b*) **2.** (*d*) **3.** (*a*) **4.** (*c*) **5.** (*a*) **6.** (*b*)

General Principles and Processes of Isolation of Elements

Chapter–6

basic concepts

1. **Minerals:** The naturally occurring chemical substances in the earth's crust which are obtained by mining.
2. **Ore:** The mineral from which the metal is conveniently and economically extracted.
3. **Gangue:** The earthy materials associated with the ores.
4. **Occurrence of metals:** Metals which have low chemical reactivity generally occur in free state. For example, gold and platinum. Metals which are chemically reactive occur in combined state. For example, aluminium, iron and zinc.

Table 6.1: Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite Kaolinite (a form of clay)	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$] $[Al_2(OH)_4Si_2O_5]$
Iron	Haematite Magnetite Siderite Iron pyrite	Fe_2O_3 Fe_3O_4 $FeCO_3$ FeS_2
Copper	Copper pyrite Malachite Copper glance Cuprite	$CuFeS_2$ $CuCO_3.Cu(OH)_2$ Cu_2S Cu_2O
Zinc	Zinc blende or Sphalerite Calamine Zincite	ZnS $ZnCO_3$ ZnO

5. **Metallurgy:** The scientific and technological process used for isolation of the metals from its ore.
6. **Concentration:** The process of removal of unwanted earthy and silicious impurities (gangue) from the ore.

   Some of the important concentration methods are:

   (*a*) **Hydraulic washing:** It is based on the differences in densities or gravities of the ore and the gangue particles. In one such process, an upward stream running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind. The oxide ores are generally concentrated by this method.

   (*b*) **Magnetic separation:** This method is based on differences in magnetic properties of ore and gangue (Fig. 6.1). For example, magnetic ores, magnetite (Fe_3O_4) and haematite (Fe_2O_3) are separated from the non-magnetic gangue by this method.

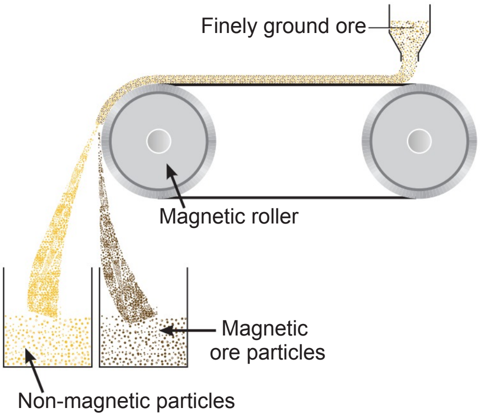


Fig. 6.1: Magnetic separation

(*c*) **Froth floatation:** This method is based on preferential wetting of ore particles by oil and gangue particles with water. The sulphide ores of zinc, copper and lead are usually concentrated by this method.

In the froth floatation process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added. The suspension is violently agitated by the rotating paddle which draws in air causing frothing (Fig. 6.2). The ore particles which are preferentially wetted by oil stick to the air bubbles, rise to the surface along with the froth while gangue particles which are preferentially wetted by water settle at the bottom. The froth is skimmed off. It is allowed to collapse and finally dried to get the concentrated ore.

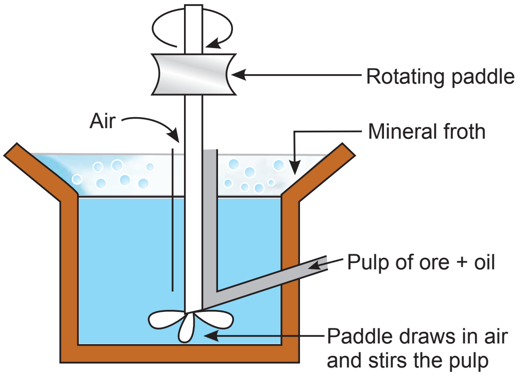


Fig. 6.2: Froth floatation process

- **Collectors:** Substances like pine oil, fatty acids, xanthates, which give water-repellant properties to the surface of the ore particles to be floated.
- **Froth stabilisers:** Substances like cresols and aniline, which stabilise the froth.
- **Depressants:** These are the substances which selectively prevent certain type of particles from forming the froth with the bubbles. For example, NaCN is added as a depressant for the separation of an ore containing ZnS and PbS. NaCN acts as a depressant for ZnS but not for PbS. NaCN forms a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of ZnS, thereby, preventing it from forming froth.

(*d*) **Leaching:** This method consists of treating the powdered ore with a suitable reagent which can selectively dissolve the ore but not the impurities. The impurities are filtered out and ore recovered from solution. For example, bauxite ore containing SiO_2, iron oxide and titanium oxide as impurities are concentrated by this method.

Leaching of aluminium from bauxite: Finely powdered bauxite ore is digested with an aqueous solution of sodium hydroxide at 473–523 K and 35–36 bar pressure. Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving impurities behind.

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

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation.

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

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to get back pure Al_2O_3.

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

7. **Extraction of Crude Metal from Concentrated Ore:** The process used to obtain metals in free state from the concentrated ore is called extraction. It involves the following two major steps:

(*a*) Conversion of the ore into metal oxide and

(*b*) Reduction of the oxide to metal.

(*a*) **Conversion of the ore into metal oxide:** The following two methods are used for conversion of ores into their respective oxides.

(*i*) **Calcination:** It is the process of heating an ore below its melting point either in the absence or limited supply of air. During calcination,

- Moisture present in the ore is expelled.
- Hydrated ores become anhydrous. For example,

$$\underset{\text{(Bauxite)}}{Al_2O_3.2H_2O(s)} \xrightarrow{\text{Heat}} \underset{\text{(Alumina)}}{Al_2O_3(s)} + 2H_2O(g)$$

$$\underset{\text{Limonite}}{Fe_2O_3.3H_2O(s)} \xrightarrow{\text{Heat}} \underset{\text{Ferric oxide}}{Fe_2O_3(s)} + 3H_2O(g)$$

Carbonates are converted into their respective oxides.

$$\underset{\text{Calamine}}{ZnCO_3(s)} \xrightarrow{\text{Heat}} \underset{\text{Zinc oxide}}{ZnO(s)} + CO_2\uparrow$$

$$\underset{\text{Limestone}}{CaCO_3(s)} \xrightarrow{\text{Heat}} \underset{\text{Calcium oxide}}{CaO(s)} + CO_2\uparrow$$

***(ii)* Roasting:** It is the process of heating the ore below its melting point in excess of air. The following changes occur during roasting:

- Moisture is driven away.
- Organic matter is destroyed.
- Non-metallic impurities such as sulphur, phosphorus and arsenic are oxidised and are removed as volatile gases.

$$S_8(s) + 8O_2(g) \xrightarrow{\text{Heat}} \underset{\text{Sulphur dioxide}}{8SO_2\uparrow}$$

$$P_4(s) + 5O_2(g) \xrightarrow{\text{Heat}} \underset{\text{Phosphorus pentaoxide}}{2P_2O_5(s)}$$

- Sulphide ores are converted into metallic oxides.

$$\underset{\text{Zinc sulphide}}{2ZnS(s)} + 3O_2(g) \longrightarrow \underset{\text{Zinc oxide}}{2ZnO(s)} + 2SO_2\uparrow$$

$$\underset{\text{Lead sulphide}}{2PbS(s)} + 3O_2(g) \longrightarrow \underset{\text{Lead oxide}}{2PbO(s)} + 2SO_2\uparrow$$

$$\underset{\text{Cuprous sulphide}}{2Cu_2S(s)} + 3O_2(g) \longrightarrow \underset{\text{Cuprous oxide}}{2Cu_2O(s)} + 2SO_2\uparrow$$

- The ore becomes porous and hence easily workable in subsequent stages.

***(b)* Reduction of oxide to metal:** The role of reducing agent is to provide ΔG negative and large enough to make the sum of ΔG of oxidation of reducing agent and reduction of metal oxide negative.

The free energy change, ΔG is related with other thermodynamic quantities by the expression;

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

where ΔH = enthalpy change, ΔS = entropy change, and T = temperature in kelvin

As heating, *i.e.*, increase in T, favours a negative value of $\Delta_r G$, therefore, the temperature is chosen such that sum of $\Delta_r G$ in two combined redox processes is negative.

Some of the common methods used for the reduction are given below.

***(i)* Auto-reduction:** In this method, inactive metals can be reduced simply by heating the ore in air. Extraction of copper, lead, antimony, mercury, etc. have been carried out by this process.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2\uparrow$$

$$2PbO + PbS \longrightarrow 3Pb + SO_2\uparrow$$

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2\uparrow$$

$$2HgO + HgS \longrightarrow 3Hg + SO_2\uparrow$$

***(ii)* Smelting:** In this process, metal oxide is reduced to metal with C or CO.

$$Fe_2O_3 + CO \xrightarrow{500-900\text{ K}} 2FeO + CO_2\uparrow$$

$$Fe_3O_4 + CO \xrightarrow{500-900\text{ K}} 3FeO + CO_2\uparrow$$

$$FeO + CO \xrightarrow{1123\text{ K}} Fe + CO_2\uparrow$$

$$Fe_2O_3 + 3C \xrightarrow{>1123\text{ K}} 2Fe + 3CO\uparrow$$

$$ZnO + C \longrightarrow Zn + CO\uparrow$$

$$SnO_2 + 2C \longrightarrow Sn + 2CO\uparrow$$

(*iii*) **Aluminothermic reduction:** The process of reduction of metal oxide by aluminium is known as aluminothermic reduction. Metals like manganese and chromium are extracted by thermite process.

$$3MnO_4 + 8Al \longrightarrow 4Al_2O_3 + 3Mn$$

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr + \text{Heat}$$

(*iv*) **Reduction with hydrogen:** Hydrogen is an efficient reducing agent for metal oxides. For this purpose, the roasted ore is heated in a current of hydrogen when metal oxide is reduced to metal. For example, oxides of W, Mo, etc. are reduced with hydrogen.

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

(*v*) **Hydrometallurgy:** The process of extraction of metal by dissolving the ore in a suitable reagent followed by precipitation or displacement of the metal by a more electropositive metal is known as hydrometallurgy.

For example, when native silver or gold is treated with a dilute solution (0.5%) of sodium or potassium cyanide, they go into the solution forming a soluble complex. From this soluble complex, metal is precipitated by adding zinc.

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

(*vi*) **Electrometallurgy:** The process of extraction of metal by electrolysis of their fused salt is known as electrometallurgy. This method is used for the extraction of highly reactive metals like Na, Ca, Al, etc.

In reduction of highly reactive metals, chemical reduction is not feasible, therefore electrolytic reduction is to be carried out. In reduction of molten metal salt, electrolysis is done. This method is based on electrochemical principles which can be understood with the help of equation

$$\Delta G^\circ = -nE^\circ F$$

where 'n' is the number of electrons and E° is electrode potential of the redox couple formed in the system.

More reactive metals have large negative values of E° therefore, ΔG° becomes +ve and their reduction is difficult.

If the difference in two values of E° of redox couple is +ve, then ΔG° will be –ve and less reactive metal can be obtained from its salt by more reactive metal.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

In electrolysis, metal ions are discharged at negative electrode (cathode) and deposited there. Sometimes a flux is added for making the molten mass more conducting.

8. **Flux:** A flux is a substance which when mixed with calcinated or roasted ore, chemically combine with impurities present to form an easily fusible material called **slag**.

$$\text{Flux} + \text{Impurity} \longrightarrow \text{Slag}$$

The slag is insoluble in molten metal, and being lighter, floats over the surface of molten metal.

Fluxes are of two types:

(*i*) **Acidic fluxes:** For basic impurities like lime present in the ore, acidic fluxes like silica are used.

$$\underset{\text{Basic impurity}}{CaO} + \underset{\text{Acidic flux}}{SiO_2} \longrightarrow \underset{\text{Fusible slag}}{CaSiO_3}$$

(*ii*) **Basic fluxes:** For acidic impurities like silica present in the ore, basic fluxes like limestone are used.

$$\underset{\text{Acidic impurity}}{SiO_2} + \underset{\text{Basic flux}}{CaCO_3} \longrightarrow \underset{\text{Fusible slag}}{CaSiO_3} + CO_2\uparrow$$

9. **Refining:** The process of purifying the impure metals is called refining. Various methods are available for refining of impure metals. The choice of purification method depends on the nature of the metal and the impurities present. Following methods are in general, employed for refining metals.

(*a*) **Distillation:** This method is used to remove the non-volatile impurities from volatile metals like zinc, cadmium and mercury. The impure metal is heated in a retort when the pure metal vaporises and condenses separately leaving behind the non-volatile impurities.

(*b*) **Liquation:** This is very useful for low melting metals like tin and lead. The impure metal is heated on the sloping hearth of a furnace when the molten metal flows away from the infusible impurities.

(*c*) **Electrolytic refining:** In this method, impure metal is made to act as anode. A strip of same metal in pure form is used as cathode. They are put in an electrolytic bath containing soluble salt of same metal. On passing electric current, metal ions from the electrolyte solution are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ions, *i.e.*,

At cathode: $M^{n+}(aq) + ne^- \longrightarrow M(s)$

At anode: $M(s) \longrightarrow M^{n+}(aq) + ne^-$

The voltage applied for the electrolysis is such that the impurities of more electropositive metals remain in the solution as ions whereas impurities of less electropositive metals settle down under the anode as anode mud. A large number of metals such as copper, gold, silver, zinc, aluminium, etc., are refined by this method.

(*d*) **Zone refining:** It is based on the principle that the impurities are more soluble in the molten state than in the solid state of the metal. The impure metal is heated with the help of a circular mobile heater at one end. This results in the formation of a molten zone or melt. As the heater is moved along the length of the rod, the pure metal crystallises out of the melt and impurities pass into the adjacent molten zone. This process is repeated several times till the impurities are completely driven to one end of the rod which is then cut off and discarded. This method is very useful for producing semiconductor and other metals of very high purity, *e.g.*, silicon, germanium, boron and gallium.

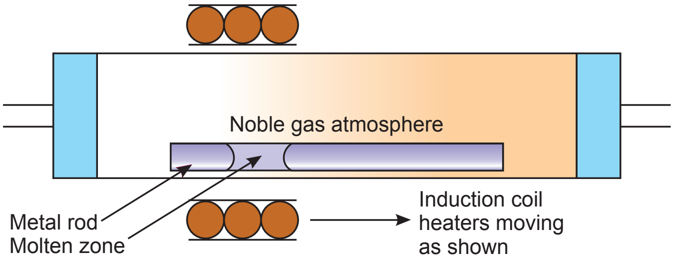


Fig. 6.3: Zone refining process

(*e*) **Vapour phase refining:** In this method, the metal is converted into its volatile compound and collected elsewhere. It is then thermally decomposed to get the pure metal.

Following examples will illustrate this technique:

(*i*) **Mond process:** In this process, nickel is heated in a stream of carbon monoxide to form a volatile complex, nickel tetracarbonyl.

$$Ni + 4CO \xrightarrow{330\text{–}350\ K} Ni(CO)_4$$

The vapour of nickel carbonyl is taken to decomposer chamber maintained at 450–470 K where it decomposes to give pure nickel.

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

(*ii*) **van Arkel method:** This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. Impure metal is heated with iodine in an evacuated vessel and the resultant tetraiodide is decomposed on a tungsten filament to get the pure metal.

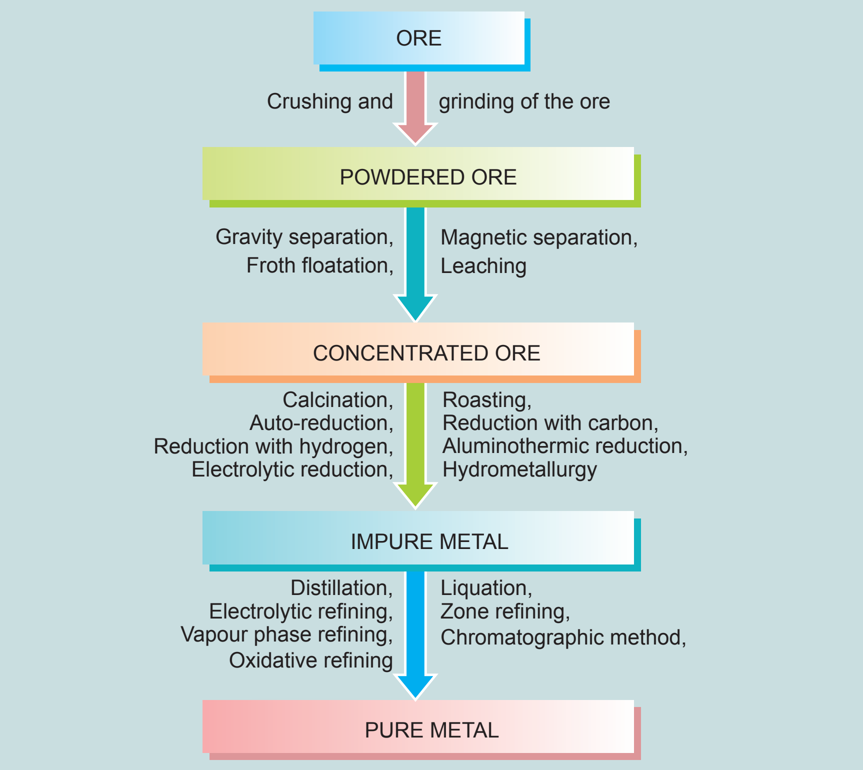
$$\underset{\text{Impure}}{\mathrm{Zr}(s) + 2\mathrm{I}_2(g)} \xrightarrow{870\ \mathrm{K}} \mathrm{ZrI}_4(g) \xrightarrow[\text{Tungsten filament}]{2075\ \mathrm{K}} \underset{\text{Pure}}{\mathrm{Zr}(s)} + 2\mathrm{I}_2(g)$$

$$\underset{\text{Impure}}{\mathrm{Ti}(s) + 2\mathrm{I}_2(g)} \xrightarrow{523\ \mathrm{K}} \mathrm{TiI}_4(g) \xrightarrow{1700\ \mathrm{K}} \underset{\text{Pure}}{\mathrm{Ti}(s)} + 2\mathrm{I}_2(g)$$

(*f*) **Chromatographic methods:** It is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture to be separated is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later, the adsorbed components are removed (eluted) by using suitable solvents (eluent). There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc. Chromatography is used for the purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

(*g*) **Oxidative refining:** In this method, the impure metal is heated to a high temperature and then exposed to air when the impurities such as carbon, phosphorus and arsenic, etc., are oxidised along with outgoing gases. Foreign metals present as impurities also form their oxides and float on the surface of molten metal from where they are skimmed off periodically. Oxidative refining of iron is carried out in the Bessemer converter by blowing air through the molten metal.

10. Flow-Sheet Diagram for Metallurgical Process:



11. Thermodynamic Principles of Metallurgy: For any process, at any specified temperature, Gibbs free energy change (ΔG) is given by the equation:

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

where ΔH is the enthalpy change and ΔS is the entropy change for the process. The change in free energy is also related to the equilibrium constant K of the reactant product system through the equation:

$$\Delta G = -RT \ln K$$

A –ve ΔG implies a +ve K in equation. And this can happen only when reaction proceeds towards products. From these facts we can draw the following conclusions:

(*i*) The criterion of feasibility of a reaction at any temperature is that the change in free energy (ΔG) must be negative. If ΔS is +ve on increasing the temperature (T), the value of $T\Delta S$ will increase and when $\Delta H < T\Delta S$, ΔG will be negative and the reaction will proceed towards products.

(*ii*) A reaction with positive ΔG can still occur when it is coupled with another reaction having large negative ΔG so that the net ΔG of the two reactions is negative.

12. (*a*) **Ellingham Diagram:** Ellingham diagram is the graphical representation of Gibbs energy. It provides a basis for considering the choice of reducing agent in the reduction of oxides and helps us in predicting the feasibility of thermal reduction of an ore.

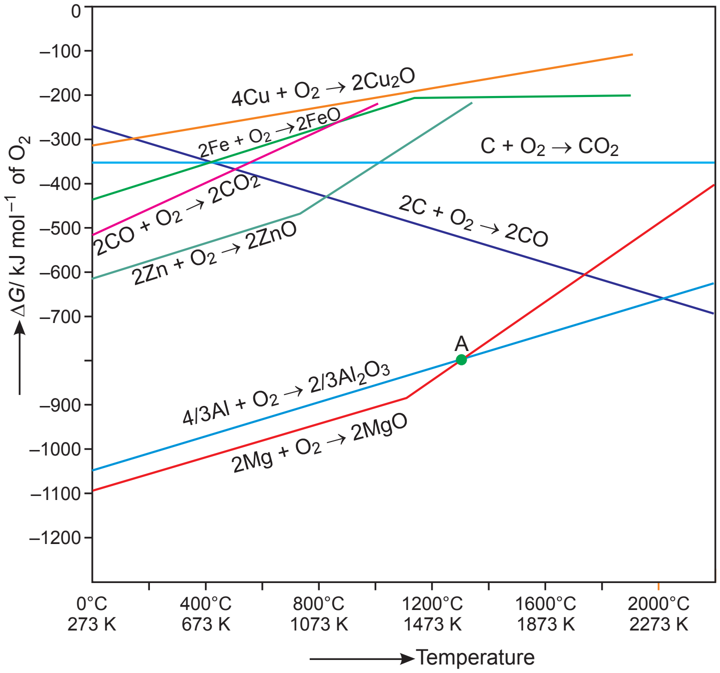


Fig. 6.4: Gibbs energy ($\Delta G°$) vs *T* plots (schematic) for formation of some oxides (Ellingham diagram)

Some salient features of Ellingham diagram are:

(*i*) Ellingham diagram normally consists of plots of $\Delta_f G°$ vs T for formation of oxides of elements, *i.e.*, for the reaction.

$$2xM(s) + O_2(g) \longrightarrow 2M_xO(s)$$

In this reaction, ΔS is –ve. Due to this ΔG shifts towards higher side despite rising T.

(*ii*) Each plot is a straight line unless some change in phase (s → liq or liq → g) takes place. The temperature at which such change occurs, is indicated by an increase in the slope on +ve side (*e.g.*, in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve).

(*iii*) There is a point in curve below which ΔG is negative, *i.e.*, M_xO is stable. Above this point, M_xO will decompose on its own.

(*iv*) In an Ellingham diagram, the plots of $\Delta G°$ for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of $\Delta_f G°$, etc. (for formation of oxides) at different temperature are depicted which make interpretation easy.

(*v*) Similar diagrams are also constructed for sulphides and halides and it becomes clear why reduction of M_xS is difficult. Therefore, the $\Delta_f G°$ of M_xS is not compensated.

(*b*) **Choice of reducing agent using Ellingham diagram:** Any metal can reduce the oxides of the other metals which lie above it in the Ellingham diagram. This is due to the fact that ΔG becomes more negative by an amount equal to the difference between the two graphs at that temperature.

(*c*) **Ellingham diagram and temperature:** As heating (*i.e.*, increasing temperature) favours a negative value of $\Delta_r G°$. Therefore, the temperature is chosen such that the sum of $\Delta_r G°$ in the two combined reactions is negative. In $\Delta_r G°$ vs T plots, this is indicated by the point of intersection of two curves (curve for M_xO and that for the oxidation of the reducing substance). After that point, the $\Delta_r G°$ value becomes more negative for the combined reaction including the reduction of M_xO. The difference in two $\Delta_r G°$ values after that point determines whether reductions of the oxide of the upper line is possible by element represented by the lower line. Larger the difference, easier is the reduction.

(*d*) Limitations of Ellingham diagram

(*i*) Ellingham diagram simply indicates whether a reaction is possible or not. It does not say about the kinetics of the reduction process, *i.e.*, how fast a reaction could be under given thermodynamic conditions.

(*ii*) The interpretation of $\Delta G°$ is based on K ($\Delta G° = -RT \ln K$). Thus, it is presumed that the reactants and products are in equilibrium. This is not always true because the reactant/ product may be solid.

13. (*a*) **Extraction of iron from its oxides:** Oxide ores of iron, after concentration through calcination or roasting are mixed with limestone and coke and fed into a blast furnace from its top. Thermodynamics help us to understand how coke reduces the oxide and why blast furnace is chosen.

$$FeO + C \longrightarrow Fe + CO$$

It can be seen as a couple of two simpler reactions.

$$FeO \longrightarrow Fe + \frac{1}{2}O_2; \qquad \Delta G_{(FeO,\, Fe)} \qquad \ldots(i)$$

$$C + \frac{1}{2}O_2 \longrightarrow CO; \qquad \Delta G_{(C,\, CO)} \qquad \ldots(ii)$$

Adding (*i*) and (*ii*), we get

$$\Delta G_{(C,\, CO)} + \Delta G_{(FeO,\, Fe)} = \Delta_r G$$

If ΔG is –ve, the reaction will take place.

In $\Delta G°$ vs T plot representing reaction (*i*) goes upward and that representing $C \rightarrow CO$ goes downward. At temperatures above 1073 K approx., the C, CO line comes below Fe, FeO line $[\Delta G_{(C,\, CO)} < \Delta G_{(Fe,\, FeO)}]$. So in this case coke will be reducing FeO to Fe and itself be oxidised to CO.

In a similar way, the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with (CO, CO_2) curve in Ellingham diagram.

Reduction of iron oxide in blast furnace: Reduction of iron oxides takes place in different temperature ranges. Coke is burnt to give temperature up to about 2200 K at lower portion itself.

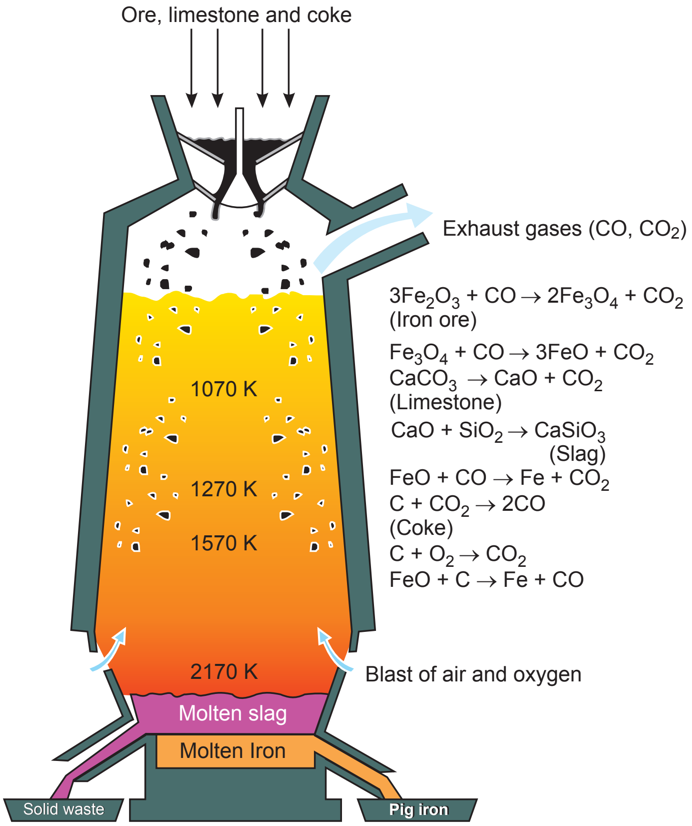


Fig. 6.5: Blast furnace

The reactions can be summarised as follows:

At 500–800 K (lower temperature range in the blast furnace):

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2\uparrow$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2\uparrow$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2\uparrow$$

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \longrightarrow 2CO(g)$$

$$FeO + CO \longrightarrow Fe + CO_2\uparrow$$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

(*b*) **Extraction of zinc from zinc oxide:** The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO\uparrow$$

The metal is distilled off and collected by rapid chilling.

14. **Extraction of Copper from Cuprous Oxide [copper (I) oxide]:** In the graph of $\Delta_r G°$ vs T for formation of oxides (Ellingham diagram), the Cu_2O line is almost at the top. So, it is quite easy to reduce Cu_2O both with C and CO at 500 to 600 K.

Concentration of ore: Cu_2S is concentrated by froth floatation process.

Roasting: Sulphide ore (Copper glance) is heated in the presence of oxygen to form Cu_2O and sulphur dioxide is formed.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

Reduction: The oxide can be reduced to metallic copper using coke as reducing agent.

$$Cu_2O + C \longrightarrow 2Cu + CO$$

Smelting: In actual process, the ore is mixed with SiO_2 and heated in a reverberatory furnace. Iron oxide reacts with SiO_2 to form iron silicate as slag.

$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

Copper is produced in the form of **copper matte**. This contains Cu_2S and FeO. Copper matte is charged into silica lined convertor. Some silica is also added and hot blast air is blown to convert the remaining FeS into FeO and Cu_2S/Cu_2O to metallic copper.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2\uparrow$$

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called **blister copper**.

Purification of copper: Copper is purified by electrolytic refining by taking impure Cu as anode, pure Cu as cathode and acidified $CuSO_4$ solution as electrolyte. The net result of electrolysis is the transfer of copper in pure form from the anode to the cathode.

At anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.

15. **Extraction of Aluminium from Bauxite:** Aluminium is extracted from bauxite $Al_2O_3.2H_2O$.

(*i*) Concentration of bauxite is done by leaching as explained in Basic Concepts Point 6.

(*ii*) **Electrolytic reduction (Hall–Heroult Process):** Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of mixture and brings electrical conductivity. Fused mixture is electrolysed using graphite rods as anode and carbon lining as cathode.

The graphite anode is useful for reduction of metal oxide to metal. The overall electrolytic reactions are:

$$Al_2O_3 \xrightarrow{\text{Electrolysis}} 2Al^{3+} + 3O^{2-}$$

Cathode: $Al^{3+}(\text{melt}) + 3e^- \longrightarrow Al\,(l)$

Anode: $C(s) + O^{2-}\,(\text{melt}) \longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}\,(\text{melt}) \longrightarrow CO_2(g) + 4e^-$

The overall reaction may be given as:

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2\uparrow$$

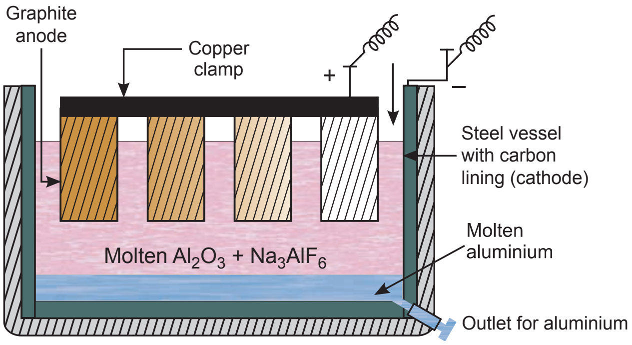


Fig. 6.6: Electrolytic cell for the extraction of aluminium

16. **Copper from Low Grade Ores and Scraps:** Copper is extracted by hydrometallurgy from low-grade copper ores and scraps. It is leached out by using acid or bacteria.

Reduction: The solution containing Cu^{2+} is treated with scrap iron or H_2.

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Fe^{2+}(aq) + Cu(s)$$

17. **Production of Chlorine:** Chlorine can be obtained from electrolysis of brine solution (saturated solution of sodium chloride).

$$2Cl^-(aq) + 2H_2O(l) \longrightarrow 2OH^-\,(aq) + H_2(g) + Cl_2(g)$$

$$\Delta G^\circ = +\,422\text{ kJ},\ E^\circ = -\,2.2\text{ V}$$

It means external e.m.f. greater than 2.2 V is required to carry out electrolysis.

18. **Table 6.2: A Summary of the Occurrence and Extraction of Some Common Metals**

Metal	Occurrence	Common Method of Extraction	Remarks
Aluminium	1. Bauxite, $Al_2O_3.xH_2O$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6.	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace.	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction.	It is self reduced in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting followed by reduction with coke.	The metal may be purified by fractional distillation.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Which of the ores mentioned in Table 6.1 can be concentrated by magnetic separation method? **[*CBSE (AI) 2019*]**

Ans. Ores in which one of the components (either the impurity or the actual ore) is magnetic can be concentrated by magnetic separation method, *e.g.*, haematite (Fe_2O_3), magnetite (Fe_3O_4), siderite ($FeCO_3$), iron pyrite (FeS_2).

Q. 2. What is the significance of leaching in the extraction of aluminium?

Ans. Leaching is significant as it helps in removing the impurities like SiO_2, Fe_2O_3, TiO_2, etc. from the bauxite ore.

Q. 3. The reaction, $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ ($\Delta G^\circ = -421$ kJ) is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?

Ans. Certain amount of energy of activation is required even for such reactions which are thermodynamically feasible, therefore heating is required.

Q. 4. Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO? What are those conditions?

Ans. Yes it is true, Ellingham diagram suggests that below 1350°C Mg can reduce Al_2O_3 and when temperature is above 1350°C Al can reduce MgO.

NCERT Textbook Exercises

Q. 1. Copper can be extracted by hydrometallurgy but not zinc. Explain.

Ans. The E^{o} of zinc ($Zn^{2+}/Zn = -0.76$ V) is lower than that of copper ($Cu^{2+}/Cu = 0.34$ V). This means that zinc is a stronger reducing agent and can displace copper from solution of Cu^{2+} ions.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

In order to extract zinc by hydrometallurgy, we need stronger reducing agent like K ($E^{o}_{K^+/K} = -2.93$ V), Mg ($E^{o}_{Mg^{2+}/Mg} = -2.37$ V), Al ($E^{o}_{Al^{3+}/Al} = -1.66$ V), etc. However, all these metals reduce water to hydrogen gas. Therefore, these metals cannot be used to displace Zn from solution of Zn^{2+} ions. Thus, copper can be extracted by hydrometallurgy but not zinc.

Q. 2. What is the role of a depressant in froth floatation process? **[*CBSE (AI) 2017*]**

Ans. In froth floatation process, the role of the depressant is to prevent certain type of particles from forming the froth with the air bubbles. For example, NaCN is used as a depressant to separate lead sulphide ore (PbS) from zinc sulphide ore (ZnS). NaCN forms a zinc complex $Na_2[Zn(CN)_4]$ on the surface of ZnS thereby preventing it from the formation of froth.

Q. 3. Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

Ans. The standard free energy ($\Delta_f G^\circ$) of formation of Cu_2S is more –ve than those of CS_2 and H_2S.

So, neither carbon nor hydrogen can reduce Cu_2S to Cu metal. On the other hand, $\Delta_f G^\circ$ of Cu_2O is much less –ve than that of CO and hence carbon can easily reduce Cu_2O to Cu.

$$Cu_2O(s) + C(s) \longrightarrow 2Cu(s) + CO(g)$$

Thus, the extraction of copper from pyrite is more difficult than from its oxide ore through reduction.

Q. 4. Explain: (*i*) Zone refining (*ii*) Column chromatography. **[*CBSE Delhi 2014*]**

Ans. (*i*) Refer to Basic Concepts Point 9(*d*).

(*ii*) Refer to Basic Concepts Point 9(*f*).

Q. 5. Out of C and CO, which is a better reducing agent at 673 K?

Ans. At 673 K (low temperature), the ΔG° (CO, CO_2) line lies below ΔG° (C, CO_2) line in the Ellingham diagram. Therefore, at 673 K, CO is a better reducing agent. On the other hand, at higher temperature, ΔG° (C, CO_2) line lies below ΔG° (CO, CO_2) line and hence at higher temperature carbon is better reducing agent than CO.

Q. 6. Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?

Ans. The common elements present in the anode mud in electrolytic refining of copper are antimony, selenium, tellurium, silver, gold and platinum. These elements, being less reactive, are not affected by $CuSO_4 + H_2SO_4$ solution and hence settle down under anode as anode mud.

Q. 7. Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

Ans. Refer to Basic Concepts Point 13.

Q. 8. Write chemical reactions taking place in the extraction of zinc from zinc blende.

Ans. The various steps involved are:

(*a*) **Concentration:** The ore is crushed and then concentrated by froth floatation process.

(*b*) **Roasting:** The concentrated ore is heated in the presence of excess of air at about 1200 K to form zinc oxide.

$$\underset{\text{Zinc blende}}{2ZnS} + 3O_2 \xrightarrow{\text{Heat}} \underset{\text{Zinc oxide}}{2ZnO} + 2SO_2\uparrow$$

(*c*) **Reduction:** ZnO obtained above is mixed with powdered coke and heated to 1673 K in a fire clay retort. It is reduced to zinc metal.

$$ZnO + C \xrightarrow{1673\text{ K}} Zn + CO\uparrow$$

At 1673 K, zinc metal being volatile (b.p. 1180 K), distills over and is condensed.

(*d*) **Electrolytic refining:** Impure zinc is made the anode and cathode consists of a sheet of pure zinc. The electrolyte consists of $ZnSO_4$ solution acidified with dil. H_2SO_4. On passing electric current, pure zinc gets deposited on the cathode.

Q. 9. State the role of silica in the metallurgy of copper.

Ans. Silica (SiO_2) acts as a flux to remove iron oxide (FeO) impurity as slag $FeSiO_3$ in the metallurgy of copper. FeS present in the copper matte is oxidised to FeO which combine with silica (SiO_2) to form $FeSiO_3$.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$\underset{\text{Impurity}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

Q. 10. Which method of refining may be more suitable if element is obtained in minute quantity?

Ans. Chromatographic method of refining is particularly suitable if the element is obtained in minute quantity.

Q. 11. Which method of refining will you suggest for an element in which impurities present have chemical properties close to the properties of that elements?

Ans. Zone refining is the method for an element in which impurities present have chemical properties close to the properties of those elements.

Q. 12. Describe the method of refining of nickel.

Ans. Refer to Basic Concepts Point 9(*e*).

Q. 13. How can you separate alumina from silica in bauxite ore associated with silica? Give equations, if any. ***[CBSE (F) 2013, 2019 (56/4/1)]***

Ans. **Leaching of aluminium from bauxite:** Finely powdered bauxite ore is digested with an aqueous solution of sodium hydroxide at 473–523 K and 35–36 bar pressure. Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving impurities behind.

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

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation.

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

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to get back pure Al_2O_3.

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

Q. 14. Giving examples, differentiate between 'roasting' and 'calcination'.

Ans.

S. No.	Roasting	Calcination
(*i*)	It is the process of heating the ore below its melting point with excess of air.	It is the process of heating the ore below its melting point in the absence or limited supply of air.
(*ii*)	Sulphide ores are converted into oxide form. $2ZnS + 3O_2 \xrightarrow{\text{Heat}} 2ZnO + 2SO_2\uparrow$	Carbonate ores are converted into oxide. $ZnCO_3 \xrightarrow{\text{Heat}} ZnO + CO_2\uparrow$
(*iii*)	Volatile impurities are removed as oxides SO_2, As_2O_3, etc.	Water and organic impurities are removed.

Q. 15. How is 'cast iron' different from 'pig iron'? *[CBSE Patna 2015; CBSE 2019 (56/5/2)]*

Ans. The iron obtained from blast furnace is called pig iron. It contains about 4% carbon and many other impurities in smaller amount (*e.g.*, S, P, Si, Mn).

Cast iron, is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Q. 16. Differentiate between "minerals" and "ores". *[CBSE (AI) 2011]*

Ans. The naturally occurring chemical substances in the form of which metals occur in the earth's crust along with impurities are called minerals. The mineral from which the metal can be extracted conveniently and profitably is called an ore. Thus, all ores are minerals but all minerals are not ores. For example, aluminium occurs in earth's crust in the form of two minerals, *i.e.*, bauxite ($Al_2O_3 . xH_2O$) and clay ($Al_2O_3 . 2SiO_2 . 2H_2O$). Out of these two minerals, Al can be conveniently and economically extracted from bauxite. Therefore, bauxite is the ore of aluminium.

Q. 17. Why copper matte is put in silica lined converter?

Ans. Copper matte consists of Cu_2S and FeS. When a blast of hot air is passed through molten matte taken in a silica lined converter, FeS present in matte is oxidised to FeO which combines with silica (SiO_2) to form $FeSiO_3$, slag.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$FeO + \underset{\text{Silica}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

When whole of iron has been removed as slag, some of the Cu_2S undergoes oxidation to form Cu_2O which then reacts with more Cu_2S to form copper metal.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2\uparrow$$

Thus, copper matte is heated in silica lined converter to remove FeS present in copper matte as $FeSiO_3$, slag.

Q. 18. What is the role of cryolite in the metallurgy of aluminium?

Ans. The role of cryolite is as follows:

(*i*) It makes alumina a good conductor of electricity.

(*ii*) It lowers the fusion temperature of the electrolytic bath from 2323 K to about 1140 K.

Q. 19. How is leaching carried in case of low grade copper ores? *[CBSE 2020 (56/5/1)]*

Ans. The leaching of the low grade copper ores is carried out with acids in the presence of air when copper goes into solution as Cu^{2+} ions.

$$2Cu(s) + 2H_2SO_4(aq) + O_2(g) \longrightarrow 2CuSO_4(aq) + 2H_2O(l)$$

or $$Cu(s) + 2H^+(aq) + \frac{1}{2}O_2(g) \longrightarrow Cu^{2+}(aq) + H_2O(l)$$

Q. 20. Why is zinc not extracted from zinc oxide through reduction using CO?

Ans. The standard free energy of formation ($\Delta_f G^\circ$) of CO_2 from CO is higher than that of the formation of ZnO from Zn. Hence, CO cannot be used to reduce ZnO to Zn.

Q. 21. The value of $\Delta_f G^\circ$ for formation of Cr_2O_3 is –540 kJ mol^{-1} and that of Al_2O_3 is –827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with aluminium?

Ans. The two equations are:

$$\frac{4}{3}\text{Al}(s) + \text{O}_2(g) \longrightarrow \frac{2}{3}\text{Al}_2\text{O}_3(s); \quad \Delta_f G^\circ = -827 \text{ kJ mol}^{-1} \qquad ...(i)$$

$$\frac{4}{3}\text{Cr}(s) + \text{O}_2(g) \longrightarrow \frac{2}{3}\text{Cr}_2\text{O}_3; \quad \Delta_f G^\circ = -540 \text{ kJ mol}^{-1} \qquad ...(ii)$$

Subtracting equation (*ii*) from equation (*i*), we get

$$\frac{4}{3}\text{Al}(s) + \frac{2}{3}\text{Cr}_2\text{O}_3(s) \longrightarrow \frac{2}{3}\text{Al}_2\text{O}_3(s) + \frac{4}{3}\text{Cr}(s); \quad \Delta_r G^\circ = -287 \text{ kJ mol}^{-1}$$

As $\Delta_r G^\circ$ of the combined redox reaction is negative, therefore, reduction of Cr_2O_3 by Al is possible.

Q. 22. Out of C and CO, which is a better reducing agent for ZnO?

Ans. The free energy of formation ($\Delta_f G^\circ$) of CO from C becomes lower at temperatures above 1120 K whereas that of CO_2 from C becomes lower above 1323 K than $\Delta_f G^\circ$ of ZnO. However, $\Delta_f G^\circ$ of CO_2 from CO is always higher than that of ZnO. Therefore, C can reduce ZnO to Zn but not CO. Therefore, out of C and CO, C is a better reducing agent than CO for ZnO.

Q. 23. The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.

Ans. Thermodynamic factor helps us in choosing a suitable reducing agent for the reduction of a particular metal oxide to the metal state as described here.

From Ellingham diagram, it is evident that metals for which the standard free energy of formation of their oxides is more negative can reduce those metal oxides for which the standard free energy of formation of their respective oxides is less negative. In other words, any metal will reduce the oxides of other metals which lie above it in the Ellingham diagram because the standard free energy change ($\Delta_r G^\text{o}$) of the combined redox reaction will be negative by an amount equal to the difference in $\Delta_f G^\text{o}$ of the two metal oxides. Hence, both Al, Zn can reduce FeO to Fe but Fe cannot reduce Al_2O_3 to Al and ZnO to Zn. Similarly, C can reduce ZnO to Zn but not CO.

Q. 24. Name the processes by which chlorine is obtained as a by-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?

Ans. In the electrolysis of NaCl by Down's process, chlorine is obtained as a by-product. This process involves the electrolysis of a fused mixture of NaCl and $CaCl_2$ at 873 K. During electrolysis, sodium is liberated at the cathode and Cl_2 is obtained at the anode.

$$\text{NaCl}(l) \xrightarrow{\text{Electrolysis}} \text{Na}^+ \text{(melt)} + \text{Cl}^- \text{(melt)}$$

At cathode: $\text{Na}^+\text{(melt)} + e^- \longrightarrow \text{Na}(s)$

At anode: $\text{Cl}^- \text{(melt)} \longrightarrow \text{Cl}(g) + e^-$

$2\text{Cl}(g) \longrightarrow \text{Cl}_2(g)$

If an aqueous solution of NaCl is electrolysed, H_2 is evolved at the cathode and Cl_2 is obtained at the anode. The reason being that the E^o of Na^+/Na redox couple is much lower (E^o = – 2.71 V) than that of H_2O ($E^\text{o}_{H_2O/H_2}$ = – 0.83 V) and hence water is reduced to H_2 in preference to Na^+ ions. However, NaOH is obtained in the solution.

$$\text{NaCl}(aq) \xrightarrow{\text{Electrolysis}} \text{Na}^+(aq) + \text{Cl}^- (aq)$$

At cathode: $2\text{H}_2\text{O}(l) + 2e^- \longrightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$

At anode: $\text{Cl}^-(aq) \longrightarrow \text{Cl}(g) + e^-$

$2\text{Cl}(g) \longrightarrow \text{Cl}_2(g)$

Q. 25. What is the role of graphite in the electrometallurgy of aluminium?

Ans. In this process, a fused mixture of alumina, cryolite and fluorspar (CaF_2) is electrolysed using graphite as anode and steel vessel with lining of carbon as cathode. During electrolysis, Al is liberated at the cathode whereas CO and CO_2 are liberated at the anode.

Cathode: $$Al^{3+}\,(\text{melt}) + 3e^- \longrightarrow Al\,(l)$$

Anode: $$C\,(s) + O^{2-}\,(\text{melt}) \longrightarrow CO\,(g) + 2e^-$$

$$C\,(s) + 2O^{2-}\,(\text{melt}) \longrightarrow CO_2\,(g) + 4e^-$$

If some other metal is used as the anode other than graphite, then O_2 liberated will not only oxidise the metal of the electrode but would also convert some of the Al liberated at the cathode back to Al_2O_3.

So, the role of graphite in electrometallurgy of Al is to prevent the liberation of O_2 at the anode which may otherwise oxidise some of the liberated Al back to Al_2O_3.

Q. 26. Outline the principles of refining of metals by the following methods:

(*i*) Zone refining

(*ii*) Electrolytic refining and

(*iii*) Vapour phase refining

Ans. (*i*) Zone refining method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

(*ii*) Refer to Basic Concepts Point 9(*c*).

(*iii*) Refer to Basic Concepts Point 9(*e*).

Q. 27. Predict conditions under which Al might be expected to reduce MgO.

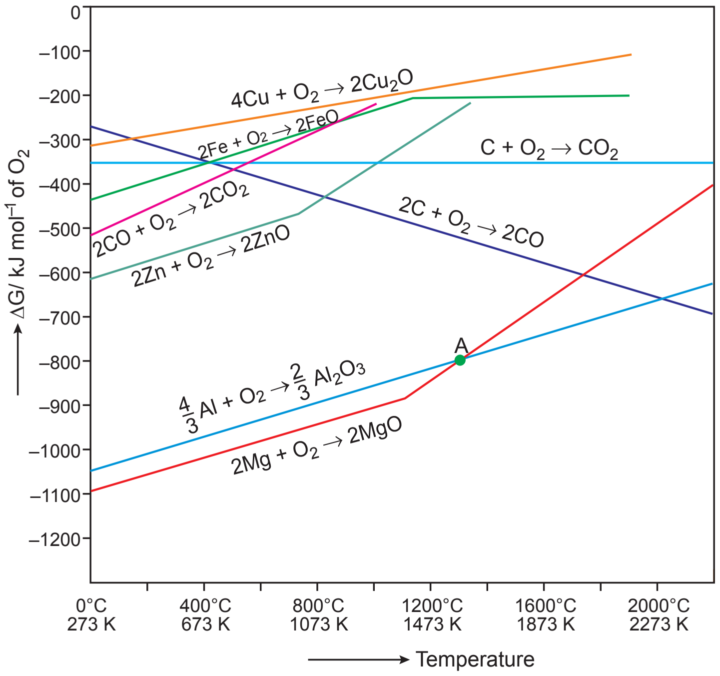
Ans. The two reactions are:

$$\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3; \qquad \Delta_f G^\circ (Al, Al_2O_3) \qquad \ldots(i)$$

$$2Mg + O_2 \longrightarrow 2MgO \qquad \Delta_f G^\circ (Mg, MgO) \qquad \ldots(ii)$$

The $\Delta_f G^\circ$ value of Al_2O_3, at temperatures below 1665 K, is less negative than that of MgO. [See Ellingham diagram]. Thus, when equation (*i*) is subtracted from equation (*ii*), $\Delta_r G^\circ$ of the two combined redox reactions, *i.e.*, equation (*iii*) is negative.

$$2Mg + \frac{2}{3}Al_2O_3 \longrightarrow 2MgO + \frac{4}{3}Al; \qquad \Delta_r G^\circ = -\text{ve} \qquad \ldots(iii)$$



Hence, below 1665 K, Mg can reduce Al_2O_3 to Al. Above 1665 K, the Δ_rG° value for Al_2O_3 is more negative than that of MgO. So, when equation (*ii*) is subtracted from equation (*i*), Δ_rG° of the two combined redox reactions, *i.e.*, equation (*iv*) is negative.

$$\frac{4}{3}Al + 2MgO \longrightarrow \frac{2}{3}Al_2O_3 + 2Mg; \qquad \Delta_rG^\circ = -ve \qquad \ldots(iv)$$

Hence, above 1665 K, Al can reduce MgO to Mg.

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Which of the following is known as 'the Wonder Material of the Orient'?

(*a*) Glass (*b*) Graphene
(*c*) Iron (*d*) Indian charcoal

2. A number of elements are available in earth's crust but most abundant elements are ______________. [*NCERT Exemplar*]

(*a*) Al and Fe (*b*) Al and Cu
(*c*) Fe and Cu (*d*) Cu and Ag

3. The salt which is least likely to be found in minerals is

(*a*) sulphide (*b*) chloride
(*c*) nitrate (*d*) sulphate

4. Which of the following is not a basic flux?

(*a*) $CaCO_3$ (*b*) CaO (*c*) SiO_2 (*d*) MgO

5. Calamine is an ore of

(*a*) Cu (*b*) Fe (*c*) Zn (*d*) Al

6. Sulphide ores are generally concentrated by

(*a*) froth floatation (*b*) roasting
(*c*) gravity (*d*) reduction of carbon

7. Heating of an ore in the absence of air below the melting point is called ________________.

(*a*) leaching (*b*) roasting
(*c*) smelting (*d*) calcination

8. Sulphide ores of metals are usually concentrated by froth floatation. Which one of the following sulphide ores is an exception and concentrated by leaching?

(*a*) Copper pyrite (*b*) Argentite
(*c*) Galena (*d*) Sphalerite

9. Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by ________________. [*NCERT Exemplar*]

(*a*) displacement of metal by some other metal from the complex ion.
(*b*) roasting of metal complex.
(*c*) calcination followed by roasting.
(*d*) thermal decomposition of metal complex.

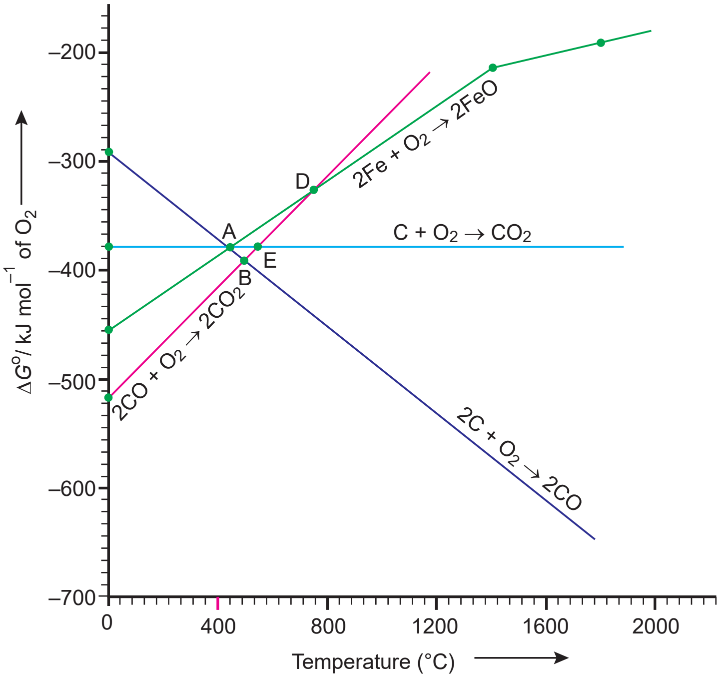
10. In aluminothermic process, Al acts as ________________.

(*a*) an oxidising agent (*b*) a flux
(*c*) a reducing agent (*d*) a solder

11. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with

(*a*) iron(II) sulphide (*b*) carbon monoxide
(*c*) copper(I) sulphide (*d*) sulphur dioxide

12. Choose the correct option of temperature at which carbon reduces FeO to iron and produces CO. *[NCERT Exemplar]*



(*a*) Below temperature at point A.

(*b*) Approximately at the temperature corresponding to point A.

(*c*) Above temperature at point A but below temperature at point D.

(*d*) Above temperature at point A.

13. Which of the following reactions taking place in the blast furnace during extraction of iron is endothermic?

(*a*) $C + O_2 \longrightarrow CO_2$

(*b*) $2C + O_2 \longrightarrow 2CO$

(*c*) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

(*d*) $CaCO_3 \longrightarrow CaO + CO_2$

14. In the blast furnace, at lower temperature range of 500–800 K

(*a*) Fe_2O_3 is first reduced to Fe_3O_4 and then to FeO

(*b*) Fe_2O_3 is first converted to FeO and then to Fe_3O_4

(*c*) Fe_3O_4 is converted to Fe_2O_3

(*d*) Fe_3O_4 is reduced to FeO

15. When copper ore is mixed with silica, in a reverberatory furnace copper matte is produced. The copper matte contains ________________. *[NCERT Exemplar]*

(*a*) sulphides of copper (II) and iron (II)

(*b*) sulphides of copper (II) and iron (III)

(*c*) sulphides of copper (I) and iron (II)

(*d*) sulphides of copper (I) and iron (III)

16. In the metallurgy of aluminium ________________. *[NCERT Exemplar]*

(*a*) Al^{3+} is oxidised to Al(*s*).

(*b*) graphite anode is oxidised to carbon monoxide and carbon dioxide.

(*c*) oxidation state of oxygen changes in the reaction at anode.

(*d*) oxidation state of oxygen changes in the overall reaction involved in the process.

17. In the extraction of aluminium by Hall-Heroult process, purified Al_2O_3 is mixed with CaF_2 to: *[NCERT Exemplar]*

(*a*) lower the melting point of Al_2O_3.

(*b*) increase the conductivity of molten mixture.

(*c*) reduce Al^{3+} into Al(*s*).

(*d*) acts as catalyst.

18. In the extraction of chlorine by electrolysis of brine ________________. [*NCERT Exemplar*]

(*a*) oxidation of Cl^- ion to chlorine gas occurs. (*b*) reduction of Cl^- ion to chlorine gas occurs.

(*c*) for overall reaction ΔG^o has negative value. (*d*) a displacement reaction takes place.

19. Electrolytic refining is used to purify which of the following metals? [*NCERT Exemplar*]

(*a*) Cu and Zn (*b*) Ge and Si (*c*) Zr and Ti (*d*) Zn and Hg

20. Zone refining is based on the principle that ________________. [*NCERT Exemplar*]

(*a*) impurities of low boiling metals can be separated by distillation.

(*b*) impurities are more soluble in molten metal than in solid metal.

(*c*) different components of a mixture are differently adsorbed on an adsorbent.

(*d*) vapours of volatile compound can be decomposed in pure metal.

21. Which method is useful for producing semiconductors and other methods of very high purity?

(*a*) Vapour phase refining (*b*) Distillation

(*c*) Electrolyte refining (*d*) Zone refining

22. Which method of purification is represented by the given equation?

$$\underset{\text{(Impure)}}{Ti} + 2I_2 \xrightarrow{500\text{ K}} TiI_4 \xrightarrow{1675\text{ K}} \underset{\text{(Pure)}}{Ti} + 2I_2$$

(*a*) Cupellation (*b*) Poling (*c*) Van Arkel (*d*) Zone refining

23. Which of the following options are correct? [*NCERT Exemplar*]

(*a*) Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast.

(*b*) In extraction of silver, silver is extracted as cationic complex.

(*c*) Nickel is purified by zone refining.

(*d*) Zr and Ti are purified by van Arkel method.

Answers

1. (*b*) **2.** (*a*) **3.** (*c*) **4.** (*c*) **5.** (*c*) **6.** (*a*) **7.** (*d*) **8.** (*b*) **9.** (*a*) **10.** (*c*)
11. (*c*) **12.** (*d*) **13.** (*d*) **14.** (*a*) **15.** (*c*) **16.** (*b*) **17.** (*a, b*) **18.** (*c*) **19.** (*a*) **20.** (*b*)
21. (*d*) **22.** (*c*) **23.** (*a*, *d*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(b) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(c) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(d) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. Assertion (*A*) : The reaction is feasible only when the value of ΔG is negative.
Reason (*R*) : ΔG is negative only when ΔS is positive.

2. Assertion (*A*) : Froth floatation process is used to concentrate the ore argentite.
Reason (*R*) : Argentite is a sulphide ore.

3. Assertion (*A*) : Sulphide ores are concentrated by Froth Floatation method.
Reason (*R*) : Cresols stabilise the froth in Froth Floatation method.

4. Assertion (*A*) : Gold is recovered from its solution containing aurocyanide complex by adding zinc dust.
Reason (*R*) : Zinc is more electropositive than gold.

5. **Assertion (*A*) :** Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.
Reason (*R*) : Copper is extracted by hydrometallurgy.

6. **Assertion (*A*) :** In smelting, roasted ore is heated with powdered coke in presence of a flux.
Reason (*R*) : Oxides are reduced to metals by C or CO. Impurities are removed as slag.

7. **Assertion (*A*) :** Iron obtained in solid state by using charcoal is called sponge iron block.
Reason (*R*) : Iron is converted into any useful product by hot forging.

8. **Assertion (*A*) :** Lead, tin and bismuth are purified by liquation method.
Reason (*R*) : Lead, tin and bismuth have low m.p. as compared to impurities.

9. **Assertion (*A*) :** To obtain metals in a high degree of purity we use zone-refining process for purification.
Reason (*R*) : During electrorefining pure metal is liberated at cathode.

10. **Assertion (*A*) :** Zone refining method is very useful for producing semiconductors.
Reason (*R*) : Semiconductors are of high purity.

11. **Assertion (*A*) :** Nickel can be purified by Mond process.
Reason (*R*) : $Ni(CO)_4$ is a volatile compound which decomposes at 460 K to give pure Ni.

12. **Assertion (*A*) :** Zirconium can be purified by Van Arkel method.
Reason (*R*) : ZrI_4 is volatile and decomposes at 1800 K.

Answers

1. (*c*) **2.** (*d*) **3.** (*b*) **4.** (*a*) **5.** (*b*) **6.** (*a*) **7.** (*b*) **8.** (*a*) **9.** (*b*) **10.** (*b*)
11. (*a*) **12.** (*a*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Ellingham diagram is the graphical representation of Gibbs energy or we can say that the plot of variation of ΔG_f° vs T for the formation of metal oxide from metals is called Ellingham diagram. It provides a basis for considering the choice of reducing agent in the reduction of oxides and helps us in predicting the feasibility of thermal reduction of an ore. The main role of a reducing agent in a metallurgical operation is to provide such a negative value of ΔG° which is large enough to make the sum of ΔG° of the oxidation and reduction reactions negative. Ellingham diagram facilitates the choice of the reducing agent for a particular metal oxide on this basis. It can also be used to determine the optimum temperature at which a particular metal can be used to reduce the metal oxide of another metal.

1. What is smelting?

Ans. The process of extracting a metal by reduction of its oxide with carbon is called smelting.

2. Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxides at high temperatures. Why? [*NCERT Exemplar*]

Ans. The reason being that at high temperatures, carbon and hydrogen form their carbides and hydrides respectively.

3. Write any one limitation of Ellingham diagram.

Ans. Ellingham diagram simply indicates whether a reaction is possible or not. It does not say about the kinetics of the reduction process, *i.e.*, how fast a reaction could be under given thermodynamics conditions.

4. What is the essential condition for understanding the theory of metallurgical transformation?

Ans. In order to understand the theory of metallurgical transformation, Gibbs energy must be known.

5. Carbon is able to reduce FeO to Fe, but it cannot reduce Al_2O_3 to Al around 800°C. Explain, why.

Ans. At 800°C, the sum of $\Delta G°$ for the reduction reaction and the oxidation reaction of carbon into carbon monoxide is negative. Hence, the reaction is feasible and carbon is able to reduce iron oxide to iron. On the other hand, at about 800°C, the sum of $\Delta G°$ for the oxidation reaction of carbon to carbon monoxide and $\Delta G°$ for the reduction reaction of Al_2O_3 to Al is not negative. Hence, carbon is unable to reduce Al_2O_3 into Al.

PASSAGE–2

For obtaining a particular metal, first we look for minerals which are naturally occurring chemical substances in the earth's crust and are obtained through mining. Out of many minerals in which a metal may be found, only a few are viable to be used as source of that metal. Such minerals are known as ores. A particular element may occur in a variety of compounds. The process of isolation of an element from its compound should be such that it is chemically feasible and commercially viable. For the purpose of extraction, bauxite is chosen for aluminium. For iron, usually the oxide ores which are abundant and do not produce polluting gases (like SO_2, that is produced in case of iron pyrites) are taken. The entire scientific and technological process used for isolation of the metal from its ore is known as metallurgy. The extraction and isolation of an element from its combined form involves various principles of chemistry. An ore is usually contaminated with earthly or undesired materials known as gangue. Removal of gangue from the ore is known as concentration of the ore. The various methods of concentration of ore are hydraulic washing, magnetic separation, froth floatation and leaching. After concentration of the ore, the two major steps are done, *i.e.*, Isolation of the metal from its concentrated ore and Purification of the metal.

1. How does mineral differ from an ore?

Ans. Minerals are the chemical compounds in which the metals occur in the earth while an ore is the mineral from which the metal is conveniently and economically extracted. Thus, all ores are the minerals but all minerals are not ores.

2. The purest form of iron is prepared by oxidizing impurities from cast iron in a reverberatory furnace. Which iron ore is used to line the furnace?

Ans. Haematite.

3. Why extraction of mineral is important?

Ans. Extraction of mineral produces metal which help us to build industries,infrastructure and important tools.

4. Out of PbS and $PbCO_3$ (ores or lead), which one is concentrated by froth floatation processes preferably?

Ans. PbS.

5. Which concentration method is used in case of aluminium?

Ans. Leaching.

Very Short Answer Questions [1 mark]

Q. 1. Name the chief ore of aluminium and zinc. *[CBSE (AI) 2014C]*

Ans.

Metal	**Chief ore**
Aluminium	Bauxite, $AlO_x(OH)_{3-2x}$, where $0 < x < 1$
Zinc	Zinc blende, ZnS

Q. 2. Copper and silver lie below in the electrochemical series and yet they are found in the combined state as sulphides in nature. Comment. *[HOTS]*

Ans. Due to high polarising power of Cu and Ag ions, their sulphides are even more stable than the metals.

Q. 3. What is the role of flux in metallurgical processes? *[NCERT Exemplar]*

Ans. Flux is used for making the molten mass more conducting.

Q. 4. What is a slag?

Ans. A slag is an easily fusible material which is formed when gangue still present in the roasted or the calcined ore combines with the flux. For example, in the metallurgy of iron, CaO (flux) combines with silica gangue to form easily fusible calcium silicate ($CaSiO_3$) slag.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (slag)}$$

Q. 5. What is meant by beneficiation process?

Ans. The process of removal of unwanted earthy and silicious impurities (gangue) from the ore is known as beneficiation process.

Q. 6. Why is it that only sulphide ores are concentrated by froth floatation process? [*CBSE (AI) 2011*]

Ans. This is because the sulphide ore particles are preferentially wetted by oil and gangue particles are preferentially wetted by water.

Q. 7. An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Name one chemical which can be used to concentrate galena selectively by froth floatation method.

Ans. NaCN (sodium cyanide) is used as a depressant to concentrate galena selectively by froth floatation method.

Q. 8. What name is given to carbon reduction process for extracting the metal?

Ans. Smelting

Q. 9. When is electrolytic reduction applied for getting a metal?

Ans. When chemical reduction is not feasible, *e.g.*, for the oxides of highly reactive metals, alkali metals, alkaline earth metals and other elements like Al, Zn, etc., electrolytic reduction is applied for getting a metal.

Q. 10. Zinc acts as a reducing agent in the extraction of silver. Comment. [*CBSE (AI) 2014*] [*HOTS*]

Ans. Zinc acts as reducing agent in the extraction of silver. It reduces Ag^+ to Ag and itself get oxidised to Zn^{2+}.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

Q. 11. What is the meant by the term pyrometallurgy?

Ans. The process of extracting the metal by heating the metal oxide with a suitable reducing agent is called pyrometallurgy.

Q. 12. What is the role of limestone in the extraction of iron from its oxides?

Ans. It provides the flux CaO which removes the impurity SiO_2 present in the ore by forming fusible calcium silicate slag.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2; \quad SiO_2 + \underset{\text{Flux}}{CaO} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

Q. 13. Which reducing agent is employed to get copper from the leached low grade copper ore? [*CBSE Delhi 2014*]

Ans. Scrap iron, $\quad Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$

or H_2 gas, $\quad Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$

Q. 14. Write a non-exothermic reaction taking place in a blast-furnace during extraction of iron.

Ans.

$$CaCO_3(s) \xrightarrow{1123\text{ K}} CaO(s) + CO_2(g); \Delta H = 179.9 \text{ kJ}$$

$$CO_2(g) + C(s) \longrightarrow 2CO(g); \Delta H = 163.2 \text{ kJ}$$

Q. 15. What is liquation?

Ans. Liquation is a method of refining of metals and is used when the impurities are not miscible with the metal and the melting temperature of the metal is lower than that of the impurities.

Q. 16. Name the method used for refining of zirconium. [*CBSE South 2016*]

Ans. Van Arkel method

Q. 17. **Name the method that is used for refining of nickel.** *[CBSE (AI) 2014]*

Ans. Mond process (Vapour phase refining)

Q. 18. **Name the method used for refining of copper metal.** *[CBSE (AI) 2014; 2020 (56/5/1)]*

Ans. Electrolytic refining

Q. 19. **Name the method of refining which is based on the principle of adsorption.**

Ans. Chromatography

Q. 20. **A mixture of X and Y was loaded in the column of silica. It was eluted by alcohol water mixture. Compound Y eluted in preference to compound X. Compare the extent of adsorption of X and Y on column.**

Ans. X is more strongly adsorbed as compared to Y.

Short Answer Questions–I [2 marks]

Q. 1. **The extraction of Au by leaching with NaCN involves both oxidation and reduction. Justify giving equations.**

Ans. $4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$

$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$

In the first reaction, Au changes into Au^+, *i.e.*, its oxidation takes place. In the second case, Au^+ changes to Au, *i.e.*, reduction takes place.

Q. 2. **What should be the considerations during the extraction of metals by electrochemical method?** *[NCERT Exemplar]*

Ans. Generally two things are considered so that proper precautions can be taken.

(*i*) Reactivity of metal produced.

(*ii*) Suitability of electrodes.

Q. 3. **Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why?**

Ans. Temperatures below the point of intersection of Al_2O_3 and MgO curves, magnesium can reduce alumina. But magnesium is a much costlier metal than aluminium and hence the process will be uneconomical.

Q. 4. **The purest form of iron is prepared by oxidising impurities from cast iron in a reverberatory furnace. Which iron ore is used to line the furnace? Explain by giving reaction.** *[NCERT Exemplar]*

Ans. Haematite.

$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$

Q. 5. **Write down the reactions taking place in blast furnace related to the metallurgy of iron in the temperature range 500–800 K.** *[NCERT Exemplar] [CBSE 2019 (56/3/2)]*

Ans. $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2\uparrow$

$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2\uparrow$

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2\uparrow$

Q. 6. (*i*) **Which solution is used for the leaching of silver metal in the presence of air in the metallurgy of silver?**

(*ii*) **Out of C and CO, which is a better reducing agent at the lower temperature range in the blast furnace to extract iron from the oxide ore?** *[CBSE Delhi 2013]*

Ans. (*i*) Dilute solution of NaCN.

(*ii*) CO.

Q. 7. (*i*) **Which of the following ores can be concentrated by froth floatation method and why?**

Fe_2O_3, ZnS, Al_2O_3.

(*ii*) **What is the role of silica in the metallurgy of copper?** *[CBSE Delhi 2013]*

Ans. (*i*) ZnS. This is because the sulphide ore particles are preferentially wetted by oil and gangue particles are preferentially wetted by water.

(*ii*) Silica acts as a flux to remove impurity, iron oxide (FeO) as slag in the metallurgy of copper.

$$\mathrm{FeO} + \underset{\text{Flux}}{\mathrm{SiO_2}} \longrightarrow \underset{\text{Slag}}{\mathrm{FeSiO_3}}$$

Q. 8. Describe the principle controlling each of the following processes:

(*i*) Preparation of cast iron from pig iron.

(*ii*) Preparation of pure alumina (Al_2O_3) from bauxite ore. ***[CBSE (AI) 2011]***

Ans. (*i*) Pig iron is melt with scrap iron and coke using hot air blast. Due to this, impurities such as C, S and P present in the pig iron are removed as CO_2, SO_2 and P_2O_5 and carbon content reduced to about 3%.

(*ii*) Bauxite is soluble in concentrated NaOH solution whereas impurities are not.

Q. 9. (*i*) Indicate the principle behind the method used for the refining of zinc.

(*ii*) Which form of the iron is the purest form of commercial iron? ***[CBSE Delhi 2010; (AI) 2014]***

Ans. (*i*) Distillation, as zinc is a low boiling metal.

(*ii*) Wrought iron is the purest form of commercial iron.

Q. 10. How are metals used as semiconductors refined? What is the principle of the method used? ***[NCERT Exemplar]***

Ans. Semiconducting metal is produced by zone refining method which is based on the principle that the impurities are more soluble in melt than in the solid state of metals.

Q. 11. Write the role of the following:

(*i*) CO in the purification of nickel. ***[CBSE 2020 (56/3/1)]***

(*ii*) Graphite rod in the electrometallurgy of aluminium. ***[CBSE (F) 2014]***

Ans. (*i*) Impure nickel when heated in a current of CO forms volatile complex nickel tetracarbonyl, $Ni(CO)_4$ leaving behind impurities.

$$\mathrm{Ni} + 4\mathrm{CO} \xrightarrow{330-350\mathrm{K}} \mathrm{Ni(CO)_4}$$

The nickel tetracarbonyl complex thus obtained is then heated to a higher temperature so that it is decomposed to give pure metal.

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

(*ii*) Graphite rod acts as anode and steel vessel lined with carbon acts as cathode in the electrometallurgy of aluminium.

Carbon reacts with oxygen liberated at anode producing CO and CO_2 otherwise oxygen liberated at the anode may oxidise some of the liberated aluminium back to Al_2O_3.

At Anode: $\mathrm{C}(s) + \mathrm{O}^{2-}(\text{melt}) \longrightarrow \mathrm{CO}(g) + 2e^-$

$\mathrm{C}(s) + 2\mathrm{O}^{2-}(\text{melt}) \longrightarrow \mathrm{CO_2}(g) + 4e^-$

At Cathode: $\mathrm{Al}^{3+}(\text{melt}) + 3e^- \longrightarrow \mathrm{Al}\,(l)$

Q. 12. Describe the principle involved in each of the following processes.

(*i*) Mond process for refining of Nickel.

(*ii*) Column chromatography for purification of rare elements. ***[CBSE Delhi 2012]***

Ans. (*i*) In Mond process, nickel is converted into its volatile complex, tetracarbonyl nickel and gets collected elsewhere. It is then decomposed to give pure nickel.

$$\underset{\substack{\text{Impure}\\\text{nickel}}}{\mathrm{Ni}} + 4\mathrm{CO} \xrightarrow{330\text{–}350\ \mathrm{K}} \underset{\substack{\text{Tetracarbonyl}\\\text{nickel (volatile)}}}{\mathrm{Ni(CO)_4}};\quad \mathrm{Ni(CO)_4} \xrightarrow{450\text{–}470\ \mathrm{K}} \underset{\substack{\text{Pure}\\\text{nickel}}}{\mathrm{Ni}} + 4\mathrm{CO}$$

(*ii*) Column chromatography is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. In purification of rare earth elements ion-exchange is used as an adsorbent.

Short Answer Questions–II [3 marks]

Q. 1. How is the concept of coupling reactions useful in explaining the occurrence of non-spontaneous thermochemical reactions? Explain by giving an example.

Ans. Many reactions which are non-spontaneous (ΔG is +ve) can be made to occur spontaneously if these are coupled with reactions having larger negative free energy. By coupling means carrying out simultaneously both non-spontaneous and spontaneous reactions. For example, decomposition of Fe_2O_3 into iron is a non-spontaneous reaction ($\Delta G^o = +1487$ kJ mol^{-1}). However, this decomposition can take place spontaneously if carbon monoxide is simultaneously burnt in oxygen ($\Delta G = -514.4$ kJ mol^{-1}).

$$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g) \quad ...(i); \quad \Delta G^o = +1487.0 \text{ kJ mol}^{-1}$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \quad ...(ii); \quad \Delta G^o = -514.4 \text{ kJ mol}^{-1}$$

Multiplying equation (*ii*) by 3 and then adding to equation (*i*), we get

$$6CO(g) + 3O_2(g) \longrightarrow 6CO_2(g); \quad \Delta G^o = -1543.2 \text{ kJ mol}^{-1}$$

$$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g); \quad \Delta G^o = +1487.0 \text{ kJ mol}^{-1}$$

$$\overline{2Fe_2O_3(s) + 6CO(g) \longrightarrow 4Fe(s) + 6CO_2(g); \quad \Delta G^o = -56.2 \text{ kJ mol}^{-1}}$$

Since, ΔG^o in the reduction of Fe_2O_3 with CO is –ve, therefore, the reaction is feasible and spontaneous.

Q. 2. Free energies of formation ($\Delta_f G$) of MgO(*s*) and CO(*g*) at 1273 K and 2273 K are given below.

$\Delta_f G[MgO(s)] = -941$ kJ/mol at 1273 K
$\Delta_f G[MgO(s)] = -314$ kJ/mol at 2273 K
$\Delta_f G[CO(g)] = -439$ kJ/mol at 1273 K
$\Delta_f G[CO(g)] = -628$ kJ/mol at 2273 K

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO(*s*).

Ans. At 1273 K,

$$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s); \quad \Delta_f G = -941 \text{ kJ/mol} \quad ...(i)$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta_f G = -439 \text{ kJ/mol} \quad ...(ii)$$

Subtracting equation (*i*) from equation (*ii*), we get

$$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g); \quad \Delta_r G = 502 \text{ kJ/mol}$$

As $\Delta_r G$ for the above reduction reaction is positive, therefore, reduction of MgO by C is not feasible at 1273 K.

At 2273 K,

$$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s); \quad \Delta_f G = -314 \text{ kJ/mol} \quad ...(iii)$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta_f G = -628 \text{ kJ/mol} \quad ...(iv)$$

Subtracting equation (*iii*) from equation (*iv*), we get

$$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g); \quad \Delta_r G = -314 \text{ kJ/mol}$$

As $\Delta_r G$ for the above reduction reaction is –ve, therefore, reduction of MgO by carbon at 2273 K is feasible and hence, carbon can be used as a reducing agent.

Q. 3. Account for the following facts: [*CBSE Sample Paper 2016*]

(*i*) The reduction of a metal oxide is easier if the metal formed is in the liquid state at the temperature of reduction.

(*ii*) Limestone is used in the manufacture of pig iron from haematite.

(*iii*) Pine oil is used in the froth floatation process used to concentrate sulphide ores.

Ans. (*i*) The entropy is higher if the metal is in liquid state than when it is in solid state. The value of entropy change (ΔS) of the reduction process is more on +ve side when the metal formed is in liquid state and the metal oxide being reduced in solid state. Since the value of $T\Delta S$ increases and that of ΔH remains constant, therefore, the value of $\Delta_r G°$ ($\Delta G = \Delta H - T\Delta S$) becomes more –ve and hence the reduction becomes easier.

(*ii*) Limestone provides the flux, CaO which combines with impurity, SiO_2 to form easily fusible $CaSiO_3$ slag. Thus, it helps in the removal of impurity silica, SiO_2.

(*iii*) Pine oil (collector) enhances the non-wettability of the ore particles, which become lighter and hence rise to the surface along with the froth.

Q. 4. (*i*) Give one example of each of the following:

(*a*) Acidic flux **(*b*) Basic flux**

(*ii*) What happens when:

(*a*) Cu_2O undergoes self reduction in a silica line converter.

(*b*) Haematite oxidises carbon to carbon monoxide. [*CBSE Sample Paper 2013*]

Ans. (*i*) (*a*) Acidic flux: SiO_2

(*b*) Basic flux: CaO

(*ii*) (*a*) Cu_2O undergoes self reduction to form blister copper as

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

(*b*) $Fe_2O_3 + 3C \longrightarrow 3CO + 2Fe$

Q. 5. What happens when

(*i*) Silver is leached with NaCN in the presence of air?

(*ii*) Copper matte is charged into silica lined converter and hot air blast is blown?

(*iii*) NaCN is added in an ore containing PbS and ZnS during concentration by froth floatation method? [*CBSE 2019 (56/3/2)*]

Ans. (*i*) During leaching process, Ag in the presence of O_2 combines with CN^- to form soluble complex, sodium dicyanoargentate [$Na(Ag(CN)_2)$].

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

(*ii*) When copper matte is charged into silica lined converter and hot air blast is blown the following reactions take place.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$\underset{\text{Impurity}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \uparrow$$

The solidified copper obtained has blistered appearance due to the evolution of SO_2, so it is called blister copper.

(*iii*) NaCN selectively prevents ZnS from coming to froth by forming complex sodium tetracyanozincate, $Na_2[Zn(CN)_4]$, but allows PbS to come with the froth.

$$4NaCN + ZnS \longrightarrow Na_2[Zn(CN)_4] + Na_2S$$

Q. 6. Name the chief ore of silver. Describe with chemical equations the extraction of silver from this ore.

Ans. The chief ore of silver is argentite or silver glance (Ag_2S).

The extraction of silver from argentite: Argentite ore is treated with dilute solution of NaCN in presence of oxygen to oxidise sodium sulphide to sodium sulphate to form a soluble complex.

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

Zn acts as reducing agent and displaces silver from the complex.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

The crude Ag metal thus obtained is refined by fusion with borax or by electrolysis.

Q. 7. Write the chemical reactions involved in the process of extraction of Gold. Explain the role of dilute NaCN and Zn in this process. *[CBSE 2018]*

Ans. $4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \longrightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$

$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$

In this process NaCN acts as a complexing agent whereas Zn acts as a reducing agent.

Q. 8. (*i*) Write the name of the method used for the refining of the following metals:

(*a*) Titanium **(*b*) Germanium**

(*c*) Copper *[CBSE 2019 (56/2/1)]*

(*ii*) Write the name of the method of concentration applied for the following ores:

(*a*) Zinc blende **(*b*) Haematite**

(*c*) Bauxite *[CBSE (F) 2017]*

Ans. (*i*) (*a*) Van Arkel method (vapour phase refining)

(*b*) Zone refining

(*c*) Electrolytic refining

(*ii*) (*a*) Froth floatation method

(*b*) Magnetic separation

(*c*) Leaching

Q. 9. (*i*) Write the principle of vapour phase refining.

(*ii*) Write the role of dilute NaCN in the extraction of silver.

(*iii*) What is the role of collectors in the froth floatation process? Give an example of a collector. *[CBSE (AI) 2017]*

Ans. (*i*) Refer to Basic Concepts Point 9(*e*).

(*ii*) NaCN acts as a leaching agent to form soluble complex with Ag, while the impurities remain unaffected which are then filtered off.

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow \underset{\text{Soluble complex}}{4Na[Ag(CN)_2]} + 4NaOH$$

(*iii*) Collectors enhance non-wettability of the ore particles in the froth floatation process, *e.g.*, pine oils, fatty acids, xanthates, etc.

Q. 10. (*i*) Write the principle of method used for the refining of germanium.

(*ii*) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably?

(*iii*) What is the significance of leaching in the extraction of aluminium? *[CBSE Delhi 2017]*

Ans. (*i*) The impurities are more soluble in the melt than in the solid state of the metal.

(*ii*) PbS.

(*iii*) Leaching is significant as it helps in removing impurities like SiO_2, Fe_2O_3 and TiO_2, etc. from the powdered bauxite ore by heating it with concentrated solution of NaOH.

Q. 11. ***(i)*** **Write the principle of electrolytic refining.**

(ii) **Why does copper obtained in the extraction from copper pyrites have a blistered appearance?**

(iii) **What is the role of depressants in the froth floatation process?** ***[CBSE(AI) 2017]***

Ans. (*i*) On passing electric current, the metal ions from the electrolytic solution are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolytic solution as metal ions *i.e.*,

At cathode: $M^{n+}(aq) + ne^- \longrightarrow M(s)$

At anode: $M(s) \longrightarrow M^{n+}(aq) + ne^-$

(*ii*) The blistered appearance is due to evolution of SO_2 gas.

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

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

(*iii*) Depressant selectively prevents one of the sulphide ore from coming to the froth, *e.g.*, NaCN in the concentration of PbS. It selectively prevents ZnS from coming to the froth by forming complex $Na_2[Zn(CN)_4]$ but allows PbS to come with the froth.

Q. 12. Describe how the following changes are brought about:

(i) **Pig iron into steel.**

(ii) **Zinc oxide into metallic zinc.**

(iii) **Impure titanium into pure titanium.** ***[CBSE Delhi 2010; (AI) 2010]***

Ans. (*i*) Pig iron is converted into steel by heating in a converter. A blast of oxygen diluted with carbon dioxide is blown through the converter. Oxygen reacts with impurities and raises the temperature to 2173 K. Carbon gets oxidised to CO which burns off at the mouth of the converter. Oxides of silicon and Mg form slag. When the flame is stopped, slag is tapped off and other metals like Mn, Cr, Ni, W may be added in the end.

(*ii*) The reduction of zinc oxide is done using coke, as a reducing agent. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO\uparrow$$

The metal is distilled off and collected by rapid chilling.

(*iii*) Impure titanium is heated with iodine to form volatile TiI_4, which decomposes on tungsten filament at high temperature to give pure titanium.

$$\underset{\text{Impure}}{Ti(s)} + 2I_2(g) \xrightarrow{523\text{ K}} TiI_4(g) \xrightarrow{1700\text{ K}} \underset{\text{Pure}}{Ti(s)} + 2I_2(g)$$

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. **The metal extracted by auto reduction is**

(*a*) Zn (*b*) Ag

(*c*) Cu (*d*) Fe

2. **Which of the following metals is leached by cyanide process?**

(*a*) Ag (*b*) Na

(*c*) Al (*d*) Cu

3. **Pyrolusite is a/an**

(*a*) oxide ore (*b*) sulphide ore

(*c*) carbide ore (*d*) not an ore

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. Assertion (A) : All the reactive elements occur in the combined state in nature.

Reason (R) : The compounds of reactive metals are more stable than the metals themselves.

5. Assertion (A) : The collectors used in froth floatation process help ore particles to pass on into the froth.

Reason (R) : The collectors get attached to the polar groups of the grains of mineral and make them water repellent.

6. Assertion (A) : Fe is more abundant than C on earth.

Reason (R) : Fe is a volatile element, whereas C is non-volatile.

Answer the following questions:

7. What is slag? **(1)**

8. Name the purest form of iron. What is the percentage of carbon in it? **(1)**

9. Why is an external emf of more than 2.2 V required for the extraction of Cl_2 from brine? **(2)**

10. Give two requirements for vapour phase refining. **(2)**

11. Describe the principle controlling each of the following processes:

(*i*) Refining by liquation. (*ii*) Electrolytic refining of metal. **(2)**

12. Why is it advantageous to roast a sulphide ore to the oxide before reduction? **(2)**

13. Name one chief ore each of copper and aluminium. Name the method used for concentration of these two ores. **(2)**

14. Write the chemical reactions which take place in the following operations:

(*i*) Isolation of zinc from zinc blende.

(*ii*) Recovery of silver after silver ore has been leached with NaCN solution.

(*iii*) van Arkel method for refining zirconium. **(3)**

15. What chemical principle is involved in choosing a reducing agent for getting the metal from the oxide ore? Consider the metal oxides, Al_2O_3 and FeO and justify the choice of reducing agent in each case. **(3)**

16. Explain the following:

(*i*) Partial roasting of sulphide ore is done in the metallurgy of copper.

(*ii*) Carbon and hydrogen are not used as reducing agents at high temperatures.

(*iii*) Vapour phase refining is used for the purification of Zr. **(3)**

17. What is the role of

(*i*) Depressants in froth floatation?

(*ii*) Carbon monoxide in Mond's process?

(*iii*) Concentrated sodium hydroxide in leaching of alumina from bauxite? **(3)**

Answers

1. (*c*) **2.** (*a*) **3.** (*a*) **4.** (*a*) **5.** (*a*) **6.** (*c*)

Chapter–7

The *p*-Block Elements

basic concepts

1. **p-Block Elements:** The elements of Group 13 (Boron family–B, Al, Ga, In, Tl); Group 14 (Carbon family–C, Si, Ge, Sn, Pb); Group 15 (Nitrogen family–N, P, As, Sb, Bi, Mc); Group 16 (Oxygen family–O, S, Se, Te, Po, Lv); Group 17 (Halogen family–F, Cl, Br, I, At, Ts) and Group 18 (Noble gases–He, Ne, Ar, Kr, Xe, Rn, Og) receive their last electron in their *np* orbitals. All these elements are therefore, called *p*-block elements. They are represented by general outer electronic configuration $ns^2\ np^{1–6}$.

   Common characteristics of *p*-block elements

   (*i*) *p*–Block elements exist in all the three physical states and may be metals, non-metals or metalloids.

   (*ii*) Ionisation energy increases across a period and decreases down the group.

   (*iii*) They have high value of electronegativity which decreases down the group but increases across a period. Fluorine has the highest value of electronegativity.

   (*iv*) They have high electron affinity. Generally, electron affinity increases from left to right in a period and decreases from top to bottom in a particular group.

   (*v*) The atomic and ionic radii of *p*-block elements decreases on moving across in a period and increases down a group.

   (*vi*) Except oxygen, fluorine and zero group elements, all other elements exhibit positive and negative oxidation states. Due to inert pair effect some of the *p*-block elements exhibit variable oxidation states, *e.g.*, Sn (II) and Sn (IV); Pb (II) and Pb (IV); Tl (I) and Tl (III), etc.

   (*vii*) P, O, S and halogens are very reactive while other elements of *p*-block are less reactive.

   (*viii*) As we move from Group 13 to 17 in the *p*-block, the reducing character decreases and the oxidising character increases. Thus, halogens are the best oxidising agents.

2. **Inert Pair Effect:** In the *p*-block elements as we go down a group, the intervening *d* and *f* orbitals, due to their poor screening effect result in the greater attraction on the ns^2 electrons. This pair of electrons cannot, therefore, take part in the bonding. This effect is called "inert pair effect".

3. **General Characteristics of *p*-Block Elements (Groups 15–18)**

Group 15

(A) General Information

1. **Name:** Nitrogen family
2. **Elements:** ${}_7N$, ${}_{15}P$, ${}_{33}As$, ${}_{51}Sb$, ${}_{83}Bi$
3. **Electronic Configuration:** ${}_7N = [He]\ 2s^2\ 2p^3$; ${}_{15}P = [Ne]\ 3s^2\ 3p^3$;
${}_{33}As = [Ar]\ 3d^{10}\ 4s^2\ 4p^3$; ${}_{51}Sb = [Kr]\ 4d^{10}\ 5s^2\ 5p^3$;
${}_{83}Bi = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$; ${}_{115}Mc = [Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^3$.

(B) Atomic and Physical Properties

1. **Atomic Radii:** They are smaller than the corresponding elements of Group 14 because of increase in nuclear charge. Down the group they show an increase mainly due to addition of a new shell.
2. **Oxidation States:** Because of small size, N and P can gain three electrons to complete their octets and hence show an oxidation state of – 3. In addition to – 3 oxidation state, the elements of Group 15 also show +3 and +5 oxidation states. Nitrogen exhibits all the oxidation states from – 3 to +5.
3. **Ionisation Enthalpy (IE):** IEs of these elements are much higher than the corresponding elements of Group 14 because of increase in nuclear charge and greater stability of exactly half-filled orbitals. Down the group the values decrease due to increase in atomic size.
4. **Metallic Character:** Metallic character increases down the group due to decrease in ionisation enthalpy and increase in atomic size. Thus, N and P are non-metals, As and Sb are metalloids while Bi is a typical metal.
5. **Electronegativity:** These are more electronegative than Group 14 elements because of further decrease in size. It decreases down the group because of increase in atomic size.
6. **Melting Points and Boiling Points:** Melting points first increase from N to As due to increase in nuclear charge and then decrease from Sb to Bi. The decrease is due to increase in size and weakening of interatomic forces and also due to inert pair effect resulting in the formation of 3 bonds instead of 5.
7. **Density:** The densities increase regularly down the group as usual.

(C) Chemical Properties

1. **Hydrides:** They form covalent hydrides with the formula EH_3.

   Properties of Hydrides

   (*i*) **Thermal stability:** It decreases down the group because the size of the atom increases and hence the bond dissociation enthalpy decreases.

   (*ii*) **Reducing character:** It increases down the group due to decrease in bond dissociation enthalpy. Except NH_3, all are strong reducing agents.

   (*iii*) **Basic character:** It decreases down the group because as atomic size increases, electron density decreases on central atom E, *i.e.*, the order is $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

   (*iv*) **Boiling points:** Boiling point of NH_3 is greater than PH_3 because of intermolecular hydrogen bonding. Boiling points increase from PH_3 onwards because of increase of molecular mass and hence van der Waals forces.

2. **Halides**

   Trihalides: All of these elements directly combine with halogens to form trihalides of the type EX_3. Except NBr_3 and NI_3, all are stable and have pyramidal shape. They are easily hydrolysed by water.

   Pentahalides: P, As and Sb form pentahalides of the formula EX_5. N does not form pentahalide because of non-availability of *d*-orbital in its valence shell. Bi does not form pentachloride due to inert pair effect. Pentahalides involve sp^3d hybridisation and have trigonal bipyramidal shape.

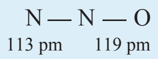
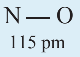
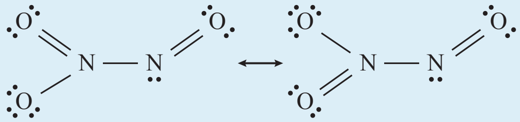
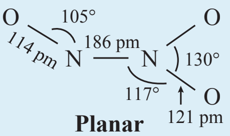
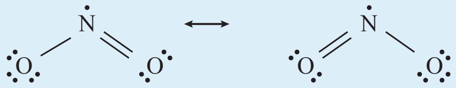
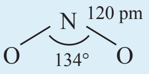
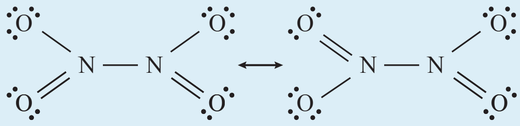
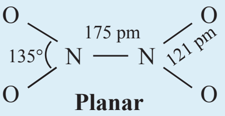
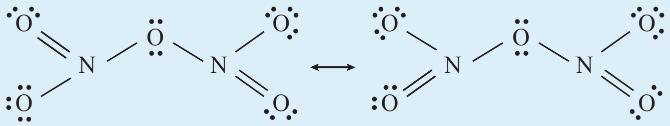
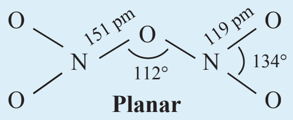
3. **Oxides:** All these elements form two types of oxides—E_2O_3 and E_2O_5. The oxide in the higher oxidation state is more acidic than that of lower oxidation state. Their acidic character decreases down the group.

Table 7.1: Oxides of Nitrogen

Name	Formula	Oxidation State of Nitrogen	Common Methods of Preparation	Physical Appearance and Chemical Nature
Dinitrogen oxide [Nitrogen (I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral

Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$	Blue solid, acidic
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$	Brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen (V) oxide]	N_2O_5	+ 5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

Table 7.2: Structures of Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O		 **Linear**
NO		
N_2O_3		 **Planar**
NO_2		 **Angular**
N_2O_4		 **Planar**
N_2O_5		 **Planar**

Oxides of phosphorus: Two important oxides of phosphorus are P_4O_6 (a dimer of P_2O_3) and P_4O_{10} (a dimer of P_2O_5). These are obtained as follows:

$$P_4 + 3O_2(\text{limited}) \xrightarrow{\Delta} P_4O_6$$

$$P_4 + 5O_2(\text{excess}) \xrightarrow{\Delta} P_4O_{10}$$

Oxides of other elements: As_4O_6 , As_2O_5 , Sb_4O_6 , Sb_2O_5 , Bi_2O_3 and Bi_2O_5.

Properties: Trioxides of N, P and As are acidic. The acidic character decreases down the group. Oxide of Sb is amphoteric while that of Bi is basic. All pentoxides are acidic. Acidic character decreases down the group. N_2O_5 is the strongest acidic oxide while Bi_2O_5 is the weakest.

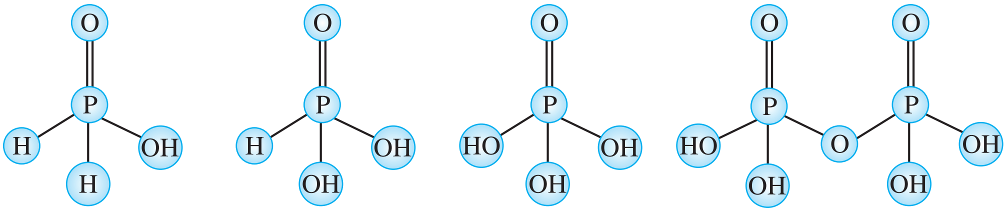
4. **Oxo-acids:** The elements of this group form a number of oxo-acids out of which those of nitrogen and phosphorus are more common.

Oxo-acids of Nitrogen:

Formula (Name)	Oxidation state of N
$H_2N_2O_2$ (Hyponitrous acid)	+ 1
HNO_2 (Nitrous acid)	+ 3
HNO_3 (Nitric acid)	+ 5

Oxo-acids of Phosphorus:

Formula (Name)	Oxidation state	Basicity
H_3PO_2 (Hypophosphorous acid)	+ 1	1
H_3PO_3 (Orthophosphorous acid)	+ 3	2
H_3PO_4 (Orthophosphoric acid)	+ 5	3
$H_4P_2O_7$ (Pyrophosphoric acid)	+ 5	4



Hypophosphorous acid (H_3PO_2) Orthophosphorous acid (H_3PO_3) Orthophosphoric acid (H_3PO_4) Pyrophosphoric acid ($H_4P_2O_7$)

Fig. 7.1: Structure of oxoacids of phosphorus

Preparation of H_3PO_3 and H_3PO_4

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Acids in +3 oxidation state of phosphorus tend to disproportionate, *e.g.*,

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

The acids which contain P–H bonds have strong reducing properties. Thus, hypophosphorus acid is a good reducing agent as it contains two P–H bonds and reduces $AgNO_3$ to metallic silver.

$$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$$

H atoms which are attached with oxygen in P–OH are ionisable and cause the basicity. Thus, H_3PO_4 and H_3PO_3 are tribasic and dibasic, respectively, as the structure of H_3PO_4 has three P–OH bonds and H_3PO_3 has two.

5. **Dinitrogen (N_2)**

In the laboratory, it is prepared by heating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l) + NaCl(aq)$$

It can also be prepared by heating ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

Properties of dinitrogen: N_2 has very little reactivity at ordinary temperature. The chemical inertness of dinitrogen is attributed to high bond enthalpy of $N \equiv N$ bond (946 kcal/mol).

It forms nitrides with highly electropositive metals like lithium, calcium and magnesium, etc.

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

It combines with dioxygen at about 2000 K to form nitric oxide, NO.

$$N_2 + O_2(g) \overset{\text{Heat}}{\rightleftharpoons} 2NO(g)$$

Uses:

1. It is used in the manufacture of ammonia.
2. Liquid nitrogen is used as a refrigerant to preserve biological materials.

6. Ammonia (NH_3)

In the laboratory, it is prepared by heating a mixture of slaked lime and ammonium chloride. Ammonia is obtained on small scale by heating ammonium salts with bases.

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\text{Heat}} 2NH_3 + CaCl_2 + 2H_2O$$

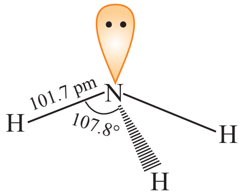
$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

Manufacture of ammonia:

Ammonia is generally manufactured by Haber's process which involves the direct combination of nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \underset{773\text{ K}}{\overset{\text{Fe/Mo}}{\rightleftharpoons}} 2NH_3(g); \quad \Delta H = -46.1\text{ kJ/mol}$$

Properties of ammonia: It has trigonal pyramidal structure with three bond pairs and one lone pair of electrons.



It is extremely soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

It forms salts with acids, *e.g.*, NH_4Cl, $(NH_4)_2SO_4$, etc.

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{(White ppt.)}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

$$2FeCl_3(aq) + 3NH_4OH(aq) \longrightarrow \underset{\text{(Brown ppt.)}}{Fe_2O_3.xH_2O(s)} + 3NH_4Cl(aq)$$

Ammonia acts as Lewis base due to the presence of a lone pair of electrons on nitrogen and hence forms a number of complexes with metal ions.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}(aq)}$$

$$\underset{\text{White ppt.}}{AgCl(s)} + 2NH_3(aq) \longrightarrow \underset{\text{Colourless}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses:

1. It is used to produce various nitrogenous fertilizers.
2. It is used in the manufacture of some inorganic nitrogen compounds like nitric acid.

7. Nitric Acid (HNO_3)

Laboratory preparation: In the laboratory, it can be prepared by heating $NaNO_3$ or KNO_3 with concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow NaHSO_4 + HNO_3$$

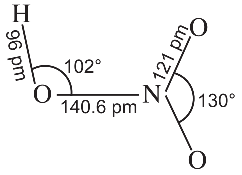
Manufacture of HNO_3 (Ostwald's process):

The reaction involving manufacture of HNO_3 are as follows:

$$4NH_3(g) + \underset{\text{(From air)}}{5O_2(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt/Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$



Properties of HNO_3: When pure, it is a colourless liquid. The impure acid is generally yellow due to the presence of NO_2 as impurity. Nitric acid containing dissolved nitrogen dioxide is known as fuming nitric acid.

In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown alongside.

In an aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Oxidising agent: Nitric acid is very strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of acid, temperature and the nature of the material undergoing oxidation.

$$3Cu + 8HNO_3(\text{dil.}) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$4Zn + 10HNO_3(\text{dil.}) \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(\text{conc.}) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

Metals such as Cr, Al do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Oxidation of non-metals:

Sulphur is oxidised to sulphuric acid.

$$\begin{array}{lll} & 2HNO_3 \longrightarrow & H_2O + 2NO_2 + (O)] \times 24 \\ S_8 + 24(O) + 8H_2O & \longrightarrow & 8H_2SO_4 \\ \hline S_8 + 48HNO_3 & \longrightarrow & 8H_2SO_4 + 48NO_2 + 16H_2O \\ \hline \end{array}$$

Carbon is oxidised to carbon dioxide.

$$\begin{array}{lll} & 2HNO_3 \longrightarrow & H_2O + 2NO_2 + (O)] \times 2 \\ C + 2(O) + H_2O & \longrightarrow & CO_2 + H_2O \\ \hline C + 4HNO_3 & \longrightarrow & CO_2 + 2H_2O + 4NO_2 \\ \hline \end{array}$$

Iodine is oxidised to iodic acid (HIO_3).

$$\begin{array}{lll} & 2HNO_3 \longrightarrow & H_2O + 2NO_2 + (O)] \times 5 \\ I_2 + 5(O) & \longrightarrow & I_2O_5 \\ I_2O_5 + H_2O & \longrightarrow & 2HIO_3 \\ \hline I_2 + 10HNO_3 & \longrightarrow & 2HIO_3 + 10NO_2 + 4H_2O \\ \hline \end{array}$$

Phosphorus is oxidised to phosphoric acid.

$$\begin{array}{lll} & 2HNO_3 \longrightarrow & H_2O + 2NO_2 + (O)] \times 10 \\ P_4 + 10(O) & \longrightarrow & P_4O_{10} \\ P_4O_{10} + 6H_2O & \longrightarrow & 4H_3PO_4 \\ \hline P_4 + 20HNO_3 & \longrightarrow & 4H_3PO_4 + 20NO_2 + 4H_2O \\ \hline \end{array}$$

Brown Ring test for NO_3^- ion:

The brown ring test for nitrates depend on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown-coloured complex.

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

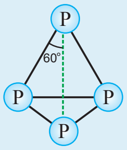
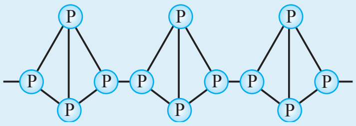
$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

8. Phosphorus

Allotropic forms of phosphorus are:

1. White or yellow phosphorus
2. Black phosphorus
3. Red phosphorus

Table 7.3: Differences between the Properties of White and Red Phosphorus

Property	White Phosphorus	Red Phosphorus
1. State	Translucent white waxy solid.	Iron grey lustrous powder.
2. Odour	Garlic smell.	Odourless.
3. Physiological action	Poisonous.	Non-poisonous.
4. Solubility	Insoluble in water but soluble in CS_2.	Insoluble in water as well as CS_2.
5. Stability	Less stable, due to angular strain in the molecule where the bond angles are only 60°.	More stable than white phosphorus.
6. Action of air	Readily catches fire in air with a greenish glow which is visible in dark.	Does not glow in dark.
7. Action of alkali	PH_3 is formed. $P_4 + 3NaOH + 3H_2O \xrightarrow{\Delta,\ CO_2} PH_3 + 3NaH_2PO_2$	No reaction.
8. Effect of heat	Changes to β-black phosphorus when heated at 473 K under high pressure and changes to red phosphorus when heated at 573 K.	Changes to α-black phosphorus when heated at 803 K in a solid tube.
9. Structure	Consists of discrete tetrahedral P_4 molecules.  	Tetrahedral units of P_4 joined together through covalent bonds to give polymeric structure. 

9. Phosphine (PH_3)

Preparation: In the laboratory, phosphine is prepared by heating white phosphorous with concentrated sodium hydroxide solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \xrightarrow{\Delta,\ CO_2} PH_3 + 3NaH_2PO_2$$

In order to purify it from the impurities, it is absorbed in HI to form PH_4I which on treating with KOH gives off phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

It can also be prepared by the reaction of calcium phosphide with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

Properties

Phosphine is a colourless gas with rotten fish smell and is highly poisonous. It is slightly soluble in water. When it is absorbed in copper sulphate or mercuric chloride solution, corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

Phosphine is weakly basic and gives phosphonium compounds with acids, *e.g.*,

$$PH_3 + HBr \longrightarrow PH_4Br$$

Uses:

The spontaneous combustion of phosphine is technically used in Holme's signal.

It is also used in smoke screens.

10. **Phosphorus Halides:** Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

Phosphorus Trichloride: It is obtained by passing dry chlorine over heated white phosphorous.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

It can also be obtained by the action of thionyl chloride on white phosphorus.

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties: It is a colourless, oily liquid and hydrolyses in the presence of moisture.

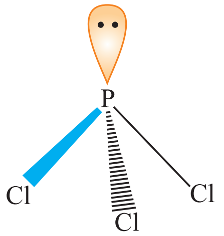
$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

It reacts with organic compounds containing —OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

It has a pyramidal shape as shown in figure alongside, in which phosphorus is sp^3 hybridised.



Phosphorus Pentachloride: It is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

Properties: PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

When heated, it sublimes but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

Finely divided metals on heating with PCl_5 give corresponding chlorides.

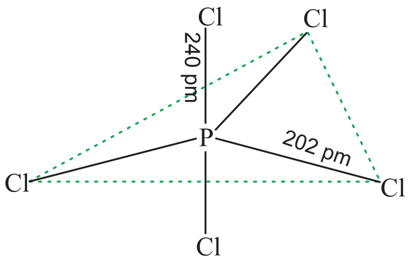
$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

It is used in the synthesis of some organic compounds, *e.g.*, C_2H_5Cl, CH_3COCl.

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown in figure alongside.

The three equatorial P—Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion from equatorial bond pairs.



In the solid state, it exists as an ionic solid, $[PCl_4]^+ [PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

Group 16

(A) General Information

1. **Name:** Oxygen family or Chalcogens
2. **Elements:** ${}_{8}O$, ${}_{16}S$, ${}_{34}Se$, ${}_{52}Te$, ${}_{84}Po$, ${}_{116}Lv$
3. **Electronic Configuration:** ${}_{8}O = [He]\ 2s^2\ 2p^4$; ${}_{16}S = [Ne]\ 3s^2\ 3p^4$
   ${}_{34}Se = [Ar]\ 3d^{10}\ 4s^2\ 4p^4$; ${}_{52}Te = [Kr]\ 4d^{10}\ 5s^2\ 5p^4$; ${}_{84}Po = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$
   ${}_{116}Lv = [Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^4$.

(B) Atomic and Physical Properties

1. **Atomic Radii:** They are smaller than the corresponding elements of Group 15 because of increase in nuclear charge. Down the group they increase mainly due to addition of a new shell.
2. **Oxidation States:** Because of high electronegativity and tendency to gain two electrons oxygen shows an oxidation state of –2 only (except in OF_2 where it has +2, and H_2O_2 where it is –1). All other elements show oxidation states of +2, +4 and +6 because of different excitations possible to empty *d*-orbitals.
3. **Ionisation Enthalpy:** First IE of these elements are lower than those of corresponding elements of Group 15 despite their smaller atomic radii. This is due to greater stability of half-filled orbitals of Group 15 elements. IE_2 values are higher than those of Group 15 because of smaller size of the ions and greater effective nuclear charge. IE decreases down the group.
4. **Electron Gain Enthalpy:** Because of small size of atom, oxygen has less negative electron gain enthalpy than sulphur. However, from sulphur onwards positive value again becomes less negative up to polonium.
5. **Metallic Character:** These elements have very little metallic character because of high IE. Down the group, the metallic character increases due to decrease in IE. Thus, O and S are non-metals, Se and Te have very little metallic character while Po is metallic.
6. **Electronegativity:** These are more electronegative than Group 15 elements because of further decrease in size. It decreases down the group because of increase in atomic size. Oxygen is the second most electronegative element.
7. **Melting and Boiling Points:** Melting and boiling points increase regularly from O to Te due to increase in size and hence greater van der Waals' forces. The element Po, has lower melting and boiling point than Te because of the maximum inert pair effect.

(C) Chemical Properties

Anomalous Behaviour of Oxygen

The anomalous behaviour of oxygen is due to its small size, high electronegativity and absence of *d*-orbitals. The absence of *d*-orbitals in oxygen limits its covalency to four.

1. **Hydrides:** They form hydrides of the formula H_2E.

   Properties of Hydrides:

   (*i*) **Thermal stability:** It decreases down the group because as the size of the atom increases the bond dissociation enthalpy decreases.

   (*ii*) **Acidic character:** It increases down the group because they can dissociate more easily to give H^+ ions.

$$H_2E + aq \rightleftharpoons H^+ + HE^-$$

$$HE^- + aq \rightleftharpoons H^+ + E^{2-}$$

   (*iii*) **Reducing nature:** Except H_2O, all are reducing agents. The reducing character increases down the group.

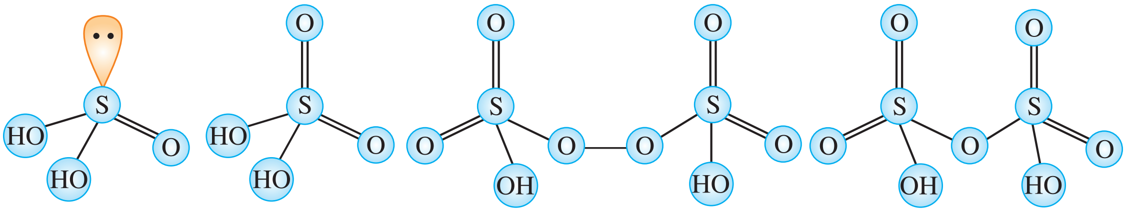
   (*iv*) **Boiling point/volatility:** H_2O has the highest boiling point because of H-bonding. After a sudden drop from H_2O to H_2S, boiling point gradually increases from H_2S to H_2Te because of increase of molecular mass and hence van der Waals' forces.

2. **Halides:** These elements form a large number of halides of the type, EX_2, EX_4 and EX_6 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order F^-, Cl^-, Br^-, I^-. Amongst hexahalides, hexafluorides are the only stable halides. SF_6 is exceptionally stable for steric reasons. It has sp^3d^2 hybridisation and thus, has octahedral structure.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 is a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structures in which one of equatorial position is occupied by a lone pair (see-saw shape). All elements except selenium form dichlorides and dibromides. These dihalides have sp^3 hybridisation and thus, have tetrahedral structure. The well known monohalides S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2, Se_2Br_2 are dimeric in nature and undergo disproportionation as given below.

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

3. **Oxides:** All these elements form oxides of the type, EO_2 and EO_3 where E is the element of the group. Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent. Both EO_2 and EO_3 types of oxides are acidic in nature.
4. **Oxo-acids:** In this family, sulphur forms a number of oxo-acids. Out of these, sulphuric acid, H_2SO_4, is the most important and is called the King of Chemicals. A few important oxo-acids of sulphur are:



Sulphurous acid (H_2SO_3)

Sulphuric acid (H_2SO_4)

Peroxodisulphuric acid ($H_2S_2O_8$)

Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Fig. 7.2: Structure of some oxoacids of sulphur

Sulphuric Acid (H_2SO_4)

Manufacture of H_2SO_4: Sulphuric acid is manufactured by the Contact process which involves the following equations:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

$$SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7(l)}$$

Oleum is diluted with water to get H_2SO_4 of desired concentration.

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$$

Properties of Sulphuric Acid:

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. Because of its low volatility, concentrated H_2SO_4 can be used to manufacture more volatile acids from their salts.

$$2MX + H_2SO_4 \longrightarrow \underset{\text{(Conc.)}}{2HX} + M_2SO_4 \qquad (M = \text{metal}, X = F, Cl, NO_3)$$

Concentrated sulphuric acid is a powerful dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

Hot concentrated H_2SO_4 is a moderately strong oxidising agent.

$$Cu + 2H_2SO_4(\text{conc.}) \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$3S + 2H_2SO_4(\text{conc.}) \longrightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4(\text{conc.}) \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

5. **Dioxygen (O_2)**

Preparation of O_2: Dioxygen can be prepared by the following ways:

1. By decomposition of oxygen rich compounds.

$$2KMnO_4(s) \longrightarrow K_2MnO_4(s) + MnO_2(s) + O_2(g)$$

$$2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$$

$$2KClO_3(s) \xrightarrow[420\text{ K}]{MnO_2} 2KCl(s) + 3O_2(g) \qquad \text{(Laboratory preparation)}$$

2. By thermal decomposition of oxides of metals which are low in electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g); \qquad 2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$$

$$2Pb_3O_4(s) \longrightarrow 6PbO(s) + O_2(g) \qquad 2PbO_2(s) \longrightarrow 2PbO(s) + O_2(g)$$

3. By decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Industrially, dioxygen is obtained by liquefaction of air followed by fractional distillation.

Properties of Dioxygen:

Dioxygen is a colourless and odourless gas. It liquefies at 90 K and freezes at 55 K. Some of the reactions of dioxygen with metals, non-metals and other compounds are given below.

$$2Ca + O_2 \longrightarrow 2CaO; \qquad 4Al + 3O_2 \longrightarrow 2Al_2O_3$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}; \qquad 4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

A binary compound of oxygen with another element is called oxide. Oxides can be simple (*e.g.*, MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). Simple oxides are further classified as acidic, basic, amphoteric and neutral oxides. An oxide which combines with water to form an acid is called an acidic oxide.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

As a general rule only non-metal oxides (*e.g.*, CO_2, SO_2, N_2O_5, Cl_2O_7) are acidic but oxides of some metals in higher oxidation state also have acidic character (*e.g.*, Mn_2O_7, CrO_3, V_2O_5). The oxide which combines with water to form a base is called a basic oxide. In general, metallic oxides (*e.g.*, Na_2O, CaO, BaO) are basic.

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

The oxides which show characteristics of both acidic as well as of basic oxides are called amphoteric oxides. For example, Al_2O_3, ZnO, SnO_2, PbO. They react with acids as well as bases.

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \longrightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[Al(OH)_6](aq)$$

The oxides which are neither acidic nor basic are called neutral oxides. For example, CO, NO, N_2O, H_2O.

Uses:

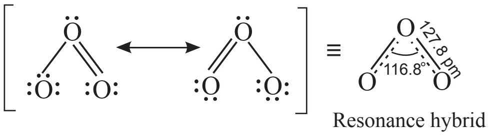
1. It is used oxyacetylene welding.
2. Oxygen cylinders are widely used in hospitals.

6. Ozone (O_3)

Preparation of Ozone: Ozone is prepared by subjecting pure and dry oxygen to silent electric discharge.

$$3O_2(g) \longrightarrow 2O_3(g); \ \Delta H^\circ(298\ K) = 142\ kJ\ mol^{-1}$$

Structure of Ozone



Resonance hybrid

Ozone is a pale blue gas having a strong characteristic smell. Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \longrightarrow O_2 + O$), it acts as a powerful oxidising agent.

$$PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$$

$$2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

Uses: Ozone is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc.

7. Sulphur (S)

Sulphur forms numerous allotropes of which the yellow rhombic (α-sulphur) and monoclinic (β-form) are the most important. Both rhombic and monoclinic sulphur have S_8 molecules. In cyclo-S_6 form, the ring adopts the chair form as shown below:

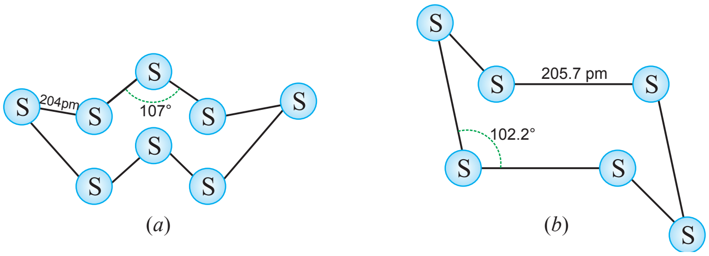


Fig. 7.3: The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

8. Sulphur Dioxide (SO_2)

Preparation of SO_2: Sulphur dioxide is formed together with a little (6–8%) sulphur trioxide when sulphur is burnt in air or oxygen.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

In the laboratory, it is prepared by treating a sulphite with dilute sulphuric acid.

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

Industrially, it is obtained as a by-product of roasting of sulphide ores.

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Properties of Sulphur Dioxide:

Sulphur dioxide is colourless gas with pungent smell and is highly soluble in water. Its aqueous solution is acidic and turns blue litmus red. It reacts readily with sodium hydroxide solution to form sodium sulphite and sodium hydrogen sulphite.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

Sulphur dioxide reacts with chlorine in the presence of charcoal as a catalyst to form sulphuryl chloride. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium pentaoxide catalyst.

$$SO_2(g) + Cl_2(g) \xrightarrow{\text{Charcoal}} SO_2Cl_2(l)$$

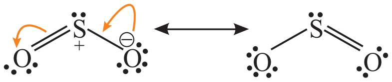
$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

In the presence of moisture, it liberates nascent hydrogen and thus acts as reducing agent.

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

The molecule of SO_2 is angular.



Structure of SO_2

Uses: Sulphur dioxide is used

(*i*) in refining petroleum and sugar,

(*ii*) in the manufacture of sulphuric acid, calcium hydrogen sulphite and sodium metabisulphite,

(*iii*) as an anti-chlor, disinfectant and preservative,

(*iv*) in bleaching wool and silk.

Group 17

(A) General Information

1. **Name:** Halogen family
2. **Elements:** $_9F$, $_{17}Cl$, $_{35}Br$, $_{53}I$, $_{85}At$, $_{117}Ts$

3. **Electronic Configuration:** ${}_{9}F = [He]\ 2s^2\ 2p^5$; ${}_{17}Cl = [Ne]\ 3s^2\ 3p^5$; ${}_{35}Br = [Ar]\ 3d^{10}\ 4s^2\ 4p^5$; ${}_{53}I = [Kr]\ 4d^{10}\ 5s^2\ 5p^5$; ${}_{85}At = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$; ${}_{117}Ts = [Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^5$.

(B) Atomic and Physical Properties

1. **Atomic Radii:** Halogens are the smallest in their respective periods due to increase in nuclear charge. Down the group, their size increases regularly due to addition of a new shell.
2. **Oxidation States:** All the halogens show –1 oxidation state. Because of highest electronegativity, fluorine shows an oxidation state of –1 only. Other elements also show oxidation states of +1, +3, +5 and +7, because of the different excitations possible due to empty *d*-orbitals.
3. **Ionisation Enthalpy:** This is higher than the corresponding members of Group 16 because of increase in nuclear charge. They are so high that these elements have little tendency to lose electrons. Down the group, the IE decreases so that I can lose electrons to form I^+.
4. **Electron Gain Enthalpy:** Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small orbitals of fluorine and thus, the incoming electron does not experience much attraction.
5. **Metallic Nature**: The elements are non-metals because of very high ionisation enthalpies. The element, I, shows some metallic character (lustre, etc.) as it can form I^+ by loss of electron.
6. **Electronegativity:** These are the most electronegative elements in their respective periods. Down the group electronegativity decreases. Thus, fluorine is the most electronegative element in the periodic table.
7. **Melting Points and Boiling Points:** Increase regularly down the group because of increase in size and nuclear charge resulting in greater van der Waals' forces of attraction. Thus, F_2 and Cl_2 are gases, Br_2 is a liquid while I_2 is a solid.
8. **Colour:** All halogens are coloured. This is due to the absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level while the remaining light is transmitted. The colour of the halogen is the colour of the transmitted light. The amount of energy required for the excitation decreases progressively from fluorine to iodine as the size of the atom increases. The energy of the transmitted light therefore goes on increasing from fluorine to iodine. For example, fluorine absorbs violet light and hence appears pale yellow while iodine absorbs yellow and green light and hence appears deep violet.
9. **Bond Dissociation Enthalpy:** Bond dissociation enthalpy decreases from Cl_2 to I_2. This is due to increase in the size of halogen atom on moving down the group from chlorine to iodine. Bond dissociation enthalpy of fluorine is smaller than chlorine or bromine. This is due to small size of fluorine which results large electron–electron repulsion among the lone pairs in F_2 molecule. Thus, the bond dissociation enthalpy decreases in the order $Cl_2 > Br_2 > F_2 > I_2$.

(C) Chemical Properties

All halogens are highly reactive. This is due to their low bond dissociation enthalpy and high negative electron gain enthalpy values. The reactivity of halogen decreases down the group. Fluorine is the strongest oxidising halogen. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \qquad (X = Cl, Br\ or\ I)$$

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \qquad (X = Br\ or\ I)$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hypohalic and hypohalous acids. I^- ion is oxidised by oxygen in acidic medium to iodine.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX\ (aq) \qquad (X = Cl\ or\ Br)$$

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(l)$$

Anomalous behaviour of fluorine:

The anomalous behaviour of fluorine is due to its small size, low F–F bond dissociation enthalpy, highest electronegativity and absence of *d*-orbitals in valence shell.

Most of the reactions of fluorine are exothermic. This is due to its small size and strong bond formed by it with other elements.

1. **Hydrides:** All elements of Group 17 form hydrides of the type HX (X = F, Cl, Br, I). The reactivity of halogen towards hydrogen decreases from fluorine to iodine.
   (*i*) **Physical state:** Except HF which is a liquid due to H-bonding, all are gases.
   (*ii*) **Thermal stability:** It decreases down the group because of decrease in bond dissociation enthalpy.
   (*iii*) **Reducing character:** It increases from HF to HI because of decrease of stability.
   (*iv*) **Acidic strength:** HF < HCl < HBr < HI. This is because bond dissociation enthalpies are in the order HF > HCl > HBr > HI.
2. **Halides:** Halogens react with metals to form metal halides. For example,

$$Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$$

Halides of metals.

(*i*) With a particular metal, ionic character is

M–F > M–Cl > M–Br > M–I.

(*ii*) With metals of low IE, halides are all ionic.

(*iii*) With metals of high IE, halides are covalent.

(*iv*) With metals showing more than one oxidation states, halides in higher oxidation state are more covalent i.e., $SnCl_4$ and $PbCl_4$ are more covalent than $SnCl_2$ and $PbCl_2$ respectively.

3. **Oxides:** Halogens form many binary compounds with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. They are called fluorine oxides because fluorine is more electronegative than oxygen. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used to remove plutonium as PuF_6 from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which oxidation states of halogens range from +1 to +7. The higher oxides of halogens tend to be more stable than the lower ones. The stability of the oxides of halogen decreases in the order, I > Cl > Br. This is because iodine–oxygen bond is stable due to greater polarity of iodine–oxygen bond. The stability of chlorine–oxygen bond is due to multiple bond formation involving *d*-orbitals of the chlorine atoms. Bromine being in between lacks both of these characteristics.

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides. They are very powerful oxidising agents. The iodine oxides, I_2O_4, I_2O_5 and I_2O_7 are insoluble solids. I_2O_5 is a very good oxidising agent and is used in estimation of carbon monoxide.

4. **Oxo-acids:** Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as hypofluorous acid. The other halogens form acid of the type HOX—hypohalous acid, HOXO—halous acid, $HOXO_2$—halic acid and $HOXO_3$—perhalic acid.

Table 7.4: Oxoacids of Halogens

F	Cl	Br	I
HOF	HOCl	HOBr	HOI
—	HOClO	—	—
—	$HOClO_2$	$HOBrO_2$	$HOIO_2$
—	$HOClO_3$	$HOBrO_3$	$HOIO_3$

The acidic strength of oxo-acids of different halogens having same oxidation state decreases in the order:

HClO > HBrO > HIO

This is because electronegativity follows the order, Cl > Br > I.

Acidic strength of oxo-acids containing the same halogen are in the order:

$$HClO < HClO_2 < HClO_3 < HClO_4$$

This is because in solution, ClO_4^- is the most stable due to dispersal of –ve charge on four O-atoms.

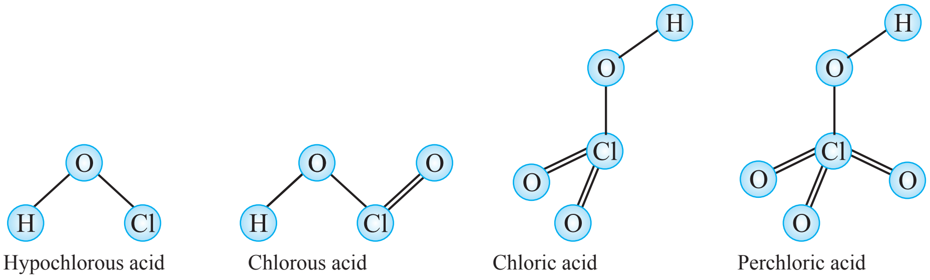


Fig. 7.4: Structures of oxoacids of chlorine

5. **Interhalogen Compounds:** Halogens combine amongst themselves to form a number of compounds known as interhalogen compounds. They can be assigned general composition as XX′, XX'_3, XX'_5, and XX'_7 where X is halogen of larger size and X′ of smaller size and X is more electropositive than X′.

$$\underset{\text{(Equal volumes)}}{Cl_2 + F_2} \xrightarrow{437\text{ K}} 2ClF; \qquad Cl_2 + \underset{\text{(Excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3$$

$$\underset{\text{(Equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl; \qquad I_2 + \underset{\text{(Excess)}}{3Cl_2} \longrightarrow 2ICl_3$$

$$\underset{\text{(Diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3; \qquad Br_2 + \underset{\text{(Excess)}}{5F_2} \longrightarrow 2BrF_5$$

Properties: All interhalogen compounds are covalent compounds and are diamagnetic in nature. In general, interhalogen compounds are more reactive than halogens (except F_2). This is because X–X′ bond in interhalogens is weaker than X–X bond in halogens except F–F bond. All of these compounds undergo hydrolysis.

$$XX' + H_2O \longrightarrow HX' + HOX$$

The molecular structures of interhalogen compounds can be explained on the basis of VSEPR theory. The XX'_3 compounds have bent 'T' shape, XX'_5 compounds have square pyramidal and IF_7 has pentagonal bipyramidal structures.

Uses:

Interhalogen compounds can be used as non-aqueous solvents. They are very useful fluorinating agents. ClF_3 and and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3(l) \longrightarrow UF_6(g) + 3ClF(g)$$

6. **Chlorine (Cl_2)**

Preparation of Cl_2: Chlorine can be prepared by heating concentrated hydrochloric acid with an oxidising agent such as manganese dioxide, potassium permanganate.

$$MnO_2 + \underset{\text{(conc.)}}{4HCl} \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In laboratory, it is prepared by heating a mixture of sodium chloride, manganese dioxide and concentrated H_2SO_4.

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

Manufacture of Chlorine:

(*i*) **Deacon's process:** In this process, hydrogen chloride gas is oxidised by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

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

(*ii*) **Electrolytic process:** Chlorine is obtained by the electrolysis of brine. Reactions involved in the process are:

At cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$; $Na^+ + OH^- \longrightarrow NaOH$

At anode: $Cl^- \longrightarrow Cl + e^-$; $Cl + Cl \longrightarrow Cl_2$

Overall reaction: $2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + Cl_2(g) + H_2$

Properties of Chlorine:

Chlorine is a greenish-yellow gas with pungent and suffocating odour. It is about 2.5 times heavier than air. It is soluble in water.

Chlorine reacts with a number of metals and non-metals to form chlorides.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3; \qquad 2Na + Cl_2 \longrightarrow 2NaCl$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3; \qquad S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3; \qquad H_2 + Cl_2 \longrightarrow 2HCl$$

It reacts with compounds containing hydrogen to form HCl.

$$H_2S + Cl_2 \longrightarrow 2HCl + S; \qquad C_{10}H_{16} + 8Cl_2 \longrightarrow 16HCl + 10C$$

$$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow \underset{\text{(explosive)}}{NCl_3} + 3HCl; \qquad \underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

With cold and dilute alkalies, chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies, it gives chloride and chlorate.

$$\underset{\text{(cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + \underset{\substack{\text{Sodium}\\\text{hypochlorite}}}{NaOCl} + H_2O$$

$$\underset{\text{(hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + \underset{\text{Sodium chlorate}}{NaClO_3} + 3I$$

With dry slaked lime, it gives bleaching powder.

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

The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$. Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. HOCl so formed gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl; \qquad HOCl \longrightarrow HCl + \underset{\text{Nascent oxygen}}{[O]}$$

It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10HCl$$

It is a powerful bleaching agent and the bleaching action is due to oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

$$\text{Coloured substance} + O \longrightarrow \text{Colourless substance}$$

Uses of Chlorine: Chlorine is used

(*i*) for bleaching cotton and textiles.

(*ii*) in sterilising drinking water.

(*iii*) in the extraction of gold and platinum.

(*iv*) in the manufacture of dyes, drugs and organic compounds such as $CHCl_3$, CCl_4, DDT, refrigerants, etc.

7. Hydrogen Chloride (HCl)

Preparation of HCl: In laboratory, it is prepared by heating sodium chloride with concentrated H_2SO_4.

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing through concentrated H_2SO_4.

Properties of Hydrogen Chloride: It is a colourless and pungent smelling gas. It is extremely soluble in water.

- When three parts of conc. HCl and one part of conc. HNO_3 are mixed, aqua regia is formed, which is used for dissolving noble metals such as gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

- It reacts with NH_3 and gives white fumes of NH_4Cl.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

- It decomposes salts of weaker acids.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2\uparrow$$

Uses of Hydrogen Chloride: Hydrochloric acid is used

(*i*) in the manufacture of chlorine, glucose and NH_4Cl.

(*ii*) for extracting glue from bones and purifying bone black.

Group 18 (Noble Gases)

(A) General Information

1. **Names:** *Rare gases* – because they are present in very small amounts in the air.
   Inert gases – old name when they were considered to be chemically unreactive (inert).
   Noble gases – this name is preferred because they do react to form compounds though to a small extent.
2. **Elements:** He, Ne, Ar, Kr, Xe, Rn and Og.
3. **Electronic Configuration:** Outer shell configuration is $ns^2\ np^6$ (except He having $1s^2$).

(B) Atomic and Physical Properties

1. **Atomic Radii:** Atomic radii increase down the group with increase in atomic number.
2. **Ionisation Enthalpy:** They have the highest IEs in their respective periods because of fully-filled orbitals and hence greatest stability. Down the group, it decreases due to increase in atomic size.
3. **Electron Gain Enthalpy:** Since noble gases have stable electronic configuration, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.
4. **Melting and Boiling Points:** They have low melting points and boiling points because of weak van der Waals' forces present between their atoms. Down the group, melting and boiling point increase because of increase in atomic size and hence increase of van der Waals' forces. Helium has the lowest boiling point (4.2 K) of any known substance.
5. **Liquefaction:** Because of weak van der Waals' forces present in them, it is difficult to liquefy them. Down the group, the ease of liquefaction increases because of increase of atomic size and hence increase of van der Waals' forces.

(C) Chemical Properties

In general, noble gases are the least reactive. Their inertness to chemical reactivity is due to following reasons:

(*i*) The noble gases except helium have completely filled ns^2np^6 electronic configuration in their valence shell.

(*ii*) They have high ionisation enthalpy and more positive electron gain enthalpy.

Chemistry of Compounds of Noble Gases: In 1962, Bartlett studied the following reaction:

$$O_2 + PtF_6 \longrightarrow \underset{\text{Dioxygenyl hexafluoro platinate}}{O_2^+[PtF_6]^-}$$

As IE of molecular oxygen was almost the same as that of xenon, the following reaction was also found to occur:

$$Xe + PtF_6 \xrightarrow{298\text{ K}} Xe^+[PtF_6]^-$$

Preparation of Xenon Fluorides: Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(Xenon in excess)}}{Xe(g)} + F_2(g) \xrightarrow{673\text{ K, 1 bar}} XeF_2(s)$$

$$\underset{(1:5\text{ ratio})}{Xe(g) + 2F_2(g)} \xrightarrow{873\text{ K, 7 bar}} XeF_4(s)$$

$$\underset{(1:20\text{ ratio})}{Xe(g) + 3F_2(g)} \xrightarrow{573\text{ K, 60-70 bar}} XeF_6(s)$$

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143 K.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

Xenon fluorides are readily hydrolysed even by traces of water.

$$2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$$

Xenon fluorides react with fluoride ion acceptor to form cationic species and fluoride ion donors to form fluoro anions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^- \qquad [M = Na, K, Rb, Cs]$$

Xenon–Oxygen Compounds: Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

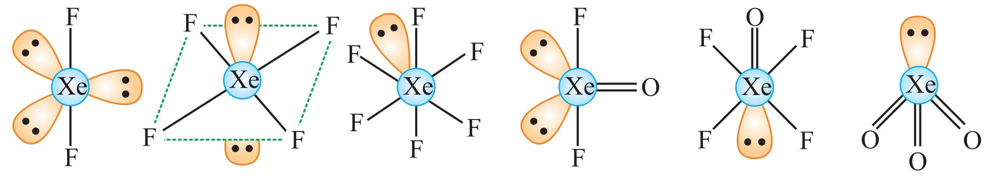
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \longrightarrow \underset{\text{Xenon oxytetrafluoride}}{XeOF_4} + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow \underset{\text{Xenon dioxydifluoride}}{XeO_2F_2} + 4HF$$

Structures of Xenon Compounds: The shapes of xenon fluoride and oxyfluorides can be explained on the basis of hybridisation and these are shown in figure given below.



$XeF_2(sp^3d)$ Linear

$XeF_4(sp^3d^2)$ Square Planar

$XeF_6(sp^3d^3)$ Distorted Octahedral

$XeOF_2(sp^3d)$ T-shaped

$XeOF_4(sp^3d^2)$ Square Pyramidal

$XeO_3(sp^3)$ Trigonal Pyramidal

Fig. 7.5: Structures of some xenon compounds

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Why are pentahalides of P, As, Sb and Bi more covalent than their trihalides?

Ans. Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.

As, in pentahalides, the central atom is in +5 oxidation state while in trihalides it is in +3 oxidation state. Therefore, pentahalides are more covalent than trihalides.

Q. 2. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements?

Ans. This is because BiH_3 is the least stable among the hydrides of Group 15.

Q. 3. Why is N_2 less reactive at room temperature?

Ans. N_2 is less reactive at room temperature because of strong $p\pi - p\pi$ overlap resulting into the triple bond ($N \equiv N$), consequently high bond enthalpy.

Q. 4. Mention the conditions to maximise the yield of ammonia.

Ans. Ammonia is prepared by the Haber's process.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{Iron oxide} + K_2O + Al_2O_3 \text{ (catalyst)}]{700\text{ K},\ 200 \times 10^5 \text{ Pa}} 2NH_3(g); \quad \Delta_f H^\circ = -92.2 \text{ kJ mol}^{-1}$$

In accordance with Le Chatelier's principle, a high pressure of 200×10^5 Pa, low temperature (optimum temperature of ~ 700 K) along with catalyst iron oxide with small amounts of K_2O and Al_2O_3 are used to maximise the yield of ammonia.

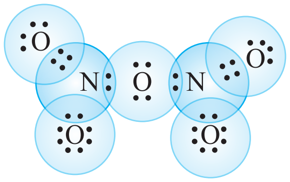
Q. 5. How does ammonia react with a solution of Cu^{2+}?

Ans. Ammonia reacts with a solution of Cu^{2+} by donating a lone pair of electron.

$$\underset{\text{Blue}}{Cu^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}(aq)}$$

Q. 6. What is the covalence of nitrogen in N_2O_5?

Ans. Covalency depends upon the number of shared pair of electrons. In N_2O_5 each nitrogen atom has four shared pairs of electrons as shown below:



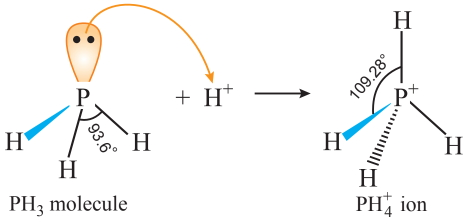
Therefore, the covalency of N in N_2O_5 is 4.

Q. 7. **(*a*) Bond angle in PH_4^+ is higher than in PH_3. Why?**

(*b*) What is formed when PH_3 reacts with an acid?

Ans. (*a*) Both are sp^3 hybridised. In PH_4^+ all the four orbitals are bonded whereas in PH_3 there is a lone pair of electrons on P, which is responsible for lone pair–bond pair repulsion in PH_3, reducing the bond angle to less than 109°28′.

(*b*) PH_3 reacts with acids like HI to form PH_4I.



PH_3 molecule (Pyramidal)

PH_4^+ ion (Tetrahedral)

Q. 8. What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2?

Ans. White phosphorus reacts with NaOH to form phosphine (PH_3).

$$\underset{\text{Phosphorus}}{P_4} + 3NaOH + 3H_2O \xrightarrow[CO_2 \text{ atmosphere}]{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

Q. 9. What happens when PCl_5 is heated?

Ans. PCl_5 has three equatorial (202 pm) and two axial (240 pm) bonds. Since axial bonds are weaker than equatorial bonds, therefore, when PCl_5 is heated, the less stable axial bonds break to form PCl_3.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2.$$

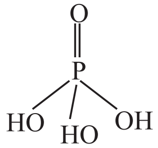
Q. 10. Write a balanced equation for the reaction of PCl_5 with water.

Ans. It reacts with heavy water to form phosphorus oxychloride $POCl_3$ and deuterium chloride (DCl).

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

Q. 11. What is the basicity of H_3PO_4?

Ans.



Three P—OH groups are present in the molecule of H_3PO_4. Therefore, its basicity is three.

Q. 12. What happens when H_3PO_3 is heated?

Ans. Orthophosphorous acid on heating disproportionates to give orthophosphoric acid and phosphine.

$$\underset{\text{Orthophosphorous acid}}{4H_3PO_3} \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + \underset{\text{Orthophosphoric acid}}{3H_3PO_4}$$

Q. 13. List the important sources of sulphur.

Ans. Sulphur mainly occurs in the earth's crust in the combined state primarily in the form of sulphates and sulphides.

Sulphates: Gypsum $CaSO_4.2H_2O$, epsom salt $MgSO_4.7H_2O$, etc.

Sulphides: Galena PbS, zinc blende ZnS, copper pyrite $CuFeS_2$.

Traces of sulphur occur as H_2S in volcanoes. Organic materials such as eggs, garlic, onion, mustard, hair and wool also contain sulphur.

Q. 14. Write the order of thermal stability of the hydrides of Group 16 elements.

Or

Arrange the following hydrides of group 16 element in the increasing order of their thermal stability

H_2O, H_2S, H_2Po, H_2Se, H_2Te *[CBSE (F) 2017]*

Ans. Since the size of the element increases down the group, the E—H bond dissociation enthalpy decreases and hence E—H bond breaks more easily. Therefore, the thermal stability of the hydrides of group 16 elements decreases down the group.

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

Q. 15. Why is H_2O a liquid and H_2S a gas?

Ans. Due to small size and high electronegativity of oxygen, molecules of water are associated through hydrogen bonding, resulting in its liquid state. On the other hand, H_2S molecules are not associated through H-bonding. Hence, it is a gas.

Q. 16. Which of the following does not react with oxygen directly?

Zn, Ti, Pt, Fe

Ans. Platinum is a noble metal. The sum of its first four ionisation enthalpies is very large. Hence, it does not react with oxygen directly. On the other hand, Zn, Ti and Fe are active metals and hence directly react with oxygen to form their respective oxides.

Q. 17. Complete the following reactions:

(*i*) $C_2H_4 + O_2 \longrightarrow$

(*ii*) $4Al + 3O_2 \longrightarrow$

Ans. (*i*) $C_2H_4 + 3O_2 \xrightarrow{\text{Heat}} 2CO_2 + 2H_2O$

(*ii*) $4Al + 3O_2 \xrightarrow{\text{Heat}} 2Al_2O_3$

Q. 18. Why does O_3 act as a powerful oxidising agent?

Ans. Due to the ease with which it liberates atoms of nascent oxygen, it acts as a powerful oxidising agent.

$$O_3 \longrightarrow O_2 + \underset{\text{(nascent oxygen)}}{O}$$

Q. 19. How is O_3 estimated quantitatively?

Ans. When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating ozone gas.

Q. 20. What happens when sulphur dioxide is passed through an aqueous solution of Fe (III) salt?

[CBSE Delhi 2019 (56/2/1)]

Ans. SO_2 acts as a reducing agent and hence reduces an aqueous solution of Fe (III) salt to Fe (II) salt.

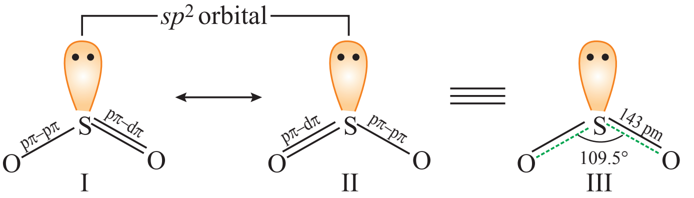
$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$$

$$\overline{2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+}$$

Q. 21. Comment upon the nature of two S—O bonds formed in SO_2 molecule. Are the two S—O bonds in this molecule equal?

Ans.



Resonating structures of SO_2

In SO_2, S is sp^2 hybridised. Two of the three sp^2 orbitals form two σ - bonds with oxygen atoms while the third contains the lone pair of electrons. Thus, S is now left with one half filled *p* orbital and one half filled *d* orbital. These orbitals form one $p\pi - p\pi$ and one $p\pi - d\pi$ double bond with oxygen atom. Due to the resonance, the two S – O bonds are equal (bond length = 143 pm).

Q. 22. How is the presence of SO_2 detected?

Ans. SO_2 is a pungent smelling gas. It can be detected by the following two tests:

(*i*) SO_2 turns acidified $K_2Cr_2O_7$ green due to reduction of $Cr_2O_7^{2-}$ to Cr^{3+} ions.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 3$$

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

$$\overline{\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 3SO_2 + 2H^+ \longrightarrow \underset{\text{(green)}}{2Cr^{3+}} + 3SO_4^{2-} + H_2O}$$

(*ii*) SO_2 turns the pink violet colour of $KMnO_4$ colourless due to reduction of MnO_4^- to Mn^{2+} ions.

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 5$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$\overline{\underset{\text{(pink violet)}}{2MnO_4^-} + 5SO_2 + 2H_2O \longrightarrow \underset{\text{(colourless)}}{2Mn^{2+}} + 5SO_4^{2-} + 4H^+}$$

Q. 23. Mention three areas in which H_2SO_4 plays an important role.

Ans. (*i*) H_2SO_4 is used in the manufacture of fertilisers, *e.g.*, ammonium sulphate, superphosphate.

(*ii*) It is used in storage batteries.

(*iii*) It is used in detergent industry.

Q. 24. Write the conditions to maximise the yield of H_2SO_4 by contact process.

Ans. The key step in the manufacture of H_2SO_4 by contact process is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta_r H^\circ = -196.6 \text{ kJ mol}^{-1}$$

The forward reaction is exothermic and proceed with decrease in number of moles. Therefore, low temperature (optimum temperature 720 K), high pressure (in practice 2 bar) and use of catalyst V_2O_5 to increase the rate of reaction at low temperature are the favourable conditions for maximum yield of H_2SO_4.

Q. 25. Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

Ans. $H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$

$HSO_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$

H_2SO_4 is a very strong acid in water mainly because its first ionisation to H_3O^+ and HSO_4^- is large. The ionisation HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. This explains why $K_{a_2} << K_{a_1}$.

Q. 26. Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2. **[*CBSE Sample Paper 2016*]**

Ans. The electrode potential depends upon the parameters indicated below:

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\Delta_{diss}H^+} X(g) \xrightarrow{\Delta_{eg}H^-} X^-(g) \xrightarrow{\Delta_{hyd}H^-} X^-(aq)$$

(Values in kJ mol^{-1})	$\Delta_{diss} H$	$\Delta_{eg} H$	$\Delta_{hyd} H$
Fluorine	158.8	– 333	515
Chlorine	242.6	– 349	381

The two factors, high hydration enthalpy of F^- ion (515 kJ mol^{-1}) and low F—F bond dissociation enthalpy compensate more than the less negative electron gain enthalpy of fluorine. Due to this, electrode potential of F_2 (+ 2.87 V) is much higher than that of Cl_2 (+1.36 V) and hence F_2 is a stronger oxidising agent than Cl_2.

Q. 27. Give two examples to show the anomalous behaviour of fluorine.

Ans. The anomalous behaviour of fluorine is due to its (*i*) small size, (*ii*) highest electronegativity, (*iii*) low F—F bond dissociation enthalpy, and (*iv*) non-availability of *d*-orbitals in its valence shell.

The two examples are:

(*i*) Fluorine forms only one oxo-acid while other halogens form a number of oxo-acids.

(*ii*) HF is a liquid due to strong H-bonding while other hydrogen halides are gases.

Q. 28. Sea is the greatest source of halogens. Comment.

Ans. Sea water contains chlorides, bromides and iodides of Na, K, Mg and Ca, but mainly sodium chloride solution (2.5% by mass). Certain forms of marine life contain iodine in their systems. For example, seaweeds contain up to 0.5% of iodine as sodium iodide.

Q. 29. Give the reason for bleaching action of Cl_2.

Ans. In presence of moisture or in aqueous solution, Cl_2 liberates nascent oxygen.

$$Cl_2 + H_2O \longrightarrow 2HCl + \underset{\text{Nascent oxygen}}{[O]}$$

This nascent oxygen brings about the oxidation of coloured substances present in vegetable and organic matter to colourless substances.

$$\text{Coloured substance} + [O] \longrightarrow \text{Colourless substance}$$

Thus, the bleaching action of Cl_2 is due to oxidation.

Q. 30. Name two poisonous gases which can be prepared from chlorine gas. **[*CBSE Delhi 2019 (56/2/1)*]**

Ans. Two poisonous gases which can be prepared from chlorine gas are:

(*i*) Phosgene gas ($COCl_2$)

(*ii*) Mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Q. 31. Why is ICl more reactive than I_2?

Ans. ICl is more reactive than I_2 because I—Cl bond is weaker than I—I bond. Consequently, ICl breaks easily to form halogen atoms which readily bring about the reactions.

Q. 32. Why is helium used in diving apparatus?

Ans. Helium is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Q. 33. Balance the following equation:

$$XeF_6 + H_2O \longrightarrow XeO_2F_2 + HF$$

Ans. $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

Q. 34. Why has it been difficult to study the chemistry of radon?

Ans. Radon is radioactive with very short half-life (3.82 days) which makes the study of chemistry of radon difficult.

NCERT Textbook Exercises

Q. 1. Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.

Ans. **Electronic configuration:** The valence shell electronic configuration of these elements is ns^2np^3. The *s*-orbital in these elements is completely filled and *p*-orbitals are half-filled, making their electronic configuration extra stable.

Oxidation state: The common oxidation states of these elements are –3, +3, and +5. The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. In fact, last member of the group, bismuth hardly forms any compound in –3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi(V) compound is BiF_5. The stability of +5 oxidation state decreases and that of +3 oxidation state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxo-acids.

Atomic size: Covalent and ionic (in a particular state) radii increase down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled *d* and/or *f* orbitals in heavier members.

Ionisation enthalpy: IE decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled *p*-orbitals electronic configuration and smaller size, the ionisation enthalpy of the Group 15 elements is much greater than that of Group 14 elements in the corresponding periods. The order of successive ionisation enthalpies as expected is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$.

Electronegativity: The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that pronounced.

Q. 2. Why does the reactivity of nitrogen differ from phosphorus?

Ans. Nitrogen exists as a diatomic molecule (N≡N). Due to the presence of a triple bond between the two N-atoms, the bond dissociation enthalpy is large (941.4 kJ mol^{-1}). Thus, nitrogen is inert and unreactive in its elemental state.

In contrast, white or yellow phosphorus exists as a tetraatomic molecule P_4. Since the P–P single bond is much weaker (213 kJ mol^{-1}) than N≡N triple bond (941.4 kJ mol^{-1}), therefore, phosphorus is much more reactive than nitrogen.

Q. 3. Discuss the trends in chemical reactivity of Group 15 elements.

Ans. Refer to Basic Concepts Point C (Group 15).

Q. 4. Why does NH_3 form hydrogen bonds but PH_3 does not?

Ans. The electronegativity of N (3.0) is much higher than that of H (2.1). Due to this, N–H bond is quite polar and hence NH_3 undergoes intermolecular H-bonding.

On the other hand, both P and H have an electronegativity of 2.1. Therefore, P–H bond is not polar and hence PH_3 does not undergo H-bonding.

Q. 5. How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

Ans. Nitrogen is prepared in the laboratory by heating an equimolar aqueous solution of ammonium chloride with sodium nitrite. The ammonium nitrite formed as a result of double displacement reaction, being unstable decompose to form dinitrogen gas.

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow NH_4NO_2(aq) + NaCl(aq)$$

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2(aq)} \xrightarrow{\text{Heat}} \underset{\text{Dinitrogen}}{N_2(g)} + 2H_2O(l)$$

Q. 6. How is ammonia manufactured industrially?

Ans. Refer to Basic Concepts Point (C) 6 (Group 15).

Q. 7. Illustrate how copper metal can give different products on reaction with HNO_3.

Ans. On heating with dil. HNO_3, copper gives copper nitrate and nitric oxide.

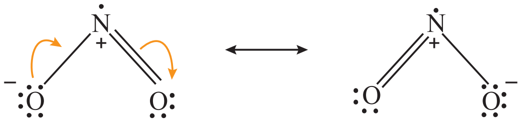
$$3Cu + 8HNO_3(\text{dil.}) \xrightarrow{\text{Heat}} 3Cu(NO_3)_2 + 4H_2O + 2NO$$

With concentrated $HNO_{3,}$ instead of NO, NO_2 is evolved.

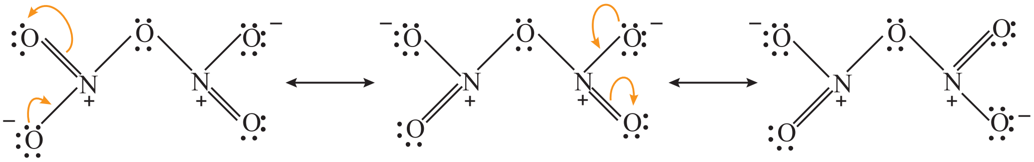
$$Cu + 4HNO_3(\text{conc.}) \xrightarrow{\text{Heat}} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Q. 8. Give the resonating structures of NO_2 and N_2O_5.

Ans. Resonating structures of NO_2 are:



Resonating structures of N_2O_5 are:



Q. 9. The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

[**Hint:** Can be explained on the basis of sp^3 hybridisation in NH_3 and only *s–p* bonding between hydrogen and other elements of the group].

Ans. As we move from N to P to As to Sb, the electronegativity of the central atom goes on decreasing. Bond pairs of electrons, lie much away from the central atom. In other words, force of repulsion between the adjacent bond pairs goes on decreasing and hence the bond angles keep on decreasing from NH_3 to SbH_3.

Q. 10. Why does $R_3P{=}O$ exist but $R_3N{=}O$ does not (R = alkyl group)?

Ans. N due to the absence of *d*-orbitals, cannot form $p\pi - d\pi$ multiple bonds. Thus, N cannot expand its covalency beyond four but in $R_3N{=}O$, N has a covalency of 5. So, the compound $R_3N{=}O$ does not exist. On the other hand, P due to the presence of *d*-orbitals forms $p\pi - d\pi$ multiple bonds and hence can expand its covalency beyond 4. Therefore, P forms $R_3P{=}O$ in which the covalency of P is 5.

Q. 11. Explain why NH_3 is basic while BiH_3 is only feebly basic.

Ans. Since the atomic size of N (70 pm) is much smaller than that of Bi (148 pm), electron density on the N-atom is much higher than that on Bi-atom. As a result, the tendency of N in NH_3 to donate its lone pair of electrons is much higher than that of Bi in BiH_3. Thus, NH_3 is much more basic than BiH_3.

Q. 12. Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Ans. Nitrogen because of its small size and high electronegativity forms $p\pi - p\pi$ multiple bonds. Thus, it exists as a diatomic molecule having a triple bond between the two N-atoms. Phosphorus due to its larger size and lower electronegativity usually does not form $p\pi - p\pi$ multiple bonds with itself. Instead it prefers to form P–P single bonds and hence it exists as tetrahedral P_4 molecules.

Q. 13. Write main differences between the properties of white phosphorus and red phosphorus.

Ans. Refer to Basic Concepts Point 8 (Group 15).

Q. 14. Why does nitrogen show catenation properties less than phosphorus?

Ans. The property of catenation depends upon the E—E bond strength of the element. Since the N—N (159 kJ mol^{-1}) bond strength is much weaker than P—P (213 kJ mol^{-1}) bond strength, hence, nitrogen shows less catenation properties than phosphorus.

Q. 15. Give the disproportionation reaction of H_3PO_3.

Ans. H_3PO_3, on heating, disproportionates to give PH_3 in which P is reduced and H_3PO_3 in which P is oxidised.

$$\underset{\text{Phosphorous acid}}{4H_3\overset{+3}{P}O_3} \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{\overset{-3}{P}H_3} + \underset{\text{Orthophosphoric acid}}{3H_3\overset{+4}{P}O_4}$$

Q. 16. Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Ans. The oxidation state of P in PCl_5 is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating electrons, therefore, PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value. So, PCl_5 acts as an oxidising agent. For example, it oxidises Ag to AgCl and Sn to $SnCl_4$.

Q. 17. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

Ans. (*i*) **Electronic configuration:**

$_8O = [He]\ 2s^2\ 2p^4$;

$_{16}S = [Ne]\ 3s^2\ 3p^4$;

$_{34}Se = [Ar]\ 3d^{10}\ 4s^2\ 4p^4$

$_{52}Te = [Kr]\ 4d^{10}\ 5s^2\ 5p^4$ and $_{84}Po = [Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$

All these elements have same (ns^2np^4) valence shell electronic configuration and hence are justified to be placed in Group 16 of the periodic table.

(*ii*) **Oxidation states:** They need two more electrons to form dinegative ions to acquire the nearest noble gas configuration. So, the minimum oxidation state of these elements should be –2. Oxygen predominantly and sulphur to some extent being electronegative show an oxidation state of –2. Since these elements have six electrons in the valence shell, therefore, at the maximum they can show an oxidation state of +6. Other positive oxidation states shown by these elements are +2 and +4. Although, oxygen due to the absence of *d*-orbitals does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group, *i.e.*, Group 16 of the periodic table.

(*iii*) **Formation of hydrides:** All the elements complete their respective octets by sharing two of their valence electrons with 1s-orbital of hydrogen to form hydrides of the general formula EH_2, *i.e.*, H_2O, H_2S, H_2Se, H_2Te and H_2Po. Therefore, on the basis of formation of hydrides of the general formula, EH_2, these elements are justified to be placed in Group 16 of the periodic table.

Q. 18. Why is dioxygen a gas but sulphur a solid?

Ans. Because of its small size, oxygen is capable of forming pπ – pπ bond and exists as diatomic O_2 molecule. The intermolecular forces in oxygen are weak van der Waals force, due to which it is a gas at room temperature. On the other hand, sulphur, due to its larger size prefers to form S–S single bond and exist as octaatomic S_8 molecule having puckered ring structure. Because of larger size the force of attraction holding the S_8 molecules together are much stronger. Hence sulphur is a solid at room temperature.

Q. 19. Knowing the electron gain enthalpy values of $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-? **[*HOTS*]**

[**Hint:** Consider lattice energy factor in the formation of compounds.]

Ans. Let us consider the reaction of a divalent metal (M) with oxygen. The formation of M_2O and MO involves the following steps:

$$M(g) \xrightarrow{\Delta_i H_1} M^+(g) \xrightarrow{\Delta_i H_2} M^{2+}(g)$$

$$O(g) \xrightarrow{\Delta_{eg} H_1} O^-(g) \xrightarrow{\Delta_{eg} H_2} O^{2-}(g)$$

$$2M^+(g) + O^-(g) \xrightarrow{\text{Lattice Energy}} M_2O(s)$$

$$M^{2+}(g) + O^{2-}(g) \xrightarrow{\text{Lattice Energy}} MO(s)$$

Although $\Delta_i H_2$ is much more than $\Delta_i H_1$ and $\Delta_{eg} H_2$ is much higher than $\Delta_{eg} H_1$ yet the lattice energy of the formation of MO(*s*) due to higher charges is much more than that of $M_2O(s)$. Thus, formation of MO is energetically more favourable than M_2O. Due to this, oxygen forms a large number of oxides having the O^{2-} species and not O^-.

Q. 20. Which aerosols deplete ozone?

Ans. Aerosols such as chlorofluorocarbons (CFCs), *i.e.*, freon (CCl_2F_2) depletes the O_3 layer by supplying Cl free radicals which convert O_3 to O_2 as shown below:

$$\underset{\text{Freon}}{Cl_2CF_2(g)} \longrightarrow \bullet Cl(g) + \bullet CClF_2(g)$$

$$\bullet Cl(g) + O_3(g) \longrightarrow ClO\bullet(g) + O_2(g)$$

$$ClO\bullet(g) + \bullet O(g) \longrightarrow \bullet Cl(g) + O_2(g)$$

Q. 21. Describe the manufacture of H_2SO_4 by contact process.

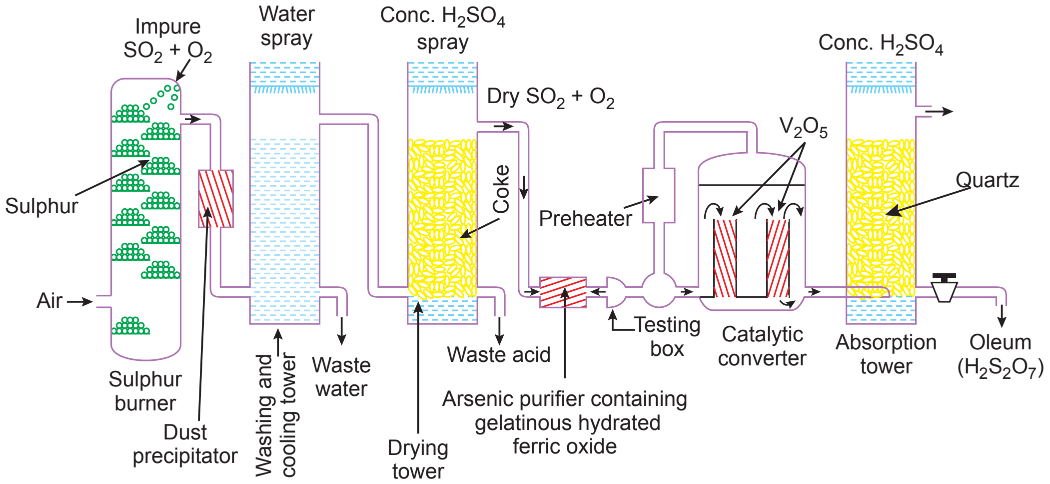
Ans. Sulphuric acid is manufactured by the contact process which involves three steps:

(*i*) Burning of sulphur or sulphide ores in air to produce SO_2.

(*ii*) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(*iii*) Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$).

A flow diagram for the manufacture of sulphuric acid is shown in figure given below. The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.



Flow diagram for the manufacture of sulphuric acid

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g); \ \Delta_r H° = -196.6 \text{ kJ mol}^{-1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise the rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives H_2SO_4 of the desired concentration.

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

The sulphuric acid obtained by contact process is 96-98% pure.

Q. 22. How is SO_2 an air pollutant?

Ans. (*i*) SO_2 dissolves in moisture present in air to form H_2SO_3 which damages building materials especially marble.

$$CaCO_3 + H_2SO_3 \longrightarrow CaSO_3 + H_2O + CO_2$$

(*ii*) Even at a low concentration of 0.03 ppm, SO_2 has a damaging effect on plants. If exposed for a long time, it slows down the formation of chlorophyll resulting in injury to the leaves including loss of green colour. This is called **chlorosis**.

(*iii*) SO_2 is strongly irritating to the respiratory tract. SO_2 at a concentration of 5 ppm causes throat and eye irritation resulting in cough, tears and redness in eyes. It causes breathlessness and affects voice box.

Q. 23. Why are halogens strong oxidising agents?

Ans. Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.

$$X + e^- \longrightarrow X^-$$

Thus, halogens act as strong oxidising agents. Their oxidising power, however, decreases from F_2 to I_2.

Q. 24. Explain why fluorine forms only one oxo acid, HOF.

Ans. Due to high electronegativity, small size and absence of *d*-orbitals, F does not form oxo-acids such as HOFO, $HOFO_2$ and $HOFO_3$ in which the oxidation state of F would be +3, +5 and +7. It just forms one oxo-acid, *i.e.*, HOF in which the oxidation state of F is +1.

Q. 25. Explain why inspite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

Ans. Although N and Cl have about the same electronegativity, yet their atomic size (covalent radii) are much different: N = 70 pm and Cl = 99 pm. Thus, electron density per unit volume on nitrogen atom is much higher than that on chlorine atom. Hence, nitrogen forms hydrogen bonds while chlorine does not though both have nearly the same electronegativity.

Q. 26. Write two uses of ClO_2.

Ans. (*a*) ClO_2 is a powerful oxidising agent and chlorinating agent. It is used for bleaching wood pulp and cellulose and for purifying drinking water.

(*b*) It is an excellent bleaching agent. Its bleaching power is about 30 times higher than that of Cl_2 and is used for bleaching flour to make white bread.

Q. 27. Why are halogens coloured?

Ans. All halogens are coloured. This is due to absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level while the remaining light is transmitted. The colour of the halogen is the colour of transmitted light.

Q. 28. Write the reactions of F_2 and Cl_2 with water.

Ans. F_2 being a strong oxidising agent oxidises H_2O to O_2 or O_3

$$2F_2(g) + 2H_2O\,(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2\,(g)$$

$$3F_2(g) + 3H_2O\,(l) \longrightarrow 6H^+(aq) + 6F^-(aq) + O_3\,(g)$$

Cl_2 reacts with H_2O to form hydrochloric acid and hypochlorous acid.

$$Cl_2\,(g) + H_2O(l) \longrightarrow \underset{\text{Hydrochloric acid}}{HCl(aq)} + \underset{\text{Hypochlorous acid}}{HOCl(aq)}$$

Q. 29. How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only. ***[CBSE 2019 (56/4/1)]***

Ans. HCl can be oxidised to Cl_2 by a number of oxidising agents like MnO_2, $KMnO_4$.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Cl_2 can be reduced to HCl by reacting with H_2 in the presence of diffused sunlight.

$$H_2 + Cl_2 \xrightarrow{\text{Diffused sunlight}} 2HCl$$

Q. 30. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6? ***[CBSE Delhi 2013]***

Ans. Neil Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid, $O_2^+\,PtF_6^-$

$$O_2(g) + PtF_6(g) \longrightarrow O_2^+[PtF_6]^-$$

Here, O_2 gets oxidised to O_2^+ by PtF_6.

Since the first ionisation enthalpy of Xe (1170 kJ mol^{-1}) is fairly close to that of O_2 molecules (1175 kJ mol^{-1}), Bartlett thought that PtF_6 should also oxidise Xe to Xe^+. This inspired Bartlett to carry out the reaction between Xe and PtF_6. When Xe and PtF_6 were mixed, a rapid reaction occurred and a red solid with the formula, $Xe^+[PtF_6]^-$ was obtained.

$$Xe + PtF_6 \xrightarrow{278\text{ K}} Xe^+[PtF_6]^-$$

Q. 31. What are the oxidation states of phosphorus in the following:

(*i*) H_3PO_3 (*ii*) PCl_3 (*iii*) Ca_3P_2 (*iv*) Na_3PO_4 (*v*) POF_3

Ans. Let the oxidation state of P be *x*.

(*i*) $\overset{+1}{H_3}\overset{x}{P}\overset{-2}{O_3}$ $\quad\therefore\ 3(1) + x + 3(-2) = 0$ or $x = +3$

(*ii*) $\overset{x}{P}\overset{-1}{Cl_3}$ $\quad\therefore\ x + 3(-1) = 0$ or $x = +3$

(*iii*) $\overset{+2}{Ca_3}\overset{x}{P_2}$ $\quad\therefore\ 3(2) + 2 \times x = 0$ or $x = -3$

(*iv*) $\overset{+1}{Na_3}\overset{x}{P}\overset{-2}{O_4}$ $\quad\therefore\ 3(1) + x + 4(-2) = 0$ or $x = +5$

(*v*) $\overset{x}{P}\overset{-2}{O}\overset{-1}{F_3}$ $\quad\therefore\ x + 1(-2) + 3(-1) = 0$ or $x = +5$

Q. 32. Write balanced equations for the following:

(*i*) NaCl is heated with sulphuric acid in the presence of MnO_2.

(*ii*) Chlorine gas is passed into a solution of NaI in water.

Ans. (*i*) Cl_2 is produced.

$$[NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$$

$$4HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O$$

(*ii*) Cl_2 being an oxidising agent oxidises NaI to I_2

$$Cl_2(g) + 2NaI\,(aq) \longrightarrow 2NaCl(aq) + I_2(s)$$

Q. 33. How are xenon fluorides XeF_2 , XeF_4 and XeF_6 obtained?

Ans. Refer to Basic Concepts Point C (Group 18).

Q. 34. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Ans. Replace O^- (9 electrons) in ClO^- by F (9 electrons). The resulting neutral molecule is ClF. Since ClF can combine further with F to form ClF_3 so, ClF is a Lewis base.

Q. 35. How are XeO_3 and $XeOF_4$ prepared?

Ans. Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

In contrast, partial hydrolysis of XeF_6 gives $XeOF_4$.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Q. 36. Arrange the following in order of property indicated for each set:

(*i*) F_2, Cl_2, Br_2, I_2 — increasing bond dissociation enthalpy.

(*ii*) HF, HCl, HBr, HI — increasing acid strength.

(*iii*) NH_3, PH_3, AsH_3, SbH_3, BiH_3 — increasing base strength. ***[CBSE Delhi 2019 (56/2/1)]***

Ans. (*i*) $I_2 < F_2 < Br_2 < Cl_2$

Bond dissociation enthalpy decreases with increase in the size of the atom as we move from Cl to I. The low F—F bond dissociation enthalpy is due to the fact that F atom is very small in size and hence the three lone pair of electrons on each F atom repel the bond pair of F—F bond very strongly.

(*ii*) As the size of atom increases from F to I, the bond dissociation enthalpy of H—X bond decreases from H—F to H—I. Therefore, the acid strength increases in the opposite order:

HF < HCl < HBr < HI.

(*iii*) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

On moving from nitrogen to bismuth, the size of the atom increases while the electron density on the atom decreases. Thus, the basic strength decreases.

Q. 37. Which one of the following does not exist?

(*i*) $XeOF_4$ **(*ii*) NeF_2**

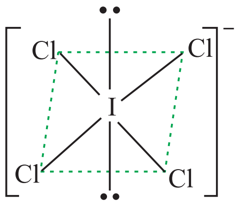
(*iii*) XeF_2 **(*iv*) XeF_6**

Ans. The sum of first and second ionisation enthalpies of Ne are much higher than those of Xe. Thus, F_2 can oxidise Xe to Xe^{2+} but cannot oxidise Ne to Ne^{2+}. In other words, NeF_2 does not exist and all the xenon fluorides (XeF_2 and XeF_6) and xenon oxyfluoride ($XeOF_4$) do exist.

Q. 38. Give the formula and describe the structure of a noble gas species which is isostructural with: (*i*) ICl_4^- (*ii*) IBr_2^- (*iii*) BrO_3^-

Ans. (*i*) **Structure of ICl_4^-:** I in ICl_4^- has four bond pairs and two lone pairs of electrons. Therefore, according to VSEPR theory, it should be square planar.

ICl_4^- has $(7 + 1 \times 4 + 1) = 12$ valence electrons. A noble gas species having 12 valence electrons is XeF_4 $(8 + 1 \times 4 = 12)$. Therefore, like ICl_4^-, XeF_4 is also square planar.

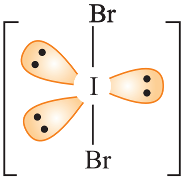


Square planar

(*ii*) **Structure of IBr_2^-:** I in IBr_2^- has two bond pairs and three lone pairs of electrons. So, according to VSEPR theory, it should be linear.

Here, IBr_2^- has $10(7 + 1 \times 2 + 1)$ valence electrons. A noble gas species having 10 valence electrons is XeF_2 $(8 + 1 \times 2 = 10)$.

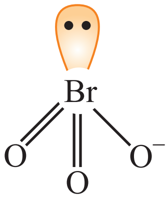
Thus, like IBr_2^-, XeF_2 is also linear.



Linear

(*iii*) **Structure of BrO_3^-:** The central atom Br has seven electrons. Four of these electrons form two double bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion. The remaining two electrons form one lone pair. Hence, in all, there are three bond pairs and one lone pair of electrons around Br atom in BrO_3^-. Therefore, according to VSEPR theory, BrO_3^- should be pyramidal.

Here, BrO_3^- has $8\ (7 + 0 \times 3 + 1)$ valence electrons. A noble gas species having 8 valence electrons is XeO_3 $(8 + 0 \times 3 = 8)$. Thus, like BrO_3^-, XeO_3 is also pyramidal.



Pyramidal

Q. 39. Why do noble gases have comparatively large atomic sizes?

Ans. Noble gases have only van der Waals' radii while others have covalent radii. As van der Waals' radii are larger than covalent radii. Hence, noble gases have comparatively large atomic sizes.

Q. 40. List the uses of neon and argon gases.

Ans. **Uses of Neon:**

(*i*) Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

(*ii*) Neon bulbs are used in botanical gardens and in green houses.

(*iii*) Neon is used in voltage regulators and indicators.

Uses of Argon:

(*i*) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.

(*ii*) It is used in the laboratory for handling substances that are air-sensitive.

(*iii*) Argon is used in radio valves and rectifiers.

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. **Out of the following halides of group 16, which does not possess reducing property?**

   (*a*) H_2Te (*b*) H_2Se (*c*) H_2S (*d*) H_2O

2. **SO_2 acts as a/an**

   (*a*) Oxidising agent (*b*) Reducing agent (*c*) Bleaching agent (*d*) All of these

3. **Which of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species?**

   (*a*) $S < O < Cl < F$ (*b*) $F < Cl < O < S$ (*c*) $Cl < F < S < O$ (*d*) $O < S < F < Cl$

4. **Which of the following is not tetrahedral in shape?** *[NCERT Exemplar]*

   (*a*) NH_4^+ (*b*) $SiCl_4$ (*c*) SF_4 (*d*) SO_4^{2-}

5. **Which of the following are peroxoacids of sulphur?** *[NCERT Exemplar]*

   (*a*) H_2SO_5 and $H_2S_2O_8$ (*b*) H_2SO_5 and $H_2S_2O_7$

   (*c*) $H_2S_2O_7$ and $H_2S_2O_8$ (*d*) $H_2S_2O_6$ and $H_2S_2O_7$

6. **Hot conc. H_2SO_4 acts as moderately strong oxidising agent. It oxidises both metals and nonmetals. Which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?** *[NCERT Exemplar]*

   (*a*) Cu (*b*) S (*c*) C (*d*) Zn

7. **In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dil. HCl, a black precipitate is obtained. On boiling the precipitate with dil. HNO_3, it forms a solution of blue colour. Addition of excess of aqueous solution of ammonia to this solution gives _______________.** *[NCERT Exemplar]*

   (*a*) deep blue precipitate of $Cu\ (OH)_2$ (*b*) deep blue solution of $[Cu\ (NH_3)_4]^{2+}$

   (*c*) deep blue solution of $Cu(NO_3)_2$ (*d*) deep blue solution of $Cu(OH)_2.Cu(NO_3)_2$

8. **Which of the following options are not in accordance with the property mentioned against them?** *[NCERT Exemplar]*

(*a*) $F_2 > Cl_2 > Br_2 > I_2$	Oxidising power.
(*b*) $MI > MBr > MCl > MF$	Ionic character of metal halide.
(*c*) $F_2 > Cl_2 > Br_2 > I_2$	Bond dissociation enthalpy.
(*d*) $HI < HBr < HCl < HF$	Hydrogen-halogen bond strength.

9. **When chlorine reacts with hot and conc. NaOH, the product(s) formed are**

   (*a*) chloride (*b*) hypochlorite

   (*c*) chlorate (*d*) mixture of chloride and chlorate

10. **If chlorine gas is passed through hot NaOH solution, two changes are observed in the oxidation number of chlorine during the reaction. These are __________ and ___________.** *[NCERT Exemplar]*

    (*a*) 0 to +5 (*b*) 0 to +3 (*c*) 0 to –1 (*d*) 0 to +1

11. **On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because:** *[NCERT Exemplar]*

    (*a*) H_2SO_4 reduces HI to I_2 (*b*) HI is of violet colour

    (*c*) HI gets oxidised to I_2 (*d*) HI changes to HIO_3

12. **Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.** *[NCERT Exemplar]*

Ion	**ClO_4^-**	**IO_4^-**	**BrO_4^-**
Reduction potential E^o/V	**$E^o = 1.19$ V**	**$E^o = 1.65$ V**	**$E^o = 1.74$ V**

    (*a*) $ClO_4^- > IO_4^- > BrO_4^-$ (*b*) $IO_4^- > BrO_4^- > ClO_4^-$

    (*c*) $BrO_4^- > IO_4^- > ClO_4^-$ (*d*) $BrO_4^- > ClO_4^- > IO_4^-$

13. The correct order of increasing bond angles in the following species is:

(*a*) $Cl_2O < ClO_2^- < ClO_2$ (*b*) $ClO_2^- < Cl_2O < ClO_2$

(*c*) $Cl_2O < ClO_2 < ClO_2^-$ (*d*) $Cl_2O < ClO_2 < ClO_2^-$

14. Which of the following is isoelectronic pair? [*NCERT Exemplar*]

(*a*) ICl_2, ClO_2 (*b*) BrO_2^-, BrF_2^+ (*c*) ClO_2, BrF (*d*) CN^-, O_3

15. The set with correct order of acidity:

(*a*) $HClO < HClO_2 < HClO_3 < HClO_4$ (*b*) $HClO_4 < HClO_3 < HClO_2 < HClO$

(*c*) $HClO < HClO_4 < HClO_3 < HClO_2$ (*d*) $HClO_4 < HClO_2 < HClO_3 < HClO$

16. In which case, order of acidic strength is not correct?

(*a*) $HClO_4 > HClO_3 > HClO_2$ (*b*) $HI > HBr > HCl$

(*c*) $HF > H_2O > NH_3$ (*d*) $HIO_4 > HBrO_4 > HClO_4$

17. Which of the statement given below is incorrect?

(*a*) ONF is isoelectronic with O_2N^- (*b*) O_3 molecule is bent

(*c*) OF_2 is an oxide of fluorine (*d*) Cl_2O_7 is an anhydride of perchloric acid

18. In the preparation of compounds of Xe, Bartlett had taken $O_2^+Pt\,F_6^-$ as a base compound. This is because: [*NCERT Exemplar*]

(*a*) both O_2 and Xe have same size.

(*b*) both O_2 and Xe have same electron gain enthalpy.

(*c*) both O_2 and Xe have almost same ionisation enthalpy.

(*d*) both Xe and O_2 are gases.

19. Two types of F × F angles are present in which of the following molecule (X = S, Xe, C):

(*a*) SF_6 (*b*) CF_4 (*c*) XeF_4 (*d*) SF_4

20. The structure of XeF_6 is

(*a*) distorted octahedral (*b*) linear (*c*) square planar (*d*) tetrahedral

21. In which of the following pairs, the two species are isostructural?

(*a*) SF_4 and XeF_4 (*b*) BF_3 and NF_3 (*c*) BrO_3^- and XeO_3 (*d*) SO_3^{2-} and NO_3^-

22. Which of the following statement is not true for helium?

(*a*) He is used in gas-cooked nuclear reactors.

(*b*) He is used as cryogenic agent for carrying out experiments at low temperature.

(*c*) He is used to fill gas balloons instead of hydrogen because it is lighter than hydrogen and non-inflammable.

(*d*) He is used as a diluent for oxygen in modern diving apparatus.

Answers

1. (*d*) **2.** (*d*) **3.** (*d*) **4.** (*c*) **5.** (*a*) **6.** (*c*) **7.** (*b*) **8.** (*b, c*) **9.** (*d*) **10.** (*a, c*)
11. (*c*) **12.** (*c*) **13.** (*b*) **14.** (*b*) **15.** (*a*) **16.** (*d*) **17.** (*c*) **18.** (*c*) **19** (*d*) **20.** (*a*)
21. (*c*) **22.** (*c*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(b) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(c) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(d) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. Assertion (*A*) : Nitrogen does not form compounds in +5 oxidation state with halogens.
Reason (*R*) : All oxidation states of nitrogen from +1 to +4 tend to disproportionate in acid solution.

2. **Assertion (*A*) :** The O—O bond length in ozone is identical with that in molecular oxygen.
Reason (*R*) : The ozone molecule is a resonance hybrid of two canonical structures.

3. **Assertion (*A*) :** Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2.
Reason (*R*) : Oxygen forms $p\pi - p\pi$ multiple bond due to small size and small bond length but $p\pi - p\pi$ bonding is not possible in sulphur.

4. **Assertion (*A*) :** The transition temperature of sulphur is 369 K.
Reason (*R*) : At 369 K, both α-sulphur and β-sulphur are stable. Below 369 K, only α-sulphur is stable whereas above 369 K, only β-sulphur is stable.

5. **Assertion (*A*) :** SO_3 has a planar structure.
Reason (*R*) : S atom in SO_3 is sp^2-hybridized and O–S–O bond angle is 120º.

6. **Assertion (*A*) :** SF_6 cannot be hydrolysed but SF_4 can be.
Reason (*R*) : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

7. **Assertion (*A*) :** NaCl reacts with concentrated H_2SO_4 to give colourless fumes with pungent smell. But on adding MnO_2 the fumes become greenish yellow.
Reason (*R*) : MnO_2 oxidises HCl to chlorine gas which is greenish yellow.

8. **Assertion (*A*) :** Salts of ClO_3^- and ClO_4^- are well known but those of FO_3^- and FO_4^- are non-existent.
Reason (*R*) : F is more electronegative than O while Cl is less electronegative than O.

9. **Assertion (*A*) :** HClO is stronger acid than HBrO.
Reason (*R*) : Greater is the electronegativity of the halogen, greater will be attraction of electron pair towards it and hence more easily the H^+ ion will be released.

10. **Assertion (*A*) :** HI cannot be prepared by the action of conc. H_2SO_4 on KI.
Reason (*R*) : HI is more volatile than H_2SO_4.

11. **Assertion (*A*) :** Hydrolysis of XeF_6 is an example of a redox reaction.
Reason (*R*) : XeF_6 when hydrolysed yields $XeOF_4$ and XeO_2F_2.

Answers

1. (*b*) **2.** (*d*) **3.** (*a*) **4.** (*a*) **5.** (*a*) **6.** (*a*) **7.** (*a*) **8.** (*a*) **9.** (*a*) **10.** (*b*)
11. (*d*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The noble gases have closed shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The chemical reactivity of noble gases involves the loss of electrons and hence it can form compounds with highly electronegative elements like F and O. Although Xe forms several fluorides, xenon tetrafluoride is the most important among fluorides. The various compounds of xenon involve xenon in first, second and third excited states. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6.

1. Noble gases are least reactive elements. Give reason.

Ans. Noble gases have fully filled outermost shells,high ionization enthalpy and positive electron gain enthalpy and therefore they are least reactive elements.

2. The majority of noble gas compounds are those of xenon only. Why?

Ans. Xe has the lowest ionisation energy among noble gases and hence can be easily oxidised by strong oxidising agent like O_2 and F_2. That is why the majority of noble gas compounds are those of xenon.

3. Noble gases have large positive values of electron gain enthalpy. Give reason.

Ans. Since noble gases have stable electronic configurations, they have no tendency to accept electrons and thus have large positive values of electron gain enthalpy.

4. What is the type of hybridisation and shape of XeF_2?

Ans. sp^3d and linear.

5. Xenon does not form fluorides such as XeF_3 and XeF_5. Give reason.

Ans. All the filled orbitals of Xe have paired electrons. The promotion of one,two or three electrons from the 5*p* filled orbital to the 5*d* vacant orbitals will give rise to two, four and six half filled orbitals respectively. So, Xe can combine with even but not odd number of F-atoms. Hence, it cannot form XeF_3 and XeF_5.

PASSAGE–2

Each halogen can combine with other halogens to form several compounds amongst themselves. These are known as interhalogens or interhalogen compounds. The main reason for the formation of these compounds is the large electronegativity and size differences among the halogens. Thus fluorine, the most electronegative element and the smallest halogen, forms the maximum number of interhalogens. lnterhalogen compound having maximum number of halogen atoms is IF_7. In interhalogens, the less electronegative halogen always written first.

1. Can FCl_3 exist? Comment.

Ans. No, because F atom has no *d*-orbital and therefore it cannot expand its valence shell. Further, three big sized Cl atoms cannot be accommodated around a small F atom.

2. In interhalogen compounds of the type AB_5 and AB_7, B is invariably fluorine. Why?

Ans. Fluorine being the strongest oxidising agent, can form interhalogen compounds in +5 and +7 oxidation state.

3. Why are interhalogens are more reactive than halogens?

Ans. This is because the bond in the interhalogen (X—X′) is weaker than X—X and X′—X′ bond in halogens.

4. What is the structure of IF_7?

Ans. Pentagonal bipyramidal.

5. Give one use of interhalogen compounds.

Ans. These compounds are used as non-aqueous solvents. They are very useful fluorinating agents.

Very Short Answer Questions [1 mark]

Q. 1. On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved which forms a blue coloured complex with Cu^{2+} ion. Identify the gas. [*CBSE Delhi 2016*] [*HOTS*]

Ans. Ammonia, NH_3.

Q. 2. On heating Cu turnings with conc. HNO_3, a brown coloured gas is evolved which on cooling dimerises. Identify the gas. [*CBSE (F) 2016*] [*HOTS*]

Ans. Nitrogen dioxide (NO_2)

Q. 3. Why is nitric oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic? [*NCERT Exemplar*]

Ans. In gaseous state NO_2 exists as monomer which has one unpaired electron but in solid state it dimerises to N_2O_4 so no unpaired electron is left hence solid form is diamagnetic.

Q. 4. BH_4^- and NH_4^+ are isolobal. Explain.

Ans. Both BH_4^- and NH_4^+ have tetrahedral shapes, *i.e.*, four lobes of sp^3-hybridised orbitals. Hence, they are isolobal.

Q. 5. In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $N(SiH_3)_3$, it has a planar geometry. Why?

Ans. $(CH_3)_3N$ is pyramidal due to sp^3 hybridisation and has a lone pair of electrons. $(SiH_3)_3$ N has sp^2 hybridisation because lone pair of nitrogen is donated to vacant *d*-orbital of Si.

Q. 6. PH_3 forms bubbles when passed slowly in water but NH_3 dissolves. Explain why. [*NCERT Exemplar*]

Ans. NH_3 forms hydrogen bonds with water therefore it is soluble in it but PH_3 cannot form hydrogen bond with water so it escapes as gas.

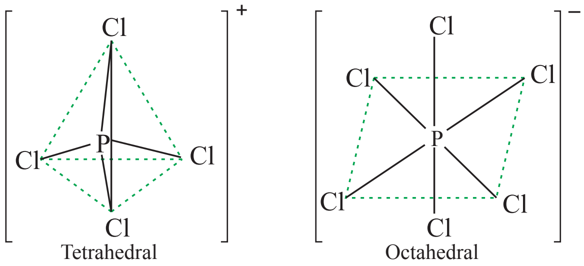
Q. 7. Write the formula of the compound of phosphorous which is obtained when conc. HNO_3 oxidises P_4. *[CBSE (AI) 2017]*

Ans. H_3PO_4

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Q. 8. Draw the structure of solid PCl_5. *[CBSE (F) 2013]*

Ans.



Tetrahedral Octahedral

Q. 9. Out of H_2O and H_2S, which one has higher bond angle and why? *[NCERT Exemplar]*

Ans. Bond angle of H_2O is larger, because oxygen is more electronegative than sulphur. Therefore, bond pair electron of O—H bond will be closer to oxygen and there will be more bond pair–bond pair repulsion between bond pairs of two O—H bonds.

Q. 10. Arrange the following hydrides of Group-16 elements in the decreasing order of their reducing character:

H_2O, H_2S, H_2Se, H_2Te *[CBSE (F) 2017]*

Ans. $H_2Te > H_2Se > H_2S > H_2O$

Q. 11. Explain why ozone is thermodynamically less stable than oxygen. *[NCERT Exemplar]*

Ans. Ozone is thermodynamically unstable with respect to oxygen as its decomposition into oxygen results in the liberation of heat (ΔH is –ve) and an increase in entropy (ΔS is +ve). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

Q. 12. On heating copper turnings with conc. H_2SO_4, a colourless gas with pungent smell is evolved which decolourises acidified $KMnO_4$ solution. Identify the gas. *[CBSE East 2016]* *[HOTS]*

Ans. Sulphur dioxide (SO_2)

Q. 13. Write the formula of the compound of sulphur which is obtained when conc. HNO_3 oxidises S_8. *[CBSE (AI) 2017]*

Ans. H_2SO_4

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

Q. 14. Why sulphurous acid acts as a reducing agent?

Ans. Due to the presence of a lone pair of electrons on the sulphur atom, sulphurous acid can be easily oxidised to sulphuric acid. Therefore, it acts as a reducing agent.

$$H_2O + Br_2 + H_2SO_3 \longrightarrow 2HBr + H_2SO_4$$

Q. 15. Concentrated H_2SO_4 is used as a dehydrating agent. Explain.

Ans. Sulphuric acid has a strong affinity for water. It, therefore, removes water not only from materials which contain it but frequently removes oxygen and hydrogen from other compounds in the proportion required to form water (H_2O).

Q. 16. Sulphur disappears when boiled with sodium sulphite. Why?

Ans. When sodium sulphite is heated with sulphur, we get sodium thiosulphate which is soluble in water that is why sulphur disappears.

$$Na_2SO_3 + S \xrightarrow{\text{heat}} Na_2S_2O_3$$

Q. 17. Fluorine exhibits only –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

Ans. Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d*-orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

Q. 18. Why is F_2O referred to as a fluoride but Cl_2O is an oxide?

Ans. F_2O is called oxygen fluoride because fluorine is more electronegative than oxygen whereas Cl_2O is called chlorine oxide because oxygen is more electronegative than chlorine.

Q. 19. Iodine forms I_3^- but F_2 does not form F_3^- ions. Why?

Ans. I_2, because of the presence of vacant *d*-orbitals, accepts electrons from I^- ions to form I_3^- ions but F_2 because of the absence of *d*-orbitals does not accept electrons from F^- ions to form F_3^- ions.

Q. 20. Why is I_2 more soluble in KI than in water?

Ans. It is due to formation of soluble complex KI_3.

$$I_2 + KI \longrightarrow KI_3$$

Q. 21. How does xenon atom form compounds with fluorine even though the xenon atom has a closed shell configuration?

Ans. This is because 1, 2 or 3 electrons from the 5*p*-orbitals can be excited to empty 5*d*-orbitals and thus making 2, 4 or 6 half-filled orbitals available for bond formation.

Q. 22. Complete the following reaction:

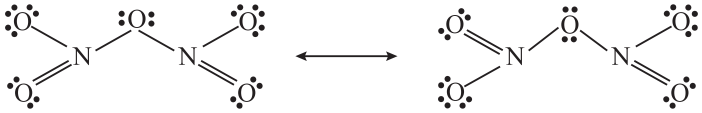
$XeF_6 + 2H_2O \longrightarrow$ **[*CBSE Delhi 2017; 2020 (56/3/2)*]**

Ans. $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

Short Answer Questions–I [2 marks]

Q. 1. Nitric acid forms an oxide of nitrogen on reaction with P_4O_{10}. Write the reaction involved. Also write the resonating structures of the oxide of nitrogen formed. **[*NCERT Exemplar*]**

Ans. $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$



Q. 2. When dilute ferrous sulphate solution is added to an aqueous solution containing nitrate ion followed by careful addition of concentrated sulphuric acid along the sides of test tube, a brown ring is formed at the interface between the solution and sulphuric acid layers. Which anion is confirmed by the appearance of brown ring? What is the composition of the brown ring? **[*CBSE 2019 (56/4/1)*]**

Ans. Nitrate ion—NO_3^-

$[Fe(H_2O)_5(NO)]^{2+}$

Q. 3. Name the two most important allotropes of sulphur. Which one of the two is stable at room temperature? What happens when the stable form is heated above 370 K? **[*CBSE (F) 2014*]**

Ans. Two most important allotropes of sulphur are rhombic sulphur and monoclinic sulphur. The stable form at room temperature is rhombic sulphur. When rhombic sulphur is heated above 370 K, it gets converted into monoclinic sulphur.

Q. 4. Complete the following equations:

(*i*) $P_4 + H_2O \longrightarrow$ **(*ii*) $XeF_4 + O_2F_2 \longrightarrow$** **[*CBSE (AI) 2014*]**

Ans. (*i*) $P_4 + H_2O \longrightarrow$ No reaction

(*ii*) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

Q. 5. Complete the following chemical equations:

(*i*) $Ca_3P_2 + H_2O \longrightarrow$ **(*ii*) $Cu + H_2SO_4(\text{conc.}) \longrightarrow$** **[*CBSE Delhi 2014*]**

Ans. (*i*) $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$

(*ii*) $Cu + 2H_2SO_4(\text{conc.}) \longrightarrow CuSO_4 + SO_2 + 2H_2O$

Q. 6. Complete the following equations:

(*i*) $2Ag + PCl_5 \longrightarrow$

(*ii*) $CaF_2 + H_2SO_4 \longrightarrow$ **[*CBSE (AI) 2014*]**

Ans. (*i*) $2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$

(*ii*) $CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4$

Q. 7. What happens when

(*i*) $(NH_4)_2Cr_2O_7$ is heated **(*ii*) H_3PO_3 is heated?**

Write the equations. *[CBSE Delhi 2017]*

Ans. (*i*) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

(*ii*) $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$

Q. 8. What happens when

(*i*) Conc. H_2SO_4 is added to Cu?

(*ii*) SO_3 is passed through water?

Write the equations. *[CBSE Delhi 2017]*

Ans. (*i*) $Cu + 2H_2SO_4\,(\text{conc.}) \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(*ii*) $SO_3 + H_2O \longrightarrow H_2SO_4$

Q. 9. What happens when

(*i*) HCl is added to MnO_2?

(*ii*) PtF_6 and xenon are mixed together? *[CBSE Delhi 2017]*

Ans. (*i*) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(*ii*) $PtF_6 + Xe \longrightarrow Xe^+[PtF_6]^-$

Q. 10. Complete the following equations:

(*i*) $C + \text{conc. } H_2SO_4 \longrightarrow$ **(*ii*) $XeF_2 + H_2O \longrightarrow$** *[CBSE (AI) 2014]*

Ans. (*i*) $C + 2H_2SO_4(\text{conc.}) \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(*ii*) $2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

Q. 11. Complete the following reactions:

(*i*) $Cl_2 + H_2O \longrightarrow$ **(*ii*) $XeF_6 + 3H_2O \longrightarrow$** *[CBSE Delhi 2017]*

Ans. (*i*) $Cl_2 + H_2O \longrightarrow HCl + HOCl$

(*ii*) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Q. 12. Complete the following chemical equations:

(*i*) $F_2 + 2Cl^- \longrightarrow$ **(*ii*) $2XeF_2 + 2H_2O \longrightarrow$** *[CBSE Delhi 2017]*

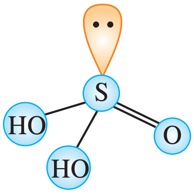
Ans. (*i*) $F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$

(*ii*) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

Q. 13. Draw the structures of the following: *[CBSE (AI) 2017]*

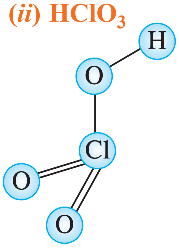
(*i*) H_2SO_3 **(*ii*) $HClO_3$**

Ans. (*i*)



Sulphurous acid
(H_2SO_3)

(*ii*)

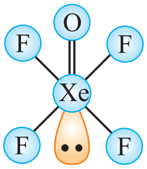


Chloric acid
($HClO_3$)

Q. 14. Draw the structures of the following:

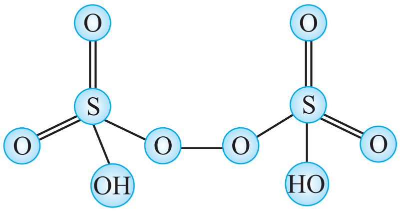
(*i*) $XeOF_4$ **(*ii*) $H_2S_2O_8$** *[CBSE Ajmer 2015; 2020 (56/5/1)]*

Ans. (*i*)



$XeOF_4(sp^3d^2)$
Square pyramidal

(*ii*)

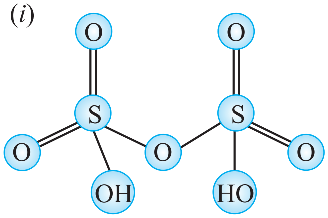


Peroxodisulphuric acid
($H_2S_2O_8$)

Q. 15. Draw the structures of the following:

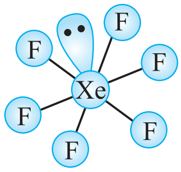
(i) **$H_2S_2O_7$** ***(ii)*** **XeF_6** ***[CBSE Delhi 2017, 2020 (56/3/2)]***

Ans. (*i*)



$H_2S_2O_7$

(*ii*)

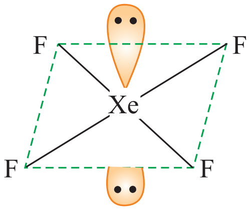


XeF_6
Distorted octahedral

Q. 16. Draw the structures of the following: ***[CBSE (AI) 2017]***

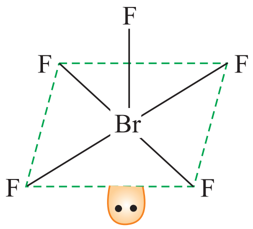
(i) **XeF_4** ***(ii)*** **BrF_5**

Ans. (*i*)



XeF_4: Square planar

(*ii*)

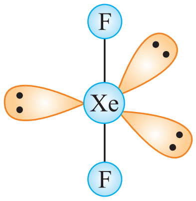


BrF_5: Square pyramidal

Q. 17. Draw the structures of the following:

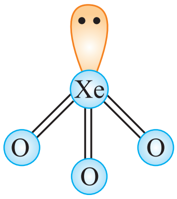
(i) **XeF_2** ***(ii)*** **XeO_3** ***[CBSE (AI) 2014]***

Ans. (*i*) There are two bond pairs and three lone pairs of electrons around central Xe atom in XeF_2. Therefore, according to VSEPR theory, XeF_2 should be linear.



XeF_2

(*ii*) There are three bond pairs and one lone pair of electrons around Xe atom in XeO_3. Therefore, according to VSEPR theory, XeO_3 should be pyramidal.



XeO_3, Pyramidal

Q. 18. Give reasons for the following:

(i) **CN^- ion is known but CP^- ion is not known.**

(ii) **NO_2 dimerises to form N_2O_4.**

Ans. (*i*) Nitrogen being smaller in size forms ρπ-ρπ multiple bonding with carbon, so CN^- ion is known, but phosphorus does not form ρπ-ρπ bond as it is larger in size.

(*ii*) This is because NO_2 is an odd electron molecule and therefore gets dimerised to stable N_2O_4.

Q. 19. Give reasons:

(*i*) NH_3 has a higher proton affinity than PH_3.

(*ii*) NO (Nitric oxide) is paramagnetic in the gaseous state but diamagnetic in the liquid and solid states.

Ans. (*i*) When NH_3 or PH_3 accepts a proton, an additional N—H or P—H bond is formed.

$$H_3N: + H^+ \longrightarrow NH_4^+$$

$$H_3P: + H^+ \longrightarrow PH_4^+$$

Due to the bigger size of P than N, P—H bond thus formed is much weaker than the N—H bond. Thus, NH_3 has higher proton affinity than PH_3.

(*ii*) NO has an odd number of electrons (11 valence electrons) and hence is paramagnetic in the gaseous state. But in liquid and solid states, it exists as a symmetrical or asymmetrical dimer and hence is diamagnetic in these states.

Q. 20. Assign a reason for each of the following:

(*i*) SCl_6 is not known but SF_6 is known.

(*ii*) Sulphur hexafluoride is used as a gaseous electrical insulator. **[*NCERT Exemplar*]**

Ans. (*i*) Due to small size of fluorine, six F^- ions can be accommodated around sulphur whereas chloride ion is comparatively larger in size, therefore, there will be interionic repulsion.

(*ii*) SF_6 is a colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. Because of its inertness and high tendency to suppress internal discharges, it is used as a gaseous electrical insulator in high voltage generators and switch gears.

Q. 21. How would you account for the following:

(*i*) H_2S is more acidic than H_2O.

(*ii*) Both O_2 and F_2 stabilise higher oxidation states but the ability of oxygen to stabilise the higher oxidation state exceeds that of fluorine. **[*CBSE (AI) 2011*]**

Ans. (*i*) This is because bond dissociation enthalpy of H—S bond is lower than that of H—O bond.

(*ii*) This is due to tendency of oxygen to form multiple bonds with metal atom.

Q. 22. Account for the following:

(*i*) Bleaching of flowers by chlorine is permanent while that by sulphur dioxide is temporary.

(*ii*) Sulphur exhibits greater tendency for catenation than selenium.

Ans. (*i*) Cl_2 bleaches coloured material by oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

$$\text{Coloured material} + [O] \longrightarrow \text{Colourless}$$

Hence, bleaching is permanent.

In contrast, SO_2 bleaches coloured material by reduction and hence bleaching is temporary since when the bleached colourless material is exposed to air, it gets oxidised and the colour is restored.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

$$\text{Coloured material} + H \longrightarrow \text{Colourless material} \xrightarrow[\text{oxidation}]{\text{aerial}} \text{Coloured material}$$

(*ii*) As we move from S to Se, the atomic size increases and hence the strength of E—E bond decreases. Thus, S—S bond is much stronger than Se—Se bond. Consequently, S shows greater tendency for catenation than selenium.

Q. 23. Account for the following:

(*i*) Iron on reaction with HCl forms $FeCl_2$ and not $FeCl_3$.

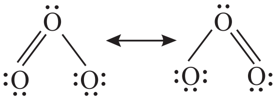
(*ii*) The two O—O bond lengths in the ozone molecule are equal. **[*CBSE (AI) 2014*]**

Ans. (*i*) Iron reacts with HCl to form $FeCl_2$ and H_2.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

H_2 thus produced prevents the oxidation of $FeCl_2$ to $FeCl_3$.

(*ii*) Ozone is a resonance hybrid of the following two main structures:



As a result of resonance, the two O—O bond lengths in O_3 are equal.

Q. 24. Account for the following observations:

(*i*) Among the halogens, F_2 is the strongest oxidising agent.

(*ii*) Acidity of oxo-acids of chlorine is $HOCl < HOClO < HOClO_2 < HOClO_3$.

Ans. (*i*) This is due to the

(*a*) low enthalpy of dissociation of F—F bond.

(*b*) high hydration enthalpy of F^-.

(*ii*) Oxygen is more electronegative than chlorine, therefore, dispersal of negative charge present on chlorine increases from ClO^- to ClO_4^- ion because number of oxygen atoms attached to chlorine is increasing. Therefore, stability of ions will increase in the order given below:

$ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$

This is due to increase in stability of conjugate base, acidic strength of corresponding acid increases in the following order:

$HClO < HClO_2 < HClO_3 < HClO_4$

Q. 25. (*i*) Why is HF acid stored in wax coated glass bottles?

(*ii*) ClF_3 exists but FCl_3 does not. Explain.

Ans. (*i*) HF does not attack wax but reacts with glass. It dissolves SiO_2 present in glass forming hydrofluorosilicic acid.

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

(*ii*) (*a*) Cl has vacant *d*-orbitals and hence can show an oxidation state of +3 but F has no *d*-orbitals, so, it cannot show positive oxidation states. Since F can show only –1 oxidation state, FCl_3 does not exist.

(*b*) Because of bigger size, Cl can accommodate three small F atoms around it while F being smaller cannot accommodate three large sized Cl atoms around it.

Q. 26. (*i*) Boiling points of interhalogens are little higher as compared to pure halogens. Why?

(*ii*) Out of He and Xe, which one can easily form compound and why? **[*CBSE South 2016*]**

Ans. (*i*) This is due to some amount of polarity associated with X—X′ bond in interhalogens whereas pure halogens are non-polar.

(*ii*) Xe, due to much lower ionisation enthalpy of Xe (1170 kJ mol^{-1}) than He (2372 kJ mol^{-1}).

Short Answer Questions–II [3 marks]

Q. 1. Complete the following equations:

(*i*) $PCl_3 + H_2O \longrightarrow$ **(*ii*) $XeF_2 + PF_5 \longrightarrow$**

(*iii*) $NaN_3 \xrightarrow{Heat}$ **[*CBSE (F) 2013*]**

Ans. (*i*) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

(*ii*) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

(*iii*) $2NaN_3 \xrightarrow{Heat} 2Na + 3N_2$

Q. 2. Illustrate how copper and zinc give different products on reaction with HNO_3. **[*HOTS*]**

Ans. With conc. HNO_3:

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$
$$Cu + O \longrightarrow CuO$$
$$CuO + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$
$$\underline{\overline{Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2}}$$

$$\begin{array}{l}
\text{Zn} + 2\text{HNO}_3 \longrightarrow \text{Zn(NO}_3)_2 + 2\text{H} \\
\text{HNO}_3 + \text{H} \longrightarrow \text{H}_2\text{O} + \text{NO}_2] \times 2 \\
\hline
\text{Zn} + 4\text{HNO}_3 \longrightarrow \text{Zn(NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2 \\
\hline
\end{array}$$

With dil HNO_3:

$$\begin{array}{l}
2\text{HNO}_3 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + 3\text{O} \\
\text{Cu} + \text{O} \longrightarrow \text{CuO}] \times 3 \\
\text{CuO} + 2\text{HNO}_3 \longrightarrow \text{Cu(NO}_3)_2 + \text{H}_2\text{O}] \times 3 \\
\hline
3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu (NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO} \\
\hline
\text{Zn} + 2\text{HNO}_3 \longrightarrow \text{Zn(NO}_3)_2 + 2\text{H}] \times 4 \\
\text{HNO}_3 + 8\text{H} \longrightarrow 3\text{H}_2\text{O} + \text{NH}_3 \\
\text{NH}_3 + \text{HNO}_3 \longrightarrow \text{NH}_4\,\text{NO}_3 \\
\text{NH}_4\,\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \\
\hline
4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn(NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O} \\
\hline
\end{array}$$

Q. 3. (*i*) Complete the following chemical equations.

(*a*) $NH_4Cl\ (aq) + NaNO_2\ (aq) \longrightarrow$

(*b*) $P_4 + 3NaOH + 3H_2O \longrightarrow$

(*ii*) Why does orthophosphoric acid acid exist as a syrupy liquid?

Ans. (*i*) (*a*) $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$

(*b*) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$

(*ii*) Orthophosphoric acid contains three -OH groups and hence undergoes extensive hydrogen bonding.

Q. 4. Give reasons for the following:

(*i*) N_2O_5 is more acidic than N_2O_3. *[CBSE (AI) 2017]*

(*ii*) H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 does not.

(*iii*) Both NO and ClO_2 are odd electron species but NO dimerises while ClO_2 does not.

Ans. (*i*) In N_2O_5, N is in +5 oxidation state whereas in N_2O_3 it is in +3 oxidation state. Higher the +ve oxidation state of the atom, more will be its acidic character.

(*ii*) Both H_3PO_2 and H_3PO_3 have P—H bonds, so they act as reducing agents. H_3PO_4, has no P—H bond but has O—H bonds, so it cannot act as a reducing agent.

(*iii*) In NO, the odd electron on N is attracted by only one O-atom but in ClO_2, the odd electron on Cl is attracted by two O-atoms. Thus, the odd electron on N in NO is localised while the odd electron on Cl in ClO_2 is delocalised. Consequently, NO has a tendency to dimerise but ClO_2 does not.

Q. 5. Account for the following:

(*i*) NH_3 has a higher boiling point than PH_3. *[CBSE Guwahati 2015]*

(*ii*) Bond angle in NH_4^+ is higher than NH_3. *[CBSE (F) 2015]*

(*iii*) The molecules NH_3 and NF_3 have dipole moments which are of opposite directions. *[CBSE (F) 2014]*

Ans. (*i*) Due to small size and high electronegativity of N, NH_3 undergoes extensive intermolecular H-bonding and hence exist as an associated molecule. In contrast due to low electronegativity of P, PH_3 does not undergo H-bonding and thus exist as a discrete molecule. That is why, boiling point of NH_3 is higher than PH_3.

(*ii*) N atom both in NH_3 and NH_4^+ is sp^3 hybridised. In NH_4^+ all the four orbitals are bonded whereas in NH_3 there is a lone pair on N , which is responsible for lone pair-bond pair repulsion in NH_3 reducing the bond angle from 109°28′ to 107°.

(*iii*) This is because in NH_3 nitrogen is more electronegative than hydrogen while in NF_3, nitrogen is less electronegative than fluorine.

Q. 6. Complete the following chemical equations:

(*i*) $Fe^{3+} + SO_2 + H_2O \longrightarrow$ **(*ii*) $P_4 + 10SOCl_2 \longrightarrow$**

(*iii*) $XeF_6 + \underset{\text{(excess)}}{H_2O} \longrightarrow$ *[CBSE (F) 2011]*

Ans. (*i*) $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4H^+ + SO_4^{2-}$

(*ii*) $P_4 + 10SOCl_2 \longrightarrow 4PCl_5 + 10SO_2$

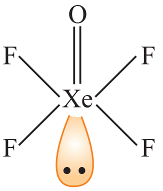
(*iii*) $XeF_6 + \underset{\text{(excess)}}{3H_2O} \longrightarrow XeO_3 + 6HF$

Q. 7. (*i*) Draw the structures of the following molecules:

(*a*) $XeOF_4$ **(*b*) H_2SO_4**

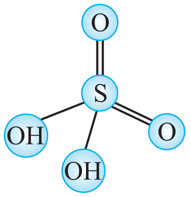
(*ii*) Write the structural difference between white phosphorus and red phosphorus. *[CBSE Delhi 2014]*

Ans. (*i*) (*a*)



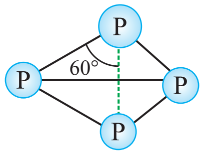
$XeOF_4$

(*b*)

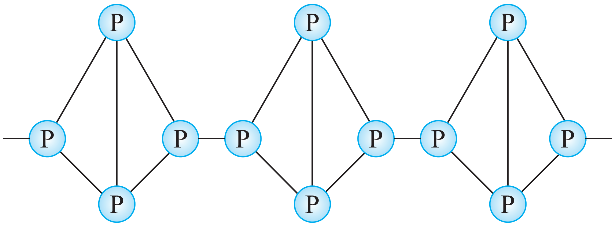


H_2SO_4

(*ii*) White phosphorus consists of discrete tetrahedral P_4 molecule with six P—P covalent bonds.



Red phosphorus has polymeric structure in which P_4 tetrahedra are linked together through P—P covalent bond to form chain.



Q. 8. Give reasons for the following:

(*i*) Nitric oxide becomes brown when released in air.

(*ii*) Solid phosphorus pentachloride exhibits some ionic character.

(*iii*) Ammonia acts as a ligand.

Ans. (*i*) Nitric oxide readily combines with O_2 of air to form nitrogen dioxide which is brown in colour.

$$\underset{\substack{\text{Nitric oxide}\\\text{(Colourless)}}}{2NO} + O_2 \longrightarrow \underset{\substack{\text{Nitrogen dioxide}\\\text{(Brown)}}}{2NO_2}$$

(*ii*) Solid PCl_5 exists as $[PCl_4]^+ [PCl_6]^-$ and hence exhibits some ionic character.

(*iii*) Due to the presence of lone pair of electrons on N, NH_3 acts as a ligand.

$$\underset{\text{Silver chloride}}{AgCl} + 2NH_3 \longrightarrow \underset{\text{Diamminesilver (I) chloride}}{[Ag(NH_3)_2]Cl}$$

Q. 9. Give reasons for the following:

(*i*) Reducing character decreases from SO_2 to TeO_2. *[CBSE (F) 2015]*

(*ii*) Bond angle decreases from H_2O to H_2Te.

(*iii*) Halogens have the maximum negative electron gain enthalpy. *[CBSE Chennai 2015]*

Ans. (*i*) Because the stability of + 4 oxidation state increases from S to Te on moving down the group in group 16 due to inert pair effect.

(*ii*) As we move down the group from O to Te, the size of central atom goes on increasing and its electronegativity goes on decreasing. Consequently, the bond pairs of electrons tend to lie away from the central atom as we move from H_2O to H_2Te. As a result of this the force of repulsion between the bond pairs decreases as we move from O to Te and hence the bond angle decreases in the same order.

(*iii*) Halogens have one electron less than the nearest noble gas configuration. Therefore, they have a strong tendency to accept an additional electron to acquire nearest noble gas configuration and hence they have maximum negative electron gain enthalpy.

Q. 10. How would you account for the following:

(*i*) The electron gain enthalpy with negative sign is less for oxygen than that for sulphur.

(*ii*) Fluorine never acts as the central atom in polyatomic interhalogen compounds. ***[CBSE (AI) 2010]***

(*iii*) H_2S has lower boiling point than H_2O. ***[CBSE (F) 2015]***

Ans. (*i*) This is due to smaller size of oxygen the electron cloud is distributed over a small region of space, making electron density high which repels the incoming electrons.

(*ii*) Fluorine never acts as the central atom in polyatomic interhalogen compounds since it is the most electronegative element of the group.

(*iii*) Due to high electronegativity and small size of oxygen, H_2O undergoes extensive intermolecular H-bonding and exists as an associated molecule. On the other hand, due to low electronegativity of S, H_2S is unable to form effective H-bonds and exists as a discrete molecule which are held by weak van der Waal forces. To overcome these forces only small amount of energy is required. Therefore, H_2S has lower boiling point than H_2O.

Q. 11. Assign appropriate reasons for each of the following statements:

(*i*) Metal fluorides are more ionic in nature than metal chlorides.

(*ii*) Addition of Cl_2 to KI solution gives it a brown colour but excess of Cl_2 turns it colourless.

(*iii*) Perchloric acid is a stronger acid than sulphuric acid.

Ans. (*i*) According to Fajan's rule, a bigger anion is more easily polarised than a smaller anion. As a result, same metal cation can polarise a bigger Cl^- ion more easily than the smaller F^- ion. In other words, for the same metal, the metal fluoride is more ionic than metal chloride. So, in general, we can easily say that metal fluorides are more ionic than metal chlorides.

(*ii*) Cl_2 being a stronger oxidising agent than I_2 first oxidises KI to give I_2 which imparts brown colour to the solution.

$$2KI(aq) + Cl_2(g) \longrightarrow 2KCl(aq) + \underset{\text{Brown}}{I_2(s)}$$

If Cl_2 is passed in excess, the I_2 thus formed gets further oxidised to iodic acid (HIO_3) which is colourless.

$$5Cl_2 + I_2 + 6H_2O \longrightarrow 10HCl + \underset{\text{(Colourless)}}{2HIO_3}$$

(*iii*) The oxidation state of Cl in perchloric acid is +7 while that of S in sulphuric acid is +6. Greater the oxidation state of central atom, more readily the O–H bond breaks and hence stronger is the acid.

Q. 12. Explain the following observations:

(*i*) H_2S is more acidic than H_2O.

(*ii*) Fluorine does not exhibit any positive oxidation state.

(*iii*) Helium forms no real chemical compound. ***[CBSE (AI) 2012]***

Ans. (*i*) Due to smaller size of O as compared to S, the bond dissociation enthalpy of O–H bond is higher than that of S–H bond. As a result, in aqueous solution, S–H bond can break more easily to form H^+ ion than O–H bond. Hence, H_2S is more acidic than H_2O.

(*ii*) This is because fluorine is the most electronegative element and it does not have *d* orbitals.

(*iii*) This is because the valence shell orbital of helium is completely filled ($1s^2$) and it has high ionisation enthalpy and more positive electron gain enthalpy.

Q. 13. **A colourless inorganic salt A decomposes at about 250°C to give only two products B and C leaving no residue. The oxide C is a liquid at room temperature and is neutral to litmus paper while B is neutral oxide. White phosphorus burns in excess of B to produce strong dehydrating agent. Give balanced equations for above processes.** ***[HOTS]***

Ans. A = NH_4NO_3 (Ammonium nitrate), B = N_2O (Nitrous oxide), C = H_2O

Reactions involved:

$$\underset{\substack{\text{Ammonium nitrate}\\ \text{(A)}}}{NH_4NO_3} \xrightarrow{250°\text{C}} \underset{\substack{\text{Nitrous oxide}\\ \text{(B)}}}{N_2O} + \underset{\text{(C)}}{2H_2O}$$

$$\underset{\text{(B)}}{10N_2O} + P_4 \longrightarrow 10N_2 + \underset{\substack{\text{Phosphorus pentoxide}\\ \text{(dehydrating agent)}}}{P_4O_{10}}$$

Q. 14. **On reaction with Cl_2, phosphorus forms two types of halides 'A' and 'B'. Halide A is yellowish-white powder but halide 'B' is colourless oily liquid. Identify A and B and write the formulas of their hydrolysis products.** ***[NCERT Exemplar]***

Ans. A = PCl_5 (Yellowish white powder)

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

B = PCl_3 (Colourless oily liquid)

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Hydrolysis products are formed as follows:

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Long Answer Questions [5 marks]

Q. 1. **(*i*) Although nitrogen and chlorine have nearly same electronegativity yet nitrogen forms hydrogen bonding while chlorine does not. Why?** ***[CBSE (F) 2017]***

(*ii*) What happens when F_2 reacts with water?

(*iii*) Write the name of the gas evolved when Ca_3P_2 is dissolved in water.

(*iv*) Write the formula of a noble gas species which is isostructural with IBr_2^-.

(*v*) Complete the equation:

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow$$

Ans. (*i*) Atomic size of nitrogen is smaller than chlorine. Due to this, electron density per unit volume on nitrogen atom is higher than that of chlorine atom. Therefore, nitrogen form hydrogen bonds while chlorine does not although nitrogen and chlorine have nearly same electronegativity.

(*ii*) It oxidises H_2O to O_2.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

(*iii*) Phosphine (PH_3).

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(*iv*) XeF_2.

IBr_2^- has 2 bond pairs and 3 lone pairs of electrons, therefore, it should be linear. Like IBr_2^-, XeF_2 has 2 bond pairs and 3 lone pairs of electrons, therefore, it is also linear.

(*v*) $$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(Brown ring)}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

Q. 2. **(*i*) Draw the structures of ClF_3.**

(*ii*) Explain the following observations:

(*a*) Oxygen is a gas but sulphur is a solid.

(*b*) Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water.

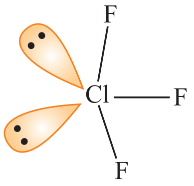
(*c*) The halogens are coloured. ***[CBSE (AI) 2012]***

Ans. (*i*) No. of electron pairs around central atom Cl = 5

No. of bond pairs = 3

No of lone pairs = 2

The shape would be slightly bent "T".



ClF_3

(*ii*) (*a*) Because of its small size, oxygen is capable of forming ρπ–ρπ bond and exists as diatomic O_2 molecule. The intermolecular forces in oxygen are weak van der Waals force, due to which it is a gas at room temperature. On the other hand, sulphur, due to its larger size prefers to form S–S single bond and exist as octaatomic S_8 molecule having puckered ring structure. Because of larger size the force of attraction holding the S_8 molecules together are much stronger. Hence sulphur is a solid at room temperature.

(*b*) This is because in H_2O hydrogen bond formed is three dimensional whereas in H–F it is linear.

(*c*) All halogens are coloured. This is due to absorption of radiation in visible region which results in the excitation of outer electrons to higher energy level while the remaining light is transmitted. The colour of the halogen is the colour of transmitted light.

Q. 3. (*i*) When conc. H_2SO_4 was added into an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were also added into this test tube. On cooling, the gas (A) changed into a colourless gas (B).

(*a*) Identify the gases A and B.

(*b*) Write the equations for the reactions involved.

(*ii*) Arrange the following in order of property indicated for each set:

(*a*) F_2, Cl_2, Br_2, I_2 —increasing bond dissociation enthalpy.

(*b*) HF, HCl, HBr, HI—increasing acidic strength.

Ans. (*i*) A = $NO_2(g)$, B = $N_2O_4(g)$

$$MNO_3 + H_2SO_4 \xrightarrow{\text{Heat}} MHSO_4 + HNO_3$$

$$4HNO_3 \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitrogen dioxide}\\ \text{(Brown gas)}}}{4NO_2} + 2H_2O + O_2$$

$$\underset{\text{Copper turnings}}{Cu} + 4HNO_3 \xrightarrow{\text{Heat}} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$\underset{\text{(Brown gas)}}{2NO_2} \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} \underset{\text{(Colourless)}}{N_2O_4}$$

(*ii*) Refer to Ans. 36 of NCERT Textbook Exercises.

Q. 4. (*i*) Arrange the following in the order of property indicated against each set:

(*a*) HF, HCl, HBr, HI — increasing bond dissociation enthalpy

(*b*) H_2O, H_2S, H_2Se, H_2Te — increasing acidic character

(*ii*) X_2 is a greenish yellow gas with pungent smell and used in purification of water. On dissolving water it gives a solution which turns blue litmus red. When it is passed through NaBr solution Br_2 is obtained.

(*a*) Identify the gas.

(*b*) What are products obtained when X_2 reacts with ammonia? Give chemical equations.

(*c*) What happens when X_2 reacts with cold and dilute NaOH solution? Write chemical equation and give the name of reaction.

Ans. (*i*) (*a*) Shorter the bond length, higher is the bond dissociation enthalpy of hydrogen halide. As the atomic size increases down the group the E–H (E = F, Cl, Br, I) bond length increases and hence the bond dissociation enthalpy increases in the reverse order *i.e.*,

$$HI < HBr < HCl < HF$$

(*b*) $H_2O < H_2S < H_2Se < H_2Te$

The increase in acidic character from H_2O to H_2Te is due to decrease in bond enthalpy for dissociation of H—E (E = O, S, Se, Te) bond down the group.

(*ii*) (*a*) $X_2 = Cl_2$

(*b*) $\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow \underset{\text{(oxidation)}}{NCl_3} + 3HCl$

(*c*) $\underset{\text{(cold and dil.)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$, Disproportionation reaction

Q. 5. (*i*) Give reasons for the following:

(*a*) Bond enthalpy of F_2 is lower than that of Cl_2.

(*b*) PH_3 has lower boiling point than NH_3.

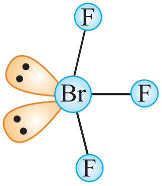
(*ii*) Draw the structures of the following molecules:

(*a*) BrF_3 (*b*) $(HPO_3)_3$ (*c*) XeF_4 **[*CBSE Delhi 2013*]**

Ans. (*i*) (*a*) Bond dissociation enthalpy decreases as the bond distance increases from F_2 to I_2 because of the corresponding increase in the size of the atom as we move from F to I. The F—F bond dissociation enthalpy is, however, smaller than that of Cl—Cl and even smaller than that of Br—Br. This is because F atom is very small and hence the three lone pairs of electrons on each F atom repel the bond pair holding the F-atoms in molecule resulting lower bond enthalpy than Cl_2.

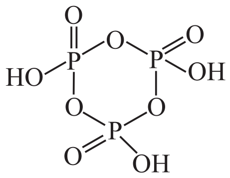
(*b*) Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

(*ii*) (*a*) BrF_3

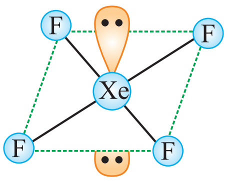


Slightly bent 'T'

(*b*) $(HPO_3)_3$



(*c*) XeF_4



Square planar

Q. 6. (*i*) Which allotrope of phosphorus is more reactive and why?

(*ii*) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers?

(*iii*) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(*iv*) Which noble gas is used in filling balloons for meteorological observations?

(*v*) Complete the equation: $XeF_2 + PF_5 \longrightarrow$ **[*CBSE Delhi 2015*]**

Ans. (*i*) White or yellow phosphorus is more reactive than the other allotropes because it is less stable due to angular strain in the P_4 molecule of white phosphorus where the angles are only 60°.

(*ii*) Nitrogen oxides (particularly nitric oxide) emitted from the exhaust system of supersonic jet aeroplanes are responsible for depletion of ozone layer.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

(*iii*) Bond dissociation enthalpy of F_2 is lower than Cl_2 due to small size of fluorine and relatively larger electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

(*iv*) Helium, as it is non-inflammable and light gas.

(*v*) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

Q. 7. (*i*) Account for the following: **[*CBSE 2019 (56/2/1)*]**

(*a*) Acidic character increases from H_2O to H_2Te.

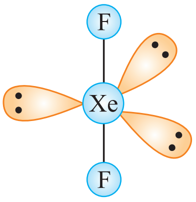
(*b*) F_2 is more reactive than CIF_3, whereas CIF_3 is more reactive than Cl_2.

(*ii*) Draw the structure of (*a*) XeF_2, (*b*) $H_4P_2O_7$.

Ans. (*i*) (*a*) The increase in acidic character from H_2O to H_2Te is due to decrease in bond enthalpy for the dissociation of H—E bond down the group.

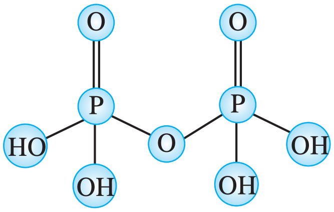
(*b*) F_2 is more reactive than ClF_3 because F–F bond in F_2 is weaker than Cl–F bond in ClF_3. In contrast Cl—F bond in ClF_3 is weaker that Cl—Cl in Cl_2, therefore, ClF_3 is more reactive than Cl_2.

(*ii*) (*a*) There are two bond pairs and three lone pairs of electrons around central Xe atom in XeF_2. Therefore, according to VSEPR theory XeF_2 should be linear.



XeF_2

(*b*)



Pyrophosphoric acid
($H_4P_2O_7$)

Q. 8. **(*i*) Give one example to show the anomalous reaction of fluorine.** **[*CBSE 2019 (56/2/1)*]**

(*ii*) What happens when XeF_6 reacts with NaF?

(*iii*) Why is H_2S a better reducing agent than H_2O?

(*iv*) Arrange the following acids in the increasing order of their acidic character:

HF, HCl, HBr and HI

Ans. (*i*) (*a*) Fluorine is the strongest oxidising agent among halogens. It oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic acid and hypohalic acid.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq) \qquad \text{(where X = Cl or Br)}$$

(*b*) As fluorine usually does not show positive oxidation states, therefore, F_2 does not undergo disproportionation reaction in alkaline medium while other halogens do.

$$X_2 + 2NaOH \xrightarrow{\text{Cold}} NaX + NaOX + H_2O \qquad \text{(where X = Cl, Br, I)}$$

(*c*) Due to small size and high electronegativity:

- Fluorine forms only one oxo acid, HOF, the other halogen form several oxo acids.
- Fluorine in HF forms intermolecular H-bonds which results in association of HF molecules. Therefore HF is a liquid (b.p. 293 K) while other hydrogen halides are gases.

(*ii*) $XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$

(*iii*) Lesser the bond dissociation enthalpy lesser is the stability of the hydride and hence stronger is the reducing agent. Since bond dissociation enthalpy of S—H bond is lesser than O—H therefore, H_2S is a stronger reducing agent than H_2O.

(*iv*) $HF < HCl < HBr < HI$

Q. 9. **(*i*) What happens when**

(*a*) chlorine gas is passed through a hot concentrated solution of NaOH?

(*b*) sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt?

[*CBSE 2019 (56/2/1)*]

(*ii*) Answer the following:

(*a*) Why does fluorine not play the role of a central atom in interhalogen compounds?

(*b*) Why do noble gases have very low boiling points? **[*CBSE (AI) 2011*]**

Ans. (*i*) (*a*) $3Cl_2 + \underset{\text{(Hot and conc.)}}{6NaOH} \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

(*b*) $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

(*ii*) (*a*) This is due to smaller size and absence of *d* orbitals in the valence shell of fluorine.

(*b*) Noble gases being monoatomic gases have no interatomic forces except weak dispersion forces, therefore they have low boiling points.

Q. 10. **(*i*) Draw structure and name the shape of the following:** [*CBSE 2019 (56/5/2)*]

(*a*) SF_4 **(*b*) ICl_3**

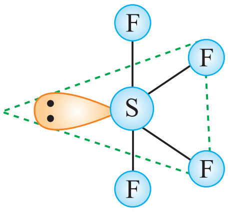
(*ii*) What happens when (Support your answer with equation)

(*a*) Chlorine gas is passed through hot and concentrated sodium hydroxide solution?

(*b*) Xenon hexafluoride is subjected to complete hydrolysis?

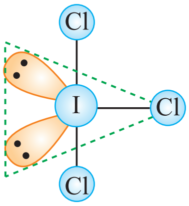
(*c*) Concentrated sulphuric acid is poured over cane sugar?

Ans. (*i*) (*a*)



SF_4
See-saw

(*b*)



ICl_3
T-shaped

(*ii*) (*a*) It forms sodium chlorate and sodium chloride.

$$\underset{\text{hot and conc.}}{6NaOH} + 3Cl_2 \longrightarrow NaClO_3 + 5NaCl + 3H_2O$$

(*b*) Xenon hexafluoride on complete hydrolysis gives XeO_3.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(*c*) Charring of cane sugar takes place.

$$C_{12}H_{22}O_{11} + \text{conc.}\,H_2SO_4 \longrightarrow 12C + 11H_2O$$

Q. 11. **Explain the following:**

(*i*) Hydrogen fluoride is a weaker acid than hydrogen chloride in aqueous solution.

(*ii*) SF_6 is inert towards hydrolysis.

(*iii*) H_3PO_3 is diprotic.

(*iv*) Out of noble gases only xenon is known to form established chemical compounds.

[*CBSE Sample Paper 2016*]

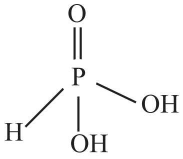
Ans. (*i*) It is due to

(*a*) Higher H—F bond dissociation energy than H—Cl.

(*b*) Stronger H-bonding of F^- ion with H_3O^+ than Cl^-,

(*ii*) In SF_6, S atom is sterically protected by six F atoms and does not allow water molecules to attack the S atom. Further, F does not have *d*-orbitals to accept the electrons donated by H_2O molecules. Due to these reasons, SF_6 is kinetically an inert substance.

(*iii*)



Since it contains only two ionisable H-atoms which are present as OH-groups, it is diprotic.

(*iv*) Except radon which is radioactive, xenon has least ionization enthalpy among noble gases hence it forms compounds particularly with O_2 and F_2.

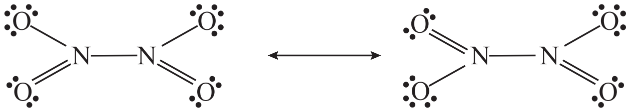
Q. 12. **On heating, lead (II) nitrate gives a brown gas "A". The gas "A" on cooling changes to colourless solid "B". Solid "B" on heating with NO changes to a blue solid 'C'. Identify 'A', 'B', 'C' and also write reactions involved and draw the structures of 'B' and 'C'.** [*NCERT Exemplar*] [*HOTS*]

Ans. $$2Pb(NO_3)_2 \xrightarrow[673\text{ K}]{\Delta} 2PbO + \underset{\substack{\text{(A)}\\ \text{(Brown colour)}}}{4NO_2} + O_2$$

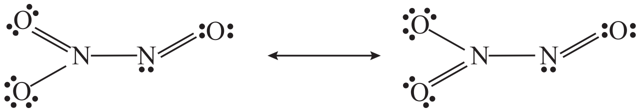
$$2NO_2 \underset{\text{On heating}}{\overset{\text{On cooling}}{\rightleftharpoons}} \underset{\substack{\text{(B)}\\ \text{(Colourless solid)}}}{N_2O_4}$$

$$2NO + N_2O_4 \xrightarrow[250\text{ K}]{\Delta} \underset{\substack{\text{(C)}\\ \text{(Blue solid)}}}{2N_2O_3}$$

Structure of N_2O_4



Structure of N_2O_3



Q. 13. **A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous KOH liberates a highly poisonous gas (C) having rotten fish smell. With excess of chlorine it forms (D) which hydrolyses to compound (E). Identify compounds (A) to (E).** **[*HOTS*]**

Ans. A = White phosphorus B = Red phosphorus

C = Phosphine (PH_3) D = Phosphorus pentachloride (PCl_5)

E = Phosphoric acid (H_3PO_4)

Reactions are:

$$\underset{\substack{\text{White phosphorus}\\ \text{(A)}}}{P_4(s)} \xrightarrow[\text{Inert gas}]{\Delta} \underset{\substack{\text{Red phosphorus}\\ \text{(B)}}}{P_4(s)}$$

$$\underset{\substack{\text{White phosphorus}\\ \text{(A)}}}{P_4(g)} + 3KOH(aq) + 3H_2O \xrightarrow{\Delta} \underset{\substack{\text{Potassium}\\ \text{hypophosphite}}}{3KH_2PO_2(aq)} + \underset{\substack{\text{Phosphine}\\ \text{(C)}}}{PH_3(g)}$$

$$\underset{\substack{\text{Phosphine}\\ \text{(C)}}}{PH_3(g)} + 4Cl_2(g) \longrightarrow \underset{\substack{\text{Phosphorus}\\ \text{pentachloride}\\ \text{(D)}}}{PCl_5(g)} + 3HCl(g)$$

$$\underset{\substack{\text{Phosphorus pentachloride}\\ \text{(D)}}}{PCl_5(g)} + 4H_2O(l) \longrightarrow \underset{\substack{\text{Phosphoric acid}\\ \text{(E)}}}{H_3PO_4(aq)} + 5HCl(aq)$$

Q. 14. **(*i*) When concentrated sulphuric acid was added to an unknown salt present in a test tube a brown gas (*A*) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, the gas (*A*) changed into a colourless solid (*B*).**

(*a*) Identify (*A*) and (*B*).

(*b*) Write the structures of (*A*) and (*B*).

(*c*) Why does gas (*A*) change to solid on cooling?

(*ii*) Arrange the following in the decreasing order of their reducing character:

HF, HCl, HBr, HI

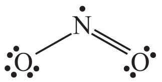
(*iii*) Complete the following reaction:

$$XeF_4 + SbF_5 \longrightarrow$$ **[*CBSE 2018*]**

Ans. (*i*) (*a*) *A* = $NO_2(g)$, Nitrogen dioxide

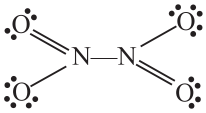
B = $N_2O_4(s)$, Dinitrogen tetroxide

(*b*)



(A)

;



(B)

(*c*) $NO_2(A)$ contains odd number of valence electrons. On cooling it undergoes dimerisation, and converted to stable $N_2O_4(B)$ molecule with even number of electrons.

(*ii*) $HI > HBr > HCl > HF$

(*iii*) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

Q. 15. (*i*) Complete the following reactions:

(*a*) $PbS(s) + O_3 \longrightarrow$

(*b*) $XeF_6 + NaF \longrightarrow$

(*ii*) Arrange the following in increasing order of property indicated, giving reason:

(*a*) Hydrides of group 15 — boiling points

(*b*) Hydrides of group 17 — acidic strength

(*c*) Hydrides of group 16 — reducing character *[CBSE 2019 (56/4/3)]*

Ans. (*i*) (*a*) $PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$

(*b*) $XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$

(*ii*) (*a*) $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

(*b*) $HF < HCl < HBr < HI$

(*c*) $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. The most powerful oxidising agent is:

(*a*) fluorine (*b*) chlorine

(*c*) bromine (*d*) iodine

2. Geometry of $XeOF_4$ molecule is:

(*a*) square planar (*b*) square pyramidal

(*c*) triangular pyramidal (*d*) octahedral

3. The hybridisation state of XeF_6 is

(*a*) sp^3d (*b*) sp^3d^2

(*c*) d^2sp^3 (*d*) sp^3d^3

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. (3 × 1 = 3)

4. **Assertion (*A*) :** Higher noble gases are soluble in water.
Reason (*R*) : Noble gases are monoatomic in nature.

5. **Assertion (*A*) :** SO_2 acts as a Lewis base.
Reason (*R*) : S atom in SO_2 contains one lone pair of electrons.

6. **Assertion (*A*) :** HI cannot be prepared by the reaction of KI with concentrated H_2SO_4.
Reason (*R*) : HI has lowest H–X bond strength among halogen acids.

Answer the following questions:

7. Complete the equation: **(1)**

$$XeF_4 + O_2F_2 \longrightarrow$$

[*CBSE Delhi 2014; (AI) 2014*]

8. Why does PCl_3 fumes in moisture? **(1)**

9. Complete the following equations:

(*i*) $\underset{\text{excess}}{Br_2} + F_2 \longrightarrow$

(*ii*) $PH_3 + HgCl_2 \longrightarrow$ **[*CBSE (F) 2011*] (2)**

10. Give reasons for the least reactivity of nitrogen molecule. **(2)**

11. Give reasons for the following:

(*i*) Noble gases are mostly inert.

(*ii*) Noble gases form compounds with fluorine and oxygen only. **(2)**

12. Give reasons for the following:

(*i*) Solid phosphorus pentachloride behave as an ionic compounds.

(*ii*) Sulphur in vapour state exhibits paramagnetism. **(2)**

13. Explain the following:

(*i*) The N—O bond in NO_2^- is shorter than the N—O bond in NO_3^-. **[*CBSE Delhi 2011*]**

(*ii*) H_3PO_2 is stronger reducing agent than H_3PO_3. **[*CBSE (F) 2014*]**

(*iii*) White phosphorus is more reactive than red phosphorus. **[*CBSE (F) 2013*] (3)**

14. Explain why:

(*i*) NH_3 is a good complexing agent.

(*ii*) iron dissolves in HCl to form $FeCl_2$ and not $FeCl_3$.

(*iii*) group 16 elements are called Chalcogens. **(3)**

15. Predict the shape and the asked angle (90° or more or less) in each of the following cases:

(*i*) SO_3^{2-} and the angle O—S—O

(*ii*) ClF_3 and the angle F—Cl—F

(*iii*) XeF_2 and the angle F—Xe—F **[*CBSE Delhi 2012*] (3)**

16. On heating compound (*A*) gives a gas (*B*) which is a constituent of air. This gas when treated with 3 mol of hydrogen (H_2) in the presence of a catalyst gives another gas (*C*) which is basic in nature. Gas *C* on further oxidation in moist condition gives a compound (*D*) which is a part of acid rain. Identify compounds (*A*) to (*D*) and also give necessary equations of all the steps involved. **(5)**

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*b*)

Chapter–8

The *d*- and *f*- Block Elements

basic concepts

1. ***d*-Block Elements:** The *d*-block elements are those elements in which the last electron enters the *d*–subshell of penultimate shell. The general electronic configuration of these elements is $(n-1)\,d^{1-10}\,ns^{1-2}$, where n is outermost shell. The *d*-block consisting of groups 3–12 occupies the large middle section of the periodic table.
2. **Transition Elements:** The elements of *d*-block are known as transition elements as they possess properties that are transitional between the *s* and *p* block elements. A transition element is defined as an element which has incompletely filled *d*-orbitals in its ground state or any one of its oxidation states. There are four series of transition elements spread between group 3 and 12.

   First transition series or 3*d*-series: Scandium ($_{21}$Sc) to Zinc ($_{30}$Zn)
   Second transition series or 4*d*-series: Yttrium ($_{39}$Y) to Cadmium ($_{48}$Cd)
   Third transition series or 5*d*-series: Lanthanum ($_{57}$La) and Hafnium ($_{72}$Hf) to Mercury ($_{80}$Hg) (Omitting $_{58}$Ce to $_{71}$Lu)
   Fourth transition series or 6*d*-series: Begins with Actinium ($_{89}$Ac) is still incomplete.

   Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end elements of the three transition series, their chemistry is studied along with the chemistry of the transition elements.
3. **General Characteristics of Transition Elements**
   - **(*a*) Atomic radii:** The atomic radii of transition elements are smaller than those of *s*-block elements and larger than those of *p*-block elements in a period. In a transition series, as the atomic number increases, the atomic radii first decreases till the middle, becomes almost constant and then increases towards the end of the period. The decrease in atomic radii in the beginning is due to the increase in the effective nuclear charge with the increase in atomic number. However, with the increase in the number of electrons in $(n-1)$ *d*–subshell, the screening effect of these *d*-electrons on the outermost *ns*-electrons also increases. This increased screening effect counterbalances the effect of increased nuclear charge, therefore, the atomic radii remain almost constant in the middle of the series. Increase in atomic radii towards the end may be attributed to the electron–electron repulsion. The pairing of electrons in the *d*-orbitals of the penultimate shell occurs only after the *d*–subshell is half filled. The repulsive interactions between the paired electrons in *d*-orbitals (of the penultimate shell) become very dominant towards the end of the series and causes the expansion of the electron cloud and thus, resulting in increased atomic size.

     The atomic radii usually increase down the group. But the atomic radii of the elements of second and third transition series belonging to a particular group are almost equal. This is due to lanthanoid contraction.
   - **(*b*) Ionic radii:** The ionic radii of the transitional elements follow the same order as their atomic radii. In general, the ionic radii decrease with increase in oxidation state.
   - **(*c*) Ionisation enthalpies:** The first ionisation enthalpies of transition elements are higher than those of *s*-block elements but lower than *p*-block elements. In a particular transition series, ionisation enthalpy increases gradually with increase in atomic number, though some irregularities are observed.

Reason: The increase in ionisation enthalpy is due to increase in nuclear charge with increase in atomic number which tends to attract the electron cloud with greater force.

The addition of *d*-electron in penultimate shell with increase in atomic number provides a screening effect and shield the outer *s*-electrons from inward nuclear pull. Thus, the effect of increased nuclear charge and increased magnitude of screening effect tend to oppose each other. Consequently, the increase in ionisation enthalpy along the series of transition element is very small. The irregular variations of first and second ionisation enthalpies in the first transition series is mainly due to varying degree of stability of different 3*d*-configuration. For example, Cr has low first ionisation enthalpy because loss of one electron gives stable $3d^5$ configuration and Zn has very high first ionisation enthalpy because the electron has to be removed from 4*s*-orbital of the stable $3d^{10}4s^2$ configuration.

The first ionisation enthalpies of 5*d*-transition elements are higher than those of 3*d* and 4*d* elements. This is due to greater effective nuclear charge acting on the outer valence electrons in these elements because of the ineffective shielding of the nucleus by 4*f*-electrons.

(*d*) **Metallic character:** All the transition elements are metallic in nature. They show gradual decrease in electropositive character in moving from left to right in a series. The metallic bond in transition metals are very strong. This is due to greater effective nuclear charge, low ionisation energies and large number of vacant orbitals in their outermost shell. Nearly, all the transition metals are hard, possess high density and high enthalpy of atomisation. This is due to presence of strong metallic bonds.

(*e*) **Melting and boiling points:** Except zinc, cadmium and mercury all the other transition elements generally have high melting and boiling points. This is due to strong metallic bonds and presence of partially filled *d*-orbitals in them. Because of these half-filled orbitals some covalent bonds also exist between atoms of transition elements. As zinc, mercury and cadmium have fully filled *d*-orbitals, therefore, there is no covalent bonding amongst the atoms of these elements. This accounts for their low melting and boiling points.

In moving along series from left to right, the melting and boiling points of transition elements first increase to a maximum and then decrease towards the end of the period. As the number of unpaired electrons increases, the tendency to form metallic and covalent bonds also increases. In first transition series after chromium, the number of unpaired electrons decreases, hence the melting point also decreases. Manganese possesses anomalous melting and boiling points because it has stable $3d^5 4s^2$ configuration, *i.e.*, electrons are held tightly by nucleus so that the delocalisation is less and the metallic bond is much weaker than that of preceding element.

(*f*) **Oxidation states:** All transition elements except first and last member of the series exhibit variable oxidation states as $(n-1)d$ and *ns* orbitals have comparable energies so that both can enter into chemical bond formation. The maximum oxidation state shown by first series increases from Sc to Mn and then decreases. The common oxidation state of first series is +3 (except Sc). The highest oxidation state of transition elements is 8 (Os and Ru).

The compounds of transition elements in lower states +2 and +3 are mostly ionic and of higher oxidation states are covalent, *e.g.*, $ZnCl_2$ and $CdCl_2$ are ionic whereas $Cr_2O_7^{2-}$ and MnO_4^- are covalent in nature, higher oxidation state of transition elements are shown in oxides and oxoacids (*e.g.*, MnO_4^-). Transition metals with fluorine and oxygen exhibit higher oxidation state due to higher electronegative nature of fluorine and oxygen. Transition metals also exhibit +1 and 0 oxidation states. For example:

Cu_2Cl_2, $AgCl$, Hg_2Cl_2 (OS of metal is +1)
$Ni(CO)_4$, $Fe(CO)_5$ (OS of metal is 0)

When the metal exhibit more than one OS, their relative stabilities can be known from their standard electrode potential, *e.g.*,

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^o_{red} = 0.34 \text{ volt}$$
$$Cu^{+}(aq) + e^- \longrightarrow Cu(s) \qquad E^o_{red} = 0.52 \text{ volt}$$

Lower standard reduction potential indicates Cu^{2+} is more stable than Cu^+ in aqueous medium.

(*g*) **Standard electrode potential:** Electrode potential is the electric potential developed on a metal electrode when it is in equilibrium with a solution of its own ions, taking electrons from the electrode. There is irregular variation in electrode potential due to irregular variation in ionisation enthalpy, sublimation energy and energy of hydration. The $E°$ value decreases from left to right across the series; Mn, Ni and Zn have higher values than expected because of their half-filled or completely filled 3*d*-orbitals in case of Mn^{2+} and Zn^{2+} respectively and the highest negative enthalpy of hydration, Ni^{2+}.

(*h*) **Magnetic properties:** Substances containing unpaired electrons are said to be paramagnetic. A diamagnetic substance is one in which all the electrons are paired. Except the ions of d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Cu^+, Zn^{2+}) configurations, all other simple ions of transition elements contain unpaired electrons in their $(n - 1)$ *d* subshell and are, therefore, paramagnetic. The magnetic moments (μ) of the elements of first transition series can be calculated with the unpaired electrons (*n*) by the spin only formula.

$$\mu = \sqrt{n(n+2)} \text{ BM (Bohr Magneton)}$$

(*i*) **Complex formation:** The tendency to form complex ions is due to

- (*i*) the high charge on the transition metal ions,
- (*ii*) the availability of *d*-orbitals for accommodating electrons donated by the ligand atoms.

(*j*) **Catalytic property:** Most of the transition metals and their compounds possess catalytic properties. The catalytic activity of transition metal ions is attributed to the following two reasons:

- (*i*) Variable oxidation states due to which they can form a variety of unstable intermediate products.
- (*ii*) Large surface area so that the reactants are adsorbed on the surface and come close to each other facilitating the reaction process.

(*k*) **Colour:** Most of the transition metal ions in solution as well as in solid states are coloured. This is due to the partial absorption of visible light. The absorbed light promotes the electron from one orbital to another orbital of the same *d*-subshell. Since the electronic transition occurs within the *d*-orbitals of the transition metal ions, they are called *d–d* transitions. It is because of these *d–d* transitions occurring in a transition metal ion by absorption of visible light that they appear coloured.

(*l*) **Alloy formation:** The transition metals have similar radii and other characteristics. Therefore, these metals can mutually substitute their position in their crystal lattices and form alloys. The alloys so formed are hard and often have high melting point. Various types of steel, brass, bronze are examples of this type of alloy.

(*m*) **Interstitial compounds:** Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals because small-sized atoms of H, B, C, N, etc., can easily occupy positions in the voids present in the crystal lattices of transition metals.

4. **Some Important Compounds of Transition Elements:** Though the transition elements are sufficiently electropositive, yet they are not very reactive because of

- (*i*) their high enthalpies of sublimation, and
- (*ii*) their high ionisation enthalpies.

Oxides: Transition metals form oxides of the general composition MO, M_2O_3, MO_2, M_2O_5 and MO_6. Oxides in the lower oxidation states are generally basic in nature and those in the higher oxidation states are amphoteric or acidic in nature. For example,

+2	+3	+8/3	+4	+7
MnO	Mn_2O_3	Mn_3O_4	MnO_2	Mn_2O_7
Basic	Amphoteric	Amphoteric	Amphoteric	Acidic

(*a*) **Potassium Dichromate, $K_2Cr_2O_7$:** It is prepared from the chromite ore. Different reactions involved in the preparation of potassium dichromate from chromite ore are:

$$\underset{\text{Chromite ore}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Roasted}} \underset{\text{Sodium chromate}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 2NaCl$$

$K_2Cr_2O_7$ is separated by fractional crystallisation.

Properties: When potassium dichromate is heated with any ionic chloride (*e.g.*, NaCl, $BaCl_2$, etc.) and concentrated H_2SO_4, red vapours of chromyl chloride are obtained.

$$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \longrightarrow \underset{\text{Chromyl chloride}}{2CrO_2Cl_2}\uparrow + 6KHSO_4 + 3H_2O$$

Potassium dichromate is a powerful oxidising agent. In acidic medium, its oxidation action can be represented as follows:

$$\begin{array}{rcll} K_2Cr_2O_7 + 4H_2SO_4 & \longrightarrow & K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O] & \\ Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O & (E^\circ = +1.31\ V) \end{array}$$

(*i*) It oxidises ferrous to ferric.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^-\ ] \times 6 \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 6Fe^{3+} + 7H_2O \\ \hline \end{array}$$

(*ii*) It oxidises stannous to stannic.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ Sn^{2+} & \longrightarrow & Sn^{4+} + 2e^-\ ] \times 3 \\ \hline Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 3Sn^{4+} + 7H_2O \\ \hline \end{array}$$

(*iii*) It oxidises sulphur dioxide to sulphuric acid.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ SO_2 + 2H_2O & \longrightarrow & SO_4^{2-} + 4H^+ + 2e^-\ ] \times 3 \\ \hline Cr_2O_7^{2-} + 3SO_2 + 2H^+ & \longrightarrow & 2Cr^{3+} + 3SO_4^{2-} + H_2O \\ \hline \end{array}$$

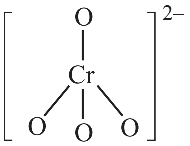
(*iv*) It oxidises hydrogen sulphide to sulphur.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ H_2S & \longrightarrow & 2H^+ + S + 2e^-\ ] \times 3 \\ \hline Cr_2O_7^{2-} + 3H_2S + 8H^+ & \longrightarrow & 2Cr^{3+} + 3S + 7H_2O \\ \hline \end{array}$$

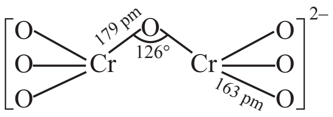
(*v*) It oxidises iodides to iodine.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ 2I^- & \longrightarrow & I_2 + 2e^-\ ] \times 3 \\ \hline Cr_2O_7^{2-} + 6I^- + 14H^+ & \longrightarrow & 2Cr^{3+} + 3I_2 + 7H_2O \\ \hline \end{array}$$

Structures of chromate and dichromate ions:



Chromate ion



Dichromate ion

The chromate and dichromate ions are interconvertible in aqueous solution depending upon the pH of the solution.

$$2CrO_4^{2-} + 2H^+ \longrightarrow \underset{\substack{\text{Dichromate ion} \\ \text{(orange red)}}}{Cr_2O_7^{2-}} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow \underset{\substack{\text{Chromate ion} \\ \text{(yellow)}}}{2CrO_4^{2-}} + H_2O$$

Potassium dichromate is used as primary standard in volumetric analysis.

(*b*) **Potassium permanganate, $KMnO_4$:** It is prepared by fusion of pyrolusite, MnO_2, with KOH in the presence of an oxidising agent like KNO_3. This produces the dark green potassium manganate, K_2MnO_4 which disproportionates in a neutral or acidic solution to give purple permanganate.

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{Potassium manganate}}{2K_2MnO_4} + 2H_2O$$

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

Or,

$$3K_2MnO_4 + 4H^+ \longrightarrow \underset{\substack{\text{Potassium}\\ \text{permanganate}}}{2KMnO_4} + MnO_2 + 2H_2O + 4K^+$$

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

$$MnO_2 \xrightarrow[\text{oxidised with air or } KNO_3]{\text{Fused with KOH}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic Oxidation}} \underset{\text{Permanganate ion}}{MnO_4^-}$$

In the laboratory, $KMnO_4$ is prepared by oxidation of manganese (II) ion salt by peroxodisulphate.

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

Properties:

Potassium permanganate is a dark purple crystalline solid.

On heating, it decomposes at 513 K and O_2 is evolved.

$$2KMnO_4 \xrightarrow{\text{Heat}} \underset{\text{Potassium manganate}}{K_2MnO_4} + MnO_2 + O_2$$

Potassium permanganate acts as a powerful oxidising agent in acidic, alkaline and neutral media. Few important oxidation reactions of $KMnO_4$ are given below:

1. In acidic medium potassium permanganate oxidises:

(*i*) Iodide to iodine

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\longrightarrow Mn^{2+} + 4H_2O] \times 2 \\ 2I^- &\longrightarrow I_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 10I^- + 16H^+ &\longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O \end{aligned}$$

(*ii*) Ferrous to ferric

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\longrightarrow Mn^{2+} + 4H_2O \\ Fe^{2+} &\longrightarrow Fe^{3+} + e^-] \times 5 \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ &\longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \end{aligned}$$

(*iii*) Oxalate to carbon dioxide

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\longrightarrow Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} &\longrightarrow 2CO_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5\,C_2O_4^{2-} + 16H^+ &\longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \end{aligned}$$

(*iv*) Hydrogen sulphide to sulphur

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\longrightarrow Mn^{2+} + 4H_2O] \times 2 \\ S^{2-} &\longrightarrow S + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5S^{2-} + 16H^+ &\longrightarrow 2Mn^{2+} + 5S + 8H_2O \end{aligned}$$

(*v*) Sulphite to sulphate

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O\ ] \times 2 \\ SO_3^{2-} + H_2O & \longrightarrow & SO_4^{2-} + 2H^+ + 2e^-\ ] \times 5 \\ \hline 5SO_3^{2-} + 2MnO_4^- + 6H^+ & \longrightarrow & 2Mn^{2+} + 5SO_4^{2-} + 3H_2O \\ \hline \end{array}$$

(*vi*) Nitrite to nitrate

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O\ ] \times 2 \\ NO_2^- + H_2O & \longrightarrow & NO_3^- + 2H^+ + 2e^-\ ] \times 5 \\ \hline 2MnO_4^- + 5NO_2^- + 6H^+ & \longrightarrow & 2Mn^{2+} + 5NO_3^- + 3H_2O \\ \hline \end{array}$$

2. In neutral or faintly alkaline solutions potassium permanganate oxidises:

(*i*) **Iodide to iodate**

$$2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$$

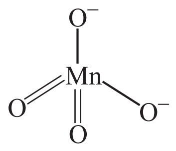
(*ii*) **Thiosulphate to sulphate**

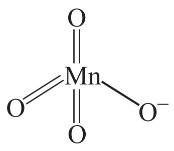
$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(*iii*) **Manganous salt to MnO_2 in presence of zinc sulphate or zinc oxide**

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

The MnO_4^{2-} and MnO_4^- are tetrahedral; the green MnO_4^{2-} is paramagnetic with one unpaired electron but the purple MnO_4^- is diamagnetic.


Tetrahedral manganate ion
(green)


Tetrahedral permanganate ion
(purple)

Inner Transition Elements (f-Block Elements)

The inner transition elements consist of lanthanoids and actinoids. They are characterised by filling of the '*f*' orbitals.

5. Lanthanoids

The series involving the filling of 4*f*-orbitals following lanthanum La (Z = 57) is called the lanthanoid series. There are 14 elements in this series, starting with cerium Ce (Z =58) to lutetium Lu (Z = 71). The lanthanoids

- are highly dense metals.
- have high melting points.
- form alloys easily with other metals.
- are soft, malleable and ductile with low tensile strength.

(*i*) **Oxidation state:** The most characteristic oxidation state of lanthanoid elements is +3. Some of the elements also exhibit +2 and +4 oxidation states.

(*ii*) **Colour:** Some of the trivalent ions of lanthanoids are coloured. This is due to the absorption in visible region of the spectrum, resulting in *f*-*f* transitions because they have partly filled orbitals.

(*iii*) **Magnetic properties:** Among lanthanoids, La^{3+} and Lu^{3+}, which have $4f^0$ or $4f^{14}$ electronic configurations are diamagnetic and all the other trivalent lanthanoid ions are paramagnetic because of the presence of unpaired electrons.

(*iv*) **Reactivity:** All lanthanoids are highly electropositive metals and have an almost similar chemical reactivity.

(*v*) **Lanthanoid contraction:** In lanthanoids, with increasing atomic number, the atomic and ionic radii decreases from one element to the other, but the decrease is very small. It is because, for every additional proton in the nucleus, the corresponding electron goes into a 4*f*-subshell, which is too diffused to screen the nucleus as effectively as the more localised inner shell. Hence, the attraction of the nucleus for the outermost electrons increases steadily with the atomic number.

(*vi*) **Uses of lanthanoids:** The pure metals have no specific use. So they are used as alloys or compounds.

- ➡ As alloys lanthanoids are used in making a misch metal which consists of lanthanoid metals (~95%) and iron (~5%) and traces of sulphur, carbon, calcium and aluminium. Magnesium mixed with 3% misch metal is used for making jet engine parts.
- ➡ Steel mixed with La, Ce, Pr and Nd is used in the manufacture of flame throwing tanks.
- ➡ Lanthanoid oxides are used for polishing glass. Neodymium and praseodymium oxides are used for making coloured glasses for goggles.
- ➡ Cerium salts are used in dyeing cotton and also as catalysts.
- ➡ Lanthanoid compounds are used as a catalyst for hydrogenation, dehydrogenation and petroleum cracking.
- ➡ Pyrophoric alloys are used for making tracer bullets and shells.

6. **Actinoids:** The elements following actinium, Ac (Z = 89), up to lawrencium (Z = 103), are called actinoids. The actinoids

- ➡ are highly dense metals with a high melting point and form alloys with other metals, specially iron.
- ➡ are silvery white metals, which are highly reactive.
- ➡ get tarnished when exposed to alkalis and are less reactive towards acids.

(*i*) **Actinoid contraction:** The atomic and ionic size decreases with an increase in atomic number. Electrons are added to the 5*f*-subshell, as a result the nuclear charge increases causing the shells to shrink inwards.

(*ii*) **Electronic configuration:** The actinoids involve the filling of 5*f*-subshells. Actinium has the electronic configuration $6d^1\ 7s^2$. From thorium ($Z = 90$) onwards, 5*f*-orbitals get progressively filled up. Because of equal energy of 5*f* and 6*d* subshells, there are some uncertainities regarding the filling of 5*f* and 6*d* subshells. Most of their properties are comparable to that of lanthanoids.

(*iii*) **Oxidation state:** Generally +3 oxidation state is preferred in actinoids. The elements in the first of actinoid series frequently exhibit higher states. For example, the maximum oxidation increases from +4 in Th to +5, +6 and +7 in Pa, U and Np, respectively, but decreases in succeeding elements.

(*iv*) **Colour:** The actinoid ions are coloured.

(*v*) **Magnetic properties:** Many of the actinoid ions are paramagnetic.

(*vi*) **Reactivity:** They are also highly electropositive and form salts as well as complexes. Many of these elements are radioactive.

(*vii*) **Uses of actinoids:**

- Thorium is used in the treatment of cancer and in incandescent gas mantles.
- Uranium is used in the glass industry, textile industry, in medicines and as nuclear fuel.
- Plutonium is used in atomic reactors and in atomic bombs.

7. **Differences between Lanthanoids and Actinoids**

S.No.	Lanthanoids	Actinoids
(*i*)	4*f*-orbital is progressively filled.	5*f*-orbital is progressively filled.
(*ii*)	+3 oxidation state is most common along with +2 and +4.	They show +3, +4, +5, +6, +7 oxidation states.
(*iii*)	Only promethium (Pm) is radioactive.	All are radioactive.
(iv)	They are less reactive than actinoids.	They are more reactive.
(*v*)	Magnetic properties are less complex.	Magnetic properties are more complex.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Silver atom has completely filled *d*-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Ans. Silver ($Z = 47$) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.

Q. 2. In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest, *i.e.*, 126 kJ mol^{-1}. Why?

Ans. In the formation of metallic bonds, no electrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds. That is why, the enthalpy of atomisation of zinc is the lowest in the series.

Q. 3. Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?

Ans. Manganese (Z = 25), as it has the maximum number of unpaired electrons in *d*-subshell. Thus, it shows oxidation states from +2 to +7 (+2, +3, +4, +5, +6 and +7) which is the maximum number.

Q. 4. The E^o (M^{2+}/M) value for copper is positive (+0.34 V). What is possible reason for this?

(Hint: Consider its high $\Delta_a H^\ominus$ and low $\Delta_{hyd} H^\ominus$)

Ans. E^o (M^{2+}/M) for any metal is related to the sum of the enthalpy change taking place in the following steps:

$$M(s) + \Delta_a H \longrightarrow M(g), \qquad (\Delta_a H = \text{Enthalpy of atomisation})$$

$$M(g) + \Delta_i H \longrightarrow M^{2+}(g), \qquad (\Delta_i H = \text{Ionisation enthalpy})$$

$$M^{2+}(g) + aq \longrightarrow M^{2+}(aq) + \Delta_{hyd}H, \quad (\Delta_{hyd} H = \text{Hydration enthalpy})$$

Copper has high enthalpy of ionisation and relatively low enthalpy of hydration. So, $E^o_{(Cu^{2+}/Cu)}$ is positive. The high energy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

Q. 5. How would you account for the irregular variation of ionisation enthalpies (first and second) in first series of the transition elements?

Ans. Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d* configuration (*e.g.*, d^0 , d^5 , d^{10} are exceptionally stable).

Q. 6. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Ans. Due to small size and high electronegativity, oxygen or fluorine can oxidise a metal to its highest oxidation state. As a result of this they can oxidise a metal to its highest oxidation state.

Q. 7. Which is a stronger reducing agent— Cr^{2+} or Fe^{2+} and why? ***[HOTS]***

Ans. Cr^{2+} is a stronger reducing agent than Fe^{2+} because after the loss of one electron Cr^{2+} becomes Cr^{3+} which has more stable t^3_{2g} (half-filled) configuration in a medium like water.

Q. 8. Calculate the 'spin only' magnetic moment of $M^{2+}(aq)$ ion (Z = 27).

OR

Calculate the spin-only magnetic moment of Co^{2+}(Z=27) by writing the electronic configuration of Co and Co^{2+}. ***[CBSE 2020 (56/1/1)]***

Ans. Electronic configuration of M atom with Z = 27 is [Ar] $3d^7\,4s^2$.

$\therefore$ Electronic configuration of M^{2+} = [Ar] $3d^7$, *i.e.*, $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Hence, it has three unpaired electrons.

$$\therefore \text{ Spin only magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM}$$

$$= \sqrt{3(3+2)} \text{ BM} = \sqrt{15}\text{BM} = \mathbf{3.87\ BM}$$

Q. 9. Explain why Cu^+ ion is not stable in aqueous solutions? ***[HOTS]***

Ans. In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2Cu^+ (aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

The higher stability of Cu^{2+} in aqueous solution may be attributed to its greater negative $\Delta_{hyd.}H^o$ than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

Q. 10. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Ans. This is because the 5*f* electrons themselves provide poor shielding from element to element in the series.

NCERT Textbook Exercises

Q. 1. Write down the electronic configuration of

(*i*) Cr^{3+} (*ii*) Cu^{+} (*iii*) Co^{2+} (*iv*) Mn^{2+} (*v*) Pm^{3+}

(*vi*) Ce^{4+} (*vii*) Lu^{2+} (*viii*) Th^{4+}

Ans. (*i*) Cr^{3+} = [Ar] $3d^3$ (*ii*) Cu^{+} = [Ar] $3d^{10}$

(*iii*) Co^{2+} = [Ar] $3d^7$ (*iv*) Mn^{2+} = [Ar] $3d^5$

(*v*) Pm^{3+} = [Xe] $4f^4$ (*vi*) Ce^{4+} = [Xe]

(*vii*) Lu^{2+} = [Xe] $4f^{14}\,5d^1$ (*viii*) Th^{4+} = [Rn]

Q. 2. Why are Mn^{2+} compounds more stable than Fe^{2+} compounds towards oxidation to their +3 state?

Ans. Electronic configuration of Mn^{2+} is $3d^5$ which is half-filled and hence stable. So, 3rd ionisation enthalpy is very high, *i.e.*, 3rd electron cannot be easily lost. In case of Fe^{2+}, electronic configuration is $3d^6$. Thus, it can lose one electron easily to give the stable configuration $3d^5$.

Q. 3. Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

Ans. As the atomic number increases from 21 to 25, the number of electrons in the 3*d*-orbital also increases from 1 to 5. +2 oxidation state is attained by the loss of the two 4*s* electrons by these metals. Sc does not exhibit +2 oxidation state. As the number of *d*- electrons in +2 state increases from Ti to Mn, the stability of +2 state increases (*d*-orbital gradually becoming half filled). Mn(+2) has d^5 electrons which is highly stable.

Q. 4. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with example.

Ans. The stability of oxidation states in the first series of the transition elements are related to their electronic configurations.

The first five elements of the first transition series up to Mn in which the 3*d*-subshell is not more than half-filled, the minimum oxidation state is given by the number of electrons in the outer *s*-subshell and the maximum oxidation state is given by the sum of the outer *s* and *d*-electrons. For example, Sc does not show +2 oxidation state. Its electronic configuration is $3d^1\,4s^2$. It loses all the three electrons to form Sc^{3+}. +3 oxidation state is very stable as by losing all three electrons, it attains the stable configuration of Argon. For Mn, +2 oxidation state is very stable, as after losing two 4*s* electrons, the *d*-orbitals become half-filled.

Q. 5. What may be the stable oxidation state of the transition element with the following *d*-electron configuration in the ground state of their atoms?

$3d^3$, $3d^5$, $3d^8$ and $3d^4$

Ans. Stable oxidation states:

$3d^3$ (vanadium): +2, +3, +4, +5 $3d^5$ (chromium): +3, +4, +6

$3d^5$ (manganese): +2, +4, +6, +7 $3d^8$ (nickel): +2, +4

$3d^4$: There is no d^4 configuration in the ground state.

Q. 6. Name the oxo-metal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

Ans. $Cr_2O_7^{2-}$ and CrO_4^{2-} (group no. = oxidation state of Cr = 6)

MnO_4^- (group no. = oxidation state of Mn = 7)

Vanadate: VO_3^- (group no. = oxidation state of V = 5)

Q. 7. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Ans. Refer to Basic Concepts Point 5 (*v*).

The consequences of lanthanoid contraction are as follows:

(*i*) The properties of second and third transition series are similar.

(*ii*) Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.

(*iii*) Lanthanide contraction makes separation of lanthanoids possible.

Q. 8. What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

Ans. Characteristics of the transition elements: Refer to Basic Concepts Point 3.

The *d*-block elements are called transition elements because these elements represent change (or transition) in properties from the most electropositive *s*-block elements to the least electropositive *p*-block elements.

The electronic configuration of Zn, Cd and Hg are represented by the general formula $(n-1)\,d^{10}\,ns^{2}$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

Q. 9. In what way is the electronic configuration of transition elements different from that of the non-transition elements?

Ans. Transition elements contain incompletely filled *d*-subshell, *i.e.*, their electronic configuration is $(n-1)\,d^{1-10}\,ns^{1-2}$ whereas non-transition elements have no *d*-subshell or their subshell is completely filled and have ns^{1-2} or $ns^2\,np^{1-6}$ in their outermost shell.

Q. 10. What are the different oxidation states exhibited by lanthanoids?

Ans. +2, +3 and +4 (+3 being most common).

Q. 11. Explain giving reasons:

(*i*) Transition metals and many of their compounds show paramagnetic behaviour.

(*ii*) The enthalpies of atomisation of the transition metals are high.

(*iii*) The transition metals generally form coloured compounds.

(*iv*) Transition metals and their many compounds act as good catalyst.

Ans. (*i*) Refer to Basic Concepts Point 3(*h*).

(*ii*) The transition elements exhibit high enthalpy of atomisation because they have large number of unpaired electrons in their atoms. Due to this they have stronger interatomic interaction.

(*iii*) Refer to Basic Concepts Point 3(*k*).

(*iv*) The transition metals and their compounds are known for their catalytic activity. This activity is due to their ability to adopt multiple oxidation states and to form complexes. Vanadium oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some examples to mention. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also, since the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

An explanation of this catalytic action is given as under:

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Q. 12. What are interstitial compounds? Why are such compounds well known for transition metals?

Ans. Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice. Interstitial compounds are well known for transition metals because small-sized atoms of H, B, C, N, etc., can easily occupy positions in the voids present in the crystal lattices of transition metals.

Q. 13. How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

Ans. The oxidation states of transition elements differ from each other by unity *e.g.*, Fe^{2+} and Fe^{3+}, Cu^+ and Cu^{2+} (due to incomplete filling of *d*-orbitals) whereas oxidation states of non-transition elements normally differ by two units *e.g.*, Pb^{2+} and Pb^{4+}, Sn^{2+} and Sn^{4+}, etc.

Q. 14. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

Ans. For preparation of potassium dichromate from iron chromite ore refer to Basic Concepts Point 4(*a*).

In aqueous solution, dichromate and chromate ions exist in equilibrium. On increasing the pH, *i.e.*, on making the solution alkaline, dichromate ions (orange coloured) are converted into chromate ions and thus, the solution turns yellow.

Q. 15. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (*i*) iodide (*ii*) iron (II) solution (*iii*) H_2S.

Ans. (*i*) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

(*ii*) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

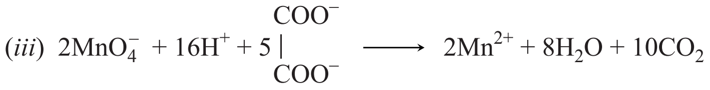
(*iii*) $Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

Q. 16. Describe the preparation of potassium permanganate. How does the acidified permanganate react with (*i*) iron (II) ions (*ii*) SO_2 (*iii*) oxalic acid? Write the ionic equations for the reaction.

Ans. For preparation, refer to Basic Concepts Point 4(*b*).

(*i*) $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(*ii*) $2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 4H^+ + 5SO_4^{2-}$



(*iii*) $2MnO_4^- + 16H^+ + 5\begin{array}{c}COO^-\\ |\\ COO^-\end{array} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

Q. 17. For M^{2+}/M and M^{3+}/M^{2+} systems, E^o values for some metals are as follows:

$Cr^{2+}/Cr = -0.9$ V | **$Cr^{3+}/Cr^{2+} = -0.4$ V**

$Mn^{2+}/Mn = -1.2$ V | **$Mn^{3+}/Mn^{2+} = +1.5$ V**

$Fe^{2+}/Fe = -0.4$ V | **$Fe^{3+}/Fe^{2+} = +0.8$ V** **[*CBSE Sample Paper 2016*]**

Use this data to comment upon

(*i*) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}.

(*ii*) the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

Ans. (*i*) Higher the reduction potential of a species, greater is the ease with which it undergo reduction. Among these pairs, Mn^{3+}/Mn^{2+} has largest positive reduction potential. Hence Mn^{3+} can be easily reduced to Mn^{2+} *i.e.*, Mn^{3+} is least stable. Cr^{3+}/Cr^{2+} has a negative E^o value, therefore, Cr^{3+} is most stable. Fe^{3+}/Fe^{2+} has a positive value but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+}.

(*ii*) Lower the reduction potential or higher the oxidation potential of a species, greater is the ease with which it undergo oxidation. Among these pairs, Mn^{2+}/Mn has the most negative reduction potential or most positive oxidation potential. Therefore, it will be most easily oxidised. Thus, the decreasing order of their ease of oxidation is Mn > Cr > Fe.

Q. 18. Predict which of the following will be coloured in aqueous solution?
$Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}$. Give reasons for each.

Ans. An ion is coloured when it has one or more unpaired electrons. Thus, Ti^{3+}, V^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+} are coloured, due to the presence of unpaired electrons and *d-d* transitions. Cu^+ and Sc^{3+} are colourless.

Q. 19. Compare the stability of +2 oxidation state for the elements of the first transition series.

Ans. Refer to Ans. 3. of NCERT Textbook Exercises.

Q. 20. Compare the chemistry of actinoids with that of lanthanoids with special reference to

(*i*) electronic configuration **(*ii*) oxidation states**

(*iii*) atomic and ionic sizes **(*iv*) chemical reactivity.**

OR

Give three points of difference between lanthanoids and actinoids. **[*CBSE 2020 (56/1/1)*]**

Ans. (*i*) **Electronic configuration:** The general electronic configuration of lanthanoids is $[Xe]^{54}\, 4f^{1-14}\, 5d^{0-1}\, 6s^2$ whereas that of actinoids is $[Rn]^{86}\, 5f^{1-14}\, 6d^{0-1}\, 7s^2$. Thus, lanthanoids belong to 4*f*-series whereas actinoids belong to 5*f*-series.

(*ii*) **Oxidation states:** Lanthanoids show limited oxidation states (+2, +3, +4), out of which, +3 is most common. This is because of a large energy gap between 4*f*, 5*d* and 6*s* subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between 5*f*, 6*d* and 7*s* subshells.

(*iii*) **Atomic and ionic sizes:** Both show decrease in size of their atoms or ions in +3 oxidation state. In lanthanoids, the decrease is called lanthanoid contraction whereas in actinoids, it is called actinoid contraction. However, the contraction is greater from element to element in actinoids due to poorer shielding by 5*f*-electrons.

(*iv*) **Chemical reactivity:**

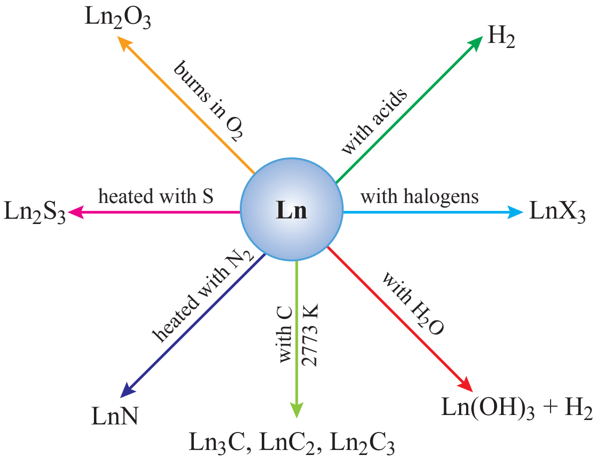
Lanthanoids: In general, the earlier members of the series are quite reactive (similar to calcium) but with increasing atomic number, they behave more like aluminium.

Values for E^o for the half-reaction:

$$Ln^{3+}(aq) + 3e^- \longrightarrow Ln(s)$$

are in the range of –2.2 to –2.4 V except for Eu for which the value is –2.0 V. This is ofcourse, a small variation.

The metals combine with hydrogen when gently heated in the gas. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides and hydroxides—M_2O_3 and $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides, basic like alkaline earth metal oxides and hydroxides.



Chemical reactions of the lanthanoids

Actinoids: The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non-metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalis have no action.

Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

Q. 21. How would you account for the following:

(*i*) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidising.

(*ii*) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(*iii*) The d^1 configuration is very unstable in ions.

Ans. (*i*) $E°$ value for Cr^{3+}/Cr^{2+} is negative (–0.41 V) whereas $E°$ value for Mn^{3+}/Mn^{2+} is positive (+1.57 V). Thus, Cr^{2+} ions can easily undergo oxidation to give Cr^{3+} ions and, therefore, act as strong reducing agent. On the other hand, Mn^{3+} can easily undergo reduction to give Mn^{2+} and hence act as oxidising agent.

(*ii*) This is because in presence of complexing reagents the CFSE value compensates more than the third ionisation energy of cobalt.

(*iii*) The ions with d^1 configuration have the tendency to lose the only electron present in *d*-subshell to acquire stable d^0 configuration. Therefore, they are unstable and undergo oxidation or disproportionation.

Q. 22. What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

Ans. Disproportionation reactions are those reactions in which the same substance undergoes oxidation as well as reduction. In disproportionation reaction, oxidation number of an element increases as well as decreases to form two different products. For example,

$$3\overset{\text{VI}}{\text{MnO}_4^{2-}} + 4\text{H}^+ \longrightarrow 2\overset{\text{VII}}{\text{MnO}_4^-} + \overset{\text{IV}}{\text{MnO}_2} + 2\text{H}_2\text{O}$$

$$3\overset{\text{V}}{\text{CrO}_4^{3-}} + 8\text{H}^+ \longrightarrow 2\overset{\text{VI}}{\text{CrO}_4^{2-}} + \overset{\text{III}}{\text{Cr}^{3+}} + 4\text{H}_2\text{O}$$

Q. 23. Which metal in the first transition series exhibits +1 oxidation state most frequently and why?

Ans. Cu has the electronic configuration $3d^{10}\ 4s^1$. It can easily lose $4s^1$ electron to give the stable $3d^{10}$ configuration. Hence, it shows +1 oxidation state.

Q. 24. Calculate the number of unpaired electrons in the following gaseous ions:
(*i*) Mn^{3+}, (*ii*) Cr^{3+}, (*iii*) V^{3+} and (*iv*) Ti^{3+}.

Which one of these is the most stable in aqueous solution?

Ans. (*i*) $Mn^{3+} = 3d^4$ = 4 unpaired electrons (*ii*) $Cr^{3+} = 3d^3$ = 3 electrons
(*iii*) $V^{3+} = 3d^2$ = 2 electrons (*iv*) $Ti^{3+} = 3d^1$ = 1 electron.

Cr^{3+} is the most stable in aqueous solution because it has half-filled t_{2g} level (*i.e.*, t^3_{2g}).

Q. 25. Give example and suggest reasons for the following features of the transition metal chemistry:

(*i*) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(*ii*) A transition metal exhibits higher oxidation states in oxides and fluorides.

(*iii*) The highest oxidation state is exhibited in oxo-anions of a metal.

Ans. (*i*) The lowest oxide of transition metal is basic because the metal atom has low oxidation state. This means that it can donate valence electrons which are not involved in bonding to act like a base. Whereas the highest oxide is acidic due to the highest oxidation state as the valence electrons are involved in bonding and are unavailable. For example, MnO is basic whereas Mn_2O_7 is acidic.

(*ii*) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size (and strongest oxidising agents). For example, osmium shows an oxidation states of +6 in OsF_6 and vanadium shows an oxidation state of +5 in V_2O_5.

(*iii*) Oxometal anions have the highest oxidation state, *e.g.*, Cr in $Cr_2O_7^{2-}$ has an oxidation state of +6 whereas Mn in MnO_4^- has an oxidation state of +7. This is again due to the combination of the metal with oxygen, which is highly electronegative and oxidising element.

Q. 26. Indicate the steps in the preparation of

(*i*) $K_2Cr_2O_7$ from chromite ore.

(*ii*) $KMnO_4$ from pyrolusite ore.

Ans. (*i*) Refer to Basic Concepts Point 4(*a*).

(*ii*) Refer to Basic Concepts Point 4(*b*).

Q. 27. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

Ans. An alloy is a homogeneous mixture of two or more metals, or metals and non-metals. An important alloy containing lanthanoid metals is misch metal which contains 95% lanthanoid metals and 5% iron alongwith traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flints.

Q. 28. What are inner-transition elements? Decide which of the following atomic numbers are the numbers of the inner-transition elements: 29, 59, 74, 95, 102, 104.

Ans. The *f*-block elements, *i.e.*, in which the last electron enters into *f*-subshell are called inner-transition elements. These include lanthanoids (58–71) and actinoids (90–103). Thus, elements with atomic numbers 59, 95 and 102 are inner-transition elements.

Q. 29. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

Ans. Lanthanoids show a limited number of oxidation state, *viz.*, +2, +3 and +4 (out of which +3 is the most common). This is because of a large energy gap between 4*f*, 5*d* and 6*s* subshells. The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation states also, *e.g.*, uranium ($Z = 92$) and plutonium ($Z = 94$) show +3, +4, +5 and +6, neptunium ($Z = 94$) shows +3, +4, +5 and +7, etc. This is due to small energy difference between 5*f*, 6*d* and 7*s* subshells of the actinoids.

Q. 30. Which is the last element of the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

Ans. Last actinoid = Lawrencium ($Z = 103$)

Electronic configuration = $[Rn]^{86}\ 5f^{14}\ 6d^1\ 7s^2$

Possible oxidation state = +3

Q. 31. Use Hund's rule to derive the electronic configuration of Ce^{3+} ion and calculate its magnetic moment on the basis of spin only formula.

Ans. $_{58}Ce = [Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$

$Ce^{3+} = [Xe]^{54}\ 4f^1$, *i.e.*, there is only one unpaired electron, *i.e.*, $n = 1$.

Hence, $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = \mathbf{1.73\ BM}$

Q. 32. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements.

Ans. $+4 = {}_{58}Ce,\ {}_{59}Pr,\ {}_{60}Nd,\ {}_{65}Tb,\ {}_{66}Dy$

$+2 = {}_{60}Nd,\ {}_{62}Sm,\ {}_{63}Eu,\ {}_{69}Tm,\ {}_{70}Yb$

+2 oxidation state is exhibited when the lanthanoid has the configuration $5d^0\ 6s^2$ so that 2 electrons are easily lost. +4 oxidation state is exhibited when the configuration left is close to $4f^0$ (*e.g.*, $4f^0$, $4f^1$, $4f^2$) or close to $4f^7$ (*e.g.*, $4f^7$ or $4f^8$)

Q. 33. Compare the chemistry of the actinoids with that of landthanoids with reference to:

(*i*) electronic configuration **(*ii*) oxidation states and**

(*iii*) chemical reactivity

Ans.

S.No.	Characteristics	Lanthanoids	Actinoids
(*i*)	Electronic configuration	$[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$	$[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$
(*ii*)	Oxidation states	Besides +3 O.S lanthanoids show +2 and +4 O.S only in a few cases.	Besides +3 O.S actinoids show higher O.S of +4, +5, +6, +7 also because of smaller energy gap between 5*f*, 6*d* and 7*s* subshell.
(*iii*)	General chemical reactivity of elements	These are less reactive metals.	These are highly reactive metals.
		Lesser tendency towards complex formation.	Greater tendency towards complex formation.
		Do not form oxocation.	Form oxocation.
		Compounds are less basic.	Compounds are more basic.

Q. 34. Write the electronic configurations of the elements with atomic numbers 61, 91, 101 and 109.

Ans. Z = 61 (Promethium, Pm), E.C. = $[Xe]\ 4f^5\ 5d^0\ 6s^2$

Z = 91 (Protactium, Pa), E.C. = $[Rn]\ 5f^2\ 6d^1\ 7s^2$

Z = 101 (Mendelevium, Md), E.C. = $[Rn]\ 5f^{13}\ 6d^0\ 7s^2$

Z = 109 (Meitnerium, Mt), E.C. = $[Rn]\ 5f^{14}\ 6d^7\ 7s^2$

Q. 35. Compare the general characteristics of the first series of transition metals with those of the second and third series metals in the respective vertical columns on the basis of following points:

(*i*) electronic configurations, **(*ii*) oxidation states,**

(*iii*) ionisation enthalpies, and **(*iv*) atomic sizes.**

Ans. (*i*) **Electronic configurations:** The elements in the same vertical column generally have similar electronic configurations. Although, the first series shows only two exceptions, *i.e.*, Cr = $[Ar]\ 3d^5\ 4s^1$ and Cu = $[Ar]\ 3d^{10}\ 4s^1$ but the second series shows more exceptions, *e.g.*, Mo(42) = $[Kr]\ 4d^5\ 5s^1$, Ru(44) = $[Kr]\ 4d^7\ 5s^1$, Rh(45) = $[Kr]\ 4d^8\ 5s^1$, Pd(46) = $[Kr]\ 4d^{10}\ 5s^0$, Ag(47) = $[Kr]\ 4d^{10}\ 5s^1$. Similarly, in the third series, W(74) = $[Xe]\ 4f^{14}\ 5d^4\ 6s^2$, Pt(78) = $[Xe]\ 4f^{14}\ 5d^9\ 6s^1$ and Au(79) = $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^1$. Hence, in the same vertical column, in a number of cases, the electronic configuration of the three series are not similar.

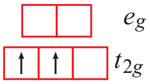
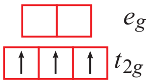
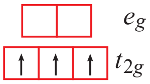
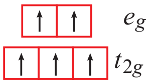
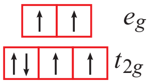
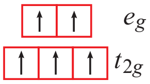
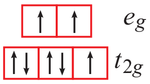
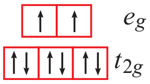
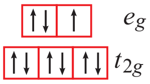
(*ii*) **Oxidation states:** The elements in the same vertical column generally show similar oxidation states. The number of oxidation states shown by the elements in the middle of each series is maximum and minimum at the extreme ends.

(*iii*) **Ionisation enthalpies:** The first ionisation enthalpies in each series generally increase gradually as we move from left to right though some exceptions are observed in each series. The first ionisation enthalpies of some elements in the second (4*d*) series are higher while some of them have lower value than the elements of 3*d*- series in the same vertical column. However, the first ionisation enthalpies of third (5*d*) series are higher than those of 3*d* and 4*d*- series. This is because of weak shielding of nucleus of 4*f*-electrons in the 5*d*-series.

(*iv*) **Atomic sizes:** Generally, ions of the same charge or atoms in a given series show progressively decrease in radius with increasing atomic number though the decrease is quite small. But the size of the atoms of the 4*d*-series is larger than the corresponding elements of the 3*d*-series whereas those of corresponding elements of the 5*d*-series are nearly the same as those of 4*d*-series due to lanthanoid contraction.

Q. 36. Write down the number of 3*d* electrons in each of the following ions:
Ti^{2+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.
Indicate how would you expect the five 3d-orbitals to be occupied for these hydrated ions (octahedral).

Ans.

	Ions	**Electronic Configurations**	**No. of 3*d* electrons**	**3*d*-orbitals occupied**	
(*i*)	Ti^{2+}	$[Ar]3d^2$	2	t_{2g}^2	
(*ii*)	V^{2+}	$[Ar]3d^3$	3	t_{2g}^3	
(*iii*)	Cr^{3+}	$[Ar]3d^3$	3	t_{2g}^3	
(*iv*)	Mn^{2+}	$[Ar]3d^5$	5	$t_{2g}^3 e_g^2$	
(*v*)	Fe^{2+}	$[Ar]3d^6$	6	$t_{2g}^4 e_g^2$	
(*vi*)	Fe^{3+}	$[Ar]3d^5$	5	$t_{2g}^3 e_g^2$	
(*vii*)	Co^{2+}	$[Ar]3d^7$	7	$t_{2g}^5 e_g^2$	
(*viii*)	Ni^{2+}	$[Ar]3d^8$	8	$t_{2g}^6 e_g^2$	
(*ix*)	Cu^{2+}	$[Ar]3d^9$	9	$t_{2g}^6 e_g^3$	

Q. 37. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements. **[*HOTS*]**

Ans. The given statement is true. Some evidences in support of this statement are:

(*i*) Atomic radii of the heavier transition elements (4*d* and 5*d*- series) are larger than those of the corresponding elements of the first transition series though those of 4*d* and 5*d*- series are very close to each other.

(*ii*) Ionisation enthalpies of 5*d*- series are higher than the corresponding elements of 3*d* and 4*d*- series.

(*iii*) Enthalpies of atomisation of 4*d* and 5*d*- series are higher than the corresponding elements of the first series.

(*iv*) Melting and boiling points of heavier transition elements are greater than those of the first transition series due to stronger intermetallic bonding.

Q. 38. What can be inferred from the magnetic moment values of the following complex species?

Example	**Magnetic Moment (BM)**
$K_4[Mn(CN)_6]$	**2.2**
$[Fe(H_2O)_6]^{2+}$	**5.3**
$K_2[MnCl_4]$	**5.9**

Ans. Magnetic moment (μ) = $\sqrt{n\,(n+2)}$ BM

For $n = 1$, $\mu = \sqrt{1\,(1+2)} = \sqrt{3} = 1.73$; For $n = 2$, $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$

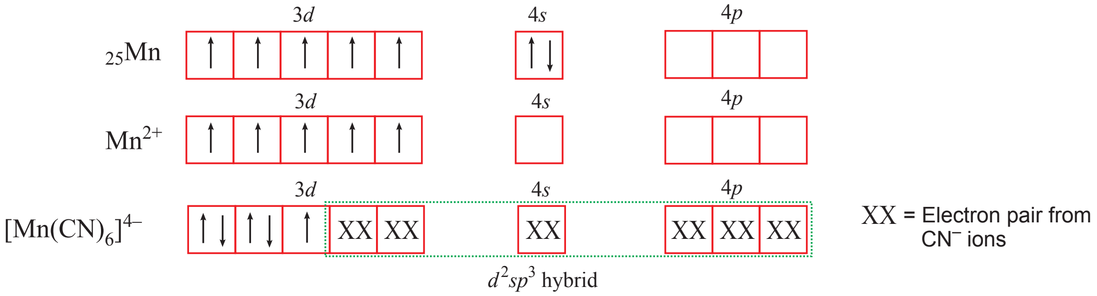
For $n = 3$, $\mu = \sqrt{3\,(3+2)} = \sqrt{15} = 3.87$; For $n = 4$, $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.90$

For $n = 5$, $\mu = \sqrt{5\,(5+2)} = \sqrt{35} = 5.92$

$K_4[Mn(CN)_6]$

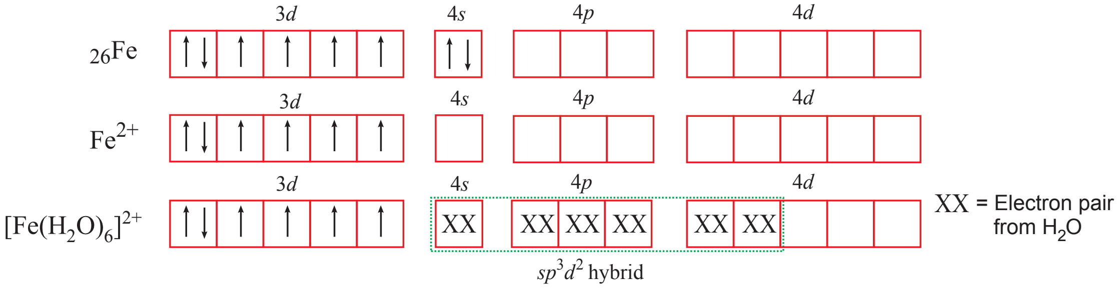
Here, Mn is in +2 oxidation state, *i.e.*, as Mn^{2+}, μ = 2.2 BM shows that it has only one unpaired electron. Hence, when CN^- ligands approach Mn^{2+} ion, the electrons in 3*d*-subshell pair up.

Hence, CN^- is a strong ligand. The hybridisation involved is d^2sp^3 forming inner orbital octahedral complex.



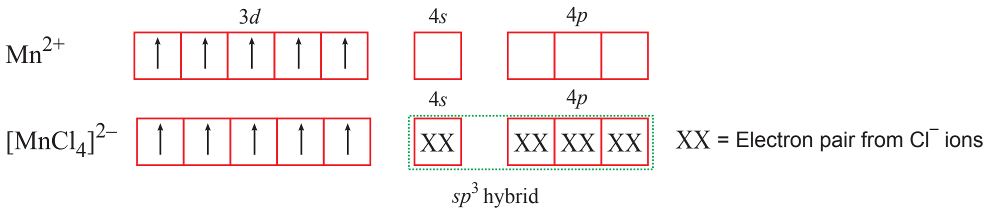
$[Fe(H_2O)_6]^{2+}$

Here, Fe is in +2 oxidation state, *i.e.*, as Fe^{2+}. μ = 5.3 BM shows that there are four unpaired electrons. This means that the electrons in 3*d*-subshell do not pair up when the ligand H_2O molecules approach. Hence, H_2O is a weak ligand. To accommodate the electrons donated by six H_2O molecules, the hybridisation will be sp^3d^2. Hence, it will be an outer orbital octahedral complex.



$K_2[MnCl_4]$

Here, Mn is in +2 state, *i.e.*, as Mn^{2+}. μ = 5.9 BM shows that there are five unpaired electrons. Hence, the hybridisation involved will be sp^3 and the complex will be tetrahedral.



Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. **Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number?** [*NCERT Exemplar*]

   (*a*) 25 (*b*) 26 (*c*) 27 (*d*) 24

2. **Metallic radii of some transition elements are given below. Which of these elements will have highest density?**

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

   [*NCERT Exemplar*]

   (*a*) Fe (*b*) Ni (*c*) Co (*d*) Cu

3. **Which of the following statements is not correct?** [*NCERT Exemplar*]

   (*a*) Copper liberates hydrogen from acids.

   (*b*) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.

   (*c*) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.

   (*d*) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

4. **Which of the following is amphoteric oxide?**

   Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4 [*NCERT Exemplar*]

   (*a*) V_2O_5, Cr_2O_3 (*b*) Mn_2O_7, CrO_3

   (*c*) CrO, V_2O_5 (*d*) V_2O_5, V_2O_4

5. **Which one of the following does not correctly represent the correct order of the property indicated against it ?**

   (*a*) $Ti < V < Cr < Mn$, increasing number of oxidation states

   (*b*) $Ti < V < Mn < Cr$, increasing second ionisation enthalpy

   (*c*) $Ti < V < Cr < Mn$, increasing melting point

   (*d*) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$, increasing magnetic moment

6. **The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is ______________.** [*NCERT Exemplar*]

   (*a*) 2.87 B.M. (*b*) 3.87 B.M. (*c*) 3.47 B.M. (*d*) 3.57 B.M.

7. **Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?** [*NCERT Exemplar*]

   (*a*) Co^{2+} (*b*) Cr^{2+} (*c*) Mn^{2+} (*d*) Cr^{3+}

8. **The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of he following is correct?** [*NCERT Exemplar*]

   (*a*) Cu(II) is more stable

   (*b*) Cu(II) is less stable

   (*c*) Cu(I) and Cu(II) are equally stable

   (*d*) Stability of Cu(I) and Cu(II) depends on nature of copper salts

9. **Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?** [*NCERT Exemplar*]

   (*a*) Ag_2SO_4 (*b*) CuF_2 (*c*) ZnF_2 (*d*) Cu_2Cl_2

10. **Which of the following statement about transition element is not correct?**

    (*a*) They show variable oxidation states.

    (*b*) They exhibit diamagnetic and paramagnetic properties.

    (*c*) All ions are coloured.

    (*d*) They exhibit catalytic property.

11. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following. [*NCERT Exemplar*]

(*a*) Mn_2O_7 (*b*) MnO_2 (*c*) $MnSO_4$ (*d*) Mn_2O_3

12. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured? [*NCERT Exemplar*]

(*a*) $KMnO_4$ (*b*) $Ce(SO_4)_2$ (*c*) $TiCl_4$ (*d*) Cu_2Cl_2

13. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because [*NCERT Exemplar*]

(*a*) CO_2 is formed as the product. (*b*) Reaction is exothermic.

(*c*) MnO_4^- catalyses the reaction. (*d*) Mn^{2+} acts as autocatalyst.

14. Which of the following reactions are disproportionation reactions? [*NCERT Exemplar*]

(*i*) $Cu^+ \longrightarrow Cu^{2+} + Cu$

(*ii*) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(*iii*) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(*iv*) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

(*a*) (*i*), (*ii*) (*b*) (*i*), (*ii*), (*iii*) (*c*) (*ii*), (*iii*), (*iv*) (*d*) (*i*), (*iv*)

15. $KMnO_4$ acts an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is [*NCERT Exemplar*]

(*a*) $\frac{2}{5}$ (*b*) $\frac{3}{5}$ (*c*) $\frac{4}{5}$ (*d*) $\frac{1}{5}$

16. $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to ____________. [*NCERT Exemplar*]

(*a*) I_2 (*b*) IO^- (*c*) IO_3^- (*d*) IO_4^-

17. Which of the following oxidation state is common for all lanthanoids? [*NCERT Exemplar*]

(*a*) +2 (*b*) +3 (*c*) +4 (*d*) +5

18. Gadolinium belongs to 4*f* series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? [*NCERT Exemplar*]

(*a*) $[Xe]\, 4f^7 5d^1 6s^2$ (*b*) $[Xe]\, 4f^6 5d^2 6s^2$

(*c*) $[Xe]\, 4f^8 6d^2$ (*d*) $[Xe]\, 4f^9 5s^1$

19. Identify the incorrect statement among the following:

(*a*) Lanthanoid contraction is the accumulation of successive shrinkages.

(*b*) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

(*c*) As a result of lanthanoid contraction, the properties of 4*d* series of the transition elements have no similarities with the 5*d* series of elements.

(*d*) Shielding power of 4*f* electrons is quite weak.

20. Actinoids exhibit greater number of oxidation states than lanthanoids. The main reason being

(*a*) more energy difference between 5*f* and 6*d* than between 4*f* and 5*f* orbitals

(*b*) 4*f* orbitals are more diffused than the 5*f* orbitals

(*c*) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals

(*d*) more reactive nature of the actinoids than the lanthanoids.

Answers

1. (*b*)	**2.** (*d*)	**3.** (*a*)	**4.** (*a*)	**5.** (*c*)	**6.** (*b*)	**7.** (*a, d*)	**8.** (*a*)	**9.** (*b*)	**10.** (*c*)
11. (*a*)	**12.** (*a, b*)	**13.** (*d*)	**14.** (*a*)	**15.** (*a*)	**16.** (*c*)	**17.** (*b*)	**18.** (*a*)	**19.** (*c*)	**20.** (*c*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion (*A*) :** In transition elements *ns* orbital is filled up first and $(n-1)d$ afterwards, during ionization *ns* electrons are lost prior to $(n-1)d$ electrons.
   Reason (*R*) : The effective nuclear charge felt by $(n-1)d$ electrons is higher as compared to that by *ns* electrons.
2. **Assertion (*A*) :** Zn, Cd and Hg cannot be regarded as transition elements.
   Reason (*R*) : These elements do not belong to the *d*-block of the periodic table.
3. **Assertion (*A*) :** Transition metals are strong reducing agents.
   Reason (*R*) : Transition metals form numerous alloys with other metals.
4. **Assertion (*A*) :** Amongst Cu^{2+} and Cu^{+} ions, the more stable ions is Cu^{2+}.
   Reason (*R*) : For determination of stability of an ion its electrode potential is more important factor than its electronic configuration.
5. **Assertion (*A*) :** Transition metals form complexes.
   Reason (*R*) : Transition metals have unpaired electrons.
6. **Assertion (*A*) :** A solution of ferric chloride on standing gives a brown precipitate.
   Reason (*R*) : $FeCl_3$ possesses covalent bonds and chlorine bridge structure.
7. **Assertion (*A*) :** Members of 4*d* and 5*d* series of transition elements have nearly same atomic radii.
   Reason (*R*) : Atomic and ionic radii for transition elements are smaller than their corresponding *s*-block elements.
8. **Assertion (*A*) :** The most common oxidation state exhibited by actinoids is +2.
   Reason (*R*) : All actinoids possess two electrons in 7*s* subshell.
9. **Assertion (*A*) :** Ce^{4+} is used as an oxidising agent in volumetric analysis.
   Reason (*R*) : Ce^{4+} has the tendency of attaining +3 oxidation state.
10. **Assertion (*A*) :** The degree of complex formation in actinides decreases in the order
    $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$
    Reason (*R*) : Actinides form complexes with π-bonding ligands such as alkyl phosphines and thioethers.

Answers

1. (*a*) **2.** (*c*) **3.** (*d*) **4.** (*b*) **5.** (*b*) **6.** (*b*) **7.** (*b*) **8.** (*d*) **9.** (*a*) **10.** (*b*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The *d*-block elements are those elements in which the last electron enters the *d*-subshell of the penultimate shell. The general electronic configuration of these elements is $(n-1)\,d^{1-10}\,ns^{1-2}$, where *n* is outermost shell. The *d*-block consisting of groups 3–12 occupies the large middle section of the periodic table. The elements of *d*-block are also known as transition elements as they possess properties that are transitional between the *s* and *p* block elements. A transition element is defined as an element which has incompletely filled *d*-orbitals in its ground state or any one of its oxidation states. There are four series of transition elements spread between group 3 and 12. First transition series or 3*d*-series: Scandium ($_{21}$Sc) to Zinc ($_{30}$Zn), Second transition series or 4*d*-series: Yttrium ($_{39}$Y) to Cadmium ($_{48}$Cd), Third transition series or 5*d*-series: Lanthanum ($_{57}$La) and Hafnium ($_{72}$Hf) to Mercury ($_{80}$Hg) (Omitting $_{58}$Ce to $_{71}$Lu), Fourth transition series or 6*d*-series: Begins with Actinium ($_{89}$Ac) is still incomplete.

1. In what way is the electronic configuration of transition elements different from that of the non-transition elements?

Ans. Transition elements contain incompletely filled *d*-subshell, *i.e.*, their electronic configuration is $(n-1)\,d^{1-10}\,ns^{1-2}$ whereas non-transition elements have no *d*-subshell or their subshell is completely filled and have ns^{1-2} or $ns^2\,np^{1-6}$ in their outermost shell.

2. Why is zinc not regarded as a transition clement? **[*CBSE Guwahati 2015*]**

Ans. As zinc atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as in oxidised state, therefore, it is not regarded as a transition element.

3. Why does a transition series contain 10 elements?

Ans. There are five *d*-orbitals in an energy level and each orbital can contain two electrons. As we move from one element to the next, an electron is added and for complete filling of the five *d*-orbitals, 10 electrons are required.

4. Name the element which shows outer electronic configuration $3d^3\,4s^2$.

Ans. Vanadium

5. What are interstitial compounds?

Ans. Interstitial compounds are those in which small atoms occupy the interstitial sites in the crystal lattice.

PASSAGE–2

Potassium permanganate, ($KMnO_4$) is prepared by fusion of pyrolusite, MnO_2 with KOH in the presence of an oxidising agent like KNO_3. This produces the dark green potassium manganate, K_2MnO_4 which disproportionates in a neutral or acidic solution to give purple permanganate ion. Potassium permanganate is an important oxidising agent in acidic, alkaline as well as neutral medium.

1. What is the state of hybridisation of Mn in MnO_4^-?

Ans. sp^3

2. Write an application of potassium permanganate.

Ans. It is used for the estimation of hydrogen peroxide.

3. What are the products formed after heating potassium permanganate?

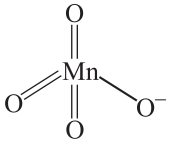
Ans. K_2MnO_4, O_2 and MnO_2 will be formed after heating of potassium permanganate.

4. How many electrons are involved in oxidation by $KMnO_4$ in an acidic medium?

Ans. Five electrons are involved in oxidation by $KMnO_4$ in an acidic medium.

5. Draw the structure of permanganate ion. Is it paramagnetic or diamagnetic?

Ans.



Tetrahedral permanganate ion
(purple)

It is diamagnetic.

Very Short Answer Questions [1 mark]

Q. 1. Copper atom has completely filled *d*-orbitals in its ground state but it is a transition element. Why? **[*CBSE Chennai 2015*]**

Ans. Copper exhibits +2 oxidation state wherein it has incompletely filled *d* orbitals ($3d^9\,4s^0$) hence, a transition element.

Q. 2. **Give reason:**

Zn is soft whereas Cr is hard. *[CBSE South 2016]*

Ans. Cr ($3d^5\ 4s^1$) has five unpaired electrons in its *d*-orbitals whereas Zn ($3d^{10}\ 4s^2$) has no unpaired electrons in its *d*-orbitals. As a result of this weak metallic bonds exist in Zn whereas strong metallic bonds exist in Cr. Hence, Zn is soft whereas Cr is hard.

Q. 3. **Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.** *[NCERT Exemplar]*

Ans. It is due to regular increase in ionisation enthalpy.

Q. 4. **Arrange the following in increasing order of acidic character:** *[HOTS]*

CrO_3, CrO, Cr_2O_3

Ans. CrO < Cr_2O_3 < CrO_3. Higher the oxidation state, more will be acidic character.

Q. 5. **Why does copper not replace hydrogen from acids?** *[NCERT Exemplar]*

Ans. Cu shows E^o positive value.

Q. 6. **Which divalent metal ion has maximum paramagnetic character among the first transition metals? Why?**

Ans. Mn^{2+} has the maximum paramagnetic character because of the maximum number of unpaired electrons, *viz*., 5.

Q. 7. **Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 BM and that of Co^{2+} is 4.87 BM. Why?** *[NCERT Exemplar]* *[HOTS]*

Ans. Due to symmetrical electronic configuration there is no orbital contribution in Cr^{3+} ion. However, appreciable orbital contribution takes place in Co^{2+} ion.

Q. 8. **Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?** *[NCERT Exemplar]* *[HOTS]*

Ans. $CuCl_2$ is more stable than Cu_2Cl_2. The stability of $Cu^{2+}(aq)$ is more than $Cu^{+}(aq)$ due to the much more negative $\Delta_{hyd}H^o$ of $Cu^{2+}(aq)$ than $Cu^{+}(aq)$.

Q. 9. **Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why?** *[CBSE Patna 2015]*

Ans. Cu^{2+} ($3d^9\ 4s^0$) has one unpaired electron in *d*-subshell which absorbs radiation in visible region resulting in *d-d* transition and hence Cu^{2+} salts are coloured. Zn^{2+} ($3d^{10}\ 4s^0$) has completely filled *d*-orbitals. No radiation is absorbed for *d-d* transition and hence Zn^{2+} salts are colourless.

Q. 10. **Write any one use of pyrophoric alloys.**

Ans. Pyrophoric alloys emit sparks when struck. Hence, they are used in making flints for lighters.

Short Answer Questions–I [2 marks]

Q. 1. **Use the data to answer the following and also justify giving reason:** *[CBSE 2019 (56/4/1)]*

	Cr	Mn	Fe	Co
$E^o_{M^{2+}/M}$	–0.91	–1.18	–0.44	–0.28
$E^o_{M^{3+}/M^{2+}}$	–0.41	–1.57	–0.77	+1.97

(*i*) **Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?**

(*ii*) **Which is the most stable ion in +2 oxidation and why?**

Ans. (*i*) Cr^{2+}, due to lower standard reduction potential (E^o)/Higher standard oxidation potential.

(*ii*) Mn^{2+}, due to highest negative standard reduction potential.

Q. 2. **In the following ions:**

Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}

(Atomic no. : Mn = 25, V = 23, Cr = 24, Ti = 22)

(*i*) **Which ion is most stable in an aqueous solution?**

(*ii*) **Which ion is the strongest oxidizing agent?**

(*iii*) **Which ion is colourless?**

(*iv*) **Which ion has the highest number of unpaired electrons?** *[CBSE (F) 2017]*

Ans. (*i*) Cr^{3+} because of half filled t_{2g} level.

(*ii*) Mn^{3+}, as the change from Mn^{3+} to Mn^{2+} results in stable half filled (d^5) configuration.

(*iii*) Ti^{4+}, as Ti^{4+} has empty *d*-orbitals therefore *d*-*d* transition cannot occur in Ti^{4+}.

(*iv*) Mn^{3+} ($3d^4 4s^0$). It has 4 unpaired electrons.

Q. 3. Give reasons for the following:

(*i*) E^o values of Mn, Ni and Zn are more negative than expected.

(*ii*) $[Ti(H_2O)]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. **[*HOTS*]**

OR

Ti^{3+} is coloured whereas Sc^{3+} is colourless in aqueous solution. **[*CBSE 2020 (56/5/1)*]**

Ans. (*i*) Negative E^o values for Mn^{2+} and Zn^{2+} are related to stabilities of half-filled and fully filled configurations, respectively. But for Ni^{2+}, E^o value is related to the highest negative enthalpy of hydration.

(*ii*) This is due to *d*-*d* transition of electron in $[Ti(H_2O)_6]^{3+}$ complex. Ti^{3+} has one electron in *d*-orbital ($3d^1$) which absorbs energy corresponding to blue-green region and jumps from t_{2g} to e_g set of *d*-orbitals ($t^1_{2g}\,e^0_g \longrightarrow t^0_{2g}\,e^1_g$). But Sc^{3+} has no electron in the *d*-orbital.

Q. 4. How would you account for the following:

(*i*) Mn (III) undergoes disproportionation reaction easily.

(*ii*) Co (II) is easily oxidised in the presence of strong ligands. **[*CBSE (F) 2011*]**

Ans. (*i*) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half filled *d*-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

(*ii*) Co (II) has electronic configuration $3d^7\,4s^0$, *i.e.*, it has three unpaired electrons. In the presence of strong ligands, two unpaired electrons in 3*d*-subshell pair-up and third unpaired electron shifts to higher energy subshell from where it can be easily lost and hence oxidised to Co(III).

Q. 5. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured (C). An acidified solution of compound (C) oxidises Na_2SO_3 to (D). Identify (A), (B), and (D.) **[*CBSE 2019 (56/2/1)*]**

Ans. $A = \underset{\text{Sodium chromate}}{Na_2CrO_4}$, $B = \underset{\text{Sodium dichromate}}{Na_2Cr_2O_7}$, $C = \underset{\text{Potassium dichromate}}{K_2Cr_2O_7}$, $D = \underset{\text{Sodium sulphate}}{Na_2SO_4}$

Q. 6. Complete the following chemical reaction equations:

(*i*) $MnO_4^-\,(aq) + C_2O_4^{2-}\,(aq) + H^+\,(aq) \longrightarrow$

(*ii*) $Cr_2O_7^{2-}\,(aq) + Fe^{2+}\,(aq) + H^+\,(aq) \longrightarrow$

Ans. (*i*)

$$\begin{array}{r}
[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2 \\
[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-\,] \times 5 \\ \hline
MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \\ \hline
\end{array}$$

(*ii*)

$$\begin{array}{r}
Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\
Fe^{2+} \longrightarrow Fe^{3+} + e^-\,] \times 6 \\ \hline
Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \\ \hline
\end{array}$$

Q. 7. Complete the following chemical equations:

(*i*) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$

(*ii*) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow$ **[*CBSE Delhi 2016*]**

Ans. (*i*)

$$\begin{array}{r}
8MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-\,] \times 8 \\
S_2O_3^{2-} + 10OH^- \longrightarrow 2SO_4^{2-} + 5H_2O + 8e^-\,] \times 3 \\ \hline
8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^- \\ \hline
\end{array}$$

(*ii*)

$$\begin{array}{r}
Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\
Sn^{2+} \longrightarrow Sn^{4+} + 2e^-\,] \times 3 \\ \hline
Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O \\ \hline
\end{array}$$

Q. 8. Complete and balance the following equations: **[*CBSE 2019 (56/5/2)*]**

(*i*) $MnO_4^- + I^- + H^+ \longrightarrow$

(*ii*) $Na_2Cr_2O_7 + KCl \longrightarrow$

Ans. (*i*) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

(*ii*) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Q. 9. Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions? **[*NCERT Exemplar*]**

Ans. Reaction between iodide and persulphate ions is:

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe(III)} I_2 + 2SO_4^{2-}$$

Role of Fe(III) ions:

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Q. 10. Explain each of the following observations:

(*i*) **Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.** **[*CBSE Delhi 2012*]**

(*ii*) **Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.** **[*CBSE (AI) 2012*]**

Ans. (*i*) $Mn^{3+}(d^4)$ is less stable than Mn^{2+} (d^5, half filled) while Fe^{3+} (d^5, half filled) is more stable than Fe^{2+} (d^4). That is why Mn^{2+} is more resistance than Fe^{2+} towards oxidation.

(*ii*) Lanthanoid metals show +2 and +4 oxidation states to attain extra stable f^0 and f^7 configurations.

Q. 11. Explain each of the following observations:

(*i*) **Actinoids exhibit a much larger number of oxidation states than the lanthanoids.** **[*CBSE 2019 (56/2/1)*]**

(*ii*) **There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.** **[*CBSE (F) 2012*]**

Ans. (*i*) This is due to small energy gap between 5*f*, 6*d* and 7*s* subshells in actinoids.

(*ii*) This is because with increase in atomic number in a series, the increased nuclear charge is partly cancelled by the increased shielding effect of electrons in the *d*-orbitals of penultimate shell.

Short Answer Questions–II [3 marks]

Q. 1.

$E^o_{Mn^{2+}/Mn}$	Cr	Mn	Fe	Co	Ni	Cu
	– 0.91	– 1.18	– 0.44	– 0.28	– 0.25	+0.34

From the given data of E^o values, answer the following questions:

(*i*) **Why is $E^o_{(Cu^{2+}/Cu)}$ value exceptionally positive?**

(*ii*) **Why is $E^o_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?**

(*iii*) **Which is a stronger reducing agent Cr^{2+} or Fe^{2+}? Give reason.** **[*CBSE Patna 2015*] [*HOTS*]**

Ans. (*i*) Copper has high enthalpy of atomisation and low enthalpy of hydration. Since the high energy to transform Cu(*s*) to Cu^{2+}(*aq*) is not balanced by hydration enthalpy, therefore, $E^o_{Cu^{2+}/Cu}$ value is exceptionally positive.

(*ii*) This is due to extra stability of half-filled 3*d*-orbitals of $Mn^{2+}(3d^5)$.

(*iii*) Refer to NCERT Intext Questions, Q. 7.

Q. 2. The elements of 3*d* transition series are given as:

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn ***[CBSE East 2016]***

Answer the following:

(*i*) Copper has exceptionally positive $E^{o}_{M^{2+}/M}$ value. Why?

(*ii*) Which element is a strong reducing agent in +2 oxidation state and why?

(*iii*) Zn^{2+} salts are colourless. Why?

Ans. (*i*) Because the sum of sublimation enthalpy and hydration enthalpy to convert Cu(*s*) to Cu^{2+}(*aq*) is so high that it is not balanced by its hydration enthalpy.

(*ii*) Cr is strongest reducing agent in +2 oxidation state. Cr^{2+} has configuration $3d^4$. After losing one electron it forms Cr^{3+} which has stable half filled t_{2g} level.

(*iii*) $Zn^{2+}(3d^{10})$ has completely filled *d*-orbitals. As a result of this, *d*-*d* transition cannot occur and hence, Zn^{2+} salts are colourless.

Q. 3. (*i*) For M^{2+}/M and M^{3+}/M^{2+} systems, E^o values for some metals are as follows:

$Cr^{2+}/Cr = -0.9$ V $Cr^{3+}/Cr^{2+} = -0.4$ V

$Mn^{2+}/Mn = -1.2$ V $Mn^{3+}/Mn^{2+} = +1.5$ V

$Fe^{2+}/Fe = -0.4$ V $Fe^{3+}/Fe^{2+} = +0.8$ V

Use this data to comment upon

(*a*) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}.

(*b*) the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

(*ii*) What can be inferred from the magnetic moment of the complex $K_4[Mn(CN)_6]$, Magnetic moment: 2.2 BM? ***[CBSE Sample Paper 2016]***

Ans. (*i*) (*a*) Higher the reduction potential of a species, greater is the ease with which it undergo reduction. Among these pairs, Mn^{3+}/Mn^{2+} has largest positive reduction potential. Hence Mn^{3+} can be easily reduced to Mn^{2+} *i.e.*, Mn^{3+} is least stable. Cr^{3+}/Cr^{2+} has a negative $E°$ value, therefore, Cr^{3+} is most stable. Fe^{3+}/Fe^{2+} has a positive value but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+}.

(*b*) Lower the reduction potential or higher the oxidation potential of a species, greater is the ease with which it undergo oxidation. Among these pairs, Mn^{2+}/Mn has the most negative reduction potential or most positive oxidation potential. Therefore, it will be most easily oxidised. Thus, the decreasing order of their ease of oxidation is Mn > Cr > Fe.

(*ii*) In the complex $K_4[Mn(CN)_6]$, Mn is in +2 oxidation state. Magnetic moment 2.2 BM indicates that it has only one unpaired electron and hence forms inner orbital or low spin octahedral complex. In presence of CN^-, a strong ligand the hybridisation involved is d^2sp^3.

Q. 4. Account for the following:

(*i*) Eu^{2+} is a strong reducing agent.

(*ii*) Orange colour of dichromate ion changes to yellow in alkaline medium.

(*iii*) $E^{o}_{M^{2+}/M}$ values for transition metals show irregular variation. ***[CBSE (F) 2017]***

Ans. (*i*) This is because Eu^{2+} tends to change to Eu^{3+} as +3 is the common oxidation state of lanthanoids.

(*ii*) In alkaline medium, the orange colour of the solution changes to yellow due to conversion of dichromate ($Cr_2O_7^{2-}$) ion to chromate (CrO_4^{2-}) ion.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \rightleftharpoons \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

(*iii*) The irregularity is due to the irregular variation of ionisation enthalpies ($\Delta_i H + \Delta_i H_2$) and also the sublimation enthalpies which are relatively much less for Mn (240 kJ mol^{-1}) and V (470 kJ mol^{-1}).

Q. 5. Complete the following reactions: *[CBSE 2019 (56/4/1)]*

(*i*) $MnO_2 + KOH + O_2 \longrightarrow$

(*ii*) $I^- + MnO_4^- + H^+ \longrightarrow$

(*iii*) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$

Ans. (*i*) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

(*ii*) $10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

(*iii*) $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

Q. 6. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A and B.

[NCERT Exemplar] *[HOTS]*

Ans. A = MnO_2 [Manganese (IV) oxide]

B = Cl_2 (Chlorine)

C = NCl_3 (Nitrogen trichloride)

$$\underset{(A)}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{(B)}{Cl_2}\uparrow + 2H_2O$$

$$NH_3 + \underset{(excess)}{3Cl_2} \longrightarrow \underset{(C)}{NCl_3} + 3HCl$$

Q. 7. A solution of $KMnO_4$ on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out? *[NCERT Exemplar]*

Ans. Oxidising behaviour of $KMnO_4$ depends on pH of the solution.

In acidic medium (pH < 7),

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow \underset{(Colourless)}{Mn^{2+}} + 4H_2O$$

In alkaline medium (pH > 7),

$$MnO_4^- + e^- \longrightarrow \underset{(Green)}{MnO_4^{2-}}$$

In neutral medium (pH = 7),

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow \underset{(Brown\ precipitate)}{MnO_2} + 2OH^-$$

Q. 8. (*i*) How would you account for the following:

(*a*) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.

(*b*) Transition metals and their compounds show catalytic properties. *[CBSE 2020 (56/5/1)]*

(*ii*) Complete the following equation:

$3MnO_4^{2-} + 4H^+ \longrightarrow$ *[CBSE (F) 2015]*

Ans. (*i*) (*a*) As oxygen stabilises manganese more than fluorine by forming multiple bonds.

(*b*) The catalytic activity of transition metals and their compounds is attributed to the following reasons:

- Due to their tendency to show variable oxidation states transition metals form unstable intermediate compounds and provide a new path for the reaction with lower activation energy.
- In some cases, the transition metals provide a suitable large surface area with free valencies on which reactants are adsorbed.

(*ii*) $$\underset{Manganate\ ion}{3MnO_4^{2-}} + 4H^+ \longrightarrow \underset{Permanganate\ ion}{2MnO_4^-} + MnO_2 + 4H_2O$$

Q. 9. Explain the following observations:

(*i*) The enthalpies of atomisation of transition metals are quite high.

(*ii*) There is a close similarity in physical and chemical properties of the 4*d* and 5*d* series of the transition elements, much more than expected on the basis of usual family relationship.

(*iii*) The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series. **[*NCERT Exemplar*]**

Ans. (*i*) This is because transition metals have strong metallic bonds as they have large number of unpaired electrons.

(*ii*) This is because 5*d* and 4*d*-series elements have virtually the same atomic and ionic radii due to lanthanoid contraction. Due to equality in size of Zr and Hf, Nb and Ta, Mo and W, etc., the two elements of each pair have the same properties.

(*iii*) The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series due to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies.

Q. 10. Account for the following:

(*i*) Mn_2O_7 is acidic whereas MnO is basic.

(*ii*) Though copper has completely filled *d*-orbital (d^{10}) yet it is considered as a transition metal.

(*iii*) Actinoids show wide range of oxidation states. **[*CBSE (F) 2016*]**

Ans. (*i*) Mn has + 7 oxidation state in Mn_2O_7 and + 2 in MnO. In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.

(*ii*) Copper exhibits +2 oxidation state wherein it will have incompletely filled *d*-orbitals ($3d^9$), hence a transition metal.

(*iii*) This is due to comparable energies of 5*f*, 6*d* and 7*s* orbitals.

Long Answer Questions [5 marks]

Q. 1. (*i*) The elements of 3*d* transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

(*a*) Which element has the highest m.p. and why?

(*b*) Which element is a strong oxidising agent in +3 oxidation state and why?

(*c*) Which element is soft and why?

(*ii*) Write the equations involved in the preparation of potassium dichromate from sodium chromate (Na_2CrO_4). **[*CBSE (F) 2016*]**

Ans. (*i*) (*a*) Cr, the highest melting point of Cr is attributed to the involvement of greater number of electrons(5) from 3*d* in addition to 4*s* electrons in interatomic metallic bonding.

(*b*) Mn, because the change from Mn^{3+} (d^4) to Mn^{2+} (d^5) results in the half filled configuration which has extra stability.

(*c*) Zn, in Zn ($3d^{10}\ 4s^2$) all the electrons present in *d*-orbitals are paired and hence metallic bonds present in it are weak. That is why, it is soft.

(*ii*) Sodium chromate is acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Q. 2. **(*i*) Is the variability in oxidation number of transition elements different from that of non-transition elements? Illustrate with examples.**

(*ii*) Give reasons:

(*a*) *d*-block elements exhibit more oxidation states than *f*-block elements.

(*b*) Orange solution of potassium dichromate turns yellow on adding sodium hydroxide to it.

(*c*) Zirconium (Z = 40) and Hafnium (Z = 72) have almost similar atomic radii.

[CBSE Sample Paper 2017]

Ans. (*i*) In transition elements, the oxidation states differ from each other by unity, *e.g.*, Fe^{3+} and Fe^{2+} etc., while in non-transition elements (*p*-block elements), the oxidation states differ by two, *e.g.*, Pb^{4+} and Pb^{2+}, etc.

In transition elements the higher oxidation states are more stable for the heavier elements in a group, *e.g.*, Mo(VI) is more stable than Cr(VI) whereas in non-transition elements (*p*-block elements), the lower oxidation states are more stable for heavier elements due to inert pair effect, *e.g.*, Pb(II) is more stable than Pb(IV).

(*ii*) (*a*) *d*–block elements exhibit more oxidation states because of less energy gap between *d* and *s* subshell whereas *f*-block elements have large energy gap between *f* and *d* subshell.

(*b*) On adding NaOH, pH of solution increases and the orange colour of the solution changes to yellow due to conversion of dichromate ion to chromate ion.

$$\underset{\substack{\text{Dichromate ion}\\ \text{(Orange)}}}{Cr_2O_7^{2-}} + 2OH^- \rightleftharpoons \underset{\substack{\text{Chromate ion}\\ \text{(Yellow)}}}{2CrO_4^{2-}} + H_2O$$

(*c*) This is due to filling of 4*f*-orbitals which have poor shielding effect (Lanthanoid contraction).

Q. 3. **(*i*) Describe the preparation of potassium permanganate from pyrolusite ore. Write balanced chemical equation for one reaction to show the oxidizing nature of potassium permanganate.**

(*ii*) Draw the structures of chromate and dichromate ions. ***[CBSE Sample Paper 2017]***

Ans. (*i*) Conversion of pyrolusite (MnO_2) into potassium manganate (K_2MnO_4).

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Electrolytic oxidation:

$$K_2MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$

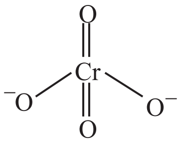
At anode: $MnO_4^{2-} \longrightarrow MnO_4^- + e^-$

At cathode: $H^+ + e^- \longrightarrow H$, $2H \longrightarrow H_2$

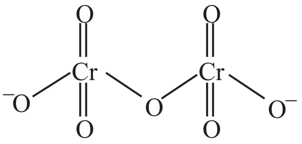
It oxidises oxalate ($C_2O_4^{2-}$) to carbon dioxide (CO_2) in acidic medium.

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 10CO_2 + 8H_2O \\ \hline \end{array}$$

(*ii*)



Chromate ion



Dichromate ion

Q. 4. **(*i*) Compare non transition and transition elements on the basis of their**

(*a*) Variability of oxidation states

(*b*) Stability of oxidation states.

(*ii*) Give chemical reactions for the following observations:

(*a*) Potassium permanganate is a good oxidising agent in basic medium.

(*b*) Inter convertibility of chromate ion and dichromate ion in aqueous solution depends upon pH of the solution.

(*c*) Potassium permanganate is thermally unstable at 513K. [*CBSE Sample Paper 2013*]

Ans. (*i*) (*a*) Oxidation states of transition elements differ from each other by unity. In non-transition elements oxidation states normally differ by a unit of two.

(*b*) In transition elements higher oxidation states are favoured by heavier elements whereas in non-transition elements lower oxidation state is favoured by heavier elements.

(*ii*) (*a*)

$$\begin{array}{rcl} MnO_4^- + 2H_2O + 3e^- & \longrightarrow & MnO_2 + 4OH^-] \times 2 \\ I^- + 6OH^- & \longrightarrow & IO_3^- + 3H_2O + 6e^- \\ \hline 2MnO_4^- + I^- + H_2O & \longrightarrow & IO_3^- + 2MnO_2 + 2OH^- \\ \hline \end{array}$$

(*b*) $2CrO_4^{2-} + 2H^+ \underset{\text{Alkali (pH more than 7)}}{\overset{\text{Acid (pH less than 7}}{\rightleftharpoons}} Cr_2O_7^{2-} + H_2O$

(*c*) $2KMnO_4 \xrightarrow{513\ K} K_2MnO_4 + MnO_2 + O_2$

Q. 5. **(*i*) In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, why is dil. H_2SO_4 used instead of dil. HCl?**

(*ii*) Give reasons:

(*a*) Among transition metals, the highest oxidation state is exhibited in oxoanions of a metal.

(*b*) Ce^{4+} is used as an oxidising agent in volumetric analysis. [*CBSE 2019(56/2/3)*]

(*c*) Zn^{2+} salts are white while Cu^{2+} salts are blue.

OR

Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution? [*CBSE 2020 (56/3/1)*]

Ans. (*i*) Dil. H_2SO_4 is an oxidising agent and oxidises $FeSO_4$ to $Fe_2(SO_4)_3$. Dil. HCl is a reducing agent and liberates chlorine on reacting with $KMnO_4$ solution.

Hence, the part of the oxygen produced from $KMnO_4$ is used up by HCl.

(*ii*) (*a*) In these oxoanions the oxygen atoms are directly bonded to the transition metal.

Since oxygen is highly electronegative, the oxoanions bring out the highest oxidation state of the metal.

(*b*) Ce^{4+} has the tendency to attain +3 oxidation state which is more stable and so it is used as an oxidising agent in volumetric analysis.

(*c*) Zn^{2+} ion has all its orbitals completely filled whereas in Cu^{2+} ion there is one half-filled 3*d*-orbital. Therefore, due to *d*-*d* transition Cu^{2+} has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.

Q. 6. **A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. H_2SO_4 and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.** [*NCERT Exemplar*] [*HOTS*]

Ans. A = $KMnO_4$ (Potassium permanganate), B = K_2MnO_4 (Potassium manganate),

C = MnO_2 (Manganese (IV) oxide), D = $MnCl_2$ (Manganese (II) chloride)

$$\underset{\text{(A)}}{2KMnO_4} \xrightarrow{\Delta} \underset{\text{(B)}}{K_2MnO_4} + \underset{\text{(C)}}{MnO_2} + O_2$$

$$\underset{(C)}{MnO_2} + 2KOH + KNO_3 \longrightarrow \underset{(B)}{K_2MnO_4} + H_2O + KNO_2$$

$$MnO_2 + 4NaCl + 4H_2SO_4 \longrightarrow \underset{(D)}{MnCl_2} + 4NaHSO_4 + 2H_2O + Cl_2$$

Q. 7. **When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.** **[*NCERT Exemplar*] [*HOTS*]**

Ans. A = MnO_2 (Manganese (IV) oxide), B = K_2MnO_4 (Potassium manganate),
C = $KMnO_4$ (Potassium permanganate), D = KIO_3 (Potassium iodate)

$$\underset{(A)}{2MnO_2} + 4KOH + O_2 \longrightarrow \underset{(B)}{2K_2MnO_4} + 2H_2O$$

$$3K_2MnO_4 + 4H^+ \longrightarrow \underset{(C)}{2KMnO_4} + MnO_2 + 2H_2O + 4K^+$$

$$2MnO_4^- + H_2O + KI \longrightarrow \underset{(A)}{2MnO_2} + 2OH^- + \underset{(D)}{KIO_3}$$

Q. 8. **(*i*) Write balanced equations to represent what happens when**

(*a*) Cu^{2+} is treated with KI.

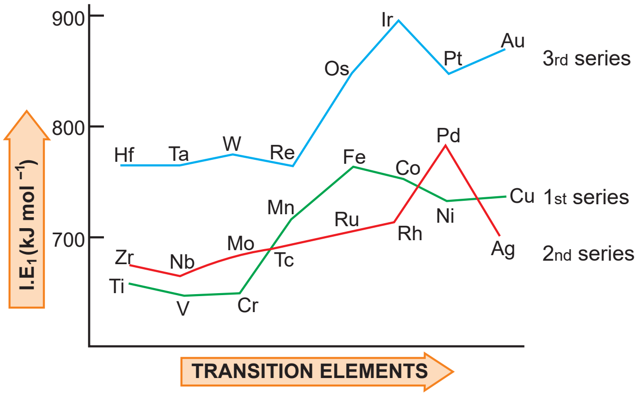
(*b*) Acidified potassium dichromate solution is reacted with iron (II) solution. (ionic equation)

(*ii*) (*a*) The figure given illustrates the first ionization enthalpies of first, second and third series of transition elements. Answer the question that follows:

Which series amongst the first, second and third series of transition elements have the highest first ionization enthalpy and why?

(*b*) Separation of lanthanoid elements is difficult. Explain. **[*CBSE 2020 (56/5/1)*]**

(*c*) Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidising agent. Why? **[*CBSE Sample Paper 2015*]**



Ans. (*i*) (*a*) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$

(*b*) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

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

(*ii*) (*a*) Third series has the highest first ionization energy due to poorest shielding effect of the fully filled 4*f* subshell.

(*b*) Due to lanthanoid contraction, some pair of elements have almost similar size and as a result, such pairs have very similar properties which makes their separation difficult.

(*c*) Sm^{2+}, Eu^{2+} and Yb^{2+} ions are good reducing agents as they tend to acquire common oxidation state of + 3 shown by lanthanoids by the loss of one electron while Ce^{4+} gains one electron to attain + 3. Hence, Ce^{4+} is an oxidising agent.

Q. 9. (*i*) Account for the following:

(*a*) Transition metals form large number of complex compounds. **[*CBSE 2019 (56/2/1)*]**

(*b*) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(*c*) E^o value for the Mn^{3+}/Mn^{2+} couple is highly positive (+ 1.57 V) as compare to Cr^{3+}/Cr^{2+}.

(*ii*) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements. **[*CBSE Delhi 2017*]**

Ans. (*i*) (*a*) The tendency to form complex compounds is due to:

—Small size and high charge on metal ion.

—The availability of *d* orbitals for accommodating electrons donated by the ligand.

(*b*) In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.

(*c*) Much large third ionisation energy of Mn (where the required change is stable half filled d^5 to d^4) is mainly responsible for this.

(*ii*) **Similarities**

— Both show mainly an oxidation state of +3.

— Actinoids show actinoid contraction like lanthanoid contraction is shown by lanthanoids.

— Both are electropositive and very reactive. (*Any one*)

Differences

— Except promethium (Pm) lanthanoids are non-radioactive whereas actinoids are radioactive.

— Lanthanoids do not form oxocation whereas actinoids form oxocation.

— Lanthanoids have less tendency towards complex formation whereas actinoids have greater tendency towards complex formation. (*Any one*)

Q. 10. Assign reasons for the following:

(*i*) The enthalpies of atomisation of transition elements are high.

(*ii*) The transition metals and many of their compounds act as good catalysts.

(*iii*) From element to element, the actinoid contraction is greater than the lanthanoid contraction.

(*iv*) The E^0 value for the Mn^{3+}/Mn^{2+} couple is much more positive than that of Cr^{3+}/Cr^{2+}.

(*v*) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element. **[*CBSE 2019 (56/2/3)*]**

Ans. (*i*) This is because transition metals have strong metallic bonds as they have a large number of unpaired electrons.

(*ii*) The catalytic activity of transition metals is attributed to the following reasons:

(*a*) Because of their variable oxidation states, transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.

(*b*) In some cases, the transition metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

(*iii*) This is due to poorer shielding by 5*f*-electrons in actinoids than that by 4*f*-electrons in the lanthanoids.

(*iv*) This is due to much larger third ionisation energy of Mn as Mn^{2+} is very stable on account of stable d^5 configuration.

(*v*) This is because scandium has partially filled *d*-orbitals in the ground state ($3d^1\ 4s^2$).

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. **Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?**
   (*a*) Both HCl and $KMnO_4$ act as oxidising agents.
   (*b*) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent.
   (*c*) $KMnO_4$ is a weaker oxidising agent than HCl.
   (*d*) $KMnO_4$ acts as a reducing agent in the presence of HCl.
2. **Which element among the lanthanides has the smallest atomic radius?**
   (*a*) Cerium
   (*b*) Lutetium
   (*c*) Europium
   (*d*) Gadolinium
3. **In acidic medium, one mole of MnO_4^- ion accepts how many moles of electrons in a redox process?**
   (*a*) 1
   (*b*) 2
   (*c*) 5
   (*d*) 6

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. **Assertion (A) :** Separation of Zr and Hf is difficult.
   Reason (R) : Because Zr and Hf lie in the same group of the periodic table.
5. **Assertion (A) :** Actinoids form relatively less stable complexes as compared to lanthanoids.
   Reason (R) : Actinoids can utilise their 5*f* orbitals along with 6*d* orbitals in bonding but lanthanoids do not use their 4*f* orbital for bonding.
6. **Assertion (A) :** Cu cannot liberate hydrogen from acids.
   Reason (R) : Because it has positive electrode potential.

Answer the following questions:

7. Why lanthanoids are called as *f*-block elements? **(1)**
8. Name a member of the lanthanoid series which is known to exhibit +4 oxidation state. **(1)**
9. Account for the following:.
   (*i*) Cobalt (III) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidised.
   (*ii*) The d^1 configuration is very unstable in ions. **(2)**
10. Complete the following equations:
   (*i*) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$
   (*ii*) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$ **(2)**

11. (*i*) Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

(*ii*) While filling up of electrons in the atomic orbitals, the 4*s* orbital is filled before the 3*d* orbital but reverse happens during the ionisation of the atom. Explain why.

[*NCERT Exemplar*] **(2)**

12. Explain the following observations:

(*i*) Colour of $KMnO_4$ disappears when oxalic acid is added to its solution in acidic medium.

(*ii*) A green solution of potassium manganate turns purple when CO_2 gas is passed through the solution. **(2)**

13. Assign suitable reasons for the following:

(*i*) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

(*ii*) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

(*iii*) The highest oxidation state is exhibited in oxo-anions of a metal. [*CBSE (F) 2014*] **(3)**

14. When pyrolusite ore MnO_2 is fused with KOH in presence of air, a green coloured compound (*A*) is obtained which undergoes disproportionation reaction in acidic medium to give a purple coloured compound (*B*).

(*i*) Write the formulae of the compounds (A) and (B).

(*ii*) What happens when compound (B) is heated? [*CBSE (South) 2016*] **(3)**

15. (*i*) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

(*ii*) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(*iii*) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why?
(Atomic nos.: Mn = 25, Cr = 24) **(3)**

16. On the basis of lanthanoid contraction, explain the following:

(*i*) Nature of bonding in La_2O_3 and Lu_2O_3.

(*ii*) Trends in the stability of oxo salts of lanthanoids from La to Lu.

(*iii*) Stability of the complexes of lanthanoids.

(*iv*) Radii of 4*d* and 5*d* block elements.

(*v*) Trends in acidic character of lanthanoid oxides. **(5)**

Answers

1. (*b*) **2.** (*b*) **3.** (*c*) **4.** (*b*) **5.** (*d*) **6.** (*a*)

Chapter–9

Coordination Compounds

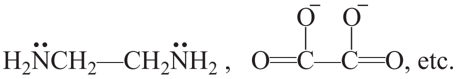
basic concepts

1. **Double Salts:** Double salts are the addition compounds which are stable in solid state but break up into constituent ions when dissolved in water or any other solvent. In these compounds the individual properties of constituent are not lost. Some common examples are:

Mohr's salt	$FeSO_4.(NH_4)_2SO_4.6H_2O$
Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Carnallite	$KCl.MgCl_2.6H_2O$

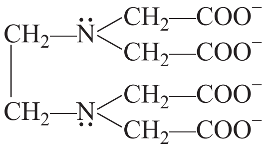
2. **Complex Ion:** An electrically charged species, carrying positive or negative charge, in which the central metal atom or ion is surrounded by fixed number of ions or molecules, *e.g.*, $[Co(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$, etc. The complex ion does not dissociate into simple ions in aqueous solutions.
3. **Coordination Compounds:** Coordination compounds are the compounds which contain complex ions, *e.g.*, $[Co(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$, etc. These compounds contain a central metal atom or cation which is attached with a fixed number of anions or molecules (called ligands) through coordinate bonds.
4. **Coordination Entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of molecules or ions (ligands), *e.g.*, $[Co(NH_3)_3Cl_3]$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, etc.
5. **Central Atom or Ion:** In a coordination entity, the atom or ion to which a fixed number of ions or molecules are bound in a definite geometrical arrangement. For example, in the complex ion $[CoCl(NH_3)_5]^{2+}$, the Co^{2+} ion is the central ion.
6. **Ligands:** Ligands are the atoms, molecules or ions which donate a pair of electrons to central metal atom or ion and form a coordinate bond with it. Depending upon the number of donor atoms available for coordination, the ligands may be classified as:

- **Unidentate ligands:** Contain one donor atom, *e.g.*, $\ddot{N}H_3$, $:\ddot{Cl}:^-$, etc.
- **Bidentate ligands:** Contain two donor atoms, *e.g.*,



$$H_2\ddot{N}CH_2—CH_2\ddot{N}H_2,\quad O{=}\overset{O^-}{\overset{|}{C}}—\overset{O^-}{\overset{|}{C}}{=}O, \text{ etc.}$$

- **Polydentate ligands:** Contain several donor atoms, *e.g.*,



Ethylenediaminetetraacetate ion (EDTA^{4-}) (Hexadentate)

- **Ambidentate ligand:** A ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal atom/ion is called an ambidentate ligand. Some common examples are given below:


$M \leftarrow N \begin{smallmatrix} O \\ O \end{smallmatrix}$

$M \leftarrow O—N{=}O$

nitrito—N
(N donor atom)

nitrito—O
(O donor atom)

M ← SCN
thiocyanato
(S donor atom)

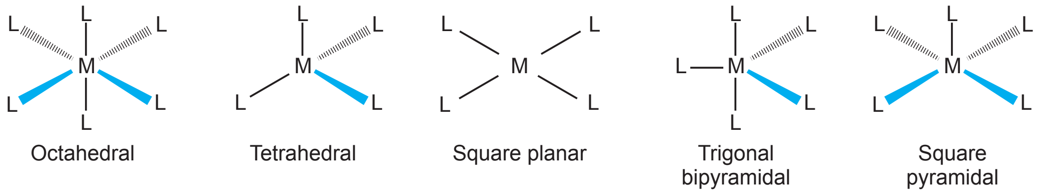
M ← NCS
isothiocyanato
(N donor atom)

M ← CN
cyano
(C donor atom)

M ← NC
isocyano
(N donor atom)

- **Chelating ligand:** When a bidentate or a polydentate ligand uses its two or more donor atoms to bind a single metal ion, then a ring-like structure is obtained. It is called chelate and the ligand is known as chelating ligand. The chelating ligands form more stable complexes than the unidentate ligands. This is because when chelation occurs entropy increases and the process becomes more favourable.

7. **Coordination Number (CN):** The coordination number of a metal ion in a complex may be defined as the total number of ligand donor atoms to which the metal ion is directly bonded. For example, in the complex ions, $[Co(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$, the coordination numbers of both Co and Fe is 6.
8. **Coordination Sphere and Counter Ions:** The central metal atom or ion and the ligands directly attached to it are enclosed in a square bracket and is collectively termed as the coordination sphere. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $[Cr(NH_3)_3(H_2O)_3]Cl_3$, the coordination sphere is $[Cr(NH_3)_3(H_2O)_3]^{3+}$ and the counter ion is Cl^-.
9. **Coordination Polyhedron:** The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion is known as the coordination polyhedron around the central atom/ion. Tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal are common shapes of coordination polyhedra.



Octahedral Tetrahedral Square planar Trigonal bipyramidal Square pyramidal

Fig. 9.1: Shapes of different coordination polyhedra.
M represents the central atom/ion and L, a unidentate ligand

10. **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.
11. **Homoleptic Complex:** The complex in which metal atom is bound to only one kind of donor groups, *e.g.*, $[Cu(CN)_4]^{3-}$.
12. **Heteroleptic Complex:** The complex in which metal atom is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$.
13. **Table 9.1: Nomenclature of Some Coordination Compounds**

S. No.	Formula	Name
(*i*)	$[Pt(NH_3)_2ClNO_2]$	diamminechloridonitrito–N–platinum(II)
(*ii*)	$[CoCl_2(en)_2]Cl$	dichloridobis(ethane-1, 2–diamine) cobalt(III) chloride
(*iii*)	$K_3[Fe(C_2O_4)_3]$	potassium trioxalatoferrate(III)
(*iv*)	$[Ag(NH_3)_2]$ $[Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I)

14. Isomerism: Two or more compounds having the same molecular formula but different arrangement of atoms and hence differ in one or more physical or chemical properties are called isomers and the phenomenon is called isomerism.

Isomerism in Coordination Compounds

Structural Isomerism
- Linkage isomerism
- Coordination isomerism
- Ionisation isomerism

Stereoisomerism
- Geometrical isomerism
- Optical isomerism

Structural isomers have different bonds. Stereoisomers have the same chemical formula and chemical bonds but differ in their spatial arrangements.

(*a*) Structural isomerism:

(*i*) Linkage isomerism: This type of isomerism arises due to the presence of an ambidentate ligand in a coordination compound. Some examples of linkage isomers are:

$[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$
$[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$

(*ii*) Coordination isomerism: This type of isomerism arises due to interchange of ligands between the cationic and anionic entities of different metal ions present in a complex. Some examples are

$[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
$[Pt(NH_3)_4]\ [PtCl_4]$ and $[PtCl(NH_3)_3]\ [PtCl_3(NH_3)]$

(*iii*) Ionisation isomerism: Ionisation 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. Some examples are:

$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]\ SO_4$
$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
$[Co(NH_3)_5NO_2]SO_4$ and $[Co(NH_3)_5SO_4]NO_2$

(*iv*) Solvate isomerism: Solvate isomers differ by whether or not a solvent molecule is directly bonded to metal ion or merely present as free solvent molecule in the crystal lattice. If water is the solvent then this form of isomerism is known as "hydrate isomerism".

Some examples in which hydrate isomerism is observed are:

$[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$
$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$
$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_2O$

(*b*) Stereoisomerism: Stereoisomerism is of two types:

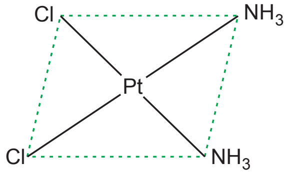
(*i*) Geometrical isomerism: This type of isomerism arises in heteroleptic complexes due to difference in geometrical arrangement of the ligand around the central metal ion. If the same kind of ligand occupy adjacent positions, the isomer is called *cis*, and if these are opposite to each other, the isomer is called *trans*.

This type of isomerism is very common in complexes with coordination number 4 and 6.

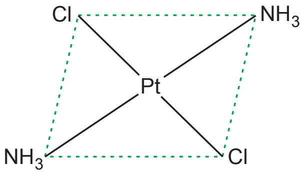
- **Isomerism in complexes with coordination number 4.**

  These complexes can either have a tetrahedral or square planar geometry. Tetrahedral complexes do not show geometrical isomerism as relative position of the ligands attached to central metal atom is same with respect to each other (adjacent). The square planar complexes on the other hand show this type of isomerism as given below:

- Tetra coordinated square planar complexes of the type $[MA_4]$, $[MA_3X]$, $[MAX_3]$ are incapable of showing geometrical isomerism because all possible arrangements of ligands in each of these complexes are exactly the same.
- **Type $[MA_2X_2]$:** $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2(NO_2)_2]$, $[Pt(Py)_2Cl_2]$

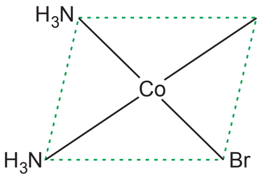


***cis*-isomer**
(similar groups on adjacent position)

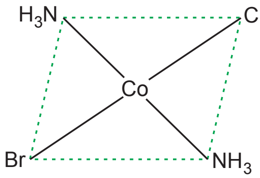


***trans*-isomer**
(similar groups on opposite position)

- **Type $[MA_2XY]$:** $[Co(NH_3)_2ClBr]$, $[Pt(Py)_2(NH_3)Cl]$

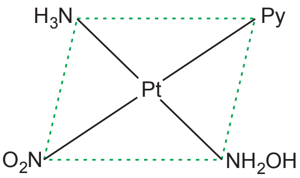


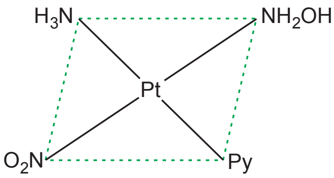
***cis*-isomer**

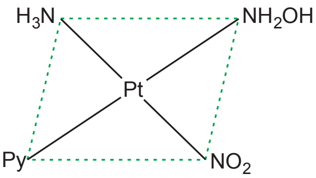


***trans*-isomer**

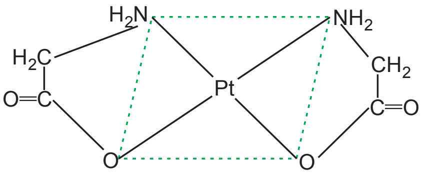
- **Type $[MABXY]$:** $[Pt(NH_3)Py(NH_2OH)(NO_2)]^+$



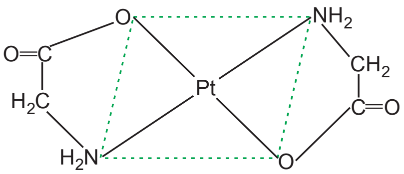




- **Type $[M(AB)_2]$:** $[Pt(gly)_2]$ where gly = $H_2NCH_2COO^-$

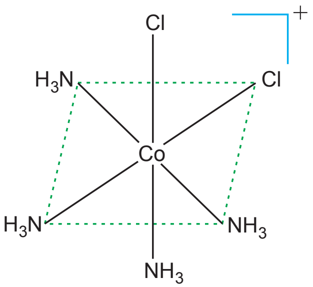


***cis*-isomer**

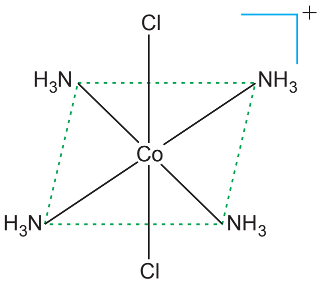


***trans*-isomer**

- **Isomerism in complexes with coordination number 6.**
  - Octahedral complexes of the type $[MA_6]$ and $[MA_5X]$ are incapable of showing geometrical isomerism.
  - **Type $[MA_4X_2]$ or $[MA_2X_4]$:** $[Co(NH_3)_4Cl_2]^+$, $[Cr(NH_3)_4Cl_2]^+$ ion

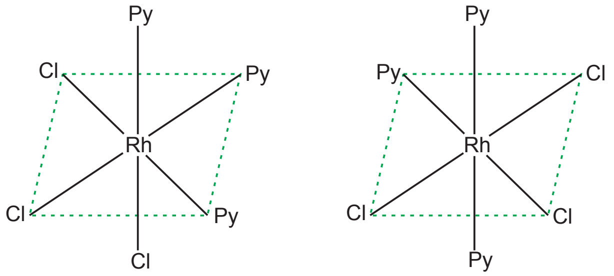


***cis*-isomer**



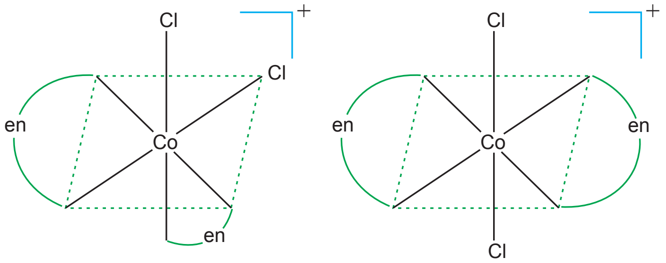
***trans*-isomer**

- **Type [MA_3X_3]:** [$Rh(Py)_3Cl_3$], [$Co(NH_3)_3Cl_3$], [$Co(NH_3)_3(NO_2)_3$]



facial or fac-isomer **meridional or mer-isomer**

- **Type [$M(AA)_2X_2$] or [$M(AA)_2XY$]:** [$Co(en)_2Cl_2$]$^+$, [$Ni(ox)_2Cl_2$]$^+$

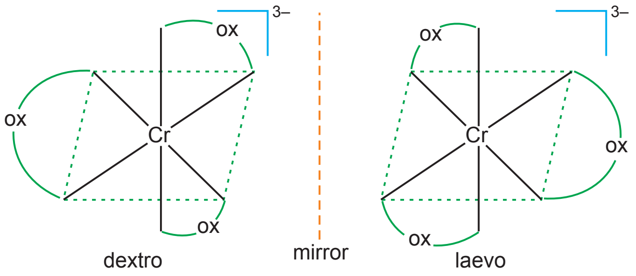


***cis*-isomer** ***trans*-isomer**

(*ii*) Optical isomerism: This type of isomerism is exhibited by chiral molecules. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers and rotate the plane of polarised light equally but in opposite directions. The isomer which rotates the plane of polarised light towards left is called laevorotatory (*l*) while which rotates the plane towards right is called dextrorotatory (*d*).

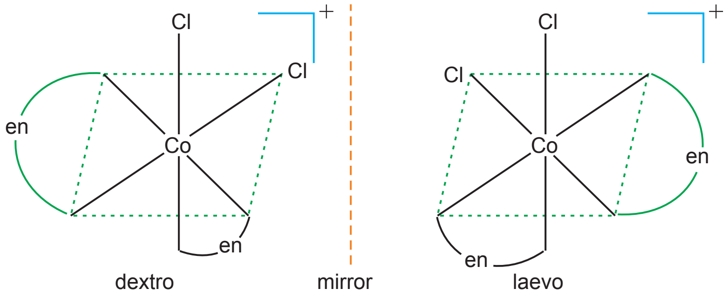
Optical isomerism is common in octahedral complexes involving bidentate ligands. Some examples of different types of octahedral complexes showing optical isomerism are given below:

- **Type [$M(AA)_3$]: [$Cr(ox)_3$]$^{3-}$, [$Co(en)_3$]$^{3+}$**



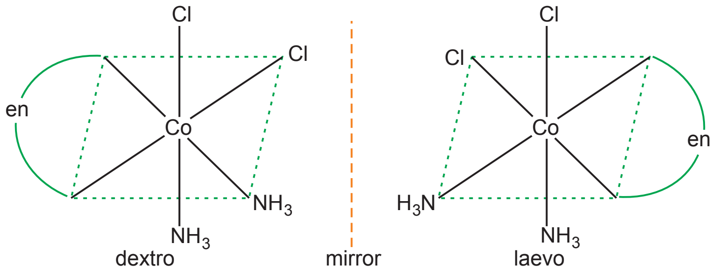
Optical isomers (*d* and *l*) of [$Cr(ox)_3$]$^{3-}$

- **Type [$M(AA)_2X_2$] or [$M(AA)_2XY$]:** *cis*-[$Co(en)_2Cl_2$]$^+$, *cis*-[$Pt(en)_2Cl_2$]$^+$, *cis*-[$Cr(ox)_2Cl_2$]$^{3-}$, etc.



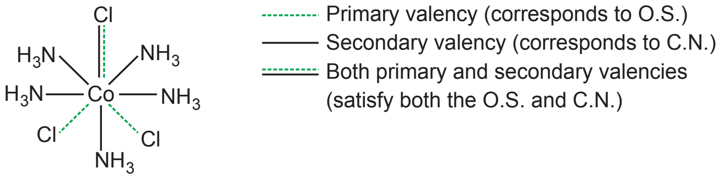
Optical isomers (*d* and *l*) of cis-[$Co(en)_2Cl_2$]$^+$

- **Type $[M(AA)X_2Y_2]$:** $[Co(en)(NH_3)_2Cl_2]$



Optical isomers (d and l) of $[Co(en)(NH_3)_2Cl_2]$

15. **Werner's Theory of Coordination Compounds:** The main postulates of this theory are:
    (*i*) In coordination compounds, metals show two types of valencies: primary and secondary.
    (*ii*) The primary valencies are normally ionisable and are satisfied by negative ions.
    (*iii*) The secondary valencies are non ionisable and are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.



Representation of $[CoCl(NH_3)_5]Cl_2$ on the basis of Werner's theory

    (*iv*) The ions or groups bound by secondary linkage to the metal have characteristic spatial arrangements corresponding to different coordination number.

16. **Bonding in Coordination Compounds**

    (*a*) **Valence bond theory:** The main features of the valence bond theory as applied to coordination compounds are as follows:

    (*i*) The number of metal–ligand coordinate bonds which can be formed in case of given metal ion depends upon the number of vacant orbitals for bonding in metal ion and is known as the coordination number of metal ion.

    (*ii*) The metal atom or ion under the influence of ligands uses its $(n-1)\ d$, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry.

Table 9.2: Number of Orbitals and Types of Hybridisations

Coordination Number	Type of Hybridisation	Distribution of Hybrid Orbitals in Space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

    (*iii*) The empty hybrid orbitals of the central metal atom or ion overlap with the filled orbitals of the ligand containing the lone pair of electrons. In this way a metal–ligand coordinate bond is formed.

    (*iv*) The inner orbital (low spin) or the outer orbital (high spin) complexes are formed depending upon whether the *d*-orbitals of inner shell or *d*-orbitals of outer shell are used in hybridisation.

    (*v*) The complex will be diamagnetic if all electrons are paired. If unpaired electrons are present then the complex will be paramagnetic.

Table 9.3: Application of Valence Bond Theory to Some Complexes

Ion/Complex	Central Metal Ion	Configuration of Metal Ion	Hybridisation of Metal Ion Involved	Geometry of the Complex	Number of Unpaired Electrons	Magnetic Behaviour
$[Ti(H_2O)_6]^{3+}$	Ti^{3+}	d^1	d^2sp^3	Octahedral	1	Paramagnetic
$[V(H_2O)_6]^{3+}$	V^{3+}	d^2	d^2sp^3	Octahedral	2	Paramagnetic
$[Cr(H_2O)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	Octahedral	3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	Octahedral	3	Paramagnetic
$[MnF_6]^{3-}$	Mn^{3+}	d^4	sp^3d^2	Octahedral	4	Paramagnetic
$[Mn(CN)_6]^{3-}$	Mn^{3+}	d^4	d^2sp^3	Octahedral	2	Paramagnetic
$[MnCl_4]^{2-}$	Mn^{2+}	d^5	sp^3	Tetrahedral	5	Paramagnetic
$[FeF_6]^{3-}$	Fe^{3+}	d^5	sp^3d^2	Octahedral	5	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	d^5	sp^3d^2	Octahedral	5	Paramagnetic
$[Fe(CN)_6]^{3-}$	Fe^{3+}	d^5	d^2sp^3	Octahedral	1	Paramagnetic
$[Fe(CN)_6]^{4-}$	Fe^{2+}	d^6	d^2sp^3	Octahedral	0	Diamagnetic
$[FeCl_4]^{2-}$	Fe^{2+}	d^6	sp^3	Tetrahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$	Co^{3+}	d^6	d^2sp^3	Octahedral	0	Diamagnetic
$[CoF_6]^{3-}$	Co^{3+}	d^6	sp^3d^2	Octahedral	4	Paramagnetic
$[Ni(CO)_4]$	Ni	$3d^8 4s^2$	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(CN)_4]^{2-}$	Ni^{2+}	d^8	dsp^2	Square planar	0	Diamagnetic
$[NiCl_4]^{2-}$	Ni^{2+}	d^8	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	d^8	sp^3d^2	Octahedral	2	Paramagnetic
$[CuCl_4]^{2-}$	Cu^{2+}	d^9	sp^3	Tetrahedral	1	Paramagnetic
$[Zn(NH_3)_4]^{2+}$	Zn^{2+}	d^{10}	sp^3	Tetrahedral	0	Diamagnetic
$[Pt(NH_3)Cl_2]$	Pt^{2+}	d^8	dsp^2	Square planar	0	Diamagnetic

➡ Limitations of valence bond theory

(*i*) It involves a number of assumptions.

(*ii*) It does not give quantitative interpretation of magnetic data.

(*iii*) It does not distinguish between weak and strong ligands.

(*iv*) It does not explain the colour exhibited by complexes.

(*v*) It does not give an exact explanation of thermodynamic or kinetic stabilities of coordination compounds.

(*vi*) It does not make exact predictions regarding the tetrahedral and square planar structures of 4 – coordinated complexes.

(*b*) Crystal field theory

- According to crystal field theory, the bonding between central metal ion and ligand is purely electrostatic. Ligands are considered as point charges in case of anions or dipoles in case of neutral molecules.
- The five *d*-orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.*, they are degenerate orbitals. However, in a complex due to asymmetrical negative field of ligands, the *d*-orbitals are no more degenerate and split into two sets of orbitals. The pattern of splitting depends upon the nature of the crystal field.

- In an octahedral environment, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy as compared to average energy in the spherical crystal field. Thus, in an octahedral complex, the degeneracy of the five *d*-orbitals is partially removed due to ligand electron–metal electron repulsions to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.
- The splitting of the degenerate orbitals due to the presence of ligands in a definite geometry is known as crystal field splitting and the difference of energy between two sets of degenerate orbitals as a result of crystal field splitting is known as crystal field stabilisation energy (CFSE). It is usually denoted by symbol Δ_o (the subscript o stands for octahedral).

It is found that e_g orbitals are $\frac{3}{5}\Delta_0$ above the average energy level and t_{2g} orbitals are $\frac{2}{5}\Delta_0$ below the average energy level.

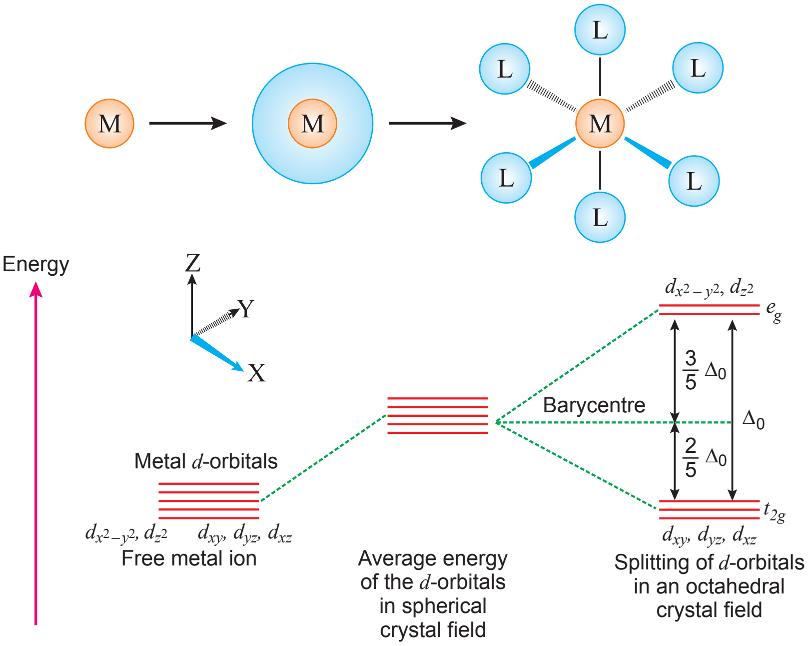


Fig. 9.2: *d*-orbital splitting in an octahedral crystal field

- The magnitude of Δ_0 depends upon the field produced by ligand and charge on the metal ion. The arrangement of ligands in a series in the order of increasing field strength is called spectrochemical series.

  $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 <$ en $< CN^- < CO$
- In d^2 and d^3 coordination entities, the *d*-electrons occupy the t_{2g} orbitals singly in accordance with Hund's rule. For d^4 ions, the electronic distribution depends on crystal field stabilisation energy (Δ_0) and pairing energy (P). The two options are:

  (*i*) If $\Delta_0 <$ P, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 <$ P are known as weak field ligands and form high spin complexes.

  (*ii*) If $\Delta_0 >$ P, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Thus, ligands for which $\Delta_o >$ P, are known as strong field ligands and form low spin complexes.

- In tetrahedral coordination entities, the *d*-orbitals splitting is inverted and is smaller as compared to the octahedral field splitting.

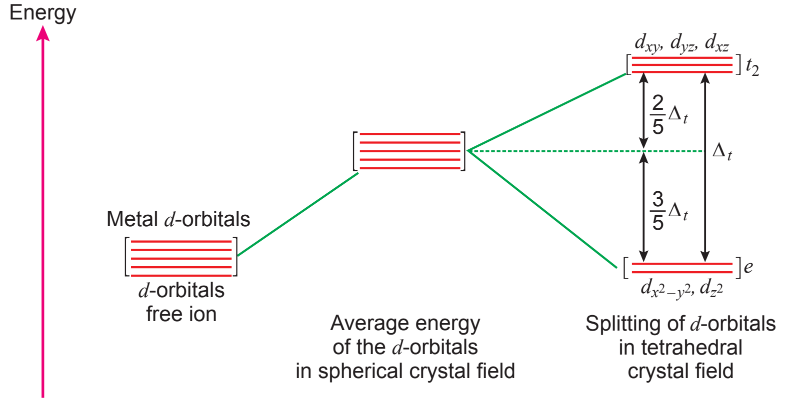
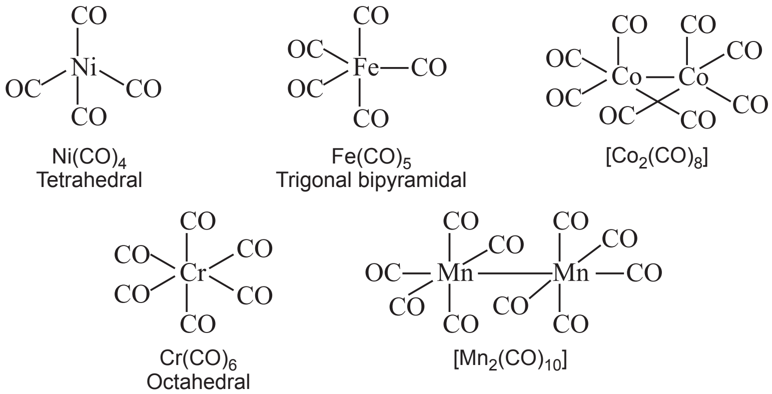


Fig. 9.3: d-orbital splitting in a tetrahedral crystal field

For the same metal, the same ligand and metal ligand distances, $\Delta_t = \frac{4}{9}\Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing, therefore, low spin configuration are rarely observed.

- **Colour in coordination compounds:** The crystal field theory attributes the colour of the coordination compounds to *d–d* transition of the electron from t_{2g} to e_g orbitals in octahedral complexes and from e_g to t_{2g} orbitals in tetrahedral complexes. In the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour.
- **Limitations of crystal field theory:**
  (*i*) As the ligands are considered as point charges, the anionic ligands should exert greater splitting effect. However, the anionic ligands are found at the low end of the spectrochemical series.
  (*ii*) It does not take into account the covalent character of metal ligand bond.

17. **Metal Carbonyls:** Metal carbonyls are the organometallic compounds in which carbon monoxide acts as the ligand. These compounds are formed by most of the transition metals. Structures of some metal carbonyls are given below:


$Ni(CO)_4$ Tetrahedral

$Fe(CO)_5$ Trigonal bipyramidal

$[Co_2(CO)_8]$

$Cr(CO)_6$ Octahedral

$[Mn_2(CO)_{10}]$

Fig. 9.4: Structures of some representative homoleptic metal carbonyls

18. **Bonding in Metal Carbonyls:** The metal–carbon bond in metal carbonyls have both σ and π character. The metal–carbon σ-bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The metal–carbon π-bond is formed by the donation of a pair of electrons from

a filled *d*-orbital of metal into the vacant anti-bonding pi-molecular orbital (π^*) of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

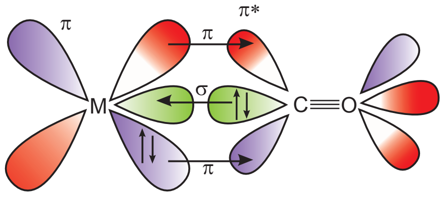


Fig. 9.5: Synergic bonding interactions in a carbonyl complex

19. **Stability of Coordination Compounds:** The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The stability of a complex ML_n is measured in terms of magnitude of (stability or formation) equilibrium constant. For a reaction of the type

$$M + nL \qquad ML_n$$

We can write stability constant as follows:

$$M + L \qquad ML \quad ; \; K_1 = [ML]/[M][L]$$

$$ML + L \qquad ML_2 \quad ; \; K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \qquad ML_3 \quad ; \; K_3 = [ML_3]/[ML_2][L]$$

....

$$ML_{n\text{-}1} + L \qquad ML_n \quad ; \; K_n = [ML_n]/[ML_{n-1}]\,[L]$$

Where K_1, K_2, K_3 etc., are referred to as stepwise stability constants.

Alternatively, we can write the overall stability constant (β_n) as:

$$M + nL \qquad ML_n \quad ; \; \beta_n = [ML_n]/[M]\,[L]^n$$

The stepwise and overall stability constant are therefore as follows:

$$\beta_n = K_1 \times K_2 \times K_3 \times \ldots \times K_n$$

➡ **Instability constant:** The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant.

20. **Factors Affecting the Stability of Complexes**

The stability of a complex depends upon

(*i*) **The nature of the central ion:** Greater the charge density (*i.e.*, charge/radius ratio) on the central metal ion, greater is the stability of the complex. For example, complexes of Fe^{3+} are more stable than Fe^{2+}. This is supported by the fact that the stability constant of $[Fe(CN)_6]^{3-}$ is 1.21×10^{31} and that of $[Fe(CN)_6]^{4-}$ is only 1.8×10^6.

(*ii*) **Nature of the ligand:** In general, more basic ligands have a tendency to donate the electron pairs to central metal ion more easily and hence the resulting complex is very stable. For example, the complexes involving F^- ions are more stable than those involving Cl^- ions or Br^- ions.

(*iii*) **Chelate effect:** When chelation occurs, entropy increases and therefore, the formation of the complex becomes more favourable. For example, chelate $[Cd(en)_4]^{2+}$ is 10,000 times more stable than the simple complex $[Cd(CH_3NH_2)_2]^{2+}$.

21. **Applications of Coordination Compounds**

➡ **In metallurgical separation:** Extraction of several metals from their ores involves complex formation. For example, silver and gold are extracted from their ores as cyanide complex.

$$4Au + 8KCN + 2H_2O + O_2 \longrightarrow \underset{\text{Potassium dicyanoaurate (I)}}{4K[Au(CN)_2]} + 4KOH$$

$$2K[Au(CN)_2] + Zn \longrightarrow \underset{\text{Potassium tetracyanozincate (II)}}{K_2[Zn(CN)_4]} + 2Au \downarrow$$

Purification of some metals can be achieved through complex formation. For example, in Mond's process, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

➡ **In analytical chemistry:** Complex formation is frequently encountered in qualitative and quantitative chemical analysis.

(*i*) Qualitative Analysis:

- Detection of Cu^{2+} is based on the formation of a blue tetraammine copper (II) ion.

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}}$$

- Ni^{2+} is detected by the formation of a red complex with dimethyl glyoxime (DMG).

$$NiCl_2 + 2DMG + 2NH_4OH \longrightarrow \underset{\substack{\text{Nickel}\\ \text{bisdimethylglyoximate}}}{[Ni(DMG)_2]} + 2NH_4Cl + 2H_2O$$

- The separation of Ag^+ and Hg^{2+} in group I is based on the fact that while AgCl dissolves in NH_3, forming a soluble complex, Hg_2Cl_2 forms an insoluble black substance.

$$AgCl(s) + 2NH_3(aq) \longrightarrow \underset{\text{Soluble complex}}{[Ag(NH_3)_2]Cl(aq)}$$

$$Hg_2Cl_2(s) + NH_3 \longrightarrow \underset{\text{Black insoluble substance}}{Hg(NH_2)Cl\,.\,Hg} + HCl$$

(*ii*) Quantitative Analysis

Gravimetric estimation of Ni^{2+} is carried out by precipitating Ni^{2+} as red nickel dimethyl oxime complex in the presence of ammonia.

$$Ni^{2+} + 2DMG \xrightarrow{NH_3} \underset{\text{Red ppt.}}{[Ni(DMG)_2]}$$

EDTA is used in the complexometric determination of several metal ions such as Ca^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, etc.

- **In Medicinal Chemistry:**
  - The platinum complex, *cis*-$[Pt(NH_3)_2Cl_2]$, known as cisplatin is used in the treatment of cancer.
  - EDTA complex of calcium is used in the treatment of lead poisoning. Ca-EDTA is a weak complex; when it is administered, calcium in the complex is replaced by the lead present in the body and is eliminated with the urine.
  - The excess of copper and iron present in animal system are removed by the chelating ligands, D-penicillamine and desferrioxime B via the formation of complexes.
- **In Biological System:**
  - Haemoglobin, the red pigment of blood which acts as oxygen carrier is a complex of Fe^{2+} with porphyrin.
  - The pigment responsible for photosynthesis, chlorophyll, is a complex of Mg^{2+} with porphyrin.
  - Vitamin B_{12} (Cyanocobalamine), the antipernicious anaemia factor, is a complex of cobalt.
- **In the Estimation of Hardness of Water:** The hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- **In Photography:** In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- **In Catalysis:** Coordination compounds are used as catalysts for many industrial processes. For example, Wilkinson's catalyst, a rhodium complex having formula $[(Ph_3P)_3RhCl]$ is used for the selective hydrogenation of alkenes.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Write the formulas for the following coordination compounds:

(*i*) tetraamminediaquacobalt(III) chloride

(*ii*) potassium tetracyanidonickelate(II)

(*iii*) tris (ethane-1, 2-diamine) chromium(III) chloride

(*iv*) amminebromidochloridonitrito-N-platinate(II)

(*v*) dichloridobis(ethane-1, 2-diamine)platinum(IV) nitrate

(*vi*) iron(III)hexacyanidoferrate(II)

Ans. (*i*) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (*ii*) $K_2[Ni(CN)_4]$

(*iii*) $[Cr(en)_3]Cl_3$ (*iv*) $[Pt(NH_3)BrCl(NO_2)]^-$

(*v*) $[PtCl_2(en)_2](NO_3)_2$ (*vi*) $Fe_4[Fe(CN)_6]_3$

Q. 2. Write IUPAC names of the following coordination compounds:

(*i*) $[Co(NH_3)_6]Cl_3$ **(*ii*) $[Co(NH_3)_5Cl]Cl_2$**

(*iii*) $K_3[Fe(CN)_6]$ **(*iv*) $K_3[Fe(C_2O_4)_3]$**

(*v*) $K_2[PdCl_4]$ **(*vi*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$**

Ans. (*i*) hexaamminecobalt(III) chloride (*ii*) pentaamminechloridocobalt(III) chloride

(*iii*) potassium hexacyanoferrate(III) (*iv*) potassium trioxalatoferrate(III)

(*v*) potassium tetrachloridopalladate(II)

(*vi*) diamminechlorido(methylamine)platinum (II) chloride

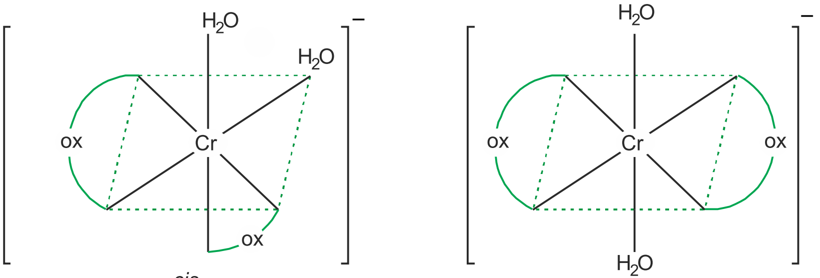
Q. 3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(*i*) $K[Cr(H_2O)_2(C_2O_4)_2]$ **(*ii*) $[Co(en)_3]Cl_3$**

(*iii*) $[Co(NH_3)_5(NO_2)](NO_3)_2$ **(*iv*) $[Pt(NH_3)(H_2O)Cl_2]$**

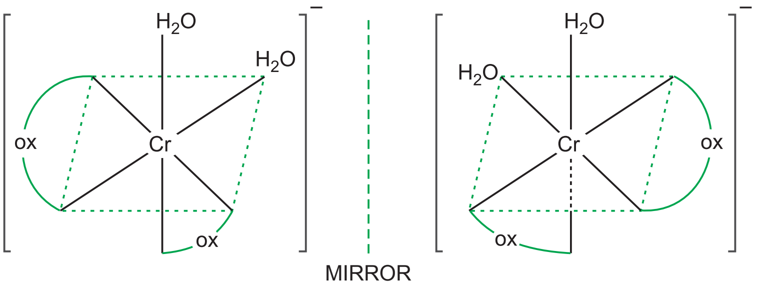
Ans. (*i*) Both geometrical (*cis–trans*) and optical isomers for *cis* can exist.

(*a*) Geometrical isomers of $K[Cr(H_2O)_2(C_2O_4)_2]$:

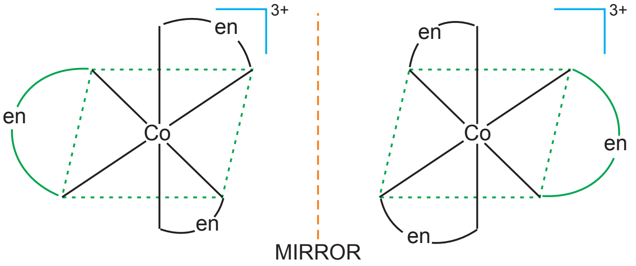


cis *trans*

(*b*) Optical isomers (*d*- and *l*-) of *cis*-$K[Cr(H_2O)_2(C_2O_4)_2]$:



(*ii*) Two optical isomers can exist.



(*iii*) Ionisation isomers:

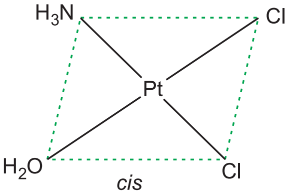
$[Co(NH_3)_5(NO_2)](NO_3)_2]$, $[Co(NH_3)_5(NO_3)](NO_2)(NO_3)]$

Linkage isomers:

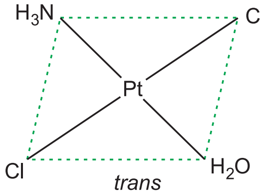
$[Co(NH_3)_5(NO_2)](NO_3)_2]$, $[Co(NH_3)_5(ONO)](NO_3)_2]$

MA_5X type complexes do not show geometrical and optical isomerism.

(*iv*) Geometrical isomers can exist.



cis



trans

Q. 4. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.

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Ans. The ionisation isomers dissolve in water to yield different ions and thus react differently with various reagents:

$$[Co(NH_3)_5Cl]SO_4 + Ba^{2+} \longrightarrow \underset{\text{Ppt}}{BaSO_4(s)\downarrow}$$

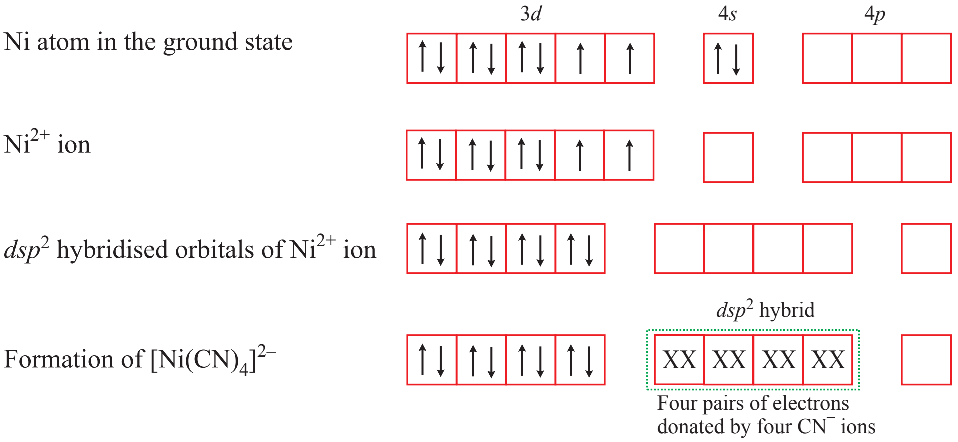
$$[Co(NH_3)_5SO_4]Cl + Ba^{2+} \longrightarrow \text{No reaction}$$

$$[Co(NH_3)_5Cl]SO_4 + Ag^{+} \longrightarrow \text{No reaction}$$

$$[Co(NH_3)_5SO_4]Cl + Ag^{+} \longrightarrow \underset{\text{Ppt}}{AgCl(s)\downarrow}$$

Q. 5. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Ans. Nickel in $[Ni(CN)_4]^{2-}$ is in the +2 oxidation state. The formation of $[Ni(CN)_4]^{2-}$ may be explained through hybridisation as follows:



Since no unpaired electrons is present, the square planar complex is diamagnetic.

In $[NiCl_4]^{2-}$, Cl^- is a weak field ligand. It is, therefore, unable to pair up the unpaired electrons of the 3*d* orbital. Hence, the hybridisation involved is sp^3 and the shape is tetrahedral. Since two electrons are unpaired, it is paramagnetic.

Q. 6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

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Ans. In $[Ni(CO)_4]$, Ni is in zero oxidation state whereas in $[NiCl_4]^{2-}$ it is in +2 oxidation state. In the presence of strong ligand, CO, the unpaired *d*-electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

Q. 7. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Ans. In presence of CN^- (a strong ligand), the $3d^5$ electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming an inner orbital complex. In the presence of H_2O (a weak ligand), 3*d* electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex containing five unpaired electrons. Hence, it is strongly paramagnetic.

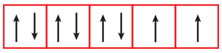
Q. 8. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Ans. In $[Co(NH_3)_6]^{3+}$, Co is in +3 oxidation state and has d^6 electrons. In the presence of NH_3, the 3*d* electrons pair up leaving two *d*-orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex.

In $[Ni(NH_3)_6]^{2+}$, Ni is in +2 oxidation state and has d^8 configuration. The hybridisation involved is sp^3d^2, forming the outer orbital complex.

Q. 9. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

Ans. In $[Pt(CN)_4]^{2-}$ ion, Pt is in +2 oxidation state, its electronic configuration is $5d^8$. It forms a square planner structure, it means the hybridisation is dsp^2.



$3d^8$

CN^- is a strong field ligand to pairing of unpaired electrons takes place. So, the number of unpaired electrons is 0.

Q. 10. The hexaaqua manganese(II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

Ans. Mn in the +2 state has the configuration $3d^5$. In the presence of H_2O a weak ligand, the distribution of these five electrons is $t_{2g}^3\,e_g^2$, *i.e.*, all the electrons remain unpaired. In the presence of CN^- a strong ligand, the distribution is $t_{2g}^5\,e_g^0$, *i.e.*, two t_{2g} orbitals contain paired electrons while the third t_{2g} orbital contains one unpaired electron.

NCERT Textbook Exercises

Q. 1. Explain the bonding in coordination compounds in terms of Werner's postulates.

Ans. Refer to Basic Concepts Point 15.

Q. 2. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why.

Ans. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio forms double salt $FeSO_4 \cdot (NH_4)_2\,SO_4 \cdot 6H_2O$ which ionises in the solution to give Fe^{2+} ions. Hence, it gives the test of Fe^{2+} ions.

$CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio forms a complex, with the formula $[Cu(NH_3)_4]SO_4$. The complex ion, $[Cu(NH_3)_4]^{2+}$ does not ionise to give Cu^{2+} ions. Hence, it does not give the test of Cu^{2+} ion.

Q. 3. Explain with two examples for each of the following:

Coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Ans. **Coordination Entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of molecules or ions (ligands), *e.g.*, $[Co(NH_3)_3Cl_3]$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, etc.

Ligands: Ligands are the atoms, molecules or ions which donate a pair of electrons to central metal atom or ion and form a coordinate bond with it.

Example: $\ddot{N}H_3$, $H_2\ddot{N}CH_2—CH_2\ddot{N}H_2$

Coordination Number (CN): The coordination number of a metal ion in a complex may be defined as the total number of ligand donor atoms to which the metal ion is directly bonded. For example, in the complex ions, $[Co(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$ the coordination numbers of both Co and Fe is 6.

Coordination Polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion is known as the coordination polyhedron around the central atom/ion. Tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal are common shapes of coordination polyhedra.

Homoleptic Complex: The complex in which metal atom is bound to only one kind of donor groups, *e.g.*, $[Cu(CN)_4]^{3-}$.

Heteroleptic Complex: The complex in which metal atom is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$.

Q. 4. What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.

Ans. A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, *e.g.*, Cl^- and NH_3.

A molecule or an ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called a bidentate ligand, *e.g.*, $NH_2—CH_2—CH_2—NH_2$ and $^-OOC—COO^-$.

A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called ambidentate ligand, *e.g.*, CN^- or NC^- and $:NO_2^-$ or $:ONO^-$.

Q. 5. Specify the oxidation numbers of the metals in the following coordination entities:

(*i*) $[Co(H_2O)(CN)(en)_2]^{2+}$ **(*ii*) $[CoBr_2(en)_2]^+$**
(*iii*) $[PtCl_4]^{2-}$ **(*iv*) $K_3[Fe(CN)_6]$**
(*v*) $[Cr(NH_3)_3Cl_3]$

Ans. (*i*) $x + (0) + (-1) + (0) = +2$ or $x = +3$

(*ii*) $x + 2(-1) + 0 = +1$ or $x = +3$

(*iii*) $x - 4 = -2$ or $x = +2$

(*iv*) $3(1) + x + 6(-1) = 0$ or $x = +3$

(*v*) $x + 0 + 3(-1) = 0$ or $x = +3$

Q. 6. Using IUPAC norms, write the formulae of the following:

(*i*) tetrahydroxozincate(II) **(*ii*) potassium tetrachloridopalladate(II)**
(*iii*) diamminedichloridoplatinum(II) **(*iv*) potassium tetracyanidonickelate(II)**
(*v*) pentaamminenitrito-O-cobalt(III) **(*vi*) hexaamminecobalt(III) sulphate**

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(*vii*) potassium tri(oxalato)chromate(III) **(*viii*) hexaammineplatinum(IV)**
(*ix*) tetrabromidocuprate(II)
(*x*) pentaamminenitrito-N-cobalt(III)

Ans. (*i*) $[Zn(OH)_4]^{2-}$ (*ii*) $K_2[PdCl_4]$
(*iii*) $[Pt(NH_3)_2Cl_2]$ (*iv*) $K_2[Ni(CN)_4]$
(*v*) $[Co(NH_3)_5(ONO)]^{2+}$ (*vi*) $[Co(NH_3)_6]_2(SO_4)_3$
(*vii*) $K_3[Cr(C_2O_4)_3]$ (*viii*) $[Pt(NH_3)_6]^{4+}$
(*ix*) $[CuBr_4]^{2-}$ (*x*) $[Co(NH_3)_5(NO_2)]^{2+}$

Q. 7. Using IUPAC norms, write the systematic names of the following:

(*i*) $[Co(NH_3)_6]Cl_3$ **(*ii*) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$**

(*iii*) $[Ti(H_2O)_6]^{3+}$ **(*iv*) $[Co(NH_3)_4Cl(NO_2)]Cl$**

(*v*) $[Mn(H_2O)_6]^{2+}$ **(*vi*) $[NiCl_4]^{2-}$**

(*vii*) $[Ni(NH_3)_6]Cl_2$ **(*viii*) $[Co(en)_3]^{3+}$**

(*ix*) $[Ni(CO)_4]$

Ans. (*i*) hexaamminecobalt(III) chloride (*ii*) diamminechlorido(methylamine)platinum (II) chloride

(*iii*) hexaaquatitanium(III) ion (*iv*) tetraamminechloridonitrito-N-cobalt(III) chloride

(*v*) hexaaquamanganese(II) ion (*vi*) tetrachloridonickelate(II)

(*vii*) hexaamminenickel(II) chloride (*viii*) tris (ethane-1, 2-diamine) cobalt(III) ion

(*ix*) tetracarbonylnickel (0)

Q. 8. List various types of isomerism possible for coordination compounds, giving an example of each.

Ans. Refer to Basic Concepts Point 14.

Q. 9. How many geometrical isomers are possible in the following coordination entities?

(*i*) $[Cr(C_2O_4)_3]^{3-}$ **(*ii*) $[Co(NH_3)_3Cl_3]$**

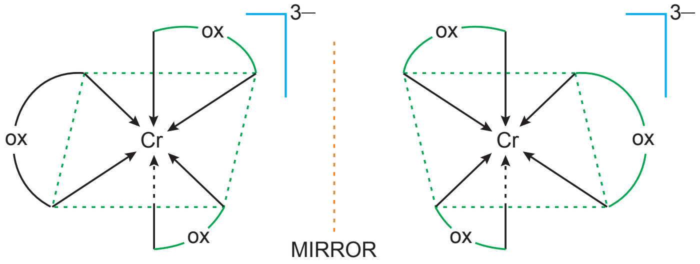
Ans. (*i*) Nil (*ii*) Two (*cis* and *trans*)

Q. 10. Draw the structures of optical isomers of

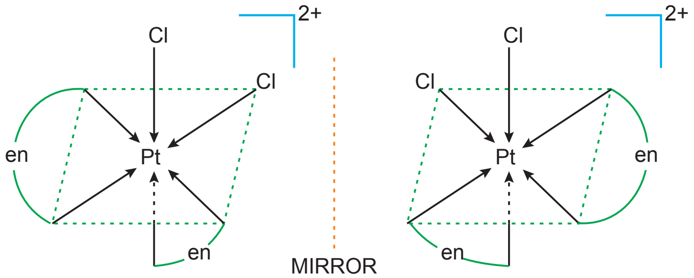
(*i*) $[Cr(C_2O_4)_3]^{3-}$ **(*ii*) $[PtCl_2(en)_2]^{2+}$**

(*iii*) $[Cr(NH_3)_2Cl_2(en)]^{+}$

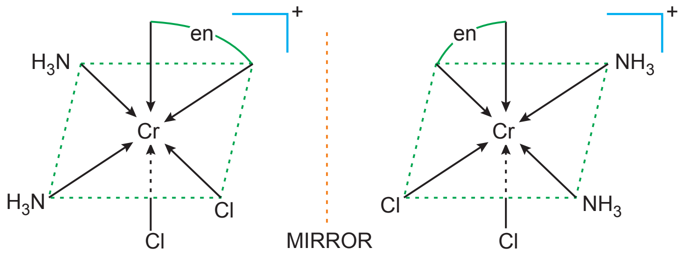
Ans. (*i*) $[Cr(C_2O_4)_3]^{3-}$



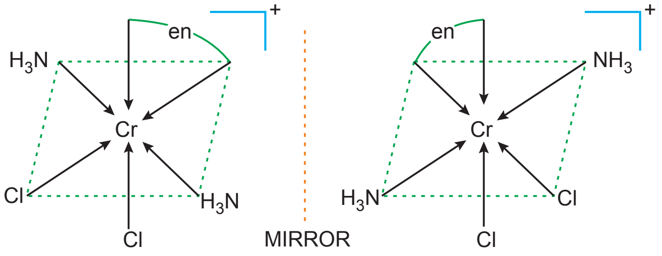
(*ii*) *cis*-$[PtCl_2(en)_2]^{2+}$:



(*iii*) (*a*) *cis*-$[Cr(NH_3)_2Cl_2(en)]^{+}$



(*b*) *trans*-$[Cr(NH_3)_2Cl_2(en)]^+$



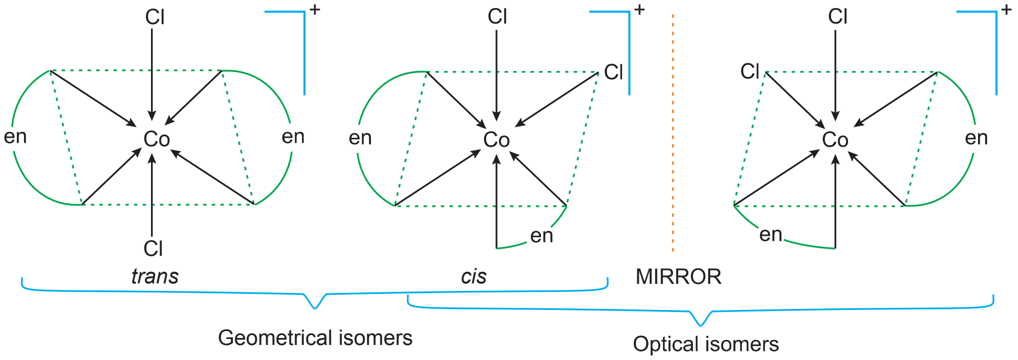
Q. 11. Draw all the isomers (geometrical and optical) of:

(*i*) $[CoCl_2(en)_2]^+$

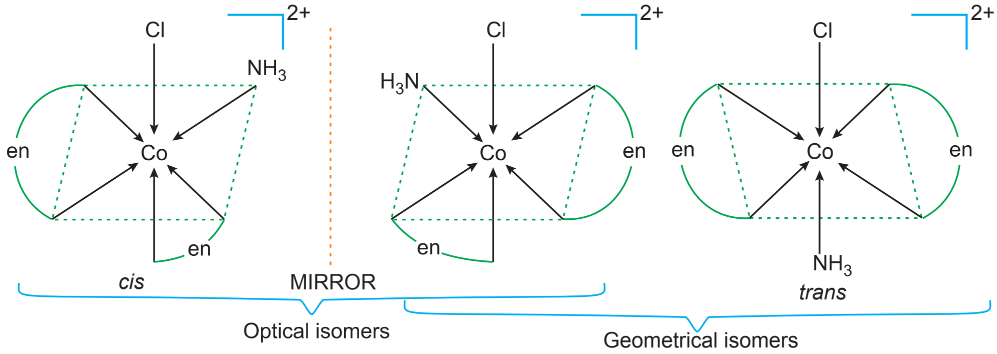
(*ii*) $[Co(NH_3)Cl(en)_2]^{2+}$

(*iii*) $[Co(NH_3)_2Cl_2(en)]^+$

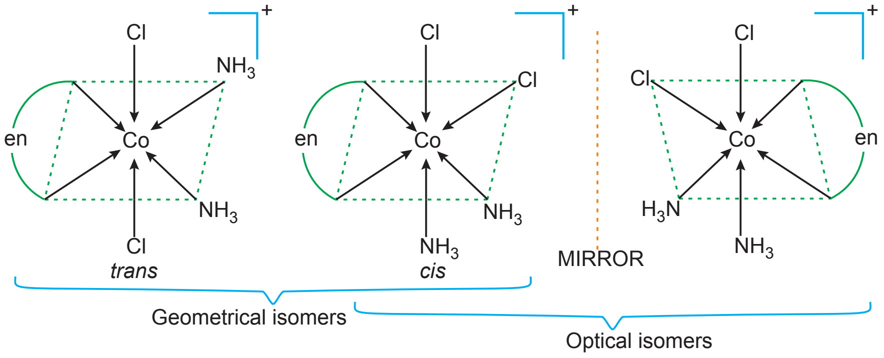
Ans. (*i*)



(*ii*)

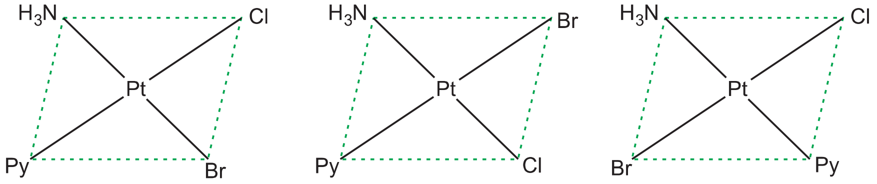


(*iii*)



Q. 12. Write all the geometrical isomers of [Pt(NH_3)(Br)(Cl)(py)] and how many of these will exhibit optical isomerism?

Ans. Three isomers are possible as follows:



Isomers of this type do not show any optical isomerism. Optical isomerism rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

Q. 13. Aqueous copper sulphate solution (blue in colour) gives (*i*) a green precipitate with aqueous potassium fluoride, and (*ii*) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Ans. Aqueous copper sulphate exists as $[Cu(H_2O)_4]SO_4$. It is a labile complex. The blue colour of the solution is due to $[Cu(H_2O)_4]^{2+}$ ions.

(*i*) When KF is added, the weak H_2O ligands are replaced by F^- ligands forming $[CuF_4]^{2-}$ ions, which is a green precipitate.

$$[Cu(H_2O)_4]^{2+} + 4F^- \longrightarrow \underset{\substack{\text{tetrafluorocuprate (II)} \\ \text{(Green ppt.)}}}{[CuF_4]^{2-}} + 4H_2O$$

(*ii*) When KCl is added, Cl^- ligands replace the weak H_2O ligands forming $[CuCl_4]^{2-}$ ion, which has bright green colour.

$$[Cu(H_2O)_4]^{2+} + 4Cl^- \longrightarrow \underset{\substack{\text{tetrachlorocuprate (II)} \\ \text{(Green solution)}}}{[CuCl_4]^{2-}} + 4H_2O$$

Q. 14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

Ans. $K_2[Cu(CN)_4]$ is formed when excess of aqueous KCN is added to an aqueous solution of $CuSO_4$.

$$\underset{\text{Copper sulphate}}{CuSO_4(aq)} + \underset{\text{Potassium cyanide}}{4KCN(aq)} \longrightarrow \underset{\substack{\text{potassium} \\ \text{tetracyanocuprate (II)} \\ \text{(soluble)}}}{K_2[Cu(CN)_4]} + K_2SO_4(aq)$$

As CN^- ions are strong ligands the complex is very stable. It is not replaced by S^{2-} ions when H_2S gas is passed through the solution and thus no precipitate of CuS is obtained.

Q. 15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(*i*) $[Fe(CN)_6]^{4-}$ **(*ii*) $[FeF_6]^{3-}$**

(*iii*) $[Co(C_2O_4)_3]^{3-}$ **(*iv*) $[CoF_6]^{3-}$** ***[CBSE 2020 (56/2/1)]***

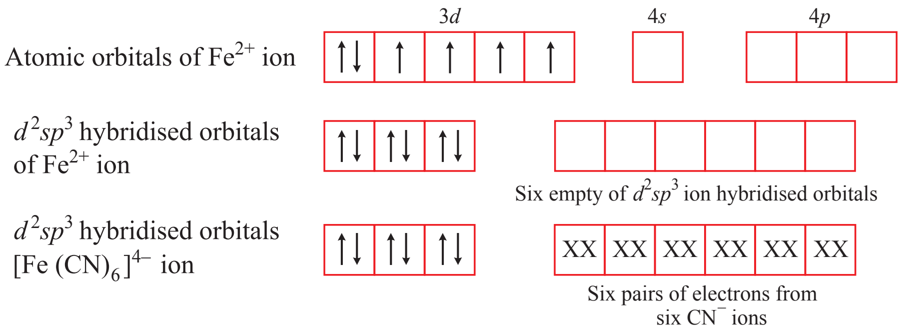
Ans. **(*i*) $[Fe(CN)_6]^{4-}$:** d^2sp^3, octahedral, diamagnetic.

In this complex ion, the oxidation state of iron is +2.

Electronic configuration of Fe = [Ar] $3d^6\,4s^2$

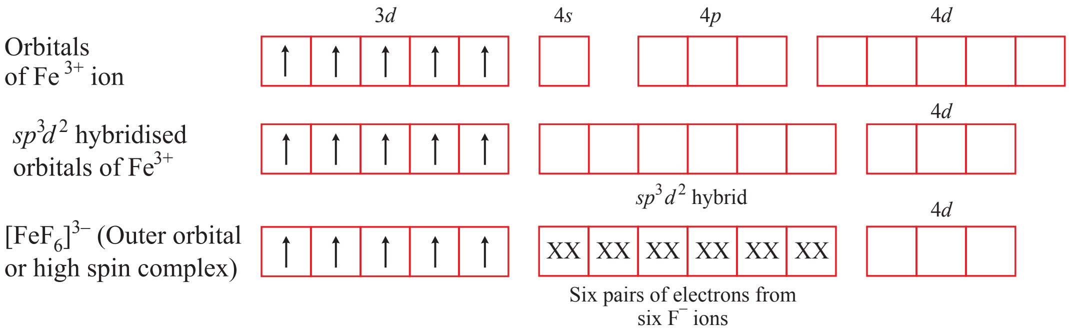
Electronic configuration of Fe^{2+} = [Ar] $3d^6$

To accommodate six pairs of electrons from six cyanide ions, the iron(II) ion must make available six empty orbitals. This can be achieved by the following hybridization scheme wherein electrons in the *d*-subshell have been paired up as CN^- ions are strong field ligands.



Thus, six pairs of electrons from six cyanide ions occupy the six hybridized orbitals of iron (II) ion. At the same time, we find no orbital which contains unpaired electron. Hence, $[Fe(CN)_6]^{4-}$ is octahedral and shows diamagnetism.

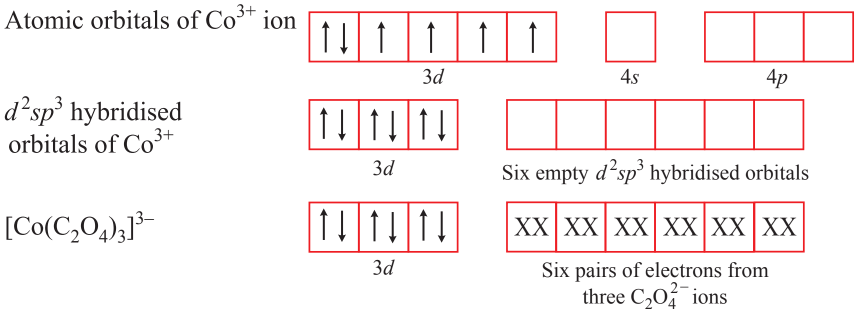
(ii) **$[FeF_6]^{3-}$**



Number of unpaired electrons (n) = 5

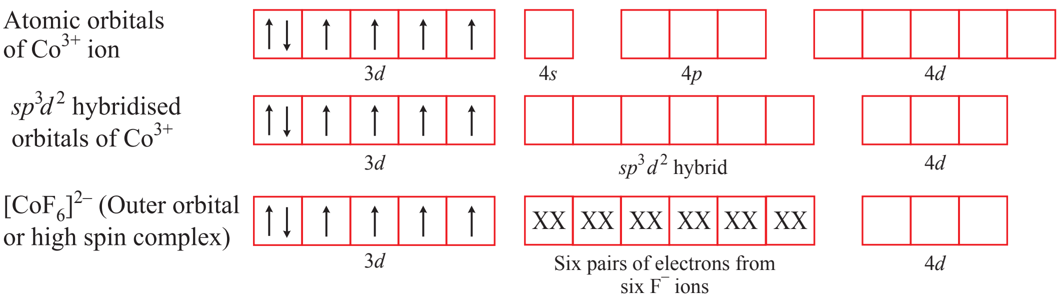
Magnetic moment (μ) = $\sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM

(iii) **$[Co(C_2O_4)_3]^{3-}$**



This complex is inner-orbital complex. It is an octahedral complex with d^2sp^3 hybridisation. As there is no orbital which contains unpaired electron, the complex is diamagnetic.

(iv) **$[CoF_6]^{3-}$**



sp^3d^2 hybridisation leads to octahedral geometry. Paramagnetic, as there are four unpaired electrons.

Q. 16. Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.

Ans. Refer to Basic Concepts Point 16 (Fig. 9.2).

Q. 17. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

Ans. The arrangement of ligands in order of their increasing field strengths, *i.e.*, increasing crystal field splitting energy (CFSE) values is called spectrochemical series.

The ligands with a small value of CFSE (Δ_0) are called weak field ligands whereas those with a large value of CFSE are called strong field ligands.

Q. 18. What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of *d*-orbitals in a coordination entity?

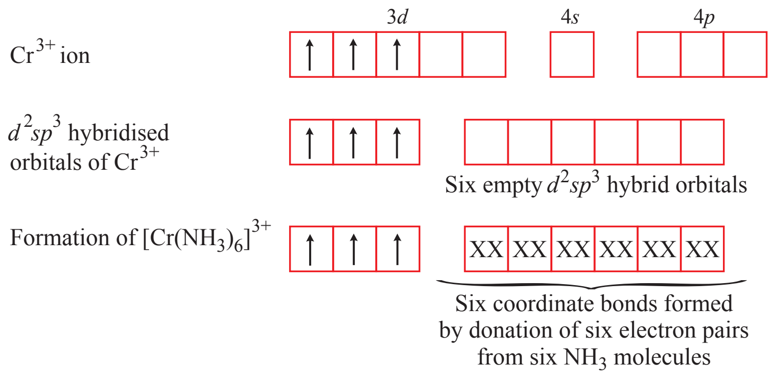
Ans. When ligands approach a transition metal ion, the *d*-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy (Δ_0) in case of octahedral field.

If $\Delta_0 < P$ (pairing energy), the 4th electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\, e_g^1$, thereby forming high spin complexes. Such ligands for which $\Delta_0 < P$ are called weak field ligands.

If $\Delta_0 > P$, the 4th electron pairs up in one of the t_{2g} orbitals giving the configuration $t_{2g}^4\, e_g^0$, thus forming low spin complexes. Such ligands for which $\Delta_0 > P$ are called strong field ligands.

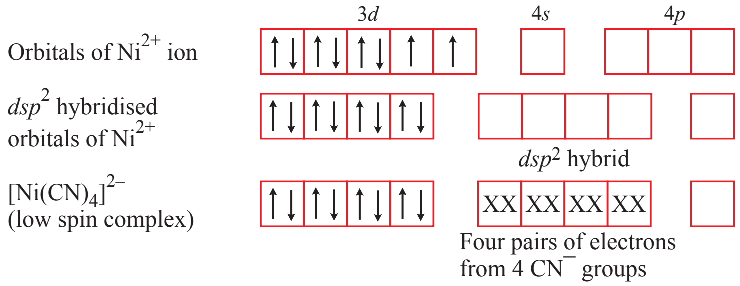
Q. 19. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why.

Ans. (*i*) **Formation of $[Cr(NH_3)_6]^{3+}$:** The oxidation state of chromium in $[Cr(NH_3)_6]^{3+}$ ion is +3. The hybridisation scheme is as shown in figure given below.



Cr^{3+} ion provides six empty orbitals to accommodate six pairs of electrons from six molecules of ammonia. The resulting complex $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridisation and is hence octahedral. The presence of three unpaired electrons in the complex explains its paramagnetic behaviour.

(*ii*) **Formation of $[Ni(CN)_4]^{2-}$:** In $[Ni(CN)_4]^{2-}$ nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in the diagram given here:



The complex $[Ni(CN)_4]^{2-}$ involves dsp^2 hybridisation and hence square planar.

Each of the dsp^2 hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

Q. 20. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Ans. In $[Ni(H_2O)_6]^{2+}$, Ni is in +2 state with the configuration $3d^8$, *i.e.*, it has two unpaired electrons which do not pair up in the presence of the weak H_2O ligand. So, it is coloured. The *d–d* transition absorbs red light and the complementary light emitted is green.

In case of $[Ni(CN)_4]^{2-}$, Ni is again in +2 state with the configuration $3d^8$ but in presence of the strong CN^- ligand, the two unpaired electrons in the 3*d* orbitals pair up. Hence, there is no unpaired electron present. Hence, it is colourless.

Q. 21. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

Ans. In both the complexes, Fe is in +2 oxidation state with d^6 configuration. As the ligands CN and H_2O possess different crystal field splitting energy (Δ_0), they absorb different components of visible light for *d-d* transition. Hence, the transmitted colours are different in dilute solutions.

Q. 22. Discuss the nature of bonding in metal carbonyls.

Ans. Refer to Basic Concepts Point 18.

Q. 23. Give the oxidation state, *d* orbital occupation and coordination number of the central metal ion in the following complexes:

(*i*) $K_3[Co(C_2O_4)_3]$ **(*ii*) *cis*-$[Cr(en)_2Cl_2]Cl$**

(*iii*) $(NH_4)_2[CoF_4]$ **(*iv*) $[Mn(H_2O)_6]SO_4$**

Ans. Let *x* be the oxidation state of central metal ion.

S.No.	Complex	Oxidation state	Coordination Number	*d*-orbital occupation
(*i*)	$K_3[Co(C_2O_4)_3]$	$3 \times 1 + x + (-2) \times 3 = +3$	6 (as $C_2O_4^{2-}$ is didentate)	$Co^{3+} = 3d^6 = t_{2g}^6\, e_g^0$
(*ii*)	*cis*-$[Cr(en)_2Cl_2]Cl$	$x + 0 \times 2 + (-2) \times 1 + (-1) \times 1 = +3$	6 (en is didentate)	$Cr^{3+} = 3d^3 = t_{2g}^3$
(*iii*)	$(NH_4)_2[CoF_4]$	$2 \times 1 + x + (-1) \times 4 = +2$	4	$Co^{2+} = 3d^7 = e_g^4\, t_{2g}^3$
(*iv*)	$[Mn(H_2O)_6]SO_4$	$x + 0 \times 6 + (-2) \times 1 = +2$	6	$Mn^{2+} = 3d^5 = t_{2g}^3\, e_g^2$

Q. 24. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(*i*) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ **(*ii*) $[Co(NH_3)_5Cl]Cl_2$**

(*iii*) $[CrCl_3(py)_3]$ **(*iv*) $Cs[FeCl_4]$** **(*v*) $K_4[Mn(CN)_6]$**

Ans. (*i*) potassiumdiaquadioxalatochromate(III)trihydrate.

Coordination number = 6 ; Shape = Octahedral

Oxidation state of Cr : $x + 0 + 2(-2) = -1,\ x = +3$

EC of $Cr^{3+} = 3d^3 = t_{2g}^3 e_g^0$; Unpaired electrons (*n*) = 3.

Magnetic moment (μ) = $\sqrt{n(n+2)} = \sqrt{3 \times 5} = \sqrt{15}$ BM = 3.87 BM

(*ii*) pentaamminechloridocobalt (III) chloride

Coordination number of Co = 6; Shape = Octahedral

Oxidation state of Co: $x + 0 - 1 = +2$ or $x = +3$

EC of $Co^{3+} = 3d^6 = t_{2g}^6\, e_g^0$

$n = 0,\ \mu = 0.$

(*iii*) trichloridotripyridinechromium (III)

Coordination number of Cr = 6; Shape = Octahedral

Oxidation state of Cr : $x - 3 + 0 = 0,\ x = +3$

EC of $Cr^{3+} = 3d^3 = t_{2g}^3\, e_g^0$

$n = 3,\ \mu = 3.87$ BM

(*iv*) caesiumtetrachloridoferrate (III)

Coordination number of Fe = 4 ; Shape = Tetrahedral

Oxidation state of Fe: $x - 4 = -1$ or $x = +3$

$$\text{EC of Fe}^{3+} = 3d^5 = e_g^2\, t_{2g}^3$$

$$n = 5, \mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

(*v*) potassiumhexacyanomanganate (II)

Coordination number of Mn = 6; Shape = Octahedral

Oxidation state of Mn : $x - 6 = -4, x = +2$

$$\text{EC of Mn}^{2+} = 3d^5 = t_{2g}^5\, e_g^0$$

$$n = 1, \mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

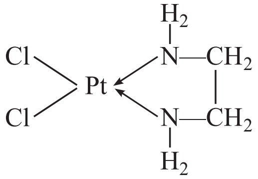
Q. 25. Explain the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory.

Ans. In $[Ti(H_2O)_6]^{3+}$, Ti is in +3 oxidation state with d^1 configuration. Therefore, the complex appears violet due to the transition of electron from t_{2g} level to the e_g level, *e.g.*,

$$(t_{2g}^1\, e_g^0 \longrightarrow t_{2g}^0\, e_g^1)$$

Q. 26. What is meant by chelate effect? Give an example. **[*CBSE 2020 (56/2/1)*]**

Ans. When a bidentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six-membered ring is formed, the effect is called chelate effect. Example, $[PtCl_2(en)]$.



Q. 27. Discuss briefly giving an example in each case, the role of coordination compounds in:

(*i*) biological systems **(*ii*) medicinal chemistry**

(*iii*) analytical chemistry **(*iv*) extraction/metallurgy of metals**

Ans. Refer to Basic Concepts Point 21.

Q. 28. How many ions are produced from the complex, $[Co(NH_3)_6]Cl_2$ in solution?

(*i*) 6 **(*ii*) 4**

(*iii*) 3 **(*iv*) 2**

Ans. The correct option is (*iii*).

Coordination number of cobalt = 6. It ionises in the solution as:

$[Co(NH_3)_6]Cl_2 \xrightarrow{aq} [Co(NH_3)_6]^{2+} + 2Cl^-$. Hence, three ions are produced.

Q. 29. Amongst the following ions which one has the highest magnetic moment value?

(*i*) $[Cr(H_2O)_6]^{3+}$ **(*ii*) $[Fe(H_2O)_6]^{2+}$**

(*iii*) $[Zn(H_2O)_6]^{2+}$

Ans. The oxidation states are: Cr (III), Fe (II) and Zn (II).

EC of $Cr^{3+} = 3d^3$, unpaired electrons = 3

EC of $Fe^{2+} = 3d^6$, unpaired electrons = 4

EC of $Zn^{2+} = 3d^{10}$, unpaired electrons = 0

As $\mu = \sqrt{n(n+2)}$, therefore, (*ii*) has the highest magnetic moment.

Q. 30. The oxidation number of cobalt in $K[Co(CO)_4]$ is:

(*i*) +1 (*ii*) +3

(*iii*) – 1 (*iv*) – 3

Ans. $K^+[Co(CO)_4]^{-1}$

$\therefore \quad 1 + x + 0 = 0, x = -1$

Therefore, (*iii*) is the correct option.

Q. 31. Amongst the following, the most stable complex is:

(*i*) $[Fe(H_2O)_6]^{3+}$ (*ii*) $[Fe(NH_3)_6]^{3+}$

(*iii*) $[Fe(C_2O_4)_3]^{3-}$ (*iv*) $[FeCl_6]^{3-}$

Ans. In each of the given complex, Fe is in +3 state. As $C_2O_4^{2-}$ is bidentate chelating ligand, it forms chelate rings and therefore, (*iii*) is the most stable complex.

Q. 32. What will be the correct order for the wavelengths of absorption in the visible region for the following: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

Ans. As metal ion is fixed, the increasing CFSE values of the ligands from the spectrochemical series are in the order:

$$H_2O < NH_3 < NO_2^-$$

Hence, the energies absorbed for excitation will be in the order:

$$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$$

As $E = \frac{hc}{\lambda}$, therefore, the wavelengths absorbed will be in the opposite order,

$$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Which of the following has highest molar conductivity?

(*a*) potassiumhexacyanoferrate (II) (*b*) hexaaquachromium(III)chloride

(*c*) tetraamminedichloridocobalt (III)chloride (*d*) diamminechlorido platinum (II)

2. When 0.1 mol $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to *[NCERT Exemplar]*

(*a*) 1:3 electrolyte (*b*) 1:2 electrolyte

(*c*) 1:1 electrolyte (*d*) 3:1 electrolyte

3. When 1 mol $CrCl_3.6H_2O$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained. The formula of the complex is: *[NCERT Exemplar]*

(*a*) $[CrCl_3(H_2O)_3].3H_2O$ (*b*) $[CrCl_2(H_2O)_4]Cl.2H_2O$

(*c*) $[CrCl(H_2O)_5]Cl_2.H_2O$ (*d*) $[Cr(H_2O)_6]Cl_3$

4. Which of the following species is not expected to be a ligand? *[NCERT Exemplar]*

(*a*) NO (*b*) NH_4^+

(*c*) $NH_2CH_2CH_2NH_2$ (*d*) CO

5. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? *[NCERT Exemplar]*

(*a*) Thiosulphato (*b*) Oxalato

(*c*) Glycinato (*d*) Ethane-1,2-diamine

6. Which of the following is π-acid ligand?

(*a*) NH_3 (*b*) CO

(*c*) F^- (*d*) ethylenediammine

7. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species? *[NCERT Exemplar]*

(*a*) $[Fe(CO)_5]$

(*b*) $[Fe(CN)_6]^{3-}$

(*c*) $[Fe(C_2O_4)_3]^{3-}$

(*d*) $[Fe(H_2O)_6]^{3+}$

8. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is *[NCERT Exemplar]*

(*a*) diamminedichloridoplatinum (II)

(*b*) diamminedichloridoplatinum (IV)

(*c*) diamminedichloridoplatinum (0)

(*d*) dichloridodiammineplatinum (IV)

9. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are *[NCERT Exemplar]*

(*a*) linkage isomers

(*b*) coordination isomers

(*c*) ionisation isomers

(*d*) geometrical isomers

10. Indicate the complex ion which shows geometrical isomerism. *[NCERT Exemplar]*

(*a*) $[Cr(H_2O)_4Cl_2]^+$

(*b*) $[Pt(NH_3)_3Cl]$

(*c*) $[Co(NH_3)_6]^{3+}$

(*d*) $[CO(CN)_5(NC)]^{3-}$

11. The geometry of $Ni(CO)_4$ and $[Ni(PPh_3)_2Cl_2]$ are

(*a*) both square planar

(*b*) tetrahedral and square planar, respectively

(*c*) both tetrahedral

(*d*) square planar and tetrahedral, respectively

12. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic? *[NCERT Exemplar]*

(*a*) $[Co(NH_3)_6]^{3+}$

(*b*) $[Mn(CN)_6]^{3-}$

(*c*) $[Fe(CN)_6]^{4-}$

(*d*) $[Fe(CN)_6]^{3-}$

13. Atomic number of Mn, Fe, Co and Ni are 25, 26 27 and 28 respectively. Which of the following outer orbital octahedral complexes have same number of unpaired electrons? *[NCERT Exemplar]*

(*a*) $[MnCl_6]^{3-}$

(*b*) $[FeF_6]^{3-}$

(*c*) $[CoF_6]^{3-}$

(*d*) $[Ni(NH_3)_6]^{2+}$

14. Crystal field stabilization energy for high spin d^4 octahedral complex is

(*a*) $-1.6\ \Delta_0 + P$

(*b*) $-1.80\ \Delta_0$

(*c*) $-1.2\ \Delta_0$

(*d*) $-0.6\ \Delta_0$

15. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be *[NCERT Exemplar]*

(*a*) 18,000 cm^{-1}

(*b*) 16,000 cm^{-1}

(*c*) 8,000 cm^{-1}

(*d*) 20,000 cm^{-1}

16. In spectrochemical series, chlorine is above water, *i.e*, $Cl > H_2O$. This is due to

(*a*) large size of Cl than H_2O

(*b*) Good π-acceptor properties of Cl

(*c*) Strong σ-donor and good π-acceptor properties of Cl

(*d*) Good π-donor properties of Cl

17. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$ *[NCERT Exemplar]*

(*a*) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(*b*) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(*c*) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(*d*) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

18. Which of the following statement is correct?

(*a*) Higher CFSE favours formation of high spin complex

(*b*) Lower CFSE favours formation of low spin complex

(*c*) t_{2g} orbital are three fold degenerate whereas e_g orbitals are two fold degenerate.

(*d*) A particular metal ion in a particular oxidation state can form either diamagnetic complexes only or paramagnetic complexes only.

19. Which of the following is an organometallic compound?
(*a*) $Ti(C_2H_4)_4$ (*b*) $Ti(OC_2H_5)$ (*c*) $Ti(OCOCH_3)_4$ (*d*) $Ti(OC_6H_5)$

20. Ziegler-Natta catalyst is $TiCl_4$ dissolved in
(*a*) triethylaluminium (*b*) ether (*c*) water (*d*) ammonia

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*b*) **7.** (*c*) **8.** (*a*) **9.** (*a*) **10.** (*a*)
11. (*c*) **12.** (*a*), (*c*) **13.** (*a*),(*c*) **14.** (*d*) **15.** (*c*) **16.** (*d*) **17.** (*c*) **18.** (*c*) **19.** (*a*) **20.** (*a*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- ***(a)*** *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- ***(b)*** *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- ***(c)*** *Assertion (A) is correct, but Reason (R) is incorrect statement.*
- ***(d)*** *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. Assertion (*A*) : Oxalate ion is a bidentate ligand.
Reason (*R*) : Oxalate ion has two donor atoms.

2. Assertion (*A*) : Linkage isomerism arises in coordination compounds containing ambidentate ligand.
Reason (*R*) : Ambidentate ligand has two different donor atoms.

3. Assertion (*A*) : Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
Reason (*R*) : Geometrical isomerism is not shown by complexes of coordination number 6.

4. Assertion (*A*) : $[Ni(CN)_4]^{2-}$ is square planar and diamagnetic.
Reason (*R*) : It has no unpaired electrons due to presence of strong ligand.

5. Assertion (*A*) : $[Ni(CO)_4]$ has square planar geometry while $[Ni(CN)_4]^{2-}$ has tetrahedral geometry.
Reason (*R*) : Geometry of any complex depends upon the nature of ligands attached.

6. Assertion (*A*) : $[FeF_6]^{3-}$ is a low spin complex.
Reason (*R*) : Low spin complexes have lesser number of unpaired electrons.

7. Assertion (*A*) : ($[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
Reason (*R*) : Because it has d^2sp^3 type hybridisation.

8. Assertion (*A*) : $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.
Reason (*R*) : Unpaired electrons are present in their *d*-orbitals.

9. Assertion (*A*) : F^- ion is a weak ligand and forms outer orbital complex.
Reason (*R*) : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.

10. Assertion (*A*) : Toxic metal ions are removed by the chelating ligands.
Reason (*R*) : Chelate complexes tend to be more stable.

Answers

1. (*a*) **2.** (*a*) **3.** (*b*) **4.** (*a*) **5.** (*d*) **6.** (*d*) **7.** (*d*) **8.** (*b*) **9.** (*a*) **10.** (*a*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

Coordination compounds are the compounds in which the central metal atom is linked to a number of ions or neutral molecules by coordinate bonds and the donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it are called ligands. Coordination number is the number of atoms or ions immediately surrounding a central atom in a complex or a crystal.

Coordination number of Ni^{2+} is 4 and it forms two complexes A and B as given below:

$$NiCl_2 + KCN \longrightarrow A \text{ (Cyano complex)}$$

$$NiCl_2 + \text{conc. } HCl \longrightarrow B \text{ (Chloro complex)}$$

1. Write the IUPAC name of complex A.

Ans. Potassium tetracyanonickelate(II).

2. Write the formula of the complex B.

Ans. $K_2[NiCl_4]$

3. Predict the magnetic nature of A.

Ans. Diamagnetic.

4. Write the state of hybridization of the complex B.

Ans. sp^3.

5. What will be the shape of the complex A?

Ans. Square planar.

PASSAGE–2

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. Formation of coordination compounds is largely used in analytical chemistry for the qualitative detection and quantitative estimation of metal ions. Coordination compounds also find several important applications in the field of medicine. Several coordination compounds are also used as antidote to poisoning caused by the ingestion of poisonous metals by human beings.

1. Which complexing material is added to vegetable oils to remove the ill effects of undesired metal ions?

Ans. EDTA

2. How would you detect the presence of nickel in a food sample?

Ans. With the help of dimethylglyoxime which forms a red complex with Ni^{2+} ions.

3. What is chelate therapy?

Ans. Chelate therapy is used for the removal of excess of metal ions present in toxic amounts in the body.

4. Which complex is used in the treatment of cancer?

Ans. Cisplatin

5. Name a vitamin which is a complex of cobalt.

Ans. Vitamin B_{12}

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Very Short Answer Questions [1 mark]

Q. 1. A coordination compound with the molecular formula $CrCl_3.4H_2O$ precipitates AgCl with $AgNO_3$ solution. Its molar conductivity is found to be equivalent to two ions. What is the structural formula and name of the compound? **[*HOTS*]**

Ans. $[Cr(H_2O)_4Cl_2]Cl$; tetraaquadichloridochromium(III) chloride

Q. 2. Arrange the following complexes in the order of increasing electrical conductivity: $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$ [*HOTS*]

Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

Q. 3. Which of the following is more stable complex and why? $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ [*CBSE Delhi 2014*]

Ans. $[Co(en)_3]^{3+}$ is more stable complex because of chelation.

Q. 4. Why is CO a stronger ligand than Cl^-? [*CBSE (F) 2011*]

Ans. CO is a stronger ligand than Cl^- as it is a π-acceptor ligand.

Q. 5. Square planar complexes with coordination number of four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?

Ans. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the ligands attached to the central metal atom are same with respect to each other.

Q. 6. How many isomers are there for octahedral complex $[CoCl_2(en)(NH_3)_2]^+$? [*NCERT Exemplar*]

Ans. There will be three isomers: *cis* and *trans* isomers. *Cis* will also show optical isomerism.

Q. 7. A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex. [*NCERT Exemplar*] [*HOTS*]

Ans. An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure, *e.g.*, *cis*-$[Pt(en)_2Cl_2]^{2+}$ or *cis*-$[Cr(en)_2Cl_2]^+$.

Q. 8. Give IUPAC name of linkage isomer of $[Co(NH_3)_5(NO_2)]^{2+}$. [*HOTS*]

Ans. The linkage isomer is $[Co(NH_3)_5(ONO)]^{2+}$. Its IUPAC name is pentaaminenitrito-O-cobalt (III) ion.

Q. 9. What type of isomerism is shown by the following complex: [*CBSE (F) 2014*]

$[Co(NH_3)_6]$ $[Cr(CN)_6]$

Ans. Coordination isomerism

Q. 10. Write IUPAC name of coordination isomer of $[Co(NH_3)_6]$ $[Cr(CN)_6]$. [*HOTS*]

Ans. The coordination isomer is $[Cr(NH_3)_6]$ $[Co(CN)_6]$, hexaamminechromium(III) hexacyanidocobaltate(III).

Q. 11. What type of isomerism is exhibited by the following complex: [*CBSE (F) 2014*]

$[Co(NH_3)_5SO_4]Cl$

Ans. Ionisation isomerism

Q. 12. What is spectrochemical series?

Ans. The series in which ligands are arranged in the order of increasing field strength is called spectrochemical series. The order is

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS < EDTA^{4-} < NH_3 < en < CN^- < CO$$

Q. 13. Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (*i*) strong field ligand, and (*ii*) weak field ligand.

(Atomic no. of Fe = 26) [*CBSE 2019 (56/3/2)*]

Ans. (*i*) $t_{2g}^5 e_g^0$

(*ii*) $t_{2g}^3 e_g^2$

Q. 14. Why are low spin tetrahedral complexes not formed? [*NCERT Exemplar*]

Ans. Because for tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy.

Q. 15. Do we call metal carbonyls as organometallics? Why?

Ans. Yes, metal carbonyls are called organometallics because C atom of CO is linked to the metal atom. In fact, the metal–carbon bonds have both σ and π character.

Short Answer Questions–I [2 marks]

Q. 1. (*i*) Write the IUPAC name of the isomer of the following complex:

$[Pt(NH_3)_2Cl_2]$

(*ii*) Write the formula for the following:

Tetraamminеaquachloridocobalt (III) nitrate ***[CBSE (F) 2017]***

Ans. (*i*) *cis*-diamminedichloridoplatinum (II) and *trans*-diamminedichloridoplatinum (II)

(*ii*) $[Co(NH_3)_4(H_2O)Cl](NO_3)_2$

Q. 2. Using IUPAC norms write the formulae for the following:

(*i*) tris(ethane-1, 2-diamine) chromium (III) chloride

(*ii*) potassium tetrahydroxozincate(II) ***[CBSE (AI) 2017]***

Ans. (*i*) $[Cr(en)_3]Cl_3$ (*ii*) $K_2[Zn(OH)_4]$

Q. 3. When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write

(*i*) structural formula of the complex.

(*ii*) IUPAC name of the complex. ***[HOTS] [CBSE Delhi 2016; 2019 (56/4/3)]***

Ans. (*i*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$

(*ii*) pentaaquachloridochromium (III) chloride monohydrate.

Q. 4. When a coordination compound $PtCl_4.6NH_3$ is mixed with $AgNO_3$, 4 moles of AgCl are precipitated per mole of the compound. Write

(*i*) structural formula of the complex.

(*ii*) IUPAC name of the complex. ***[CBSE East 2016] [HOTS]***

Ans. (*i*) $[Pt(NH_3)_6]Cl_4$

(*ii*) hexaammineplatinum (IV) chloride

Q. 5. A chloride of fourth group cation in qualitative analysis gives a green coloured complex [*A*] in aqueous solution which when treated with ethane-1, 2-diamine (en) gives pale-yellow solution [*B*] which on subsequent addition of ethane-1, 2-diamine turns to blue/purple [*C*] and finally to violet [*D*]. Write the structures of complexes [*A*], [*B*], [*C*] and [*D*]. ***[CBSE Sample Paper 2017]***

Ans. $A = [Ni(H_2O)_6]^{2+}$ $B = [Ni(H_2O)_4 (en)]^{2+}$

$C = [Ni(H_2O)_2(en)_2]^{2+}$ $D = [Ni(en)_3]^{2+}$

Q. 6. Using IUPAC norms, write the formulae for the following complexes: ***[CBSE 2019 (56/2/1)]***

(*i*) hexaaquachromium (III) chloride

(*ii*) sodium trioxalatoferrate (III)

Ans. (*i*) $[Cr(H_2O)_6]Cl_3$

(*ii*) $Na_3[Fe(C_2O_4)_3]$

Q. 7. Write IUPAC name of the complex $[Co(en)_2(NO_2)Cl]^+$. What type of structural isomerism is shown by this complex? ***[CBSE 2019 (56/2/1)]***

Ans. Chloridobis-(ethane-1, 2-diamine) nitrito-N cobalt (III) ion.

This complex shows linkage isomerism.

Q. 8. Why do compounds having similar geometry have different magnetic moment? ***[NCERT Exemplar]***

Ans. It is due to the presence of weak and strong ligands in complexes, if CFSE is high, the complex will show low value of magnetic moment and vice versa, *e.g.*, $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic and the latter is diamagnetic.

Q. 9. Give the formula of each of the following coordination entities:

(*i*) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.

(*ii*) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.

(At. nos. Co = 27, Ni = 28) ***[CBSE Delhi 2012]***

Ans. (*i*) $[Co(NH_3)Cl(en)_2]^{2+}$: amminechloridobis (ethane-1, 2-diamine)-cobalt(III) ion

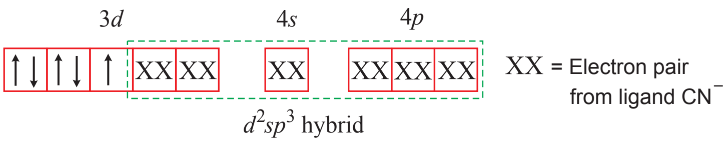
Magnetic behaviour : Diamagnetic

(*ii*) $[Ni(H_2O)_2(ox)_2]^{2-}$: diaquadioxalatonickelate (II)

Magnetic behaviour : Paramagnetic

Q. 10. For the complex $[Fe(CN)_6]^{3-}$, write the hybridisation type, magnetic character and spin nature of the complex. (At. Number : Fe = 26). ***[CBSE Delhi 2016]***

Ans. $[Fe(CN)_6]^{3-}$, $Fe^{3+}(3d^5)$



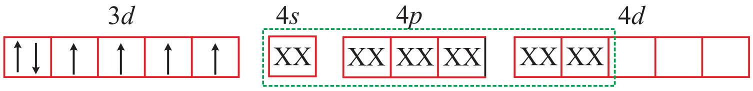
- d^2sp^3 hybridisation
- Paramagnetic in nature and low spin complex.

Q. 11. Write the state of hybridisation, shape and IUPAC name of the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27) ***[CBSE (F) 2014]***

OR

Write IUPAC name and hybridisation of the complex: $[CoF_6]^{3-}$. (Atomic number of Co = 27) ***[CBSE 2020 (56/4/2)]***

Ans. $[CoF_6]^{3-}$: hexafluoridocobaltate (III); $Co^{3+} = [Ar]3d^6$

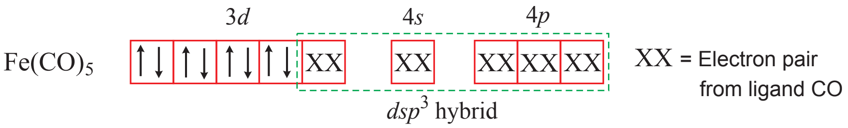


XX = Electron pair from ligand F^-

Hybridisation = sp^3d^2, Shape = Octahedral

Q. 12. For the complex $[Fe(CO)_5]$, write the hybridization, magnetic character and spin of the complex. (At. number: Fe = 26) ***[CBSE (F) 2016]***

Ans. $Fe([Ar]\ 3d^6\ 4s^2)$



Hybridisation	dsp^3
Magnetic character	Diamagnetic
Spin of the complex	Low spin complex or inner orbital complex

Q. 13. Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM. ***[NCERT Exemplar]***

Ans. $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons. This difference is due to the presence of strong CN^- and weak ligand H_2O in these complexes.

Q. 14. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when

(i) $\Delta_0 > P$ ***(ii)*** $\Delta_0 < P$ ***[CBSE (AI) 2013]***

Ans. The difference of energy between two sets of degenerate orbitals after crystal field splitting is known as crystal field splitting energy.

(*i*) $t_{2g}^4\, e_g^0$ (*ii*) $t_{2g}^3\, e_g^1$

Q. 15. The π-complexes are known for transition metals only. Why?

Ans. Transition metals have vacant *d*-orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing π-electrons, *e.g.*, C_6H_6, $CH_2{=\!=}CH_2$, etc. Thus, $d\pi - p\pi$ bonding is possible.

Q. 16. On the basis of crystal field theory explain why Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands.

[*NCERT Exemplar*]

Ans. With weak field ligands, $\Delta_0 < P$, the electronic configuration of Co(III) will be $t_{2g}^4\, e_g^2$ and it has 4 unpaired electrons and is paramagnetic. With strong field ligands, $\Delta_0 > P$ the electronic configuration will be $t_{2g}^6\, e_g^0$. It has no unpaired electrons and is diamagnetic.

Q. 17. What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex? **[*NCERT Exemplar*]**

Ans. When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

Short Answer Questions–II [3 marks]

Q. 1. Explain with two examples each of the following:

(*i*) Coordination polyhedron

(*ii*) Homoleptic complex **[*CBSE 2019 (56/2/3)*]**

(*iii*) Heteroleptic complex

Ans. Refer to NCERT Textbook Exercises, Q. 3.

Q. 2. Write the correct formulae for the following coordination compounds:

(*i*) $CrCl_3.6H_2O$ (violet with 3 chloride ions precipitated as AgCl)

(*ii*) $CrCl_3.6H_2O$ (light green colour, with 2 chloride ions precipitated as AgCl)

(*iii*) $CrCl_3.6H_2O$ (dark green colour, with 1 chloride ion precipitated as AgCl)

[*CBSE Sample Paper 2017*]

Ans. (*i*) $[Cr(H_2O)_6]Cl_3$

(*ii*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$

(*iii*) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Q. 3. Using valence bond theory, predict the hybridisation and magnetic character of the following:

(*i*) $[CoF_6]^{3-}$ **(*ii*) $[Ni(CN)_4]^{2-}$**

[Atomic number: Co = 27, Ni = 28] **[*CBSE 2019 (56/5/2)*]**

Ans. (*i*) sp^3d^2, paramagnetic

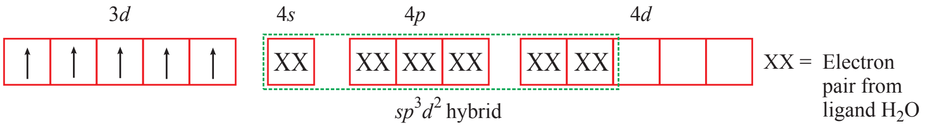
(*ii*) dsp^2, diamagnetic

Q. 4. (*i*) For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridisation, magnetic character and spin of the complex. (At. number: Fe = 26)

(*ii*) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive.

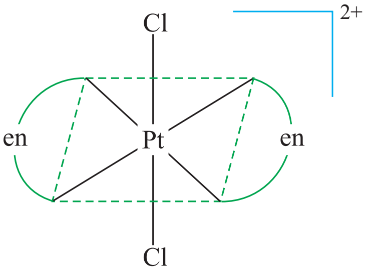
[*CBSE Central 2016*]

Ans. (*i*) $Fe^{3+}([Ar]3d^5)$



Hybridisation	sp^3d^2
Magnetic character	Paramagnetic
Spin of the complex	High spin complex

(*ii*)



trans-$[Pt(en)_2Cl_2]^{2+}$

Q. 5. Write the name, the structure and the magnetic behaviour of each one of the following complexes:

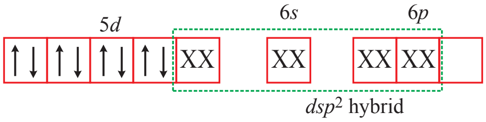
(*i*) $[Pt(NH_3)_2Cl(NO_2)]$

(*ii*) $[Co(NH_3)_4Cl_2]Cl$

(*iii*) $[Ni(CO)_4]$

(At. nos. Co = 27, Ni = 28, Pt = 78) ***[CBSE Delhi 2012, 2020 (56/2/1)]***

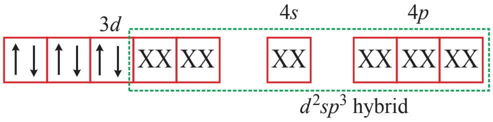
Ans. (*i*) $[Pt(NH_3)_2ClNO_2]$: diamminechloridonitrito-N-platinum (II); $Pt^{2+} = 5d^8$



XX = Electron pair from ligands NH_3, Cl^- and NO_2

Structure = Square planar; Magnetic behaviour : Diamagnetic

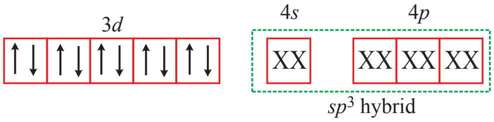
(*ii*) $[Co(NH_3)_4Cl_2]Cl$: tetraamminedichloridocobalt (III) chloride; $Co^{3+} = 3d^6$



XX = Electron pair from ligands NH_3, Cl^- and NO_2

Structure = Octahedral; Magnetic behaviour : Diamagnetic

(*iii*) $[Ni(CO)_4]$: tetracarbonyl nickel(0); Ni = $3d^8\ 4s^2$



XX = Electron pair from ligand CO

Structure = Tetrahedral; Magnetic behaviour : Diamagnetic

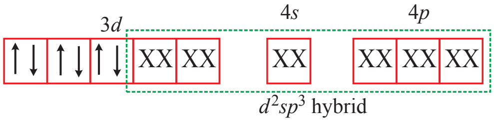
Q. 6. Name the following coordination entities and describe their structures:

(*i*) $[Fe(CN)_6]^{4-}$ **(*ii*) $[Cr(NH_3)_4Cl_2]^+$**

(*iii*) $[Ni(CN)_4]^{2-}$

(Atomic Numbers: Fe = 26, Cr = 24, Ni = 28) ***[CBSE (AI) 2012]***

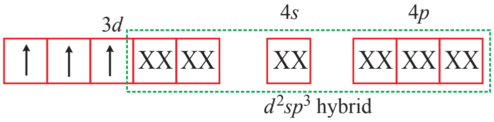
Ans. (*i*) $[Fe(CN)_6]^{4-}$ = hexacyanoferrate (II) ion; $Fe^{2+}(3d^6)$



XX = Electron pair from the CN^- ion

d^2sp^3 hybridisation in $[Fe(CN)_6]^{4-}$ leads to octahedral structure.

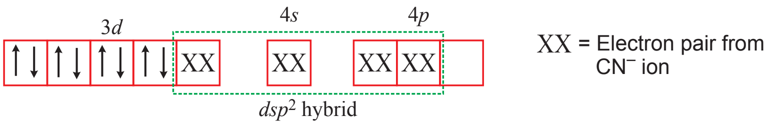
(*ii*) $[Cr(NH_3)_4Cl_2]^+$ = tetraamminedichloridochromium (III) ion; $Cr^{3+}(3d^3)$



XX = Electron pair from NH_3 molecule and Cl^- ion

d^2sp^3 hybridisation in $[Cr(NH_3)_4Cl_2]^+$ leads to octahedral structure.

(*iii*) $[Ni(CN)_4]^{2-}$ = tetracyanonickelate(II)ion; Ni^{2+} $(3d^8)$



dsp^2 hybridisation in $[Ni(CN)_4]^{2-}$ leads to square planar structure.

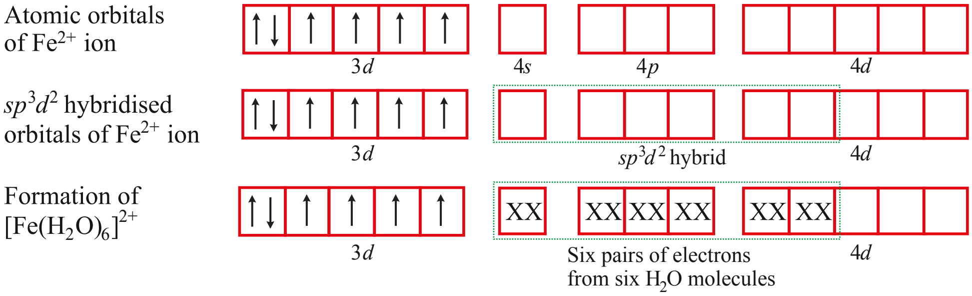
Q. 7. Describe for any two of the following complex ions, the type of hybridisation, shape and magnetic property:

(*i*) $[Fe(H_2O)_6]^{2+}$ **(*ii*) $[Co(NH_3)_6]^{3+}$**

(*iii*) $[NiCl_4]^{2-}$

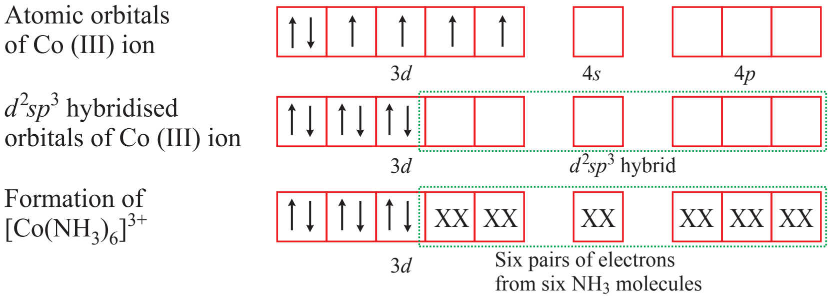
(At. Nos. Fe = 26, Co = 27, Ni = 28)

Ans. (*i*)



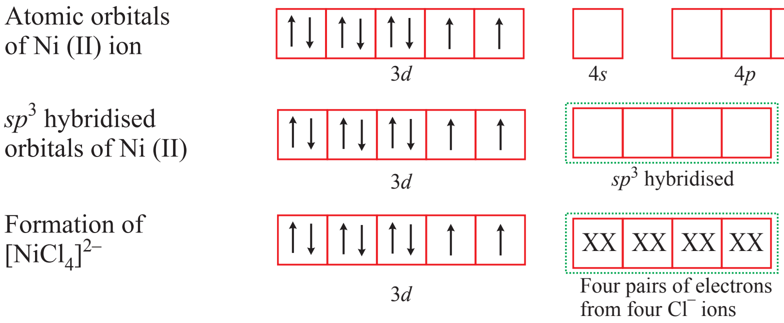
Octahedral because of sp^3d^2 hybridisation. Paramagnetic, as there are four unpaired electrons present in the complex ion.

(*ii*)



d^2sp^3 hybridisation leads to octahedral geometry. Diamagnetic, as there is no unpaired electron present in the complex.

(*iii*)



sp^3 hybridisation leads to tetrahedral geometry. Paramagnetic, as there are two unpaired electrons.

(*any two*)

Q. 8. $Fe^{3+} \xrightarrow[\text{excess}]{SCN^-} A \xrightarrow[\text{excess}]{F^-} B$

What are A and B? Give IUPAC names of A and B. Find spin only magnetic moment of B. [*HOTS*]

Ans. A = $[Fe(SCN)_3]$, B = $[FeF_6]^{3-}$

trithiocyanato iron(III) hexafluoridoferrate(III)

EC of Fe(III) = d^5,

Unpaired electrons (n) = 5

Spin only magnetic moment of B $= \sqrt{n(n+2)}$

$= \sqrt{5(5+2)}$

$=$ **5.916 BM**

Q. 9. Write the name, stereochemistry and magnetic behaviour of the following:
(At. nos. Mn = 25, Co = 27, Ni = 28)

(*i*) $K_4[Mn(CN)_6]$
(*ii*) $[Co(NH_3)_5Cl]Cl_2$
(*iii*) $K_2[Ni(CN)_4]$ **[*CBSE Delhi 2011*]**

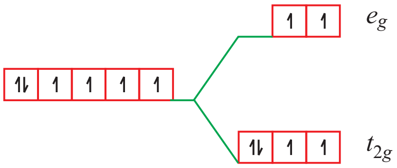
Ans.

S. No.	Name of the complex	Hybridisation of metal ion involved	Geometry of complex	Magnetic behaviour
(*i*)	potassiumhexacyanomanganate (II)	d^2sp^3	Octahedral	Paramagnetic
(*ii*)	pentaamminechloridocobalt (III) chloride	d^2sp^3	Octahedral	Diamagnetic
(*iii*)	potassiumtetracyanonickelate (II)	dsp^2	Square planar	Diamagnetic

Q. 10. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the $[Fe(H_2O)_6]^{2+}$. **[*NCERT Exemplar*]**

Ans. $[Fe(H_2O)_6]^{2+}$

$Fe^{2+} = 3d^6$



i.e., $t_{2g}^4\, e_g^2$

Number of unpaired electrons (n) = 4

Magnetic moment (μ) $= \sqrt{4(4+2)} = \sqrt{24} =$ **4.9 BM**

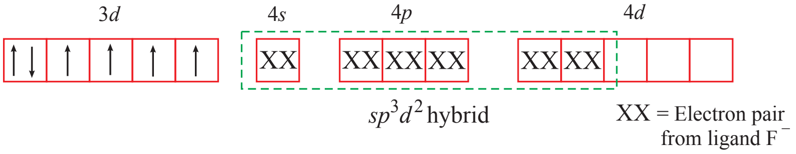
Q. 11. (*i*) What type of isomerism is shown by the complex $[Cr(H_2O)_6]Cl_3$?
(*ii*) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_0 > P$.
(*iii*) Write the hybridisation and shape of $[CoF_6]^{3-}$.
(Atomic number of Co = 27) **[*CBSE Allahabad 2015*]**

Ans. (*i*) Hydration isomerism is shown by complex $[Cr(H_2O)_6]Cl_3$.

(*ii*) If $\Delta_0 > P$, electronic configuration becomes $t_{2g}^4\, e_g^0$.

(*iii*) Co^{3+} : $3d^6\, 4s^0$

$[CoF_6]^{3-}$:
(outer orbital complex)

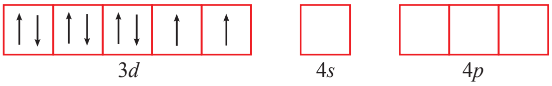


Hybridisation $= sp^3d^2$; Shape = Octahedral

Q. 12. Explain the following: **[*HOTS*]**

(*i*) Low spin octahedral complexes of nickel are not known.
(*ii*) Co^{2+} is easily oxidised to Co^{3+} in the presence of a strong ligand.
(*iii*) CO is a stronger complexing reagent than NH_3.

Ans. (*i*) Orbitals of Ni^{2+}



For the formation of low spin complex, electrons present in 3*d* electrons of Ni^{2+} should pair up. This will produce only one empty *d* orbital. Hence, d^2sp^3 hybridisation in nickel is not possible to form low spin octahedral complex.

(*ii*) With the electronic configuration $3d^7 4s^0$, Co^{2+} has three unpaired electrons. H_2O being a weak ligand, the unpaired electrons present in 3*d* orbitals of Co (II) do not pair up. In the presence of strong ligands, two unpaired electrons in 3*d* orbitals pair up and the third unpaired electron shifts to higher energy orbital from where it can be easily lost and hence shows an oxidation state of III.

(*iii*) CO has empty π-orbitals which overlap with filled *d*-orbitals (t_{2g} orbitals) of transition metals and form π-bonds by back bonding. These π-interactions increase the value of crystal field stabilisation energy (Δ_0).

As NH_3 cannot form π bonds by back bonding, therefore, CO is stronger ligand than NH_3.

Q. 13. Give the electronic configuration of the **[*HOTS*]**

(*i*) *d*-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.

(*ii*) Why is this complex coloured? Explain on the basis of distribution of electrons in the *d*-orbitals.

(*iii*) How does the colour change on heating $[Ti(H_2O)_6]^{3+}$ ion?

Ans. (*i*) In $[Ti(H_2O)_6]^{3+}$ ion, Ti is in +3 oxidation state. There is one electron in *d*-orbital and the electronic configuration is $t_{2g}^1 e_g^0$.

(*ii*) Due to *d*-*d* transition, the electron present in t_{2g} absorbs green and yellow radiation of white light for excitation to e_g and the configuration becomes e_g^1. The complementary colour is purple.

(*iii*) On heating, H_2O is lost. In the absence of ligand, crystal field splitting does not occur hence the substance becomes colourless.

Long Answer Questions [5 marks]

Q. 1. (*i*) (*a*) What type of isomerism is shown by the complex $[Co(NH_3)_6]\,[Cr(CN)_6]$?

(*b*) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At no. of Ni = 28)

(*c*) Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$. [*CBSE Delhi 2017*]

(*ii*) Differentiate between weak field and strong field coordination entity.

Ans. (*i*) (*a*) Coordination isomerism.

(*b*) In $[Ni(H_2O)_6]^{2+}$, Ni is in + 2 oxidation state with the configuration $3d^8\,4s^0$, *i.e.*, it has two unpaired electrons which do not pair up in the presence of weak H_2O ligand. The *d*–*d* transition absorbs red light and the complementary green light is emitted.

On the other hand, in $[Ni(CN)_4]^{2-}$, Ni is again in +2 oxidation state with the electronic configuration $3d^8$. In the presence of strong CN^- ligand the two unpaired electrons in the 3*d* orbitals pair up. As there is no unpaired electron in $[Ni(CN)_4]^{2-}$ therefore the complex is colourless.

(*c*) Pentaamminecarbonatocobalt(III)chloride

(*ii*)

S.No.	Weak field coordination entity	Strong field coordination entity
(*i*)	They are formed when the crystal field stabilisation energy (Δ_o) in octahedral complexes is less than the energy required for an electron pairing in a single orbital (P).	They are formed when the crystal field stabilisation energy (Δ_o) is greater than the P.
(*ii*)	They are also called high spin complexes.	They are called low spin complexes.
(*iii*)	They are mostly paramagnetic in nature.	They are mostly diamagnetic or less paramagnetic than weak field.
(*iv*)	Never formed by CN^- ligands.	Formed by CN^- like ligands.

Q. 2. A metal ion M^{n+} having d^4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_0 > P$: **[*HOTS*]**

(*i*) Explain orbital splitting during this complex formation.

(*ii*) Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.

(*iii*) What type of hybridisation will M^{n+} ion have?

(*iv*) Name the type of isomerism exhibited by this complex.

Ans. (*i*) As $\Delta_0 > P$ pairing will occur in the t_{2g} orbitals and e_g orbitals will remain vacant.

(*ii*) $t_{2g}^4\, e_g^0$

(*iii*) As there are three bidentate ligands to combine therefore hybridisation will be d^2sp^3.

(*iv*) Optical isomerism.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. Which of the following compounds can show optical isomerism?

(*a*) *trans*-$[Co(en)_2Cl_2]Br$ (*b*) $[Co(en)_3]Cl_3$

(*c*) *trans*-$[Co(NH_3)_4Cl_2]Cl$ (*d*) $[(NH_3)_5Cl]Cl_2$

2. Which one will give the test for Fe^{3+} in solution?

(*a*) $[Fe(CN)_6]^{3-}$ (*b*) $[Fe(CN)_6]^{2-}$

(*c*) $(NH_4)_2SO_4.FeSO_4.6H_2O$ (*d*) $Fe_2(SO_4)_3$

3. Ethylene diammine is a

(*a*) monodentate ligand (*b*) bidentate ligand

(*c*) hexadentate ligand (*d*) tridentate ligand

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. (3 × 1 = 3)

4. **Assertion (*A*) :** Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ is not a coordination compound.
Reason (*R*) : The aqueous solution of this salt gives the test of Fe^{2+}, NH_4^+ and SO_4^{2-} ions.

5. **Assertion (*A*) :** The tetrahedral complexes can show geometrical isomerism.
Reason (*R*) : This is because all the four ligands lie at the same distance from central metal atom in a tetrahedral geometry.

6. **Assertion (*A*) :** The complex $[Fe(H_2O)_6]^{2+}$ is paramagnetic in nature.
Reason (*R*) : It consists of two unpaired electrons.

Answer the following questions:

7. Write IUPAC name of linkage isomer of $[Cr(H_2O)_5SCN]^{2+}$. (1)

8. Name a complex used in treatment of cancer. **(1)**

9. An octahedral complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio 1 : 4, 0.1 m solution of this complex was found to freeze at 0.372°C. What is the formula of the complex? Given that molal depression constant (K_f) for water = 1.86°C/m. **(2)**

10. (*i*) What is meant by denticity of a ligand?

    (*ii*) Which compound is used to estimate the hardness of water volumetrically? **(2)**

11. Using valence bond theory explain the $[Co(NH_3)_6]^{3+}$ in relation to the terms given below:

    (*i*) Type of hybridisation

    (*ii*) Inner or outer orbital complex

    (*iii*) Magnetic behaviour

    (*iv*) Spin only magnetic moment value. **(2)**

12. $CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why? **(2)**

13. Give the name, the stereochemistry and the magnetic behaviour of the following complexes:

    (*i*) $[Co(NH_3)_5Cl]Cl_2$

    (*ii*) $K_2[Ni(CN)_4]$ **(3)**

14. (*i*) What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

    (*ii*) Write the formula of pentamminechloridoplatinum (IV).

    (*iii*) Arrange following complex ions in increasing order of crystal field splitting energy (Δ_0):

    $[Cr(Cl)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$ **(3)**

15. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following: $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$ **(3)**

16. $CoSO_4Cl.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions:

    (*i*) Identify 'A' and 'B' and write their structural formulae.

    (*ii*) Name the type of isomerism involved.

    (*iii*) Give the IUPAC name of 'A' and 'B'. **(5)**

Answers

1. (*b*) **2.** (*d*) **3.** (*b*) **4.** (*b*) **5.** (*d*) **6.** (*c*)

Haloalkanes and Haloarenes

basic concepts

1. **Haloalkanes or alkyl halides** are the compounds which have the general formula RX, where R is an alkyl or substituted alkyl group and X is a halogen (F, Cl, Br, I). Likewise, **haloarenes** or **aryl halides** are the compounds containing halogens attached directly to an aromatic ring. They have the general formula ArX (where Ar is phenyl, or substituted phenyl).

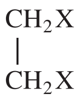
R—X	Ar—X
An alkyl halide (Haloalkane)	An aryl halide (Haloarene)
R = Alkyl or substituted alkyl	Ar = Phenyl or substituted phenyl
X = F, Cl, Br, I	X = F, Cl, Br, I

Classification:

(*a*) Classification based on the number of halogen atoms: These may be classified as mono, di, or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,

C_2H_5X

Monohaloalkane

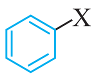


$$\begin{array}{c}CH_2X\\ |\\ CH_2X\end{array}$$

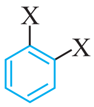
Dihaloalkane

$$\begin{array}{c}CH_2X\\ |\\ CHX\\ |\\ CH_2X\end{array}$$

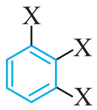
Trihaloalkane



Monohaloarene



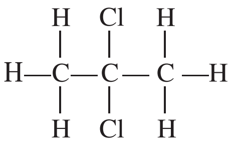
Dihaloarene



Trihaloarene

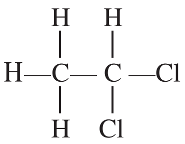
Dihalogen compounds may be further classified as discussed below:

- **Gem-dihalides:** The two halogen atoms are attached to the same carbon atom in gem-dihalides. For example,



$$\begin{array}{ccccccc} & H & & Cl & & H & \\ & | & & | & & | & \\ H— & C & — & C & — & C & —H\\ & | & & | & & | & \\ & H & & Cl & & H & \end{array}$$

Isopropylidene chloride
(2,2-Dichloropropane)



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H— & C & — & C & —Cl\\ & | & & | & \\ & H & & Cl & \end{array}$$

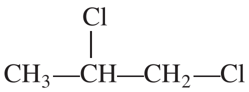
Ethylidene chloride
(1,1-Dichloroethane)

- **Vic-dihalides:** In these compounds, the two halogen atoms are attached to adjacent carbon atoms. For example,

$Cl—CH_2—CH_2—Cl$

Ethylene dichloride

(1, 2 - Dichloroethane)



$$CH_3—\overset{\displaystyle Cl}{\overset{|}{CH}}—CH_2—Cl$$

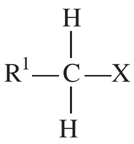
Propylene dichloride

(1, 2 - Dichloropropane)

(*b*) Classification based on hybridisation of carbon atom:

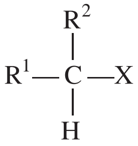
(*i*) Halogen compounds in which halogen is bonded to sp^3 hybridised carbon. This class includes:

(*a*) Haloalkanes or alkyl halides: They are the halogen compounds of saturated hydrocarbon. Their general formula is $C_nH_{2n+1}X$. They are further classified as primary haloalkane, secondary haloalkane or tertiary haloalkane according to whether the halogen atom is bonded to primary, secondary or tertiary carbon atom.



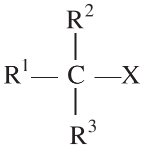
$$R^1—\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—X$$

Primary haloalkane



$$R^1—\overset{\displaystyle R^2}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—X$$

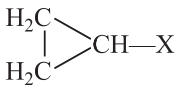
Secondary haloalkane



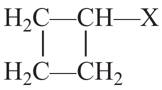
$$R^1—\overset{\displaystyle R^2}{\underset{\displaystyle R^3}{\overset{|}{\underset{|}{C}}}}—X$$

Tertiary haloalkane

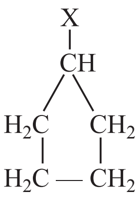
If in R—X, R is an alicyclic, *i.e.*, cyclic aliphatic hydrocarbons such as cyclopropane, cyclobutane, cyclopentane, etc., they are known as halocycloalkane or cycloalkylhalide. For example,



Halocyclopropane



Halocyclobutane



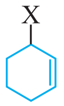
Halocyclopentane

(*b*) Allylic halides: In these compounds, halogen is bonded to allylic carbon, *i.e.*, to the sp^3 hybridised carbon atom next to a carbon–carbon double bond. Examples are:

$CH_2{=}CH—CH_2—X$

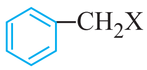
Allyl halide

(3-Halo-1-propene)

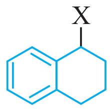


3-Halocyclohex-1-ene

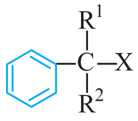
(*c*) Benzylic halides: In these halides, the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring, *i.e.*, to a benzylic carbon. For example,



Benzyl halide



1-Halo-1, 2, 3, 4 tetrahydro naphthalene



Dialkylbenzylhalide

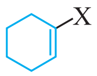
Benzylic halides may be primary, secondary or tertiary.

(*ii*) Halogen compounds in which halogen is bonded to sp^2 or *sp* hybridised carbon.

(*a*) Vinylic halides: In these halides, halogen is bonded to one of the carbon atoms of a vinylic carbon, *i.e.*, carbon–carbon double bond which is sp^2 hybridised. The examples are :

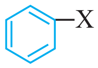
$CH_2{=}CH—X$

Vinyl halide



1-Halocyclohex-1-ene

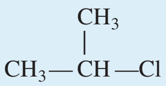
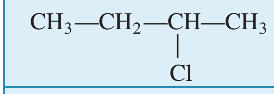
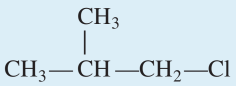
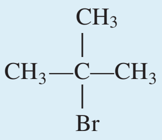
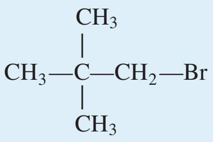
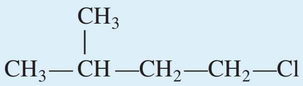
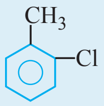
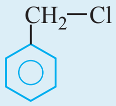
(*b*) **Aryl halides:** In these halides, the halogen atom is directly bonded to carbon atom of aromatic ring. These are called haloarene or aryl halides, *e.g.*, halobenzene.



Halobenzene

2. Common and IUPAC names of some halides:

Table 10.1: Common and IUPAC Names of Some Halides

Structure	Common Name	IUPAC Name
CH_3-Cl	Methyl chloride	Chloromethane
$CH_3-CH_2-CH_2-F$	*n*-Propyl fluoride	1-Fluoropropane
 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-Cl$	Isopropyl chloride	2-Chloropropane
$CH_3-CH_2-CH_2-CH_2-Cl$	*n*-Butyl chloride	1-Chlorobutane
 $CH_3-CH_2-\underset{Cl}{\underset{\vert}{CH}}-CH_3$	sec-Butyl chloride	2-Chlorobutane
 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-Cl$	Isobutyl chloride	1-Chloro-2-methylpropane
 $CH_3-\underset{Br}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_3$	tert-Butyl bromide	2-Bromo-2- methylpropane
 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_2-Br$	neo-Pentyl bromide	1-Bromo-2, 2-dimethylpropane
 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-CH_2-Cl$	Isopentyl chloride	1-Chloro-3-methylbutane
$CH_2{=}CH-Cl$	Vinyl chloride	Chloroethene
$CH_2{=}CH-CH_2-Br$	Allyl bromide	3-Bromoprop-1-ene
CH_2-Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
	*o*-Chlorotoluene	2-Chlorotoluene or 1-Chloro-2-methylbenzene
	Benzyl chloride	Chlorophenylmethane

3. Methods of Preparation of Haloalkanes

(*a*) From alcohols: Alkyl halides are best prepared from alcohols, which are easily accessible.

$$R—OH + HX \xrightarrow{ZnCl_2} R—X + H_2O \quad (X = Cl, Br, I)$$

$$R—OH + NaBr + H_2SO_4 \longrightarrow R—Br + NaHSO_4 + H_2O$$

$$3R—OH + PX_3 \longrightarrow 3R—X + H_3PO_3 \quad (X = Cl, Br)$$

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

$$R—OH \xrightarrow[X_2=Br_2,I_2]{\text{Red } P/X_2} R—X$$

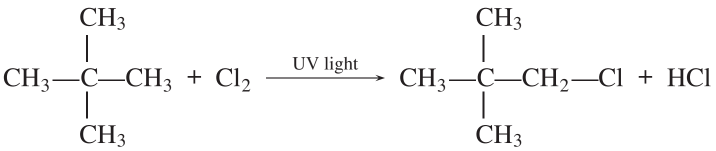
$$R—OH + SOCl_2 \longrightarrow R—Cl + SO_2 + HCl$$

The reactions of primary and secondary alcohols with HX require the presence of the catalyst, $ZnCl_2$.

(*b*) From hydrocarbons

By free radical halogenation:

$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} \underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{sec-Butyl chloride}}{CH_3CH_2CHClCH_3}$$

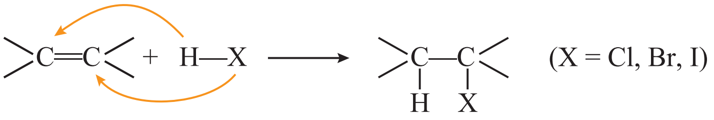


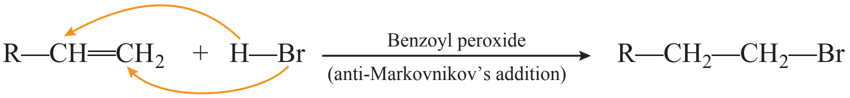
$$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3 + Cl_2 \xrightarrow{\text{UV light}} CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—Cl + HCl$$

neo-Pentane neo-Pentyl chloride

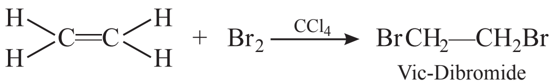
(*c*) From alkenes

(*i*) Addition of hydrogen halides





(*ii*) Addition of halogens



Vic-Dibromide

(*d*) Halide exchange

(*i*) By Finkelstein reaction

$$R—X + NaI \xrightarrow{\text{Dry acetone}} R—I + NaX \qquad (X = Cl, Br)$$

(*ii*) By Swarts reaction

$$R—X \xrightarrow{AgF,\ Hg_2F_2,\ CoF_2 \text{ or } SbF_3} R—F$$

$$CH_3—Br + AgF \longrightarrow CH_3—F + AgBr$$

4. Physical Properties of Haloalkanes

(*a*) **Melting and boiling point:** Haloalkanes have higher boiling points as compared to those of corresponding alkanes. This is due to their polar nature and strong dipole–dipole interactions between their molecules.

The boiling points of haloalkanes are in the order RCl < RBr < RI. It is because with the increase in size and mass of the halogen atom the magnitude of van der Waals forces of attraction increases.

Among isomeric alkyl halides, the boiling point decreases with increase in branching in the alkyl group. This is due to the reason that with increase in branching, the molecule attains a spherical shape with less surface area. As a result, interparticle forces become weaker resulting in lower boiling point. For example, among isomeric butyl chlorides, the straight chain isomer, n-butyl chloride has the highest boiling point whereas tert-butyl chloride has the lowest boiling point.

(*b*) **Density:** Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

(*c*) **Solubility:** Haloalkanes and haloarenes are practically insoluble in water because they are not able to form intermolecular hydrogen bonds with water molecules. However, they are soluble in organic solvents.

5. Chemical Properties of Haloalkanes

The chemical reactions of haloalkanes can be divided into following types:

(*a*) Nucleophilic substitution reactions

(*b*) Dehydrohalogenation or β-elimination reactions

(*c*) Reaction with metals

(a) **Nucleophilic substitution reactions:** When an atom or group of atoms is replaced by a nucleophile, the reaction is called nucleophilic substitution reaction.

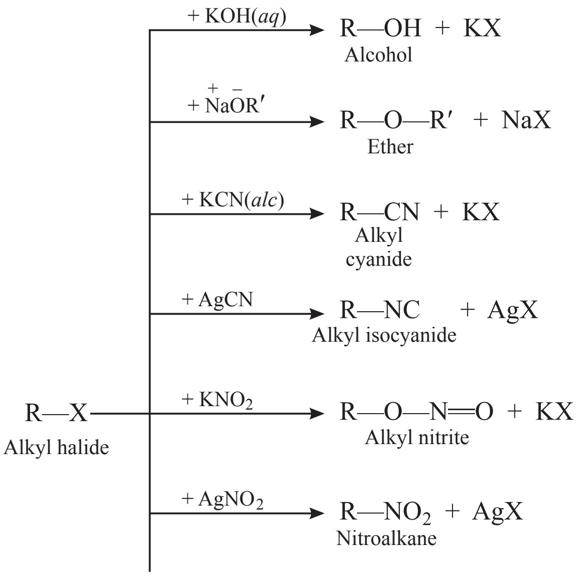
In haloalkanes, the halogen atom is attached to the carbon atom. As the halogen atom is more electronegative than carbon, the bond between carbon and halogen is polar in character.

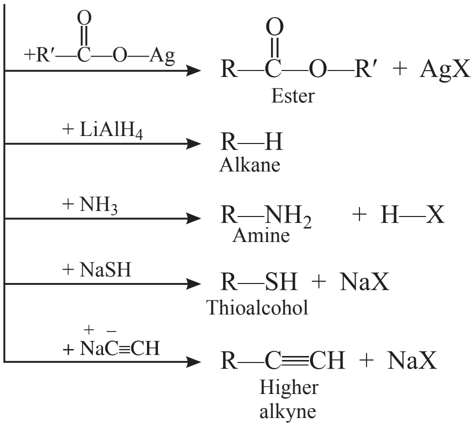
$$\overset{\delta+}{>C} - \overset{\delta-}{X}$$

Due to the presence of partial positive charge on the carbon atom, the nucleophiles can attack on electron deficient carbon thereby resulting in the displacement of weaker nucleophile, the halide ion.

$$\underset{\text{Substrate}}{\overset{\delta+}{>C} - \overset{\delta-}{X}} \;+\; \underset{\text{Nucleophile}}{:\overset{\ominus}{Z}} \longrightarrow \underset{\text{Product}}{>C-Z} \;+\; \underset{\text{Leaving group}}{:\overset{\ominus}{X}}$$

Nucleophilic Substitution of Alkyl halides (R—X)





$$R-X \xrightarrow{+R'-\overset{O}{\overset{\|}{C}}-O-Ag} \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-O-R'} + AgX$$

$$R-X \xrightarrow{+LiAlH_4} \underset{\text{Alkane}}{R-H}$$

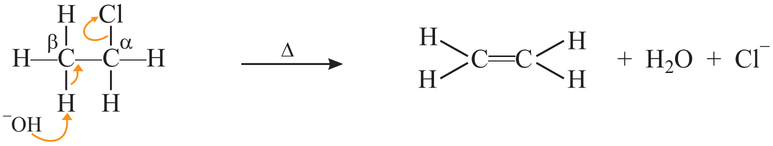
$$R-X \xrightarrow{+NH_3} \underset{\text{Amine}}{R-NH_2} + H-X$$

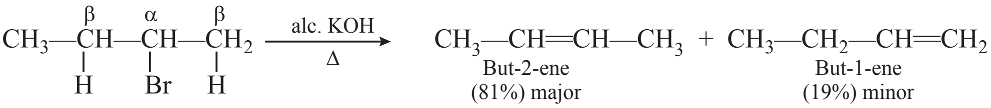
$$R-X \xrightarrow{+NaSH} \underset{\text{Thioalcohol}}{R-SH} + NaX$$

$$R-X \xrightarrow{+\overset{+}{Na}\overset{-}{C}\equiv CH} \underset{\text{Higher alkyne}}{R-C\equiv CH} + NaX$$

(*b*) **Elimination reactions:** When haloalkane with β-hydrogen atom is heated with ethanolic potassium hydroxide, there is elimination of hydrogen atom from β-carbon atom and a halogen atom from α-carbon atom. As a result, an alkene is formed. Since β-hydrogen atom is involved in elimination, it is often called β-elimination reaction.

$$CH_3-CH_2-Cl + KOH(\text{alc.}) \xrightarrow{\Delta} CH_2=CH_2 + KCl + H_2O$$





$$\underset{\substack{| \\ H}}{\overset{\beta}{CH_3-CH}}-\underset{\substack{| \\ Br}}{\overset{\alpha}{CH}}-\underset{\substack{| \\ H}}{\overset{\beta}{CH_2}} \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\substack{\text{But-2-ene} \\ (81\%)\text{ major}}}{CH_3-CH=CH-CH_3} + \underset{\substack{\text{But-1-ene} \\ (19\%)\text{ minor}}}{CH_3-CH_2-CH=CH_2}$$

(*c*) **Reaction with metals**

(*i*) Reaction with magnesium

$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide} \\ \text{(Grignard reagent)}}}{RMgX}$$

$$CH_3-CH_2-Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium bromide}}{CH_3-CH_2-MgBr}$$

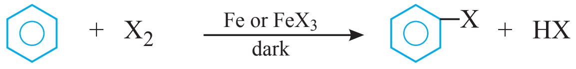
(*ii*) Reaction with sodium (**Wurtz reaction**)

$$R-\boxed{X + 2Na + X}-R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2NaX$$

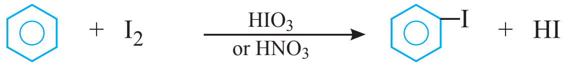
$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-}\boxed{Cl + 2Na + Cl}-CH_2-CH_3 \xrightarrow{\text{Dry ether}} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} + 2NaCl$$

6. Preparation of Haloarenes

(*a*) By direct halogenation of benzene

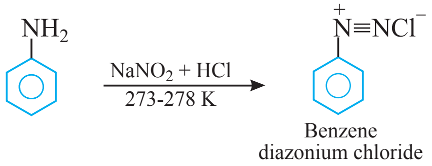


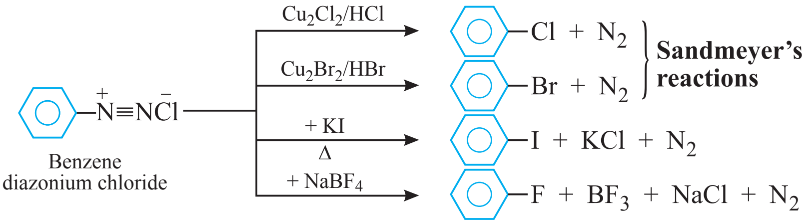
(X = Cl, Br)



Iodobenzene

(*b*) From diazonium salts





7. Physical Properties of Haloarenes

(*a*) Melting and boiling points: Boiling point of isomeric dihalobenzenes are very nearly same. However *p*-isomer have higher melting point as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho and meta isomers.

(*b*) Nature of C—X bond: The C—X bond is polar as 'X' is more electronegative than carbon. The carbon has partial positive charge whereas halogen has slight negative charge because shared pair of electrons are more towards halogen atoms.

$$—\overset{\delta+}{C}—\overset{\delta-}{X}$$

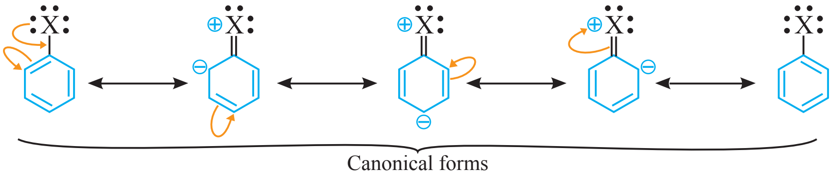
Dipole moment of CH_3Cl is higher than CH_3F due to greater bond length in C—Cl bond.

8. Chemical Properties of Haloarenes:

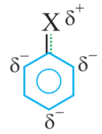
(*a*) Nucleophilic substitution reactions of haloarenes

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(*i*) Resonance effect: In arylhalides C—X bond acquires a partial double bond character due to resonance. As a result C—X bond cleavage in aryl halides is difficult than alkyl halides and therefore they are less reactive towards nucleophilic substitution reaction.

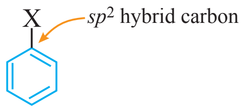


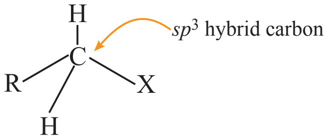
Canonical forms



Resonance hybrid structure

(*ii*) Difference in hybridisation:



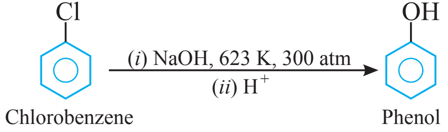


(*iii*) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore S_N1 mechanism is ruled out.

(*iv*) Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich areas.

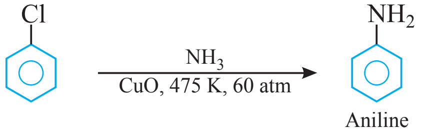
However, at high temperature and pressure several nucleophilic substitution reactions are carried out.

- Substitution by —OH group (**Dow's process**)

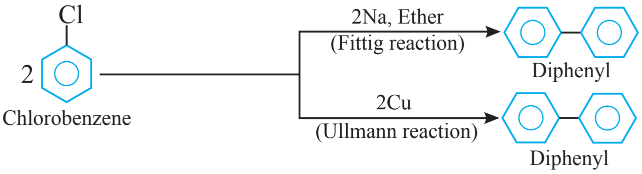


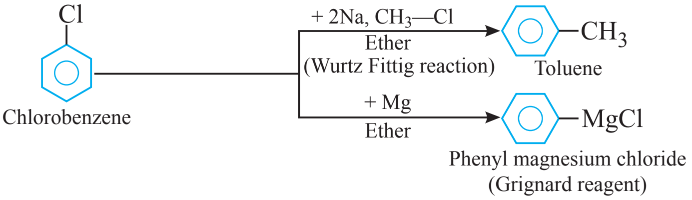
- Substitution by —CN group

- Substitution by —NH_2 group

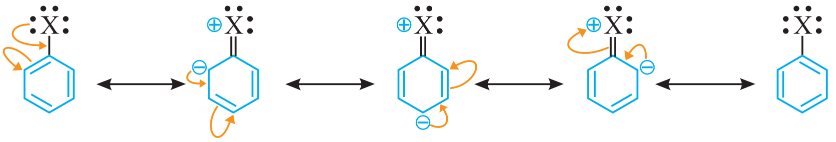


(*b*) Reactions with metals

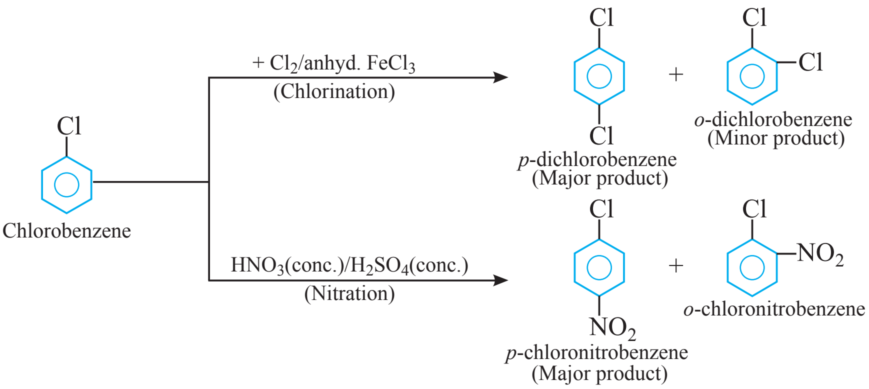


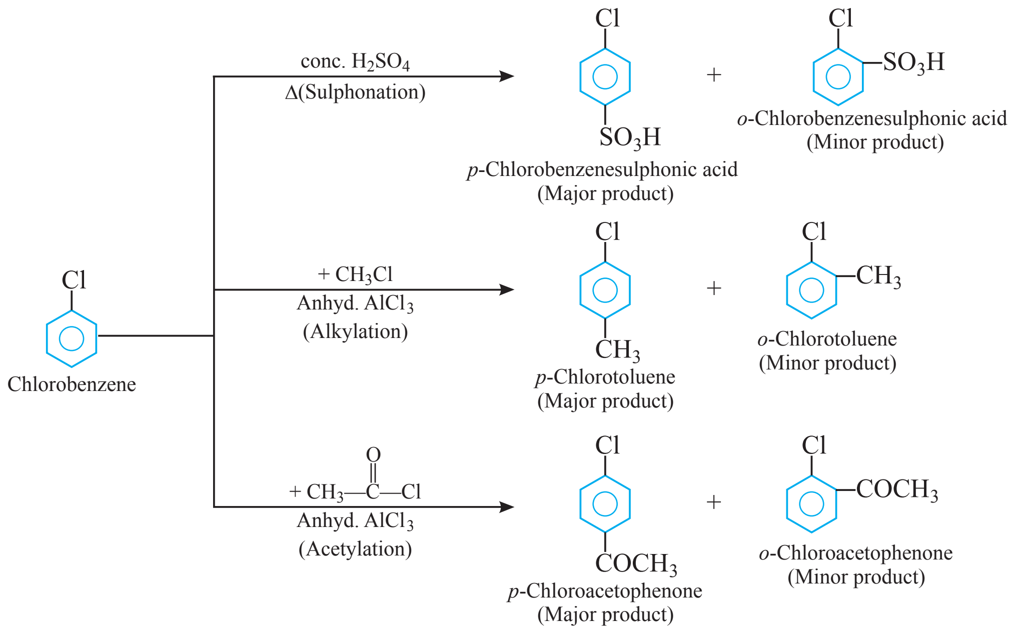


(c) Electrophilic substitution reactions of haloarenes



Due to resonance, the electron density increases more at ortho and para positions than at meta positions. Therefore, electrophilic substitution reactions take place at ortho and para positions.





9. (*a*) **Stereoisomerism:** Isomerism exhibited by two or more compounds with the same molecular and structural formulae but different spatial arrangements of atoms or groups in space is called stereoisomerism.

(*b*) **Plane-polarised light:** The beam of light whose oscillations or vibrations are confined to one plane only is called plane-polarised light. It is obtained by passing a monochromatic light (light of single wavelength) through a Nicol prism.

(*c*) **Optically active substances:** Those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solutions are called optically active substances. This phenomenon is called optical activity.

(*d*) **Optical rotation:** The property of rotating the plane of polarisation either towards left or towards right is called optical rotation.

(*i*) **Laevorotatory:** Those substances which rotate the plane of polarisation of light towards the left direction are called laevorotatory.

(*ii*) **Dextrorotatory:** Those substances which rotate the plane of polarisation of light towards right are called dextrorotatory.

Currently, dextro and laevo rotations are represented by algebraic signs of (+) and (–), respectively.

(*e*) **Specific rotation:** Specific rotation is defined as the number of degrees of rotation observed when the concentration of optically active substance is 1 g cm^{-3} and length of polarimeter tube is 1 decimetre (dm) for D-line of sodium vapour lamp at 25°C.

$$\text{Specific rotation } [\alpha] = \frac{\text{Observed rotation } (\alpha_{\text{obs}})}{\text{Length of tube (dm)} \times \text{Concentration of solution (g mL}^{-1})}$$

While reporting [α], the wavelength of light used is given as subscript and the temperature (in degrees celsius) as a superscript. It is also customary to designate the solvent and concentration.

Thus, $[\alpha]_D^{25} = -2.25°$ (C; 0.50 ethanol) means that α was measured at 25°C using sodium D-line and the sample concentration was 0.50 g/mL in ethanol.

(*f*) **Asymmetric molecule:** If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.

(*g*) **Chiral:** An object which is non-superimposable on its mirror image is said to be chiral. The property of being chiral is known as chirality.

(*h*) **Asymmetric carbon:** The carbon atom which is attached with four different groups of atoms is called asymmetric carbon. The molecule having asymmetric carbon atom is called asymmetric.

(*i*) **Enantiomers:** The stereoisomers which are non-superimposable mirror images are called enantiomers. Enantiomers rotate the plane of polarised light to the same extent but in opposite direction.

(*j*) **Racemic mixture:** An equimolar mixture of a pair of enantiomers is called racemic mixture. A racemic mixture is optically inactive due to external compensation.

(*k*) **Racemisation:** The process of conversion of an enantiomer into racemic mixture is known as racemisation.

(*l*) **Resolution of a racemic mixture:** Resolution is a process of separating a racemic mixture into its enantiomer constituents, *i.e.*, dextro *d*(+) and laevo-rotatory *l*(–) substances.

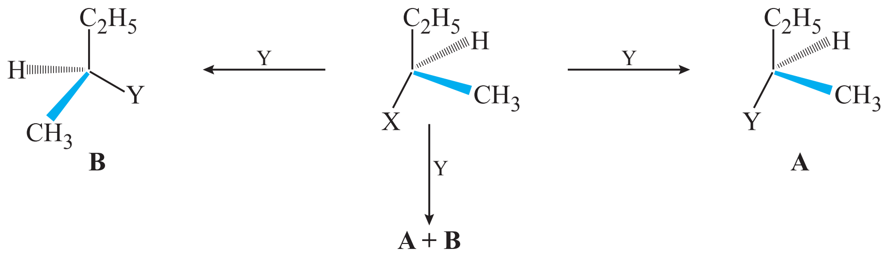
(*m*) **Meso compounds:** The compounds containing two or more chirality centres but possessing achiral molecular structure because of having plane of symmetry are called meso compounds. A meso compound is optically inactive due to internal compensation.

(*n*) **Diastereomers:** The stereoisomers which are non-superimposable and do not bear a mirror-image relationship.

(*o*) **Retention:** If in an optically active molecule the relative configuration of the atoms/groups around a chiral centre remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.

(*p*) **Inversion:** If the relative configuration of atoms/groups around a stereo centre in the product is opposite to that in reactant, the reaction is said to proceed with inversion of configuration.

There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction:



If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50 : 50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

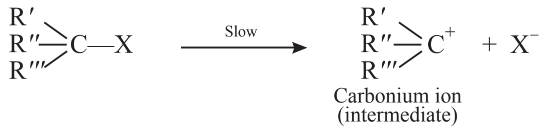
10. Mechanism of Nucleophilic Substitution in Alkyl Halides

The nucleophilic substitution reactions in alkyl halides can take place by either of two mechanisms: S_N1 and S_N2

Substitution nucleophilic unimolecular (S_N1)

It takes place in two steps and the reaction is of first order. In the first step, alkyl halide undergoes slow heterolysis to produce carbonium ion (an intermediate) and a halide ion. In the second step, nucleophile rapidly combines with the carbonium ion to complete the substitution reaction.

Step 1:

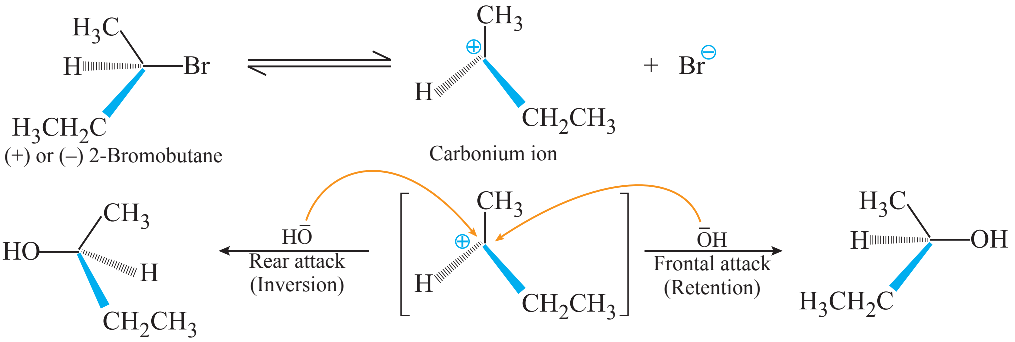


$$R'R''R'''C{-}X \xrightarrow{\text{Slow}} R'R''R'''C^+ + X^-$$

Step 2:

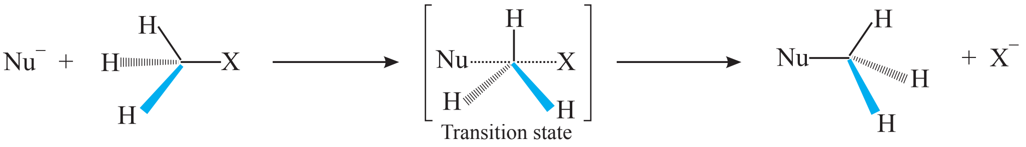
$$R'R''R'''C^+ + Nu^- \longrightarrow R'R''R'''C{-}Nu$$

S_N1 reactions of optically active halides are accompanied by racemisation. This is because the carbonium formed in the slow step being sp^2 hybridised is planar (achiral) therefore, the attack of nucleophile on it can occur from both the faces with equal ease giving a mixture containing two enantiomers in equal amounts. This may be illustrated by hydrolysis of optically active 2-bromobutane, which gives (±) butan-2-ol.



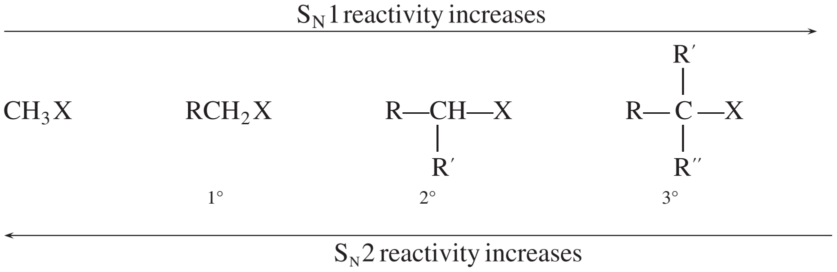
Substitution nucleophilic bimolecular (S_N2)

It takes place in one step and the reaction is of second order. In this process the nucleophile attacks the partially positive carbon of the C—X bond of the substrate, alkyl halide, from the back side of the C—X bond and the leaving group, X^-, departs simultaneously.

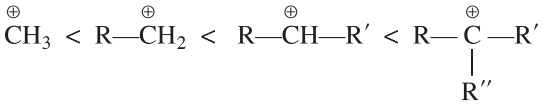


S_N2 reactions of optically active halides are accompanied by inversion of configuration. This is because the attack of nucleophile occurs from a direction opposite to the one from where the halogen atom leaves.

The order of reactivity of alkyl halides towards S_N1 and S_N2 reactions is as follows:



An alkyl group at the α-carbon, being bigger in size than H atom, tends to block the approach of the nucleophile to carbon due to steric hindrance in S_N2 mechanism and makes the reaction difficult to occur. In the S_N1 mechanism, a carbocation is formed in the first, slow step. The more stable the carbocation, more easily is the product formed. Tertiary alkyl halides undergo S_N1 reaction very fast because of the high stability of tertiary carbocation.

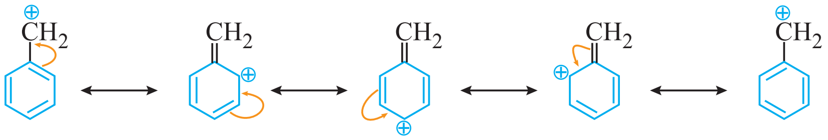


$$\overset{\oplus}{C}H_3 < R—\overset{\oplus}{C}H_2 < R—\overset{\oplus}{C}H—R' < R—\underset{R''}{\overset{\oplus}{C}}—R'$$

Primary allylic and benzylic halides show higher reactivity in S_N1 reactions than other primary halides. This is due to stabilisation of allylic and benzylic carbocation intermediates by resonance.

$$CH_2{=}CH—\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2—CH{=}CH_2$$

Resonance in allyl carbocation



Resonance stabilisation in benzyl carbocation

Thus, primary alkyl halides always react predominantly by S_N2 mechanism. Tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by both the mechanisms without much preference. Polar solvents favour S_N1 and non-polar solvents favour S_N2 reactions.

11. **Polyhalogen Compounds:** Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture.

Some polyhalogen compounds are described as follows:

(*a*) **Methylene chloride (Dichloromethane):** It is prepared industrially by the direct chlorination of methane.

$$\mathrm{CH_4 + 2Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + 2HCl}$$

Uses:

It is an effective solvent used in pharmaceutical and food industry.

(*b*) **Chloroform (Trichloromethane):** It is manufactured by chlorination of methane followed by separation by fractional distillation.

$$\mathrm{CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\nu} CHCl_3 + 3HCl}$$

Properties:

(*i*) It is a sweet smelling liquid with boiling point 61°C.

(*ii*) It is stored in dark coloured bottles because it gets oxidised in the presence of sunlight to form a poisonous gas, phosgene ($COCl_2$).

$$\mathrm{2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl}$$

It is therefore stored in closed dark coloured bottles completely filled so that air is kept out. 1% ethanol is added so as to convert phosgene gas to diethyl carbonate which is non-volatile and non-toxic.

$$\mathrm{COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5)_2CO_3} + 2HCl}$$

Uses:

(*i*) It is widely used in industry as a solvent for fats, waxes, resins, rubber, etc.

(*ii*) It was once used as an anaesthetic agent in surgery and as flavouring agent in cough syrups but now it is not used because it forms phosgene gas which is poisonous.

(*c*) **Triiodomethane (Iodoform):** Iodoform is prepared by the action of iodine and alkali on ethyl alcohol or acetone.

Reactions involved in the preparation of iodoform from ethyl alcohol are:

$$\mathrm{2NaOH + I_2 \longrightarrow NaI + \underset{\text{Sodium hypoiodite}}{NaOI} + H_2O}$$

$$\mathrm{C_2H_5OH + NaOI \xrightarrow{\text{Oxidation}} CH_3CHO + NaI + H_2O}$$

$$\mathrm{CH_3CHO + 3NaOI \xrightarrow{\text{Iodination}} \underset{\text{Iodal}}{CI_3CHO} + 3NaOH}$$

$$\mathrm{CI_3CHO + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{Iodoform}}{CHI_3\downarrow} + \underset{\text{Sodium formate}}{HCOONa}}$$

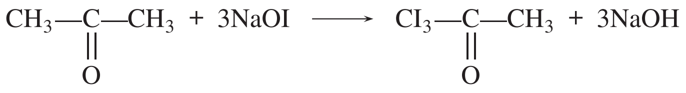
The complete reaction may be written as:

$$\mathrm{CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3\downarrow + HCOONa + 5NaI + 5H_2O}$$

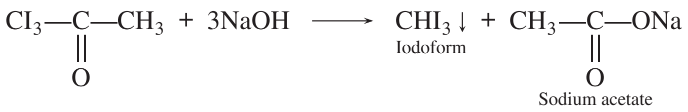
However, when sodium carbonate is used in place of sodium hydroxide then the complete reaction may be written as:

$$\mathrm{CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3\downarrow + 5NaI + HCOONa + 3CO_2 + 2H_2O}$$

Reactions involved in the preparation of iodoform from acetone are:



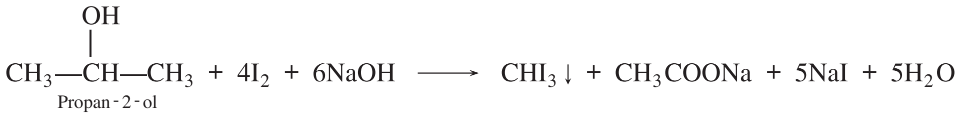
$$\mathrm{CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + 3NaOI \longrightarrow CI_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + 3NaOH}$$



$$CI_3-\underset{\underset{O}{\|}}{C}-CH_3 + 3NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + \underset{\text{Sodium acetate}}{CH_3-\underset{\underset{O}{\|}}{C}-ONa}$$

The reaction of iodine and sodium hydroxide or iodine and sodium carbonate to give yellow precipitate of iodoform is called iodoform reaction.

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCOONa + 3NaI + 3H_2O$$



$$\underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \longrightarrow CHI_3\downarrow + CH_3COONa + 5NaI + 5H_2O$$

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + CH_3COONa + 3NaI + 3H_2O$$

$$\underset{\text{Butan-2-one}}{CH_3COCH_2CH_3} + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + CH_3CH_2COONa + 3NaI + 3H_2O$$

Physical properties:

Iodoform is a yellow coloured solid having m.p. 392 K. It is insoluble in water but dissolves readily in organic solvents.

Uses:

It is used as an antiseptic for dressing wounds.

The haloform reaction is commonly used to distinguish between methyl ketones or methyl carbinols from other ketones and alcohols.

(*d*) **Carbon tetrachloride (Tetrachloromethane):** It is prepared by chlorination of methane and by action of chlorine on CS_2 in presence of $AlCl_3$ as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + \underset{\text{(Sulphur monochloride)}}{S_2Cl_2}$$

$$CH_4 + 4Cl_2 \xrightarrow{hv} CCl_4 + 4HCl$$

Properties:

(*i*) CCl_4 is a colourless liquid with boiling point 350 K.

(*ii*) It has a sickly sweet smell.

Uses:

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and generally used as a solvent. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting which can cause permanent damage to nerve cells. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer.

(*e*) **Freon:** The chlorofluorocarbon compounds of methane and ethane are collectively called freons.

It is manufactured from CCl_4 by **Swarts reaction**.

$$3CCl_4 + 2SbF_3 \xrightarrow[SbCl_5]{\text{Heat}} \underset{\text{Freon-12}}{3CCl_2F_2} + 2SbCl_3$$

Properties:

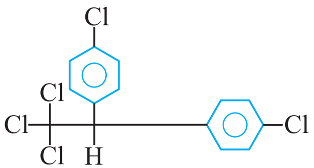
(*i*) Dichlorodifluoromethane (CCl_2F_2, Freon-12) is one of the most common freons in industrial use.

(*ii*) They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquifiable gases.

Uses:

They have also been used extensively as propellants, for aerosols and foams to spray out deodorants, cleansers, hair spray, shaving creams. Use of freon is being reduced and banned because they are responsible for ozone layer depletion.

(*f*) **DDT (*p*, *p′*-Dichlorodiphenyl trichloroethane):** It is a white powder insoluble in water, but soluble in oil. It is used as an insecticide. It results in pollution due to its extreme stability. It is non-biodegradable. Many species of insects developed resistance to DDT, and it was also discovered to have high toxicity in fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised rapidly by animals.

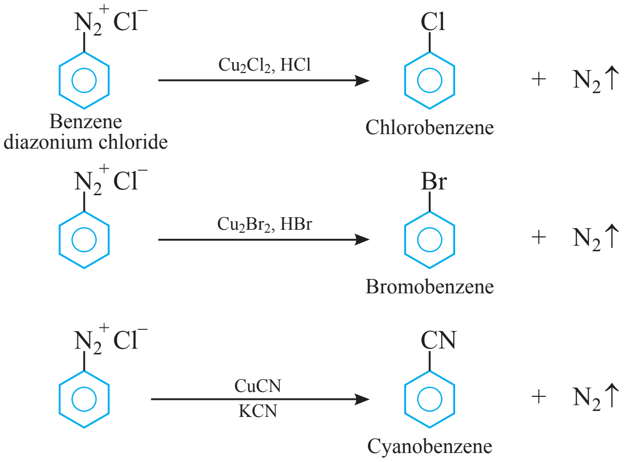


DDT

12. Important Name Reactions

(*a*) Sandmeyer's Reaction:

Benzene diazonium chloride is converted to chlorobenzene, bromobenzene, cyanobenzene on treatment with CuCl/HCl, CuBr/HBr and CuCN/KCN, respectively.



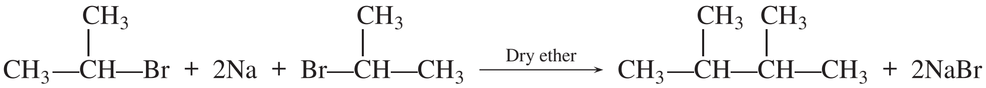
(*b*) **Finkelstein Reaction:** Chloroalkanes or bromoalkanes are converted into corresponding iodoalkanes by treating with sodium iodide dissolved in acetone.

$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + NaI \xrightarrow{\text{Dry acetone}} \underset{\text{Ethyl iodide}}{CH_3CH_2I} + NaCl$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + NaI \xrightarrow{\text{Dry acetone}} \underset{\text{Ethyl iodide}}{CH_3CH_2I} + NaBr$$

(*c*) **Wurtz Reaction:** Alkyl halides react with metallic sodium in the presence of dry ether to form alkanes. This reaction is used for the preparation of higher alkanes. For example,

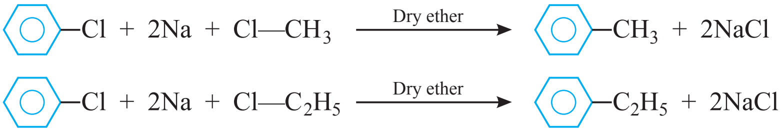
$$\underset{\text{Methyl bromide}}{CH_3Br} + 2Na + Br{-}CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$



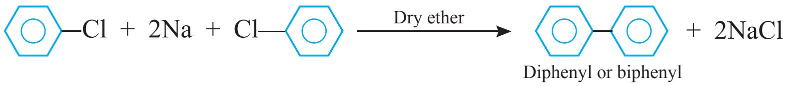
$$\underset{\text{Isopropyl bromide}}{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}Br} + 2Na + Br{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{2,3-Dimethylbutane}}{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_3} + 2NaBr$$

Wurtz reaction is only useful for the preparation of alkanes containing even number of carbon atoms and not for the alkanes containing odd number of carbon atoms.

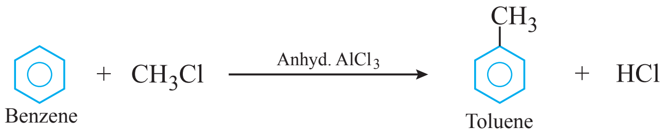
(*d*) **Wurtz–Fittig Reaction:** Aryl halides when treated with alkyl halide and sodium in dry ether give alkylbenzenes.

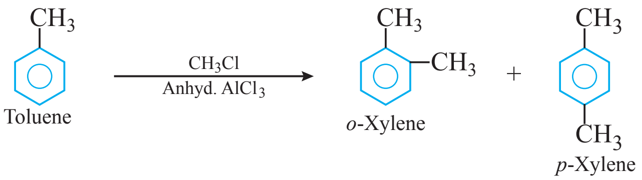


(*e*) Fittig's Reaction: In this reaction two molecules of haloarene combine with metallic sodium in the presence of dry ether to give diphenyl or biphenyl.

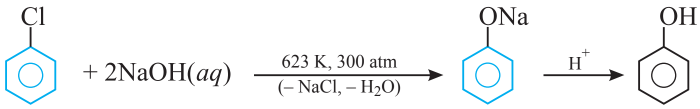


(*f*) Friedel–Crafts Alkylation: Benzene and other aromatic compounds react with alkyl halides in the presence of anhydrous $AlCl_3$ to form alkyl benzene.





(*g*) Dow's Process: When chlorobenzene is treated with an aqueous solution of NaOH at 623 K, 300 atm pressure sodium phenoxide is formed which on acidification gives phenol.



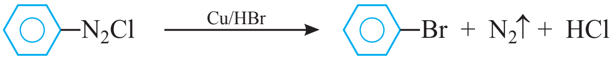
(*h*) Hunsdiecker's Reaction: Bromoalkanes are obtained by this method by refluxing silver salts of fatty acids with Br_2 in CCl_4.

$$\text{R—COOAg} + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} \text{R—Br} + AgBr + CO_2\uparrow$$

$$CH_3CH_2COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} CH_3CH_2Br + AgBr + CO_2\uparrow$$

This method can be employed to decrease the number of carbon atoms.

(*i*) Gatterman's Reaction: The reaction of diazonium salts with 'Cu' powder in the presence of corresponding halogen acids is known as Gatterman's reaction.



13. Distinctions between Pairs of Organic Compounds Containing Halogen

Silver nitrate test: In this test, the halide is warmed with aqueous or alcoholic KOH. The solution is then acidified with dil. HNO_3 followed by addition of $AgNO_3$ solution.

Alkyl, benzyl and allyl halides give precipitate.

Aryl and vinyl halides do not give precipitate.

It may be noted that the precipitate formed should be insoluble in HNO_3.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Write the structures of the following compounds:

(*i*) 2-Chloro-3-methylpentane

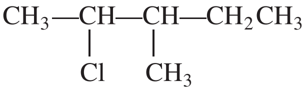
(*ii*) 1-Chloro-4-ethylcyclohexane

(*iii*) 4-tert-Butyl-3-iodoheptane

(*iv*) 1, 4-Dibromobut-2-ene

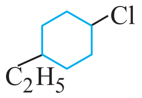
(*v*) 1-Bromo-4-sec-butyl-2- methylbenzene

Ans. (*i*)

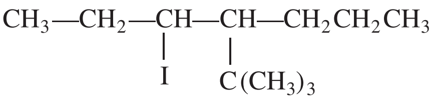


$$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_3$$

(*ii*)



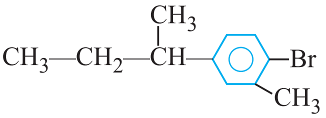
(*iii*)



$$CH_3-CH_2-\underset{I}{\underset{|}{CH}}-\underset{C(CH_3)_3}{\underset{|}{CH}}-CH_2CH_2CH_3$$

(*iv*) $BrCH_2CH{=}CHCH_2Br$

(*v*)



Q. 2. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans. H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding HI and then oxidises it to I_2.

Q. 3. Write structures of different dihalogen derivatives of propane.

Ans. (*i*) $ClCH_2CH_2CH_2Cl$ (*ii*) $ClCH_2CHClCH_3$

(*iii*) $Cl_2CHCH_2CH_3$ (*iv*) $CH_3CCl_2CH_3$

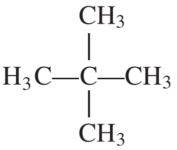
Q. 4. Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(*i*) A single monochloride *[CBSE (F) 2017]*

(*ii*) Three isomeric monochlorides

(*iii*) Four isomeric monochlorides.

Ans. (*i*) All the hydrogen atoms are equivalent and replacement of any hydrogen will give the same product.

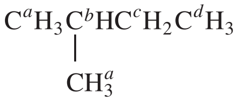


$$H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \text{ neopentane}$$

(*ii*) The equivalent hydrogens are grouped as *a*, *b* and *c*. The replacement of equivalent hydrogens will give the same product.

$$C^aH_3C^bH_2C^cH_2C^bH_2C^aH_3 \text{ pentane}$$

(*iii*) Similarly the equivalent hydrogens are grouped as *a, b, c* and *d*. Thus, four isomeric products are possible.

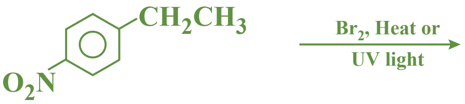


$$C^aH_3\underset{CH_3^a}{\underset{|}{C^b}}HC^cH_2C^dH_3 \quad \text{2-methylbutane}$$

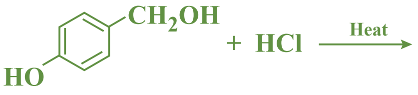
Q. 5. Draw the structures of major monohalo product in each of the following reactions:

(*i*)

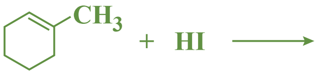
(*ii*)



(*iii*)

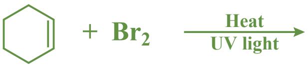


(*iv*)

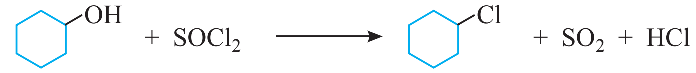


(*v*) $CH_3CH_2Br + NaI \longrightarrow$

(*vi*)

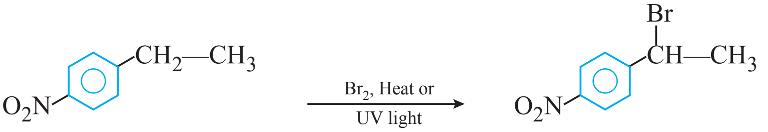


Ans. (*i*)



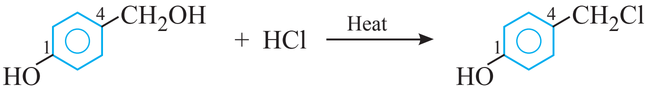
Cyclohexanol Chlorocyclohexane

(*ii*)



4-ethylnitrobenzene 4-(1-Bromoethyl) nitrobenzene

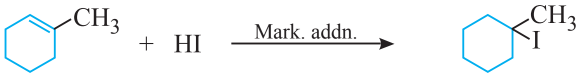
(*iii*)



4-Hydroxymethylphenol 4-Chloromethylphenol

Only alcoholic but not phenolic OH groups are replaced by Cl on heating with HCl.

(*iv*)

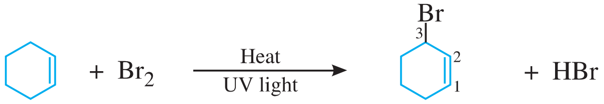


1-Methylcyclohexene 1-Iodo-1-methylcyclohexane

(*v*) $\underset{\text{Bromoethane}}{CH_3CH_2—Br} + NaI \longrightarrow \underset{\text{Iodoethane}}{CH_3CH_2—I} + NaBr$

Iodide ion is a strong nucleophile and hence it displaces bromide ion.

(*vi*)



3-Bromocyclohexene

Q. 6. Arrange each set of compounds in the order of increasing boiling points.

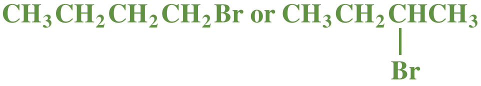
(*i*) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(*ii*) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

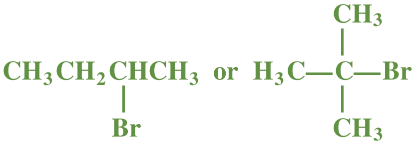
Ans. (*i*) Chloromethane < Bromomethane < Dibromomethane < Bromoform. Boiling point increases with increase in molecular mass.

(*ii*) Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane. Isopropyl chloride being branched has lower b.p. than 1-Chloropropane.

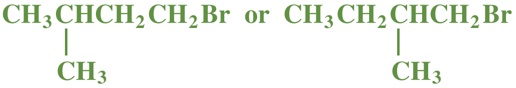
Q. 7. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.



(*i*) $CH_3CH_2CH_2CH_2Br$ **or** $CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3$

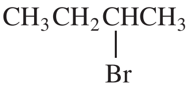


(*ii*) $CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3$ **or** $H_3C—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—Br$

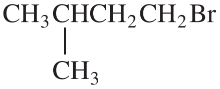


(*iii*) $CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2Br$ **or** $CH_3CH_2\underset{\underset{CH_3}{|}}{CH}CH_2Br$

Ans. (*i*) $CH_3CH_2CH_2CH_2Br$ Being primary halide, there won't be any steric hindrance.

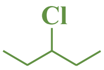
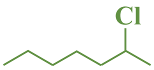


(*ii*) $CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3$ Being a secondary halide, there will be less crowding around α-carbon than tertiary halide.



(*iii*) $CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2Br$ The presence of methyl group closer to the halide group will increase the steric hindrance and decreases the rate.

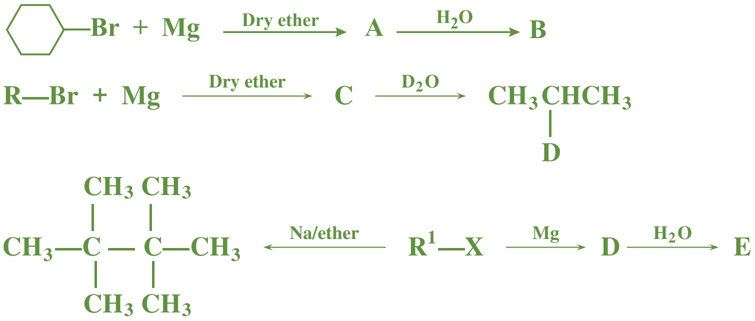
Q. 8. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

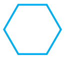
(*i*)  **and**  **(*ii*)**  **and** 

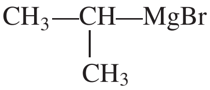
Ans. (*i*)  2-Chloro-2-methylpropane as the tertiary carbocation is more stable than secondary carbocation.

(*ii*)  2-Chloroheptane as the secondary carbocation is more stable than primary carbocation.

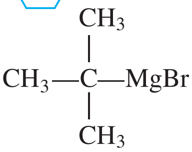
Q. 9. Identify A, B, C, D, E, R and R^1 in the following:



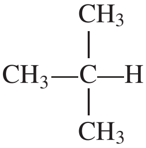
Ans. A =  B = 

C = 

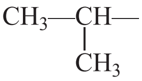
$$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}MgBr$$

D = 

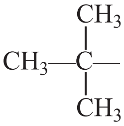
$$CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}MgBr$$

E = 

$$CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}H$$

R = 

$$CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}$$

R^1 = 

$$CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}$$

NCERT Textbook Exercises

Q. 1. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides.

(*i*) $(CH_3)_2CHCH(Cl)CH_3$
(*ii*) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$
(*iii*) $CH_3CH_2C(CH_3)_2CH_2I$
(*iv*) $(CH_3)_3CCH_2CH(Br)C_6H_5$
(*v*) $CH_3CH(CH_3)CH(Br)CH_3$
(*vi*) $CH_3C(C_2H_5)_2CH_2Br$
(*vii*) $CH_3C(Cl)(C_2H_5)CH_2CH_3$
(*viii*) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$
(*ix*) $CH_3CH{=}CHC(Br)(CH_3)_2$
(*x*) *p*-$ClC_6H_4CH_2CH(CH_3)_2$
(*xi*) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$
(*xii*) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

Ans. (*i*) 2-Chloro-3-methylbutane; 2° alkyl halide
(*ii*) 3-Chloro-4-methylhexane; 2° alkyl halide
(*iii*) 1-Iodo-2, 2-dimethylbutane; 1° alkyl halide
(*iv*) 1-Bromo-3,3-dimethyl-1-phenylbutane; 2° benzylic halide
(*v*) 2-Bromo-3-methylbutane; 2°alkyl halide
(*vi*) 1-Bromo-2-ethyl-2-methylbutane; 1° alkyl halide
(*vii*) 3-Chloro-3-methylpentane; 3° alkyl halide
(*viii*) 3-Chloro-5-methylhex-2-ene; vinylic halide

(*ix*) 4-Bromo-4-methylpent-2-ene; allylic halide

(*x*) 1-Chloro-4-(2-methylpropyl) benzene; aryl halide

(*xi*) 1-Chloromethyl-3-(2, 2-dimethylpropyl) benzene; 1° benzylic halide

(*xii*) 1-Bromo-2-(1-methylpropyl) benzene; aryl halide

Q. 2. Give the IUPAC names of the following compounds:

(*i*) $CH_3CH(Cl)CH(Br)CH_3$

(*ii*) $CHF_2CBrClF$

(*iii*) $ClCH_2C{\equiv}CCH_2Br$

(*iv*) $(CCl_3)_3CCl$

(*v*) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$

(*vi*) $(CH_3)_3CCH{=}C(Cl)C_6H_4I\text{–}p$

Ans. (*i*) 2-Bromo-3-chlorobutane

(*ii*) 1-Bromo-1-chloro-1, 2, 2-trifluoroethane

(*iii*) 1-Bromo-4-chlorobut-2-yne

(*iv*) 2-(Trichloromethyl)-1, 1, 1, 2, 3, 3, 3-heptachloropropane

(*v*) 2-Bromo-3, 3-Bis (4-chlorophenyl) butane

(*vi*) 1-Chloro-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene

Q. 3. Write the structures of the following organic halogen compounds:

(*i*) 2-Chloro-3-methylpentane

(*ii*) *p*-Bromochlorobenzene

(*iii*) 1-Chloro-4-ethylcyclohexane

(*iv*) 2-(2-Chlorophenyl)-1-iodooctane

(*v*) 2-Bromobutane

(*vi*) 4-tert. Butyl-3-iodoheptane

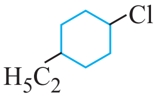
(*vii*) 1-Bromo-4-sec. butyl-2-methylbenzene

(*viii*) 1, 4-Dibromobut-2-ene

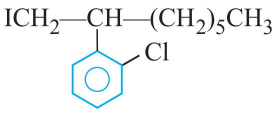
Ans. (*i*) $CH_3CH_2CH(CH_3)CHClCH_3$

(*ii*)

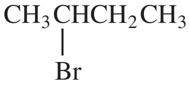
(*iii*)



(*iv*)

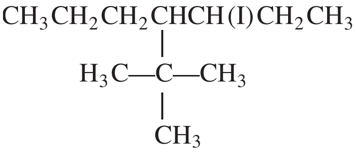


(*v*)



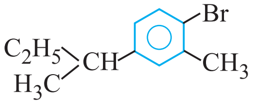
$$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_2CH_3}$$

(*vi*)



$$CH_3CH_2CH_2\underset{\displaystyle H_3C-\underset{\displaystyle \overset{|}{C}H_3}{\overset{|}{C}}-CH_3}{\underset{|}{C}H}CH(I)CH_2CH_3$$

(*vii*)



(*viii*) $BrCH_2CH{=}CHCH_2Br$

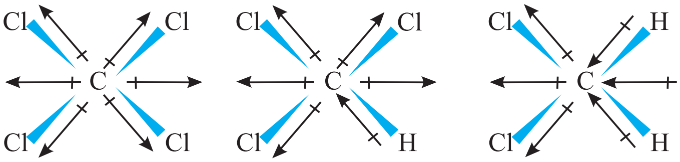
Q. 4. Which one of the following has the highest dipole moment?

(*i*) CH_2Cl_2

(*ii*) $CHCl_3$

(*iii*) CCl_4

Ans. The three-dimensional structures of the three compounds along with the direction of dipole moment in each of their bonds are given as follows:



CCl_4 being symmetrical has zero dipole moment. In $CHCl_3$, the resultant of two C—Cl dipoles is opposed by the result of C—H and C—Cl bond. As the latter resultant is expected to be smaller than the former, $CHCl_3$ has a finite dipole (1.03 D) moment.

In CH_2Cl_2, the resultant of two C—Cl dipole moments is reinforced by the resultant of two C—H dipoles, hence, CH_2Cl_2 (1.62 D) has a dipole moment higher than that of $CHCl_3$.

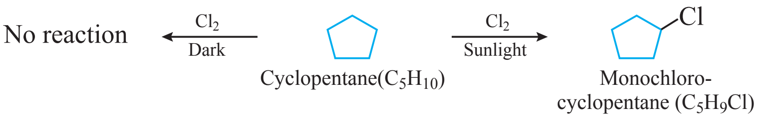
Therefore, CH_2Cl_2 has the highest dipole moment.

Q. 5. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound, C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Ans. (*i*) The hydrocarbon with molecular formula C_5H_{10} can be either a cycloalkane or an alkene.

(*ii*) Since the hydrocarbon does not react with Cl_2 in the dark, it cannot be an alkene but must be a cycloalkane.

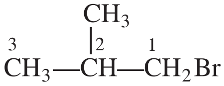
(*iii*) As the cycloalkane reacts with Cl_2 in the presence of bright sunlight, to give a single monochloro compound, C_5H_9Cl, therefore all the ten hydrogen atoms of the cycloalkane must be equivalent. Therefore, the cycloalkane is cyclopentane.



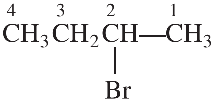
Q. 6. Write the isomers of the compound having formula C_4H_9Br.

Ans. It has the following four isomers:

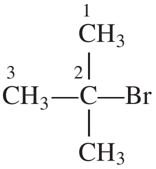
(*i*) $\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$

(*ii*)

$$\overset{3}{CH_3}-\overset{\overset{CH_3}{|\,2}}{CH}-\overset{1}{CH_2Br}$$

1-Bromo-2-methylpropane

(*iii*)

$$\overset{4}{CH_3}\overset{3}{CH_2}\underset{\underset{Br}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2-Bromobutane

(*iv*)

$$\overset{3}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{1}{CH_3}}{2\,|}}{C}}-Br$$

2-Bromo-2-methylpropane

Q. 7. Write the equations for the preparation of 1-iodobutane from (*i*) 1-butanol (*ii*) 1-chlorobutane, and (*iii*) but-1-ene.

Ans. (*i*) $$\underset{\text{1-Butanol}}{3CH_3CH_2CH_2CH_2OH} + \underset{\substack{\text{From}\\ (\text{P \& I}_2)}}{PI_3} \longrightarrow \underset{\text{1-Iodobutane}}{3CH_3CH_2CH_2CH_2I} + H_3PO_3$$

(*ii*) $$\underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + KI \xrightarrow[\text{(Finkelstein reaction)}]{\text{Acetone, heat}} \underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I} + KCl$$

(*iii*) $$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\text{Anti-Markovnikov's addition}]{\text{Peroxide}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$$

$$\xrightarrow[\text{(Finkelstein reaction)}]{\text{KI/Acetone, }\Delta} \underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I}$$

Q. 8. What are ambident nucleophiles? Explain with an example.

Ans. The nucleophiles which can attack through two different sites are called ambident nucleophiles. For example, cyanide ion is a resonance hybrid of the following two structures:

$$^{-}:C\equiv N: \longleftrightarrow :C=\ddot{N}:^{-}$$

It can attack through carbon to form cyanides and through N to form isocyanides or carbylamines.

Q. 9. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?

(*i*) CH_3Br or CH_3I **(*ii*) $(CH_3)_3CCl$ or CH_3Cl**

Ans. (*i*) Since I^- ion is a better leaving group than Br^- ion, hence, CH_3I reacts faster than CH_3Br in S_N2 reaction with OH^- ion.

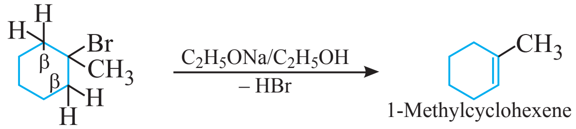
(*ii*) On steric grounds, 1° alkyl halides are more reactive than *tert*-alkyl halides in S_N2 reactions. Hence, CH_3Cl will react at a faster rate than $(CH_3)_3CCl$ in a S_N2 reaction with OH^- ion.

Q. 10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.

(*i*) 1-Bromo-1-methylcyclohexane **(*ii*) 2-Chloro-2-methylbutane**

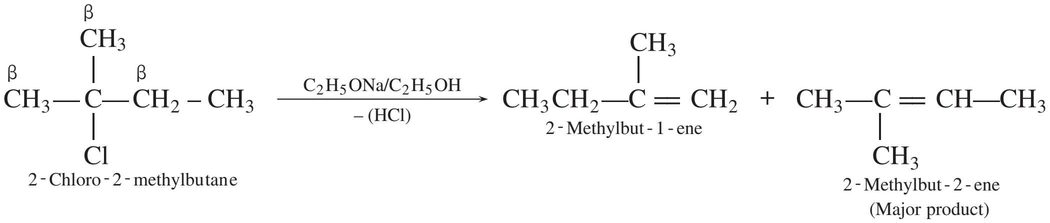
(*iii*) 2, 2, 3-Trimethyl-3-bromopentane.

Ans. (*i*) In 1-bromo-1-methylcyclohexane, the β-hydrogens on either side of the Br atom are equivalent, therefore, only 1-alkene is formed.



1-Methylcyclohexene

(*ii*) All β-hydrogens in 2-chloro-2-methylbutane are not equivalent, hence on treatment with C_2H_5ONa/C_2H_5OH, it gives two alkenes.



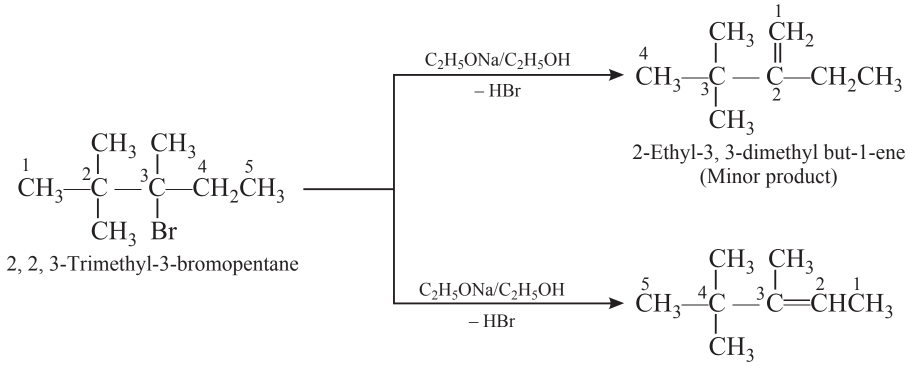
$$CH_3-\overset{\overset{\beta}{CH_3}}{\underset{Cl}{C}}-CH_2-CH_3 \xrightarrow[-(HCl)]{C_2H_5ONa/C_2H_5OH} CH_3CH_2-\overset{CH_3}{C}=CH_2 + CH_3-\underset{CH_3}{C}=CH-CH_3$$

2-Chloro-2-methylbutane

2-Methylbut-1-ene

2-Methylbut-2-ene (Major product)

(*iii*) 2, 2, 3-Trimethyl-3-bromopentane has two different sets of β-hydrogen and therefore, in principle, can give two alkenes (I and II). But according to Saytzeff rule, more highly substituted alkene (II), being more stable is the major product.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{Br}{C}}-CH_2CH_3 \xrightarrow[-HBr]{C_2H_5ONa/C_2H_5OH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_2}{\overset{\|}{C}}-CH_2CH_3$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{Br}{C}}-CH_2CH_3 \xrightarrow[-HBr]{C_2H_5ONa/C_2H_5OH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{C}=CHCH_3$$

2, 2, 3-Trimethyl-3-bromopentane

2-Ethyl-3, 3-dimethyl but-1-ene
(Minor product)

3, 4, 4-Trimethylpent-2-ene
(Major product)

Q. 11. How will you bring the following conversions?

(*i*) Ethanol to but-1-yne	**(*ii*) Ethane to bromoethene**
(*iii*) Propene to 1-nitropropane	**(*iv*) Toluene to benzyl alcohol**
(*v*) Propene to propyne	**(*vi*) Ethanol to ethyl fluoride**
(*vii*) Bromomethane to propanone	**(*viii*) But-1-ene to but-2-ene**
(*ix*) 1-Chlorobutane to *n*-octane	**(*x*) Benzene to biphenyl**

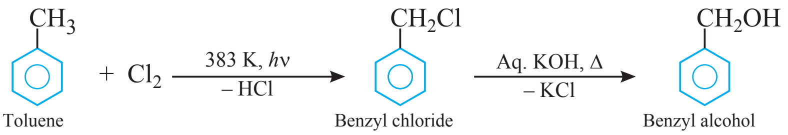
Ans. (*i*) $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Pyridine}]{+SOCl_2} CH_3CH_2Cl \xrightarrow[NaNH_2,\ \text{liq. } NH_3,\ 196\text{ K}]{+CH\equiv CH} \underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH}$$

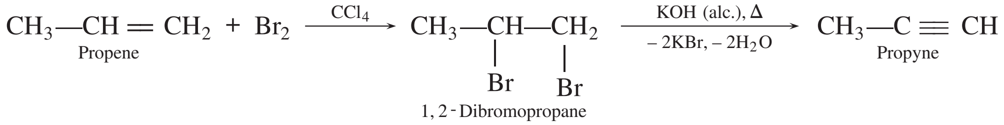
(*ii*) $$\underset{\text{Ethane}}{CH_3-CH_3} + Br_2 \xrightarrow{h\nu,\ 520-670\text{ K}} \underset{\text{Bromoethane}}{CH_3CH_2-Br} \xrightarrow[-HBr]{\text{KOH (alc.)},\ \Delta} \underset{\text{Ethene}}{CH_2=CH_2}$$

$$\xrightarrow{Br_2/CCl_4} \underset{\text{1,2-Dibromoethane}}{BrCH_2CH_2Br} \xrightarrow[\text{KOH (alc.)},\ \Delta]{-HBr} \underset{\text{Bromoethene}}{CH_2=CHBr}$$

(*iii*) $$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Peroxide}]{+HBr} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br} \xrightarrow[-AgBr]{AgNO_2,\ C_2H_5OH/H_2O} \underset{\text{1-Nitropropane}}{CH_3CH_2CH_2NO_2}$$

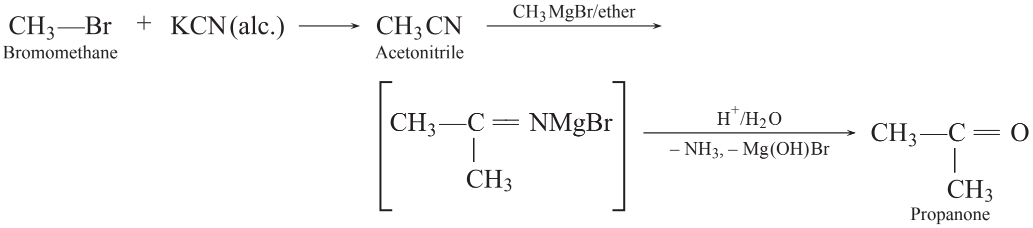
(*iv*)



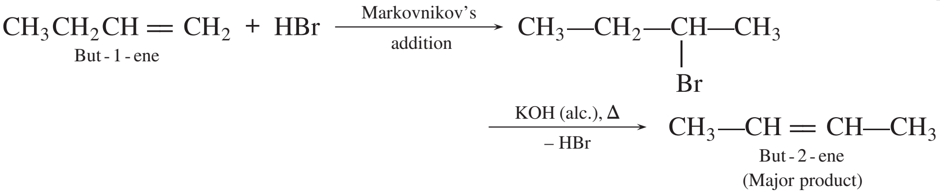
(*v*) 

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\text{1, 2 - Dibromopropane}}{CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}} \xrightarrow[-\,2KBr,\ -\,2H_2O]{KOH\ (alc.),\ \Delta} \underset{\text{Propyne}}{CH_3-C\equiv CH}$$

(*vi*) $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-\,SO_2,\ -\,HCl]{SOCl_2,\ pyridine} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[-\,Hg_2Cl_2]{Hg_2F_2} \underset{\text{Ethyl fluoride}}{CH_3CH_2F}$$

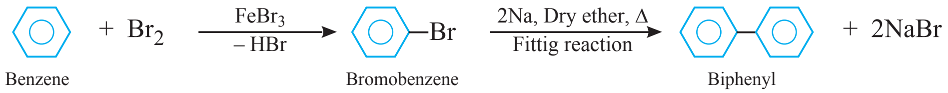
(*vii*) 

$$\underset{\text{Bromomethane}}{CH_3-Br} + KCN(alc.) \longrightarrow \underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow{CH_3MgBr/ether} \left[CH_3-\underset{CH_3}{\underset{|}{C}}=NMgBr\right] \xrightarrow[-\,NH_3,\ -\,Mg(OH)Br]{H^+/H_2O} \underset{\text{Propanone}}{CH_3-\underset{CH_3}{\underset{|}{C}}=O}$$

(*viii*) 

$$\underset{\text{But - 1 - ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\text{addition}]{\text{Markovnikov's}} CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[-\,HBr]{KOH\ (alc.),\ \Delta} \underset{\text{(Major product)}}{\underset{\text{But - 2 - ene}}{CH_3-CH=CH-CH_3}}$$

(*ix*) $$\underset{\text{1 - Chlorobutane}}{2CH_3CH_2CH_2CH_2Cl} + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{n\text{ - octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaCl$$

(*x*) 

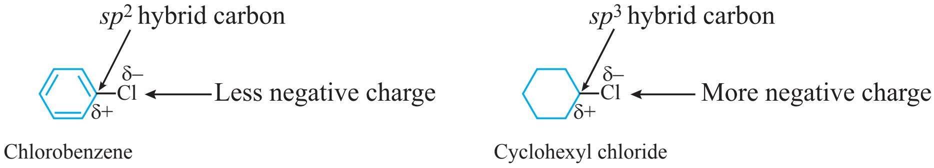
Q. 12. Explain why

(*i*) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

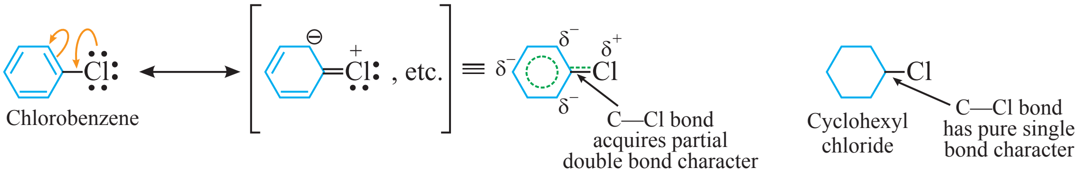
(*ii*) alkyl halides, though polar, are immiscible with water?

(*iii*) Grignard reagents should be prepared under anhydrous conditions?

Ans. (*i*) Due to greater *s*-character, sp^2 hybrid carbon atom is more electronegative than sp^3 hybrid carbon atom. Therefore, the sp^2 hybrid carbon of C–Cl bond in chlorobenzene has less tendency to release electrons to Cl than an sp^3 hybrid carbon of cyclohexyl chloride. As a result, the magnitude of negative charge is less on Cl atom of chlorobenzene than in cyclohexyl chloride.



Further, due to resonance the C—Cl bond in chlorobenzene acquires partial double bond character whereas the bond in cyclohexyl chloride is a pure single bond. In other words, C—Cl bond in chlorobenzene is shorter than in cyclohexyl chloride.



As dipole moment is a product of charge and distance. Therefore, dipole moment of chlorobenzene is less than that of cyclohexyl chloride.

(*ii*) Alkyl halides, though polar, are immiscible in water because they are unable to form hydrogen bonds with water molecules.

(*iii*) Grignard reagents are very reactive. They react with moisture present in the apparatus or the starting materials to give hydrocarbons.

$$\underset{\text{Grignard reagent}}{\overset{\delta-}{R}—\overset{\delta+}{MgX}} + H—OH \longrightarrow R—H + Mg(OH)X$$

Hence, Grignard reagent must be prepared under anhydrous conditions.

Q. 13. Give the uses of Freon-12, DDT, carbon tetrachloride and iodoform.

Ans. Refer to Basic Concepts Point 11.

Q. 14. Write the structure of the major organic product in each of the following reactions:

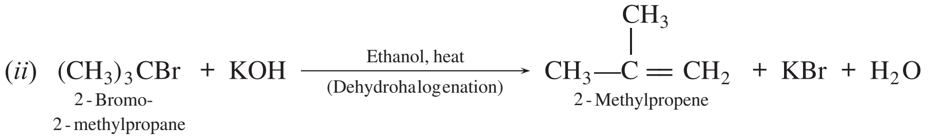
(*i*) $CH_3CH_2CH_2Cl + NaI \xrightarrow{\text{Acetone, heat}}$ **(*ii*)** $(CH_3)_3CBr + KOH \xrightarrow{\text{Ethanol, heat}}$

(*iii*) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{Water}}$ **(*iv*)** $CH_3CH_2Br + KCN \xrightarrow{\text{Aq. ethanol}}$

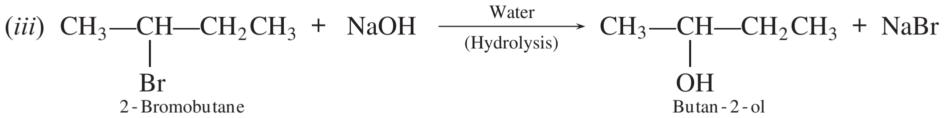
(*v*) $C_6H_5ONa + C_2H_5Cl \longrightarrow$ **(*vi*)** $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(*vii*) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}}$ **(*viii*)** $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow$

Ans. (*i*) $\underset{\text{1 - Chloropropane}}{CH_3CH_2CH_2Cl} + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{Acetone, heat}} \underset{\text{1 - Iodopropane}}{CH_3CH_2CH_2I} + NaCl$



(*ii*) $$\underset{\substack{\text{2 - Bromo-}\\\text{2 - methylpropane}}}{(CH_3)_3CBr} + KOH \xrightarrow[\text{(Dehydrohalogenation)}]{\text{Ethanol, heat}} \underset{\text{2 - Methylpropene}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2} + KBr + H_2O$$



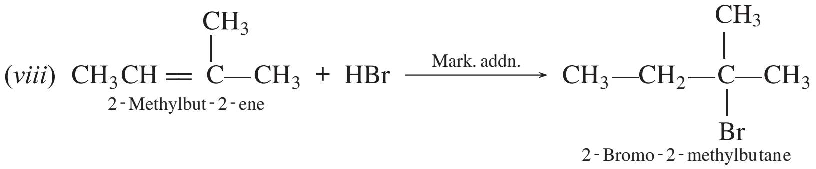
(*iii*) $$\underset{\text{2 - Bromobutane}}{CH_3—\underset{\underset{\displaystyle Br}{|}}{CH}—CH_2CH_3} + NaOH \xrightarrow[\text{(Hydrolysis)}]{\text{Water}} \underset{\text{Butan - 2 - ol}}{CH_3—\underset{\underset{\displaystyle OH}{|}}{CH}—CH_2CH_3} + NaBr$$

(*iv*) $\underset{\text{Bromoethane}}{CH_3CH_2Br} + KCN \xrightarrow[\text{(Nucleophilic substitution)}]{\text{Aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3CH_2CN} + KBr$

(*v*) $\underset{\text{Sod. phenoxide}}{C_6H_5O^-Na^+} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow[\text{synthesis}]{\text{Williamson's}} \underset{\text{Phenetol}}{C_6H_5—O—C_2H_5} + NaCl$

(*vi*) $\underset{\text{Propan - 1 - ol}}{CH_3CH_2CH_2OH} + SOCl_2 \xrightarrow[\text{substitution}]{\text{Nucleophilic}} \underset{\text{1 - Chloropropane}}{CH_3CH_2CH_2Cl} + HCl + SO_2$

(*vii*) $\underset{\text{But - 1 - ene}}{CH_3CH_2CH{=}CH_2} + HBr \xrightarrow[\text{(Anti - Mark. addn.)}]{\text{Peroxide}} \underset{\text{1 - Bromobutane}}{CH_3CH_2CH_2CH_2Br}$



(*viii*) $$\underset{\text{2 - Methylbut - 2 - ene}}{CH_3CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}—CH_3} + HBr \xrightarrow{\text{Mark. addn.}} \underset{\text{2 - Bromo - 2 - methylbutane}}{CH_3—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}—CH_3}$$

Q. 15. Write the mechanism of the following reaction: ***[HOTS]***

$$n\mathbf{BuBr} + \mathbf{KCN} \xrightarrow{\mathbf{EtOH - H_2O}} n\mathbf{BuCN}$$

Ans. The above reaction is an S_N2 reaction.

$$K^+[:C{\equiv}N: \longleftrightarrow :C{=}\ddot{N}:^-]$$

CN^- ion is an ambident nucleophile so it can attack the carbon atom of C—Br bond in *n*–BuBr through C or N. As C—C bond is stronger than C—N bond, therefore attack occurs through C to form *n*–BuCN.

$$\overset{-}{N}CK^+ + CH_3CH_2CH_2\overset{\delta+}{C}H_2\overset{\delta-}{Br} \longrightarrow CH_3CH_2CH_2CH_2CN + KBr$$

Q. 16. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

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(*i*) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane.

(*ii*) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane.

(*iii*) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

Ans. The reactivity in S_N2 reactions depends upon steric hindrance; more the steric hindrance, slower the reaction.

(*i*) Due to steric reasons, the order of reactivity in S_N2 reactions follows the order: 1° > 2° > 3°, therefore, order of reactivity of the given alkyl bromides is as follows:

1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylpentane.

(*ii*) Due to steric reasons, the order of reactivity of alkyl halides in S_N2 reactions follows the order: 1° > 2° > 3°, therefore, the order of reactivity of the given alkyl bromides is as follows:

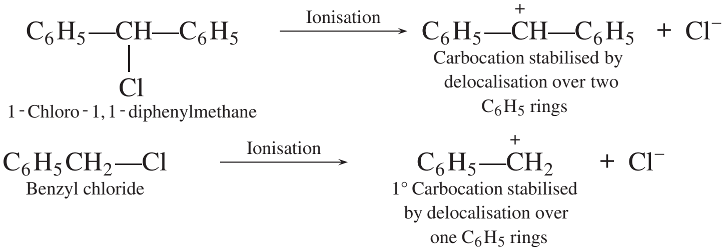
1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane.

(*iii*) As in case of 1° alkyl halides, steric hindrance increases in the order: *n*-alkyl halides, alkyl halide with a substituent at any position other than the β-position, one substituent at the β-position, two substituents at the β-position. Therefore, the reactivity decreases in the same order. Hence, the reactivity of the given alkyl bromides decreases in the order:

1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2, 2-dimethylpropane.

Q. 17. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$ which is more easily hydrolysed by aqueous KOH?

Ans. $C_6H_5CH_2Cl$ is a 1° aralkyl halide while $C_6H_5CHClC_6H_5$ is a 2° aralkyl halide.



$$C_6H_5\text{—}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{—}C_6H_5 \xrightarrow{\text{Ionisation}} C_6H_5\text{—}\overset{+}{C}H\text{—}C_6H_5 + Cl^-$$

1 - Chloro - 1, 1 - diphenylmethane

Carbocation stabilised by delocalisation over two C_6H_5 rings

$$C_6H_5CH_2\text{—}Cl \xrightarrow{\text{Ionisation}} C_6H_5\text{—}\overset{+}{C}H_2 + Cl^-$$

Benzyl chloride

1° Carbocation stabilised by delocalisation over one C_6H_5 rings

In S_N1 reactions the reactivity depends upon the stability of carbocations. Since the carbocation $C_6H_5\overset{+}{C}HC_6H_5$ (where the +ve charge is delocalised over two C_6H_5 rings) derived from $C_6H_5\text{—}CHClC_6H_5$ is more stable than the carbocation, $C_6H_5\overset{+}{C}H_2$ (where +ve charge is delocalised over one C_6H_5 ring) derived from $C_6H_5CH_2Cl$, therefore, $C_6H_5CHClC_6H_5$ gets hydrolysed more easily than $C_6H_5CH_2Cl$ under S_N1 conditions.

Although, under S_N2 conditions, the reactivity depends on steric hindrance, therefore, under S_N2 conditions, $C_6H_5CH_2Cl$ gets hydrolysed more easily than $C_6H_5CHClC_6H_5$.

Q. 18. *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.

Ans. The *p*-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger intermolecular forces of attraction than *o*- and *m*-isomers. As during melting, the crystal lattice breaks, therefore, a larger amount of energy is needed to melt the *p*-isomer than the corresponding *o*-and *m*-isomers. In other words, the melting point of the *p*-isomer is higher than the corresponding *o*- and *m*-isomers.

Q. 19. How the following conversions can be carried out?

(*i*) Propene to propan-1-ol

(*ii*) Ethanol to but-1-yne

(*iii*) 1-Bromopropane to 2-bromopropane

(*iv*) Toluene to benzyl alcohol

(*v*) Benzene to 4-bromonitrobenzene

(*vi*) Benzyl alcohol to 2-phenylethanoic acid

(*vii*) Ethanol to propanenitrile

(*viii*) Aniline to chlorobenzene

(*ix*) 2-Chlorobutane to 3, 4-dimethylhexane

(*x*) 2-Methyl-1-propene to 2-chloro-2-methylpropane

(*xi*) Ethyl chloride to propanoic acid

(*xii*) But-1-ene to *n*-butyliodide

(*xiii*) 2-Chloropropane to 1-propanol **(*xiv*) Isopropyl alcohol to iodoform**

(*xv*) Chlorobenzene to *p*-nitrophenol **(*xvi*) 2-Bromopropane to 1-bromopropane**

(*xvii*) Chloroethane to butane **(*xviii*) Benzene to diphenyl**

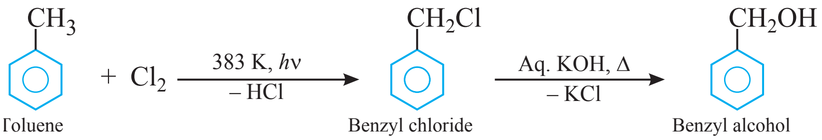
(*xix*) tert-Butyl bromide to isobutyl bromide **(*xx*) Aniline to phenylisocyanide**

Ans. (*i*) $$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{(Anti-Mark. addn.)}]{\text{+ HBr, Peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{Hydrolysis}]{\text{aq. KOH, heat}} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$$

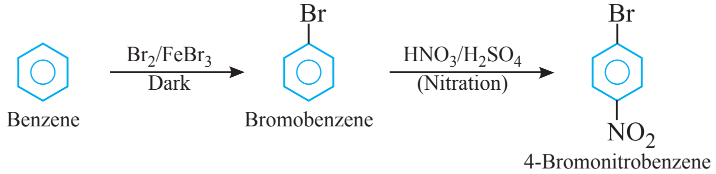
(*ii*) $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Pyridine}]{+\,SOCl_2} CH_3CH_2Cl \xrightarrow[\text{NaNH}_2\text{, liq. NH}_3\text{, 196 K}]{+CH\equiv CH} \underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH}$$

(*iii*) $$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc.), heat}} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{Mark. addn.}]{\text{HBr}} \underset{\text{2-Bromopropane}}{CH_3CHBrCH_3}$$

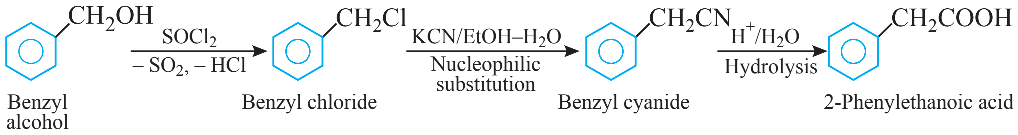
(*iv*)



(*v*)

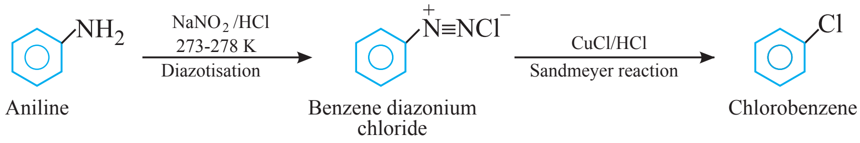


(*vi*)

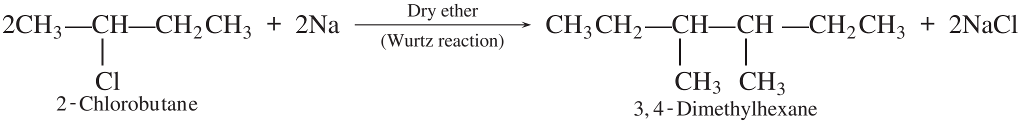


(*vii*) $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{P/I}_2\text{, Heat}} \underset{\text{1-Iodoethane}}{CH_3CH_2I} \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN. EtOH – H}_2\text{O}} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$$

(*viii*)



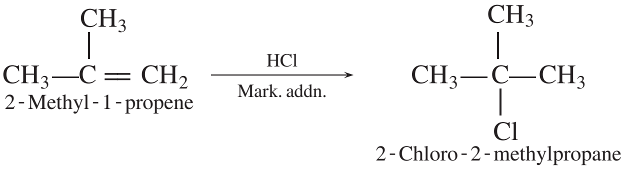
(*ix*)



$$2CH_3-\underset{\underset{\text{Cl}}{|}}{CH}-CH_2CH_3 + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + 2NaCl$$

2-Chlorobutane 3, 4-Dimethylhexane

(*x*)



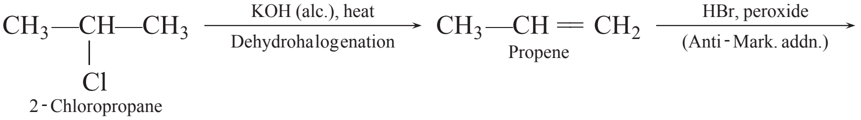
$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Mark. addn.}]{\text{HCl}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

2-Methyl-1-propene 2-Chloro-2-methylpropane

(*xi*) $$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN, EtOH – H}_2\text{O}} \underset{\text{Propanenitrile}}{CH_3CH_2CN} \xrightarrow[\text{Hydrolysis}]{H^+/H_2O} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

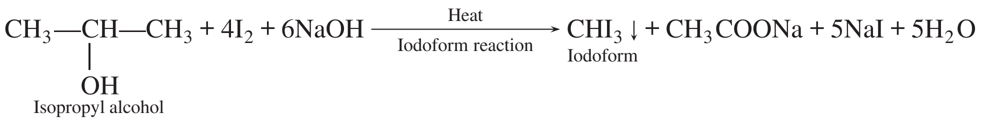
(*xii*) $$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{Anti-Mark. addn.}]{\text{HBr/RCOOR}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{Finkelstein reaction}]{\text{NaI, acetone}} \underset{n\text{-Butyl iodide}}{CH_3CH_2CH_2CH_2I}$$

(*xiii*)

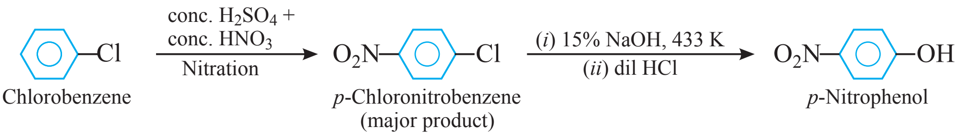


$$\underset{\text{2-Chloropropane}}{CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3} \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH (alc.), heat}} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{(Anti-Mark. addn.)}]{\text{HBr, peroxide}}$$

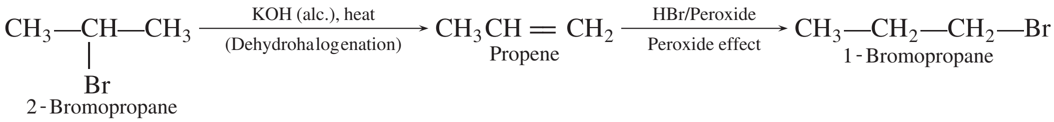
$$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KOH }(aq)\text{, }\Delta} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$$

(*xiv*) 

$$\underset{\text{Isopropyl alcohol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow[\text{Iodoform reaction}]{\text{Heat}} \underset{\text{Iodoform}}{CHI_3\downarrow} + CH_3COONa + 5NaI + 5H_2O$$

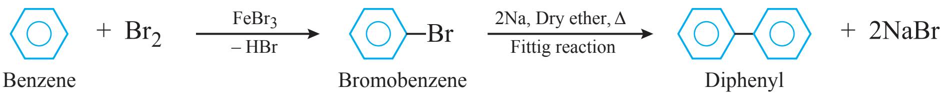
(*xv*) 

Chlorobenzene *p*-Chloronitrobenzene (major product) *p*-Nitrophenol

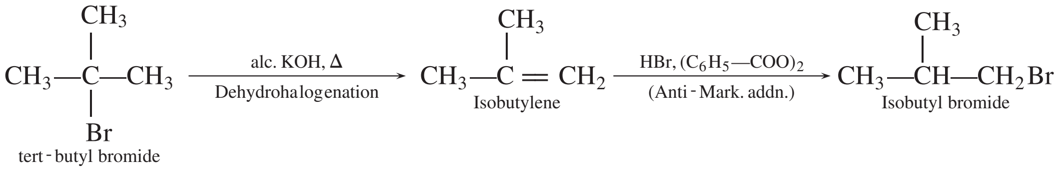
(*xvi*) 

$$\underset{\text{2-Bromopropane}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc.), heat}} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{Peroxide effect}]{\text{HBr/Peroxide}} \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

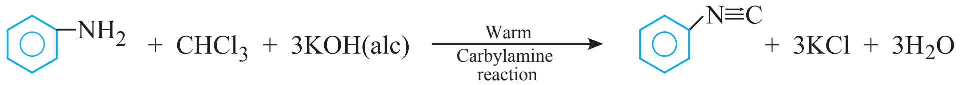
(*xvii*) $\underset{\text{Chloroethane}}{2CH_3CH_2Cl} + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether, heat}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaCl$

(*xviii*) 

Benzene Bromobenzene Diphenyl

(*xix*) 

$$\underset{\text{tert-butyl bromide}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3} \xrightarrow[\text{Dehydrohalogenation}]{\text{alc. KOH, }\Delta} \underset{\text{Isobutylene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} \xrightarrow[\text{(Anti-Mark. addn.)}]{\text{HBr, }(C_6H_5-COO)_2} \underset{\text{Isobutyl bromide}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Br}$$

(*xx*) 

Aniline Chloroform Phenylisocyanide

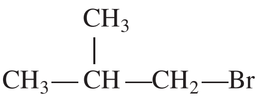
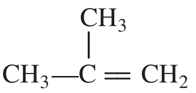
Q. 20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are major products. Explain. **[*HOTS*]**

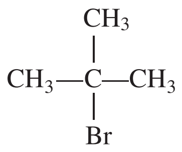
Ans. In aqueous solution, KOH is almost completely ionised to give OH^- ions which being a strong nucleophile brings about a substitution reaction on alkyl halides to form alcohols. In the aqueous solution, OH^- ions are highly hydrated. This reduces the basic character of OH^- ions which fail to abstract a hydrogen from the β-carbon of the alkyl chloride to form an alkene.

On the other hand, an alcoholic solution of KOH contains alkoxide (OR^-) ions which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

Q. 21. Primary alkyl halide C_4H_9Br (*a*) reacted with alcoholic KOH to give compound (*b*). Compound (*b*) is reacted with HBr to give (*c*) which is an isomer of (*a*). When (*a*) is reacted with sodium metal, it gives compound (*d*), C_8H_{18} which is different from the compound formed when *n*-butyl bromide is reacted with sodium. Give the structural formula of (*a*) and write the equations for all the reactions. **[*HOTS*]**

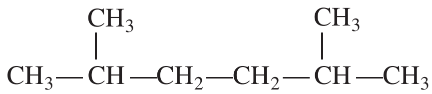
Ans.

Compound	Structural Formula	Name
(*a*)	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-Br$	1-Bromo-2-methylpropane
(*b*)	 $CH_3-\overset{\overset{CH_3}{\vert}}{C}=CH_2$	2-Methylprop-1-ene

(*c*) 

$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle Br}{|}}{C}}}-CH_3}$$

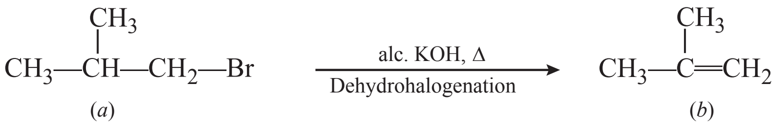
2-Bromo-2-methylpropane

(*d*) 

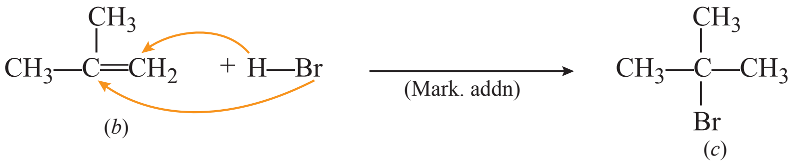
$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3}$$

2, 5-Dimethylhexane

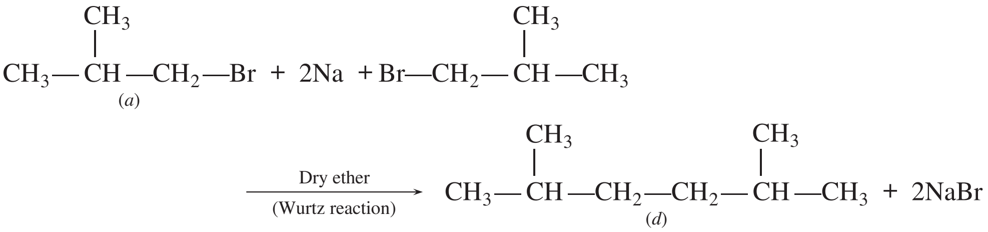
Equations of the Reactions:



$$\underset{(a)}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-Br}} \xrightarrow[\text{Dehydrohalogenation}]{\text{alc. KOH, }\Delta} \underset{(b)}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2}}$$



$$\underset{(b)}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2}} + \mathrm{H-Br} \xrightarrow[\text{(Mark. addn)}]{} \underset{(c)}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle Br}{|}}{C}}}-CH_3}}$$



$$\underset{(a)}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-Br}} + 2\mathrm{Na} + \mathrm{Br-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3}$$

$$\xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{(d)}{\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3}} + 2\mathrm{NaBr}$$

Q. 22. What happens when

(*i*) *n*-butyl chloride is treated with alcoholic KOH,

(*ii*) bromobenzene is treated with Mg in the presence of dry ether,

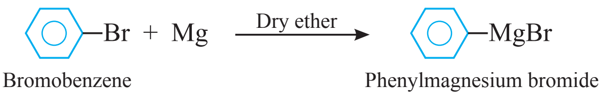
(*iii*) chlorobenzene is subjected to hydrolysis,

(*iv*) ethyl chloride is treated with aqueous KOH,

(*v*) methyl bromide is treated with sodium in the presence of dry ether,

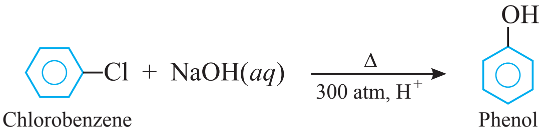
(*vi*) methyl chloride is treated with KCN?

Ans. (*i*) $\underset{n\text{-Butyl chloride}}{\mathrm{CH_3CH_2CH_2CH_2Cl}} + \mathrm{KOH(alc.)} \xrightarrow[\text{(Dehydrohalogenation)}]{\Delta} \underset{\text{But-1-ene}}{\mathrm{CH_3CH_2CH=CH_2}} + \mathrm{KCl} + \mathrm{H_2O}$

(*ii*) 

Bromobenzene

Phenylmagnesium bromide

(*iii*) 

Chlorobenzene

Phenol

(*iv*) $\underset{\text{Ethyl chloride}}{\mathrm{CH_3CH_2Cl}} + \mathrm{KOH}\,(aq) \xrightarrow[\Delta]{\text{Hydrolysis}} \underset{\text{Ethyl alcohol}}{\mathrm{CH_3CH_2-OH}} + \mathrm{KCl} + \mathrm{H_2O}$

(*v*) $\underset{\text{Methyl bromide}}{\mathrm{CH_3Br}} + 2\mathrm{Na} + \mathrm{BrCH_3} \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{\text{Ethane}}{\mathrm{CH_3CH_3}} + 2\mathrm{NaBr}$

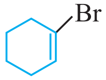
(*vi*) $\underset{\text{Methyl chloride}}{\mathrm{CH_3Cl}} + \mathrm{KCN} \xrightarrow[\text{(Nucleophilic substitution)}]{\mathrm{EtOH-H_2O},\,\Delta} \underset{\substack{\text{Methyl cyanide}\\\text{(Major product)}}}{\mathrm{CH_3C\equiv N}} + \mathrm{KCl}$

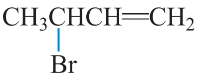
Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Which of the following is vinylic halide?

(*a*) $CH_3CH{=}CHCH_2Br$ (*b*) 

(*c*) 

(*d*) 

$CH_3\underset{\underset{Br}{|}}{C}HCH{=}CH_2$

2. The position of Br in the compound in $CH_3CH{=}CHC(Br)(CH_3)_2$ can be classified as __________. [*NCERT Exemplar*]

(*a*) Allyl (*b*) Aryl (*c*) Vinyl (*d*) Secondary

3. Which of the following is an example of vic-dihalide? [*NCERT Exemplar*]

(*a*) Dichloromethane (*b*) 1,2-dichloroethane

(*c*) Ethylidene chloride (*d*) Allyl chloride

4. Ethylidene chloride is a/an __________. [*NCERT Exemplar*]

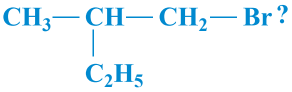
(*a*) vic-dihalide (*b*) gem-dihalide

(*c*) allylic halide (*d*) vinylic halide

5. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds. [*NCERT Exemplar*]

(*a*) 2-Bromopentane (*b*) Vinyl chloride (chloroethene)

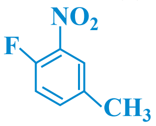
(*c*) 2-Chloroacetophenone (*d*) Trichloromethane

6. Which is the correct IUPAC name for  [*NCERT Exemplar*]

$CH_3-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-Br$?

(*a*) 1-Bromo-2-ethylpropane (*b*) 1-Bromo-2-ethyl-2-methylethane

(*c*) 1-Bromo-2-methylbutane (*d*) 2-Methyl-1-bromobutane

7. The IUPAC name of the compound  **is:**

(*a*) 4-fluoro-1-methyl-3-nitrobenzene (*b*) 1-fluoro-4-methyl-2-nitrobenzene

(*c*) 2-fluoro-5-methyl-1-nitrobenzene (*d*) 4-methyl-1-fluoro-2-nitrobenzene

8. Which of the following is most preferred to prepare alkylchloride from alcohol?

(*a*) Concentrated HCl (*b*) $SOCl_2$ (*c*) PCl_5 (*d*) PCl_3

9. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements. [*NCERT Exemplar*]

(*a*) Both the compounds form same product on treatment with alcoholic KOH.

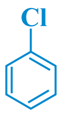
(*b*) Both the compounds form same product on treatment with aq. NaOH.

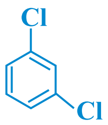
(*c*) Both the compounds form same product on reduction.

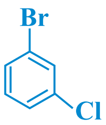
(*d*) Both the compounds are optically active.

10. Arrange the following compounds in the increasing order of their densities. [*NCERT Exemplar*]

(*i*) 

(*ii*) 

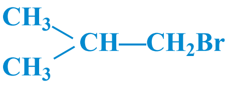
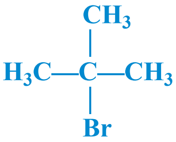
(*iii*) 

(*iv*) 

(*a*) (*i*) < (*ii*) < (*iii*) < (*iv*) (*b*) (*i*) < (*iii*) < (*iv*) < (*ii*)

(*c*) (*iv*) < (*iii*) < (*ii*) < (*i*) (*d*) (*ii*) < (*iv*) < (*iii*) < (*i*)

11. Arrange the following compounds in increasing order of their boiling points. [*NCERT Exemplar*]

(*i*)  **(*ii*)** $CH_3CH_2CH_2CH_2Br$ **(*iii*)** 

$H_3C{-}C(CH_3)(Br){-}CH_3$

(*a*) (*ii*) < (*i*) < (*iii*)
(*b*) (*i*) < (*ii*) < (*iii*)
(*c*) (*iii*) < (*i*) < (*ii*)
(*d*) (*iii*) < (*ii*) < (*i*)

12. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction? [*NCERT Exemplar*]

(*a*) Cl^-
(*b*) Cl^+
(*c*) $AlCl_3$
(*d*) $[AlCl_4]^-$

13. Which reagent will you use for the following reaction? [*NCERT Exemplar*]

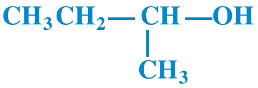
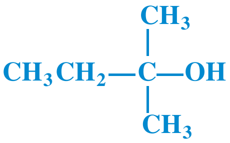
$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(*a*) Cl_2 / UV light
(*b*) $NaCl + H_2SO_4$
(*c*) Cl_2 gas in dark
(*d*) Cl_2 gas in the presence of iron in dark

14. The reagents for the following conversion is/are

(*a*) Zn/CH_3OH
(*b*) alcoholic KOH followed by $NaNH_2$
(*c*) aqueous KOH followed by $NaNH_2$
(*d*) alcoholic KOH

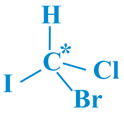
15. The order of reactivity of following alcohols with halogen acids is ___________. [*NCERT Exemplar*]

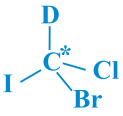
(A) $CH_3{-}CH_2{-}CH_2{-}OH$ **(B)**  **(C)** 

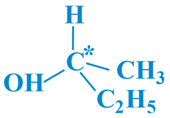
(B) $CH_3CH_2{-}CH(CH_3){-}OH$ (C) $CH_3CH_2{-}C(CH_3)_2{-}OH$

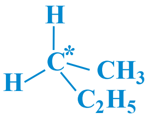
(*a*) (A) > (B) > (C)
(*b*) (C) > (B) > (A)
(*c*) (B) > (A) > (C)
(*d*) (A) > (C) > (B)

16. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric? [*NCERT Exemplar*]


(*i*)

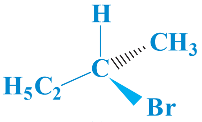

(*ii*)

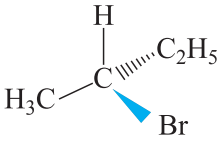

(*iii*)

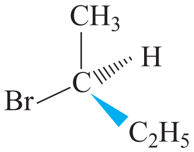

(*iv*)

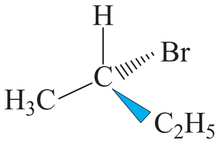
(*a*) (*i*), (*ii*), (*iii*), (*iv*)
(*b*) (*i*), (*ii*), (*iii*)
(*c*) (*ii*), (*iii*), (*iv*)
(*d*) (*i*), (*iii*), (*iv*)

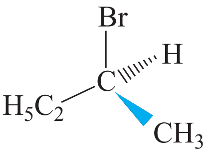
17. Which of the following structures is enantiomeric with the molecule (A) given below: [*NCERT Exemplar*]


(A)

(*a*) 

(*b*) 

(*c*) 

(*d*) 

18. Two possible stereo-structure of CH_3—CH(OH)COOH which are optically active are called
(*a*) mesomers (*b*) enantiomers (*c*) diastereomers (*d*) atropisomers

19. Alkyl halides undergoing nucleophilic bimolecular substitution involve
(*a*) retention of configuration (*b*) racemic mixture
(*c*) inversion of configuration (*d*) formation of carbocation

20. Which of the following alkyl halides will undergo S_N1 reaction most readily? [*NCERT Exemplar*]
(*a*) $(CH_3)_3C—F$ (*b*) $(CH_3)_3C—Cl$ (*c*) $(CH_3)_3C—Br$ (*d*) $(CH_3)_3C—I$

21. For the following (*i*) $I^{\ominus}$, (*ii*) $Cl^{\ominus}$, (*iii*) $Br^{\ominus}$, the increasing order of nucleophilicity would be:
(*a*) $I^{\ominus} < Br^{\ominus} < Cl^{\ominus}$ (*b*) $Br^{\ominus} < Cl^{\ominus} < I^{\ominus}$ (*c*) $Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$ (*d*) $I^{\ominus} < Cl^{\ominus} < Br^{\ominus}$

22. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is ________________. [*NCERT Exemplar*]
(*a*) Electrophilic elimination reaction (*b*) Electrophilic substitution reaction
(*c*) Free radical addition reaction (*d*) Nucleophilic substitution reaction

Answers

1. (*c*) **2.** (*a*) **3.** (*b*) **4.** (*b*) **5.** (*a, d*) **6.** (*c*) **7.** (*b*) **8.** (*b*) **9.** (*a, c*) **10.** (*a*)
11. (*c*) **12.** (*b*) **13.** (*a*) **14.** (*b*) **15.** (*b*) **16.** (*b*) **17.** (*a*) **18.** (*b*) **19.** (*c*) **20.** (*d*)
21. (*c*) **22.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion (A)** : Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.
Reason (*R*) : Phosphorus chlorides give pure alkyl halides.

2. **Assertion (*A*)** : The boiling points of alkyl halides decrease in the order:
RI > RBr > RCl > RF
Reason (*R*) : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

3. **Assertion (*A*)** : KCN reacts with methyl chloride to give methyl isocyanide
Reason (*R*) : CN^- is an ambident nucleophile.

4. **Assertion (*A*)** : *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.
Reason (*R*) : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

5. **Assertion (*A*)** : Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.
Reason (*R*) : This reaction proceeds through the formation of a carbocation.

6. **Assertion (*A*)** : 3° alkyl halides are most reactive towards S_N1 reaction.
Reason (*R*) : In S_N1 reaction, the rate of the reaction depends only on the concentration of alkyl halide.

7. **Assertion (*A*)** : Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.
Reason (*R*) : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

8. **Assertion (*A*) :** Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene.
Reason (*R*) : —NO_2 group is a *m*-directing group.

9. **Assertion (*A*) :** It is difficult to replace chlorine by –OH in chlorobenzene in comparison to that in chloroethane.
Reason (*R*) : Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

10. **Assertion (*A*) :** In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.
Reason (*R*) : Halogen atom is a ring deactivator.

11. **Assertion (*A*) :** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
Reason (*R*) : Oxidising agent oxidises I_2 into HI.

Answers

1. (*b*) **2.** (*b*) **3.** (*d*) **4.** (*a*) **5.** (*c*) **6.** (*b*) **7.** (*a*) **8.** (*d*) **9.** (*a*) **10.** (*b*) **11.** (*c*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

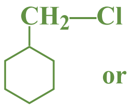
PASSAGE–1

The polarity of C—X bond is responsible for the nucleophilic substitution reactions of alkyl halides which mostly occur by S_N1 and S_N2 mechanisms. The rates of S_N1 reaction are governed by the stability of intermediate carbocations while that of S_N2 reactions are governed by steric factors. Chirality has a great role in understanding the mechanism of S_N1 and S_N2 reactions. S_N1 reactions of chiral alkyl halides are accompanied by racemisation. Whereas S_N2 reactions are characterised by inversion of configuration.

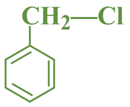
1. What do you mean by chirality?

Ans. The objects which are non-superimposable on their mirror images are called chiral and the property is known as chirality.

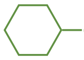
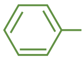
2. Which of the following compounds would undergo S_N1 reaction faster and why?



or



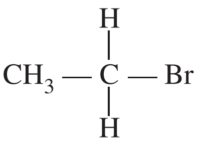
OR

Out of  **—CH_2Cl and**  **—CH_2—Cl, which will react faster in S_N1 reaction with OH?**
[*CBSE 2020 (56/4/2)*]

Ans. Benzyl chloride undergoes S_N1 reaction faster than cyclohexyl methyl chloride because in case of benzyl chloride, the carbocation formed after the loss of Cl^- is stabilised by resonance, whereas, no such stabilisation is possible in the carbocation obtained from cyclohexyl methyl chloride.

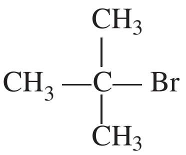
3. In the pair, $(CH_3)_3$ C—Br and CH_3—CH_2—Br, which one is more reactive towards S_N2 reaction and why?

Ans.



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-Br$$

Carbon carrying Br atom is attached to one methyl group, less steric hindrance, more reactive.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br$$

Carbon carrying Br atom is attached to three bigger methyl groups, more steric hindrance, less reactive.

4. What is meant by the term racemic mixture?

Ans. An equimolar mixture of a pair of enantiomers is known as racemic mixture.

5. Predict the order of reactivity of the four isomeric bromobutanes in S_N1 and S_N2 reactions.

Ans. $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_N1)

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_N2)

Of the two primary bromides, the carbocation intermediate derived from $(CH_3)_2CHCH_2Br$ is more stable than that derived from $CH_3CH_2CH_2CH_2Br$ because of greater electron donating inductive effect of $(CH_3)_2CH$ group. So, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 reactions. $CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Thus, the above order is followed in S_N1. The reactivity in S_N2 reactions follows the reverse order as the steric hindrance around the electrophilic carbon increases in that order.

PASSAGE–2

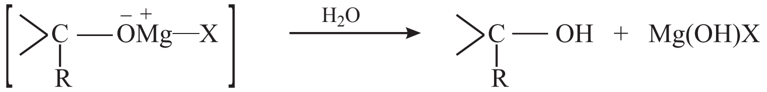
Grignard reagents are alkyl magnesium halides. Due to large electronegativity difference between carbon and magnesium, the carbon-magnesium bond has significant ionic character. The hydrocarbon part of the Grignard reagents acts as a source of carbanions. Therefore, Grignard reagents readily undergo nucleophilic addition reactions to aldehydes and ketones forming the addition products which upon hydrolysis yield alcohols.

1. Give the mechanism of addition of Grignard reagent to carbonyl compound forming an alcohol.

Ans. **Step I:** Nucleophilic addition of Grignard reagent to carbonyl group.

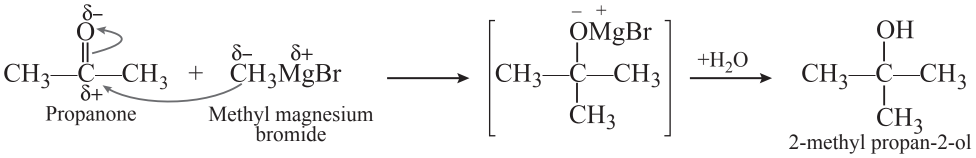
Adduct

Step II: Hydrolysis



2. How will you convert propanone to 2–methylpropan-2-ol?

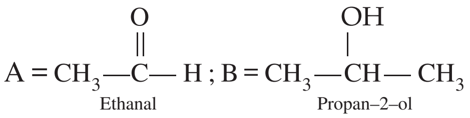
Ans.



3. Write the structures of A and B in the following reactions:

$$CH_3—CH_2—OH \xrightarrow[573\text{ K}]{Cu} A \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} B$$

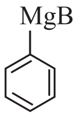
Ans.



$$A = CH_3—\overset{\overset{\displaystyle O}{\|}}{C}— H \;;\; B = CH_3—\overset{\overset{\displaystyle OH}{|}}{CH}— CH_3$$

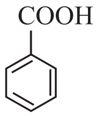
4. Complete the following:

Ans.



Phenyl Magnesium bromide

and



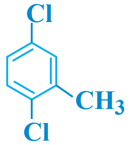
Benzoic acid

5. What will be the product formed when chlorobenzene reacts with magnesium in presence of dry ether?

Ans. Phenyl magnesium chloride (Grignard reagent)

Very Short Answer Questions [1 mark]

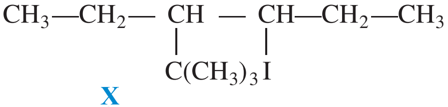
Q. 1. Write the IUPAC name of the following compound: *[CBSE (AI) 2013]*



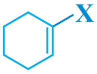
Ans. 2, 5-Dichlorotoluene/1,4-Dichloro-3-methylbenzene.

Q. 2. Draw the structure of the compound, 4-tert-butyl-3-iodoheptane.

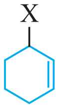
Ans.



$$CH_3{-}CH_2{-}\underset{\displaystyle C(CH_3)_3}{\underset{|}{CH}}{-}\underset{\displaystyle I}{\underset{|}{CH}}{-}CH_2{-}CH_3$$

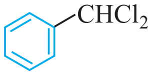
Q. 3. Out of  **and**  **, which is an example of allylic halide?** *[CBSE (AI) 2017]*

Ans.



Q. 4. Out of  **and**  **, which is an example of a benzylic halide?** *[CBSE (AI) 2017]*

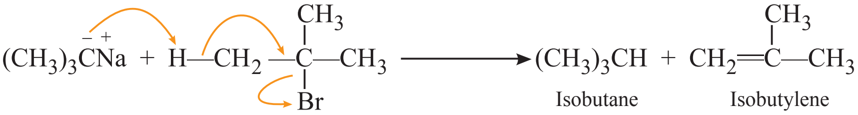
Ans.



Q. 5. Wurtz reaction fails in case of tert-alkyl halides. Why? *[HOTS]*

Ans. This is because tert-alkyl halides prefer to undergo dehydrohalogenation in the presence of sodium metal instead of undergoing Wurtz reaction.

$$\underset{\text{tert-Butyl bromide}}{(CH_3)_3C{-}Br} + 2Na \xrightarrow{-NaBr} \underset{\text{tert-Butyl sodium}}{(CH_3)_3\overset{-\ +}{C}Na}$$

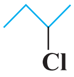


$$(CH_3)_3\overset{-\ +}{C}Na + H{-}CH_2{-}\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH_3 \longrightarrow \underset{\text{Isobutane}}{(CH_3)_3CH} + \underset{\text{Isobutylene}}{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3}$$

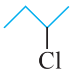
Q. 6. What happens when bromine attacks $CH_2{=}CH{-}CH_2{-}C{\equiv}CH$? *[CBSE (AI) 2012]*

Ans. The reddish brown colour of bromine is discharged.

Q. 7. Identify the chiral molecule in the following pair: *[CBSE (AI) 2014]*



Ans.



Q. 8. Out of chlorobenzene and cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why? *[CBSE 2019 (56/2/1)]*

Ans. Cyclohexyl chloride is more reactive than chlorobenzene towards nucleophilic substitution reactions. Due to resonance the C–Cl bond in chlorobenzene acquires partial double bond character which makes the substitution of chlorine more difficult in chlorobenzene than in cyclohexyl chloride where the C–Cl bond has pure single bond character.

Q. 9. Why is *t*-butyl bromide more reactive towards S_N1 reaction as compared to *n*-butyl bromide? *[CBSE 2019 (56/4/1)]*

Ans. Due to higher stability of tertiary carbocation than primary carbocation.

Q. 10. Give one chemical test to distinguish between C_2H_5Br and C_6H_5Br.

Ans. Hydrolysis of C_2H_5Br with aqueous KOH followed by acidification with dil. HNO_3 and subsequent treatment with $AgNO_3$ gives light yellow ppt. of AgBr whereas C_6H_5Br does not give this test.

Q. 11. Give reason: Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out. *[CBSE Delhi 2010]*

Ans. This is because chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas phosgene.

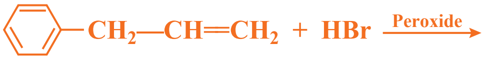
$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \xrightarrow{\text{Light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Short Answer Questions–I [2 marks]

Q. 1. Draw the structure of major monohalo product in each of the following reactions:

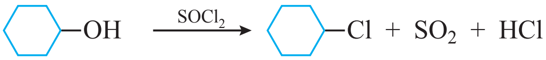
(i)

(ii)

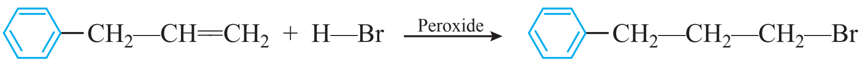


[CBSE Delhi 2014]

Ans. (*i*)



(*ii*)



Q. 2. Which one of the following compounds is more easily hydrolysed by KOH and why?

$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$ *[CBSE (AI) 2012]*

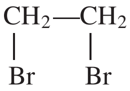
Ans. Due to +I effect of alkyl groups, the 2° carbonium ion $CH_3—\overset{+}{C}H—CH_2—CH_3$ derived from sec. butyl chloride is more stable than the 1° carbonium ion $CH_3—CH_2—\overset{+}{C}H_2$ derived from *n*-propyl chloride. Therefore sec. butyl chloride gets hydrolysed more easily than *n*-propyl chloride under S_N1 conditions.

Q. 3. How the following conversion can be carried out? *[HOTS]*

Ethanol to But-2-yne

Ans.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{+SOCl_2} \underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc.), heat}} \underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow[\text{Electrophilic addition}]{Br_2/CCl_4}$$



$$\underset{Br}{\underset{|}{CH_2}}—\underset{Br}{\underset{|}{CH_2}} \xrightarrow[196\text{ K}]{NaNH_2 \text{ in liq. } NH_3} HC \equiv CH \xrightarrow[196\text{ K}]{NaNH_2 \text{ in liq. } NH_3} \underset{\text{Disodium acetylide}}{Na^+C^- \equiv C^-Na^+}$$

$$\xrightarrow{CH_3Cl \text{ (excess)}} \underset{\text{But-2-yne}}{CH_3—C \equiv C—CH_3}$$

Q. 4. Give reasons for the following:

(*i*) Chloroethane is insoluble in water.

(*ii*) Thionyl chloride method is preferred for preparing alkyl chlorides from alcohols.

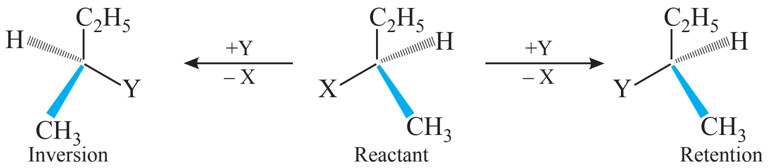
[CBSE 2019 (56/4/1)]

Ans. (*i*) Chloroethane is unable to form hydrogen bonds with water. Hence, it is insoluble in water.

(*ii*) The byproducts of the reaction, *i.e.*, SO_2 and HCl being gases escape into the atmosphere leaving behind alkyl chlorides in almost pure state.

Q. 5. Differentiate between retention and inversion.

Ans. If the relative configuration of the atoms/groups around a chiral centre in an optically active molecule remains the same before and after the reaction, the reaction is said to proceed with retention of configuration. On the other hand, if the relative configuration of the atoms/groups around a stereocentre in the product is opposite to that in the reactant, the reaction is said to proceed with inversion of configuration. For example,

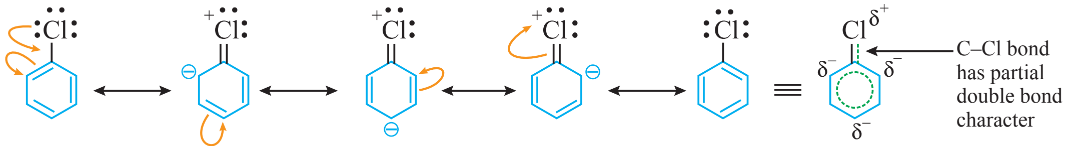


Q. 6. Give reasons: **[*CBSE Delhi 2016*]**

(*i*) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in CH_3—Cl.

(*ii*) S_N1 reactions are accompanied by racemisation in optically active alkyl halides.

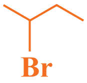
Ans. (*i*) In chlorobenzene, C—Cl bond acquires partial double bond character while in methyl chloride, C—Cl bond has pure single bond character. As a result C—Cl bond in chlorobenzene is shorter than methyl chloride.



(*ii*) Carbocations are intermediate in S_N1 reactions. Carbocations being sp^2 hybridised are planar species, therefore, attack of nucleophile on it can occur from both front and rear with almost equal ease giving a racemic mixture.

Q. 7. (*i*) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(*a*)

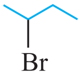


(*b*)

(*ii*) Out of S_N1 and S_N2, which reaction occurs with

(*a*) Inversion of configuration

(*b*) Racemisation **[*CBSE Delhi 2014*]**

Ans. (*i*) , 2-bromobutane is a chiral molecule.

, primary halides undergo faster S_N2 reactions than secondary halides due to less steric hinderance.

(*ii*) (*a*) S_N2 reaction occurs with inversion of configuration.

(*b*) S_N1 reaction occurs with racemisation.

Q. 8. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

$C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Ans. $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1).

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2).

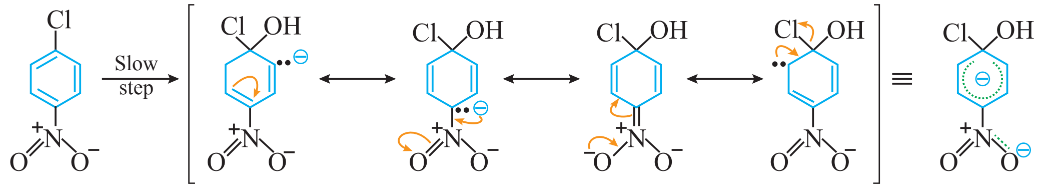
Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than that obtained from $C_6H_5CH(CH_3)Br$ because it is stabilised by two phenyl groups due to resonance. Hence, the former bromide is more reactive than the latter in S_N1 reaction. Phenyl group is bulkier than a methyl group. Thus, $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 reactions.

Q. 9. Give reasons for the following:

(*i*) *p*-nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well.

(*ii*) Iodoform is obtained by reaction of acetone with hypoiodite ion but not iodide ion.

Ans. (*i*) In *p*-nitrochlorobenzene a carbanion intermediate is formed. This is stabilised by resonance as shown below.



The –I effect of nitro group further stabilises the intermediate. Hence, *p*-nitrochlorobenzene reacts faster than chlorobenzene.

(*ii*) Hypoiodite ion can act as an oxidising agent while iodide ion does not.

Q. 10. How will you distinguish between the following pairs of compounds: [*CBSE Sample Paper 2014*]

(*i*) Chloroform and carbon tetrachloride.

(*ii*) Benzyl chloride and chlorobenzene.

Ans. (*i*) On heating chloroform and carbon tetrachloride with aniline and ethanolic potassium hydroxide separately chloroform forms pungent smelling isocyanide but carbon tetrachloride does not form this compound.

$$C_6H_5NH_2 + CHCl_3 + 3KOH\,(\text{ethanolic}) \xrightarrow{\Delta} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

(*ii*) On adding sodium hydroxide and silver nitrate to both the compounds benzyl chloride forms white precipitate but chlorobenzene does not form white precipitate.

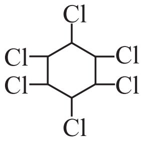
$$C_6H_5CH_2Cl + NaOH \longrightarrow C_6H_5CH_2OH + NaCl$$

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl(s)} + NaNO_3$$

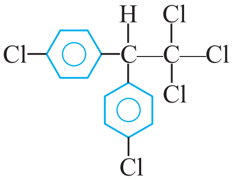
Q. 11. Give the structural formula and IUPAC name of the following compounds:

(*i*) BHC **(*ii*) DDT**

Ans. (*i*) BHC (*ii*) DDT



1,2,3,4,5,6-Hexachloro cyclohexane

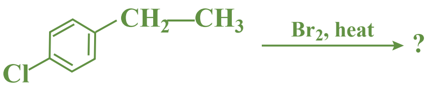


1,1'-(2,2,2-trichloroethane-1,1-diyl) bis(4-chlorobenzene)

Short Answer Questions–II [3 marks]

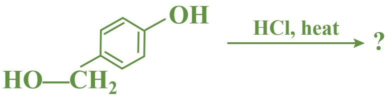
Q. 1. Draw the structures of the major monohalo product for each of the following reactions:

(*i*)



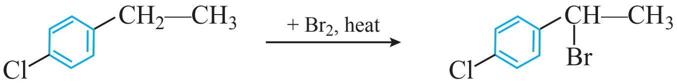
(*ii*)

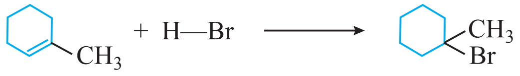
(*iii*)

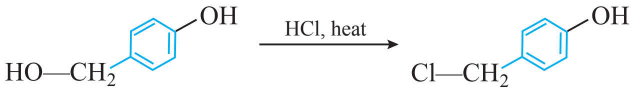


[*CBSE (F) 2017*]

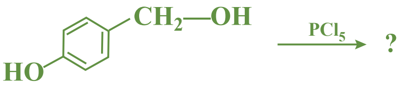
Ans. (*i*)



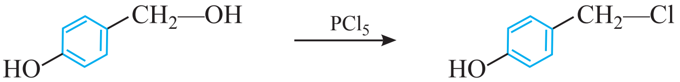
(*ii*) 

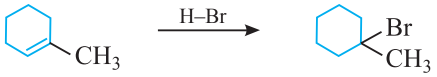
(*iii*) 

Q. 2. Write the major product(s) in the following reactions:

(*i*)  **(*ii*)** 

(*iii*) $\mathbf{CH_3CH_2Cl \xrightarrow{KNO_2} ?}$ **[*CBSE (F) 2016*]**

Ans. (*i*) 

(*ii*) 

(*iii*) $CH_3—CH_2—Cl \xrightarrow{KNO_2} CH_3—CH_2—ONO$

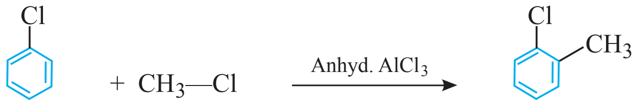
Q. 3. How do you convert the following: **[*CBSE Panchkula 2015*]**

(*i*) Prop-1-ene to 1-fluoropropane

(*ii*) Chlorobenzene to 2-chlorotoluene

(*iii*) Ethanol to propanenitrile

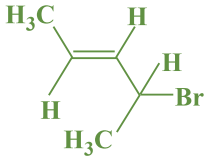
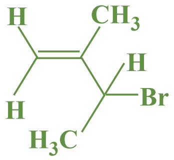
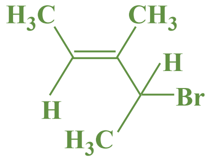
Ans. (*i*) $\underset{\text{Prop-1-ene}}{CH_3—CH=CH_2} \xrightarrow[(C_6H_5COO)_2]{+\,HBr} CH_3—CH_2—CH_2—Br \xrightarrow[\Delta]{AgF} \underset{\text{1-Fluoropropane}}{CH_3—CH_2—CH_2—F}$

(*ii*) 

Chlorobenzene Chloromethane 2-Chlorotoluene

(*iii*) $\underset{\text{Ethanol}}{CH_3—CH_2—OH} \xrightarrow{+\,PCl_5} CH_3—CH_2—Cl \xrightarrow{\text{Alk. KCN}} \underset{\text{Propanenitrile}}{CH_3—CH_2—C\equiv N}$

Q. 4. Write IUPAC names of the following: **[*CBSE (AI) 2011*]**

(*i*)  **(*ii*)**  **(*iii*)** 

Ans. (*i*) 4-Bromopent-2-ene (*ii*) 3-Bromo-2-methylbut-1-ene

(*iii*) 4-Bromo-3-methylpent-2-ene

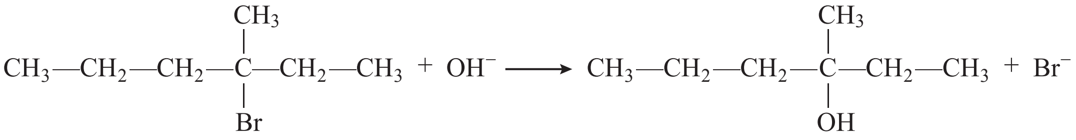
Q. 5. (*i*) Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(*ii*) An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give a racemic mixture of products. Write the mechanism involved in this reaction.

[*CBSE Sample Paper 2016*]

Ans. (*i*) Refer to Q. 12 (*i*), NCERT Textbook Exercises.

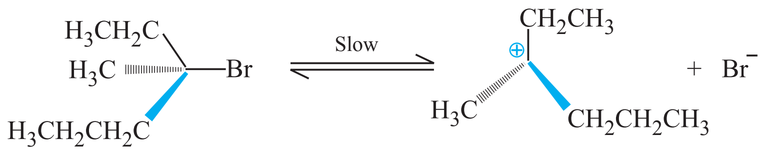
(*ii*) Since the optically active compound, $C_7H_{15}Br$ reacts with KOH forms a racemic mixture, therefore it must be tertiary alkyl halide and the reaction will follow S_N1 mechanism.



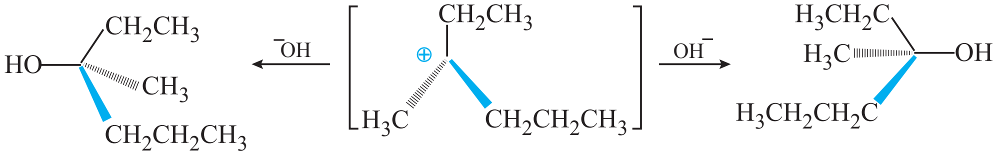
$$CH_3—CH_2—CH_2—\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{C}}—CH_2—CH_3 + OH^- \longrightarrow \underset{(\pm)\text{ 3-Methyl-hexan-3-ol}}{CH_3—CH_2—CH_2—\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{C}}—CH_2—CH_3} + Br^-$$

Mechanism:

(*a*)



(*b*)



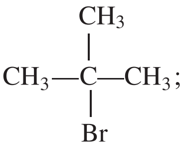
(+) 3-Methyl-hexan-3-ol (–) 3-Methyl-hexan-3-ol

Q. 6. Compound ‘A’ with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound ‘A’ only. When another optically active isomer ‘B’ of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

(*i*) Write down the structural formula of both compounds ‘A’ and ‘B’.

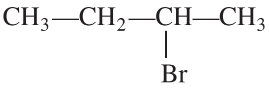
(*ii*) Out of these two compounds, which one will be converted to the product with inverted configuration? *[NCERT Exemplar]* *[HOTS]*

Ans. (*i*) Compound A:



$$CH_3-\underset{\substack{|\\Br}}{\overset{\substack{CH_3\\|}}{C}}-CH_3;$$

Compound B:

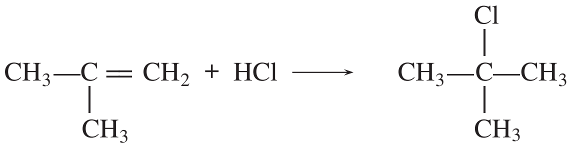


$$CH_3-CH_2-\underset{\substack{|\\Br}}{CH}-CH_3$$

(*ii*) Compound ‘B’.

Q. 7. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved. *[NCERT Exemplar]* *[HOTS]*

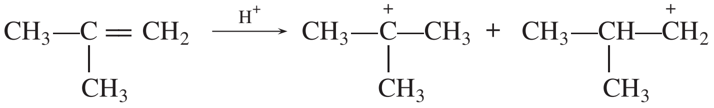
Ans.



$$\underset{\text{(Isobutylene)}}{CH_3-\underset{\substack{|\\CH_3}}{C}=CH_2} + HCl \longrightarrow \underset{\text{(2-Chloro-2-methylpropane)}}{CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{Cl\\|}}{C}}-CH_3}$$

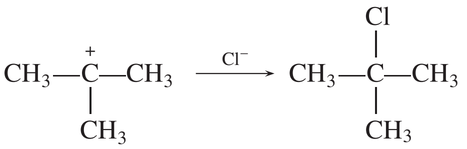
The mechanism involved in this reaction is:

Step I



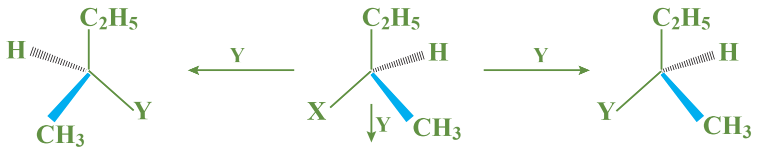
$$\underset{\text{Isobutylene}}{CH_3-\underset{\substack{|\\CH_3}}{C}=CH_2} \xrightarrow{H^+} \underset{\substack{\text{3° carbocation}\\\text{(more stable)}}}{CH_3-\underset{\substack{|\\CH_3}}{\overset{+}{C}}-CH_3} + \underset{\substack{\text{1° carbocation}\\\text{(less stable)}}}{CH_3-\underset{\substack{|\\CH_3}}{CH}-\overset{+}{C}H_2}$$

Step II



$$CH_3-\underset{\substack{|\\CH_3}}{\overset{+}{C}}-CH_3 \xrightarrow{Cl^-} CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{Cl\\|}}{C}}-CH_3$$

Q. 8. Consider the three types of replacement of group X by group Y as shown here.



(B) **(A) + (B)** **(A)**

This can result in giving compound (A) or (B) or both. What is the process called if

(*i*) (A) is the only compound obtained?

(*ii*) (B) is the only compound obtained?

(*iii*) (A) and (B) are formed in equal proportions? **[*CBSE (F) 2013*]**

Ans. (*i*) Retention (*ii*) Inversion

(*iii*) Racemisation

Q. 9. Following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(*i*) Write the compound which is most reactive towards S_N2 reaction.

(*ii*) Write the compound which is optically active.

(*iii*) Write the compound which is most reactive towards β-elimination reaction. **[*CBSE Delhi 2017*]**

Ans. (*i*) 1-Bromopentane, it is primary halide therefore undergoes S_N2 reaction faster.

(*ii*) 2-Bromopentane as carbon number two is symmetric carbon.

(*iii*) 2-Bromo-2-methyl butane, because tertiary alkyl halides on dehydrogenation form most substituted alkene which is more stable.

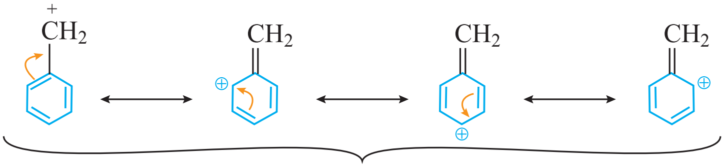
Q. 10. Give reasons for the following:

(*i*) Benzyl chloride is highly reactive towards the S_N1 reaction.

(*ii*) 2-bromobutane is optically active but 1-bromobutane is optically inactive.

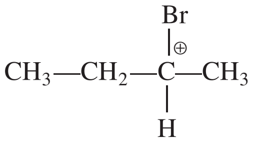
(*iii*) Electrophilic reactions in haloarenes occur slowly. **[*CBSE Bhubaneshwar 2015*] [*HOTS*]**

Ans. (*i*) Benzyl chloride is highly reactive towards the S_N1 reaction because the intermediate benzyl carbocation formed in slowest step is stabilized through resonance.



Benzyl cation stabilised by resonance

(*ii*) 2-bromobutane is a chiral molecule as it contains an asymmetric carbon atom therefore, it is optically active whereas 1-bromobutane is an achiral molecule as it does not contain asymmetric carbon atom therefore it is optically inactive.



$CH_3-CH_2-\overset{Br}{\underset{H}{\overset{|\oplus}{\underset{|}{C}}}}-CH_3$

Carbocation of 2-Bromobutane

(*iii*) Halogen in haloarenes withdraws electrons through $-I$ effect and release electrons through $+R$ effect. The inductive effect is stronger than resonance effect and causes net electron withdrawal. As a result, the electrophilic substitution reactions in haloarenes occur slowly.

Q. 11. Give reasons for the following observations:

(*i*) *p*-dichlorobenzene has higher melting point than those of *o*– and *m*– isomers.

(*ii*) Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(*iii*) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product. **[*CBSE 2019 (56/4/1)*]**

Ans. (*i*) It is due to the greater symmetry of para-isomer that fits in the crystal better as compared to ortho and meta-isomers.

(*ii*) As C–X bond in aryl halide acquires a partial double bond character due to resonance while the C–X bond in alkyl halide is a pure single bond.

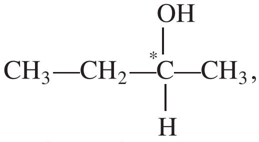
(*iii*) Alkoxide ion present in alcoholic KOH, is not only a strong nucleophile but also a strong base so preferentially eliminate a molecule of HCl from alkyl halide to form alkenes.

Q. 12. (*i*) Why are alkyl halides insoluble in water?

(*ii*) Why is butan-1-ol optically inactive but butan-2-ol is optically active?

(*iii*) Although chlorine is an electron withdrawing group, yet it is *ortho*, *para* directing in electrophilic aromatic substitution reactions. Why? **[*CBSE (F) 2015*]**

Ans. (*i*) This is due to the inability of alkyl halide molecule to form intermolecular hydrogen bonds with water molecules.

(*ii*) 

$CH_3—CH_2—\overset{*}{C}(OH)(H)—CH_3$, due to presence of a chiral carbon butan-2-ol is an optically active compound.

(*iii*) As the weaker resonance (+ *R*) effect of Cl which stabilise the carbocation formed tends to oppose the stronger inductive (– *I*) effect of Cl which destabilise the carbocation at ortho and para positions and makes deactivation less for ortho and para position.

Q. 13. Give reasons:

(*i*) *n*-Butyl bromide has higher boiling point than *t*-butyl bromide.

(*ii*) Racemic mixture is optically inactive.

(*iii*) The presence of nitro group (—NO_2) at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. [*CBSE Delhi 2015; 2019 (56/4/1)*]

Ans. (*i*) *n*-Butyl bromide being a straight chain alkyl halide has larger surface area than *tert*.butyl bromide. Larger the surface area, larger the magnitude of the van der Waal's forces and hence higher is the boiling point.

(*ii*) A racemic mixture contains the two enantiomers *d* and *l* in equal proportions. As the rotation due to one enantiomer is cancelled by equal and opposite rotation of another enantiomer, therefore, it is optically inactive.

(*iii*) The presence of NO_2 group at *o/p* position in haloarenes helps in the stabilisation of resulting carbanion by –*R* and –*I* effects and hence increases the reactivity of haloarenes towards nucleophilic substitution reactions.

Long Answer Questions [5 marks]

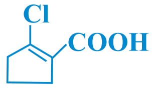
Q. 1. (*i*) Among all the isomers of molecular formula C_4H_9Br, identify [*CBSE 2019 (56/2/1)*]

(*a*) the one isomer which is optically active.

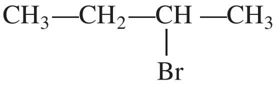
(*b*) the one isomer which is highly reactive towards S_N2.

(*c*) the two isomers which give same product on dehydrohalogenation with alcoholic KOH.

(*ii*) Give IUPAC name of the following organic compounds:

(*a*) 

(*b*) $(CH_3)_3CCH_2Br$

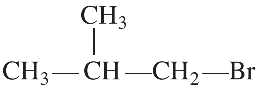
Ans. (*i*) (*a*) 

$CH_3—CH_2—CH(Br)—CH_3$

2 - Bromobutane

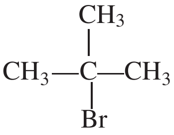
(*b*) $CH_3—CH_2—CH_2—CH_2—Br$

1 - Bromobutane

(*c*) 

$CH_3—CH(CH_3)—CH_2—Br$

1 - Bromo - 2 - methyl propane

and 

$CH_3—C(CH_3)(Br)—CH_3$

2 - Bromo - 2 - methyl propane

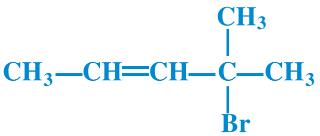
(*ii*) (*a*) 2-chloro cyclopent-1-ene-1-carboxylic acid

(*b*) 1-bromo-2, 2-dimethyl propane

Q. 2. (*i*) (*a*) Write equation for preparation of 1-iodobutane from 1-chlorobutane.

(*b*) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction and why?

(*c*) Give IUPAC name of



$CH_3—CH{=}CH—C(CH_3)(Br)—CH_3$

[*CBSE 2019 (56/4/1)*]

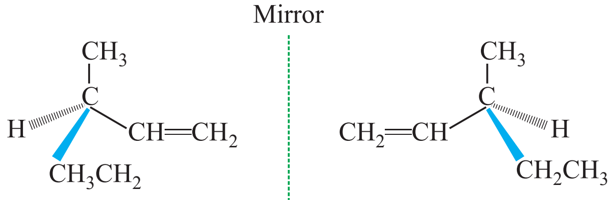
(*ii*) What are enantiomers? Draw the structures of the possible enantiomers of 3-methylpent-1-ene.

Ans. (*i*) (*a*) $CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow{\text{Dry acetone}} CH_3CH_2CH_2CH_2—I + NaCl$

(*b*) 2-Bromo-2-methylbutane is more reactive as it gives more substituted alkene on elimination.

(*c*) 4-Bromo-4-methylpent-2-ene

(*ii*) Stereoisomers which are non-superimposable mirror images of each other are called enantiomers.



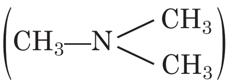
Enantiomers of 3–methylpent-1-ene

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. **Chloromethane on treatment with excess of ammonia yields mainly.**

(*a*) N, N-Dimethylmethanamine 
$\left(CH_3—N\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}\right)$

(*b*) N–methylmethanamine ($CH_3—NH—CH_3$)

(*c*) Methanamine (CH_3NH_2)

(*d*) Mixture containing all these in equal proportion

2. **Molecules whose mirror image is non superimposable over them are known as chiral. Which of the following molecules is chiral in nature?**

(*a*) 2-Bromobutane (*b*) 1-Bromobutane

(*c*) 2-Bromopropane (*d*) 2-Bromopropan-2-ol

3. **Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows ____________.**

(*a*) S_N1 mechanism

(*b*) S_N2 mechanism

(*c*) Any of the above two depending upon the temperature of reaction

(*d*) Saytzeff rule

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. **Assertion (*A*)** : Hydroxyketones are not directly used in Grignard reaction.

Reason (*R*) : Grignard reagents reacts with hydroxyl group.

5. **Assertion (*A*)** : Chlorination of ethylbenzene with Cl_2 in presence of heat and light mainly yields 1-chloro-2-phenylethane.

Reason (*R*) : The reaction occurs through intermediate formation of the radical $C_6H_5\dot{C}HCH_3$.

6. Assertion (A) : Addition of HCl on butene-1 always forms racemic mixture, while it is not so in case of addition of HBr on butene-1.

Reason (R) : Addition of HCl is not governed by Markovnikoff's rule.

Answer the following questions:

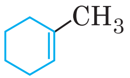
7. Give the IUPAC name of $(CCl_3)_3C—Cl$. **(1)**

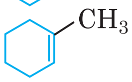
8. How will you convert aniline to bromobenzene? **(1)**

9. Illustrate the following reactions giving a suitable example for each:

(*i*) Wurtz-Fittig reaction (*ii*) Finkelstein reaction. **(2)**

10. Complete the following reaction equations:

(*i*)  $+ HBr \xrightarrow{\text{Peroxide}}$

(*ii*)  $+ HBr \longrightarrow$ **(2)**

11. Give chemical tests to distinguish between the following pairs of compounds:

(*i*) Bromobenzene and benzyl bromide

(*ii*) Ethyl chloride and vinyl chloride **(2)**

12. Give mechanism for the following reaction:

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$ **(2)**

OR

Write the mechanism of the following S_N1 reaction:

$$(CH_3)_3C—Br \xrightarrow{\text{Aq. NaOH}} (CH_3)_3C—OH + NaBr$$ **[*CBSE 2020 (56/4/2)*]**

13. (*i*) Which is a better nucleophile, a bromide ion or an iodide ion?

(*ii*) Which will have a higher boiling point?

1-Chloropentane or 2-methyl-2-chlorobutane **(2)**

14. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the structure of the hydrocarbon. **(3)**

15. How will you bring about following conversions?

(*i*) Chlorobenzene to phenol

(*ii*) Isopropyl bromide to n-propyl bromide

(*iii*) Aniline to iodobenzene **(3)**

16. Complete the following giving the structures of major organic products.

(*i*) $(CH_3)_3—C—Br \xrightarrow{Mg} .... \xrightarrow{H_2O} ....$

(*ii*) $(CH_3)_3—C—CH_2—Br \xrightarrow[\Delta]{C_2H_5ONa/C_2H_5OH} ....$

(*iii*)  $+ (CH_3)_3—C—CH_2—Br \xrightarrow{\text{anhyd. } AlCl_3} ....$ **(3)**

17. A compound 'A' having molecular formula C_4H_9Br on reaction with alcoholic KOH gives a compound 'B'. Bromination of 'B' gives compound 'C'. Compound 'C' on treatment with soda amide gives a gaseous compound 'D'. The gas 'D' when passed through ammonical silver nitrate solution forms white precipitate.

Identify compounds A, B, C and D and write down the reactions involved. **(3)**

Answers

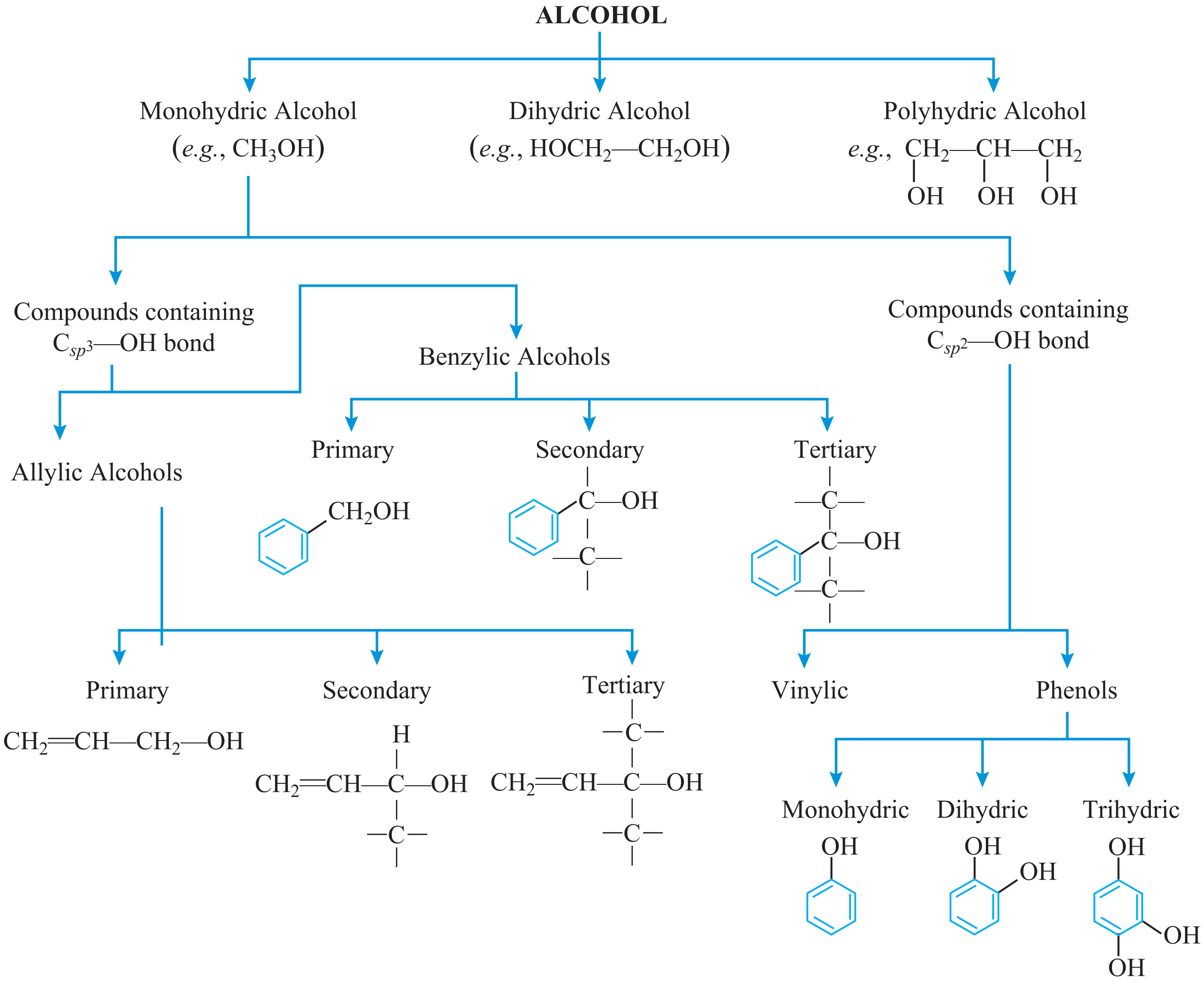
1. (*c*) **2.** (*a*) **3.** (*a*) **4.** (*a*) **5.** (*d*) **6.** (*a*)

Alcohols, Phenols and Ethers

basic concepts

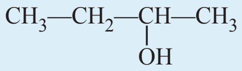
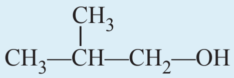
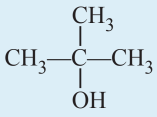
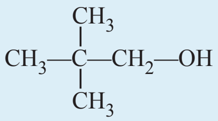
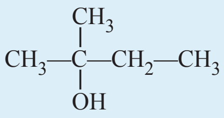
1. **Introduction:** Alcohols and phenols are the compounds containing one or more hydroxyl groups (—OH). The alcohols contain the —OH group attached to the alkyl group whereas in phenols, the —OH group is attached to the aromatic ring.

CLASSIFICATION



2. Common and IUPAC names of some alcohols:

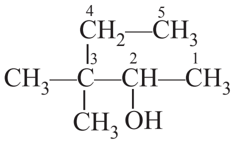
Table 11.1: Common and IUPAC Names of Some Alcohols

Common Name	Structural Formula	IUPAC Name
Ethyl alcohol	CH_3-CH_2-OH	Ethanol
n-Butyl alcohol	$CH_3-CH_2-CH_2-CH_2-OH$	Butan-1-ol
sec-Butyl alcohol	 $CH_3-CH_2-\underset{OH}{\underset{\vert}{CH}}-CH_3$	Butan-2-ol
Isobutyl alcohol	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2-OH$	2-Methylpropan-1-ol
tert-Butyl alcohol	 $CH_3-\underset{OH}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_3$	2 -Methylpropan-2-ol
neo-Pentyl alcohol	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_2-OH$	2, 2-Dimethylpropan-1-ol
tert-Pentyl alcohol	 $CH_3-\underset{OH}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_2-CH_3$	2-Methylbutan-2-ol

Some more examples of alcohols are given below:

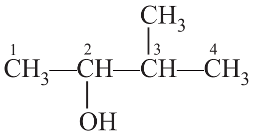
$CH_2=CH-OH$

Vinyl alcohol
(Ethen-1-ol)



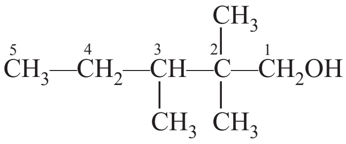
$$CH_3-\underset{CH_3}{\underset{\vert}{\overset{\overset{4}{C}H_2-\overset{5}{C}H_3}{\overset{\vert}{\overset{3}{C}}}}}-\underset{OH}{\underset{\vert}{\overset{2}{C}H}}-\overset{1}{C}H_3$$

3, 3-Dimethylpentan-2-ol



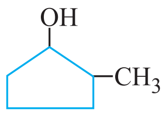
$$\overset{1}{C}H_3-\underset{OH}{\underset{\vert}{\overset{2}{C}H}}-\overset{CH_3}{\overset{\vert}{\overset{3}{C}H}}-\overset{4}{C}H_3$$

3-Methylbutan-2-ol



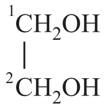
$$\overset{5}{C}H_3-\overset{4}{C}H_2-\underset{CH_3}{\underset{\vert}{\overset{3}{C}H}}-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{\overset{2}{C}}}}}-\overset{1}{C}H_2OH$$

2, 2, 3-Trimethylpentanol



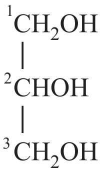
2-Methylcyclopentanol

In IUPAC system, dihydric alcohols are named as alkanediols and trihydric alcohols are named as alkanetriols.



$$\begin{array}{l} {}^{1}CH_2OH \\ \vert \\ {}^{2}CH_2OH \end{array}$$

Ethylene glycol
(Ethane-1, 2-diol)

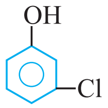


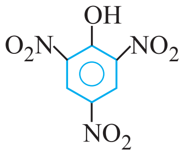
$$\begin{array}{l} {}^{1}CH_2OH \\ \vert \\ {}^{2}CHOH \\ \vert \\ {}^{3}CH_2OH \end{array}$$

Glycerol
(Propane-1, 2, 3-triol)

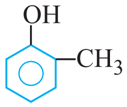
The simplest hydroxy derivative of benzene is phenol. The substituted phenols are named as derivatives of phenol.

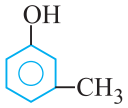

Phenol

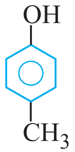

3-Chlorophenol

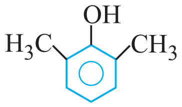

Picric acid
(2,4,6-Trinitrophenol)

Methyl phenols are known as cresols.

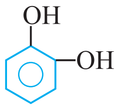

o-Cresol
(2-Methylphenol)

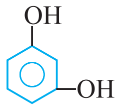

m-Cresol
(3-Methylphenol)


p-Cresol
(4-Methylphenol)

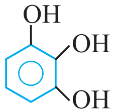

2,6-Dimethylphenol

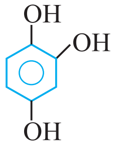
Some dihydric and trihydric phenols are given below:

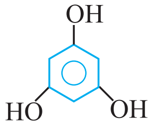

Catechol
(Benzene-1,2-diol)


Resorcinol
(Benzene-1,3-diol)

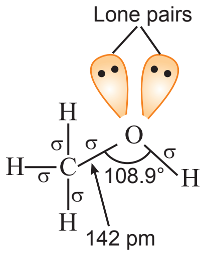

Quinol or hydroquinone
(Benzene-1,4-diol)


Pyrogallol
(Benzene-1,2,3-triol)


Hydroxyquinol
(Benzene-1,2,4-triol)


Phloroglucinol
(Benzene-1,3,5-triol)

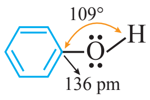
3. **Structure of R—OH:** In **alcohols**, both the carbon atoms of R, *e.g.*, —CH_3 and oxygen atom of —OH groups are sp^3 hybridised. The structure of CH_3—OH is shown below.



Structure of Methanol

The C—OH bond angle is slightly less than tetrahedral angle (109°28′) due to repulsions between lone pairs of electrons of oxygen atom. The C—O and O—H bonds are polar because of high electronegativity of oxygen atom.

In **phenols**, the –OH group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (*i*) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and (*ii*) sp^2 hybridised state of carbon to which oxygen is attached.



Structure of Phenol

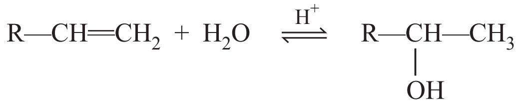
4. Methods of Preparation

Alcohols are prepared by the following methods:

(*a*) From alkenes

(*i*) By acid catalysed hydration:

Addition occurs according to Markovnikov's rule.



$$R-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} R-\underset{\substack{|\\ OH}}{CH}-CH_3$$

(*ii*) By hydroboration oxidation:

Addition occurs in accordance with anti-Markovnikov's rule.

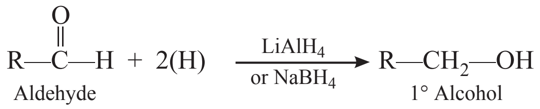
$$R-CH=CH_2 + \underset{\text{Diborane}}{\frac{1}{2}(BH_3)_2} \longrightarrow (R-CH_2-CH_2)_3B$$

$$\xrightarrow[OH^-,\ H_2O]{3H_2O_2} \underset{1^\circ\ \text{Alcohol}}{3R-CH_2-CH_2-OH} + H_3BO_3$$

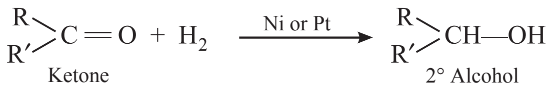
(*b*) From carbonyl compounds

(*i*) By reduction of aldehydes and ketones:

Common reducing agents used are lithium aluminium hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$), H_2 in the presence of Ni or Pt. Aldehydes on reduction give 1° alcohols whereas ketones on reduction give 2° alcohols.



$$\underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + 2(H) \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{1^\circ\ \text{Alcohol}}{R-CH_2-OH}$$



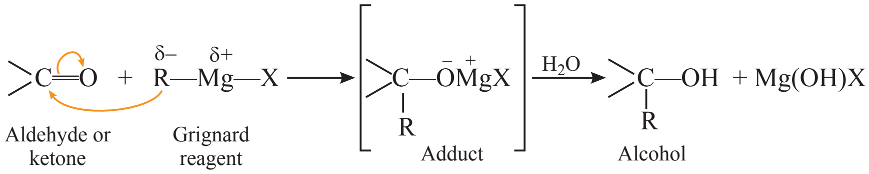
$$\underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!>C=O} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{2^\circ\ \text{Alcohol}}{\begin{matrix}R\\R'\end{matrix}\!>CH-OH}$$

(*ii*) By reduction of carboxylic acids and esters:

$$\underset{\text{Carboxylic acid}}{R-COOH} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} \underset{1^\circ\text{Alcohol}}{R-CH_2-OH}$$

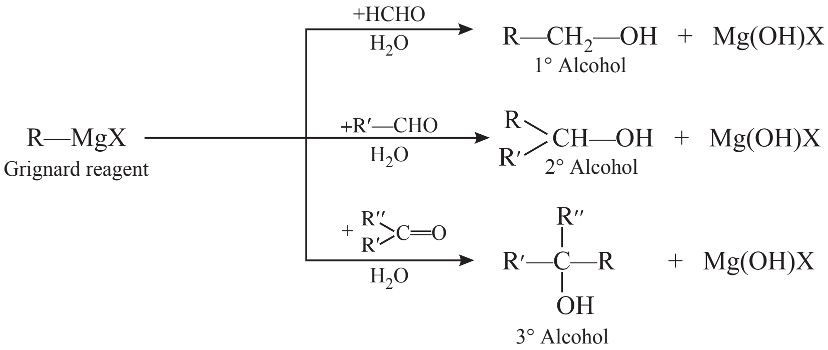
$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow[H^+]{R'OH} \underset{\text{Ester}}{R-COOR'} \xrightarrow{H_2/Pd} \underset{1^\circ\text{Alcohol}}{R-CH_2-OH} + R'-OH$$

(*c*) From Grignard's reagents



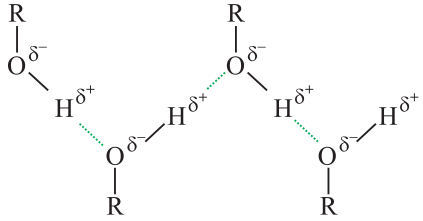
$$\underset{\text{Aldehyde or ketone}}{>C=O} + \underset{\text{Grignard reagent}}{\overset{\delta-}{R}-\overset{\delta+}{Mg}-X} \longrightarrow \left[\underset{\text{Adduct}}{>\underset{\substack{|\\ R}}{C}-\overset{-}{O}\overset{+}{Mg}X}\right] \xrightarrow{H_2O} \underset{\text{Alcohol}}{>\underset{\substack{|\\ R}}{C}-OH} + Mg(OH)X$$

The reaction of Grignard's reagents with formaldehyde produces a primary alcohol, with other aldehydes it produces secondary alcohols and tertiary alcohols with ketones.



5. Physical Properties of Alcohols:

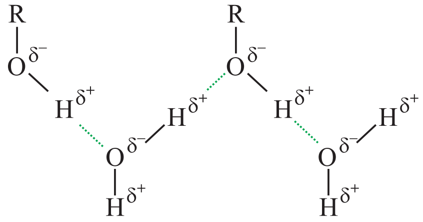
(*a*) **Boiling points:** Boiling points of alcohols are much higher than those of alkanes, haloalkanes or ethers of comparable molecular masses. This is because in alcohols strong intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.



Among isomeric alcohols, the boiling point decreases with increase in branching in the alkyl group (due to decrease in van der Waals forces with decrease in surface area). For isomeric alcohols, the boiling points generally follow the order:

Primary alcohol > Secondary alcohol > Tertiary alcohol.

(*b*) **Solubility of alcohols:** The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents like ether, benzene, etc. The solubility of lower alcohols in water is due to their ability to form hydrogen bonds with water molecules.

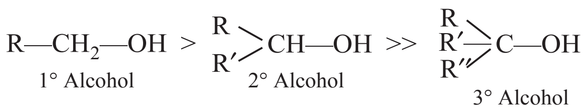


The solubility of alcohols in water decreases with increase in molecular mass because with increase in molecular mass the non-polar alkyl group becomes predominant and masks the effect of polar —OH group. In addition, among the isomeric alcohols the solubility increases with branching of chain. It is because the surface area of non-polar part in the molecule decreases, thus enhancing the solubility.

6. Chemical Properties of Alcohols:

(*a*) Reactions involving cleavage of oxygen–hydrogen (O—H) bond

Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O—H bond. An electron releasing group (alkyl group) increases electron density on oxygen tending to decrease the polarity of O—H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



$$\underset{1^\circ\ \text{Alcohol}}{R—CH_2—OH} > \underset{2^\circ\ \text{Alcohol}}{\overset{R}{\underset{R'}{>}}CH—OH} >> \underset{3^\circ\ \text{Alcohol}}{R,R',R''{>}C—OH}$$

(*i*) Reaction with metals:

$$2R—O—H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R—\overset{-}{O}\overset{+}{Na}} + H_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} + Na \longrightarrow \underset{\text{Sodium ethoxide}}{CH_3—CH_2—\overset{-}{O}\overset{+}{Na}} + \frac{1}{2}H_2$$

$$\underset{3^\circ\ \text{Butyl alcohol}}{6(CH_3)_3—C—OH} + 2Al \longrightarrow \underset{\text{Aluminium tert-butoxide}}{2((CH_3)_3—CO)_3Al} + 3H_2$$

(*ii*) Esterification:

$$\underset{\text{Carboxylic acid}}{R—COOH} + \underset{\text{Alcohol}}{R'—OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R—COOR'} + H_2O$$

$$\underset{\text{Acid anhydride}}{(R—CO)_2O} + R'—OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R—COOR'} + R—COOH$$

$$\underset{\text{Acyl chloride}}{R—COCl} + R'—OH \xrightarrow{\text{Pyridine}} \underset{\text{Ester}}{R—COOR'} + HCl$$

(*b*) Reactions involving cleavage of carbon–oxygen (C—O) bond

In such type of reactions, the order of reactivity of alcohols is

3°Alcohol > 2°Alcohol > 1°Alcohol

(*i*) Reaction with hydrogen halides:

$$\underset{\text{Alcohol}}{R—OH} + H—X \longrightarrow \underset{\text{Alkyl halide}}{R—X} + H_2O$$

$$CH_3—CH_2—OH + H—Cl \xrightarrow{\text{Anhyd. } ZnCl_2} CH_3—CH_2—Cl + H_2O$$

(ii) Reaction with phosphorus halides:

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

$$3R—OH + PCl_3 \longrightarrow 3R—Cl + H_3PO_3$$

$$3R—OH + PBr_3 \xrightarrow{\text{from } (P\ \&\ Br_2)} 3R—Br + H_3PO_3$$

$$3R—OH + PI_3 \xrightarrow{\text{from } (P\ \&\ I_2)} 3R—I + H_3PO_3$$

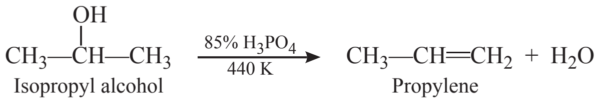
(*iii*) Reaction with thionyl chloride:

$$R—OH + SOCl_2 \longrightarrow R—Cl + SO_2\uparrow + HCl\uparrow$$

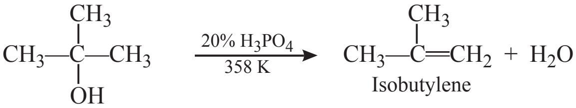
(*iv*) Dehydration: The ease of dehydration follows the following order:

3° Alcohol > 2° Alcohol > 1° Alcohol

$$\underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} \xrightarrow[443\ K]{\text{conc. } H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2O$$



$$\underset{\text{Isopropyl alcohol}}{CH_3—\overset{\overset{OH}{|}}{C}H—CH_3} \xrightarrow[440\ K]{85\%\ H_3PO_4} \underset{\text{Propylene}}{CH_3—CH{=}CH_2} + H_2O$$



$$CH_3\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_3 \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3\text{—}\overset{\overset{CH_3}{|}}{C}\text{=}CH_2 + H_2O$$

tert -Butyl alcohol Isobutylene

(*v*) Oxidation: Oxidation of alcohols involves the formation of a carbon–oxygen double bond with the cleavage of an O—H and C—H bond.

$$H\text{—}\overset{|}{\underset{|}{C}}\text{—}O\text{—}H \longrightarrow \rangle C\text{=}O$$

Bond breaking

1° alcohols on oxidation give aldehydes which on further oxidation give carboxylic acids with the same number of carbon atoms.

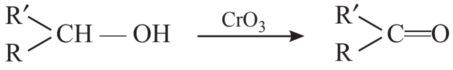
$$R\text{—}CH_2\text{—}OH + [O] \xrightarrow[\substack{\text{or alk. } KMnO_4 \\ -H_2O}]{K_2Cr_2O_7/H_2SO_4} R\text{—}CHO \xrightarrow{[O]} R\text{—}COOH$$

1° Alcohol Aldehyde Carboxylic acid

$$CH_3\text{—}CH\text{=}CH\text{—}CH_2\text{—}OH \xrightarrow{PCC} CH_3\text{—}CH\text{=}CH\text{—}CHO$$

But-2-enol But-2-enal

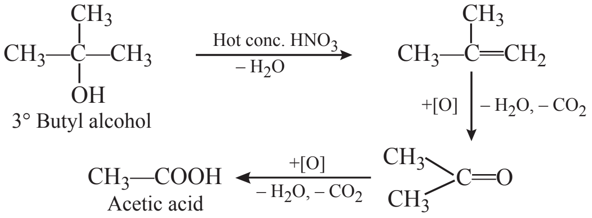
2° Alcohols are oxidised to ketones by CrO_3.



$$\begin{matrix}R'\\R\end{matrix}\rangle CH\text{—}OH \xrightarrow{CrO_3} \begin{matrix}R'\\R\end{matrix}\rangle C\text{=}O$$

2° Alcohol Ketone

3° alcohols do not undergo oxidation reaction as they do not have α-hydrogens. However, when oxidation is carried under strong reaction conditions and elevated temperature, they undergo oxidation with the cleavage of C—C bond.



$$CH_3\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_3 \xrightarrow[-H_2O]{\text{Hot conc. } HNO_3} CH_3\text{—}\overset{\overset{CH_3}{|}}{C}\text{=}CH_2 \xrightarrow[-H_2O,\ -CO_2]{+[O]} \begin{matrix}CH_3\\CH_3\end{matrix}\rangle C\text{=}O \xrightarrow[-H_2O,\ -CO_2]{+[O]} CH_3\text{—}COOH$$

3° Butyl alcohol

Acetic acid

Acetone

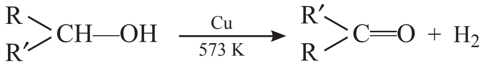
(*vi*) Dehydrogenation

Primary alcohols are dehydrogenated to aldehydes.

$$R\text{—}CH_2\text{—}OH \xrightarrow[573\ K]{Cu} R\text{—}CHO + H_2$$

1° Alcohol Aldehyde

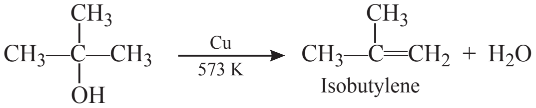
Secondary alcohols are dehydrogenated to ketones.



$$\begin{matrix}R\\R'\end{matrix}\rangle CH\text{—}OH \xrightarrow[573\ K]{Cu} \begin{matrix}R'\\R\end{matrix}\rangle C\text{=}O + H_2$$

2° Alcohol Ketone

Tertiary alcohols undergo dehydration to give alkenes.

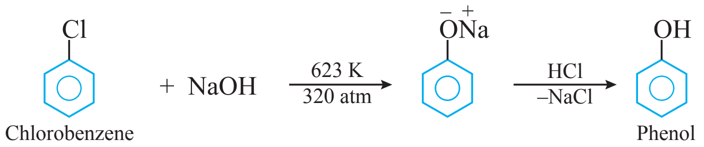


$$CH_3\text{—}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}CH_3 \xrightarrow[573\ K]{Cu} CH_3\text{—}\overset{\overset{CH_3}{|}}{C}\text{=}CH_2 + H_2O$$

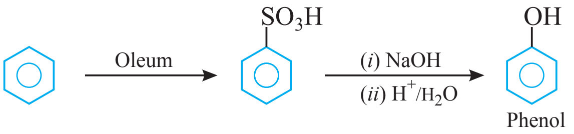
tert-Butyl alcohol Isobutylene

7. Preparation of Phenols:

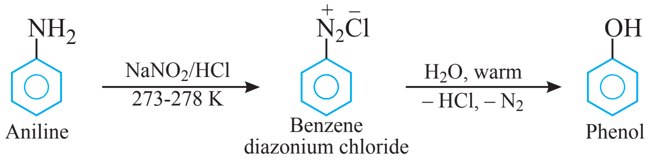
(*i*) From aryl halides



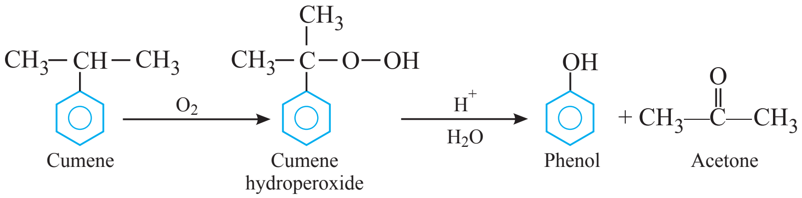
(*ii*) From benzenesulphonic acid



(*iii*) From diazonium salts

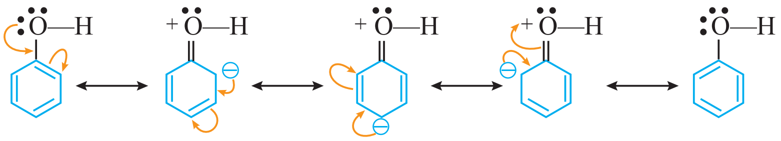


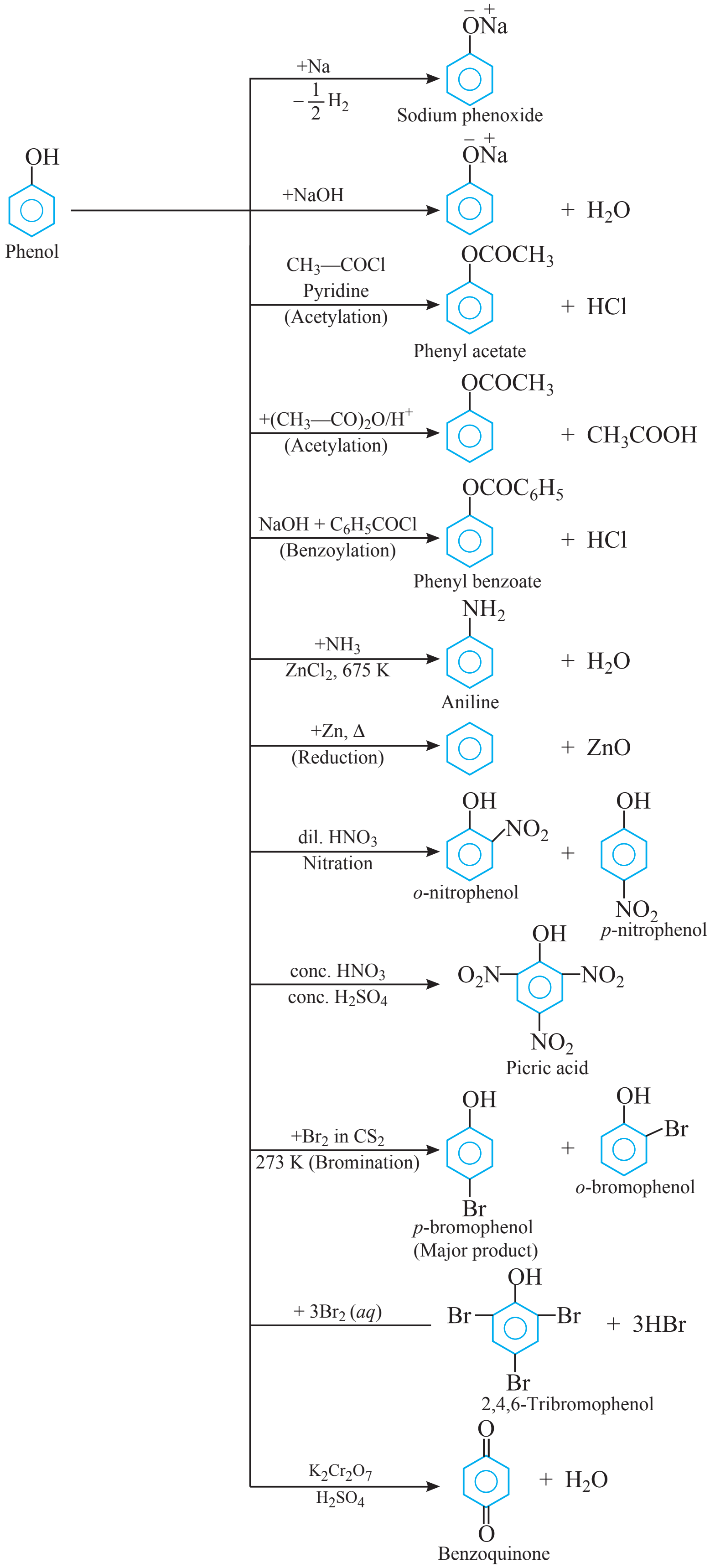
(*iv*) **From Cumene.** Cumene is oxidised in air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acids.



8. Reactions of Phenol:

Acidity of Phenol: The acidity of phenols is due to its ability to lose hydrogen ion to form phenoxide ions In a phenol molecule, the sp^2 hybridised carbon atom of the benzene ring attached directly to the hydroxyl group acts as an electron-withdrawing group. This sp^2 hybridized carbon atom of a benzene ring attached directly to the hydroxyl group has higher electronegativity in comparison to the hydroxyl group. Due to the higher electronegativity of this carbon atom in comparison to the hydroxyl group attached, electron density decreases on the oxygen atom. The decrease in electron density increases the polarity of O—H bond and results in the increase in ionization of phenols. Thus, the phenoxide ion is formed. The phenoxide ion formed is stabilized by the delocalization of negative charge due to the resonance in the benzene ring. Phenoxide ion has greater stability than phenols, as in the case of phenol charge separation takes place during resonance The resonance structures of phenoxide ions explain the delocalization of negative charge In the case of substituted phenols, the acidity of phenols increases in the presence of the electron-withdrawing group. This is due to the stability of the phenoxide ion generated. The acidity of phenols further increases if these groups are attached at ortho and para positions. This is due to the fact that the negative charge in phenoxide ion is mainly delocalised at ortho and para positions of the attached benzene ring. On the other hand, the acidity of phenol decreases in the presence of electron-donating groups as they prohibit the formation of phenoxide ion.




OH
Phenol
+Na
−½H₂
ONa
Sodium phenoxide
+NaOH
ONa
+ H₂O
CH₃—COCl
Pyridine
(Acetylation)
OCOCH₃
+ HCl
Phenyl acetate
+(CH₃—CO)₂O/H⁺
(Acetylation)
OCOCH₃
+ CH₃COOH
NaOH + C₆H₅COCl
(Benzoylation)
OCOC₆H₅
+ HCl
Phenyl benzoate
+NH₃
ZnCl₂, 675 K
NH₂
+ H₂O
Aniline
+Zn, Δ
(Reduction)
+ ZnO
dil. HNO₃
Nitration
OH
NO₂
o-nitrophenol
+
OH
NO₂
p-nitrophenol
conc. HNO₃
conc. H₂SO₄
OH
O₂N
NO₂
NO₂
Picric acid
+Br₂ in CS₂
273 K (Bromination)
OH
Br
p-bromophenol
(Major product)
+
OH
Br
o-bromophenol
+ 3Br₂ (aq)
OH
Br
Br
Br
+ 3HBr
2,4,6-Tribromophenol
K₂Cr₂O₇
H₂SO₄
O
O
+ H₂O
Benzoquinone

9. Some Commercially Important Compounds:

(*a*) Methyl alcohol: It is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature in presence of $ZnO\text{-}Cr_2O_3$ catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\text{ atm}\\573\text{-}673\text{ K}}]{ZnO—Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3—OH}$$

(*b*) Ethyl alcohol: It is obtained commercially by fermentation.

$$(i)\ \underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$(ii)\ \underset{\substack{\text{Glucose}\\\text{or}\\\text{Fructose}}}{C_6H_{12}O_6} \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

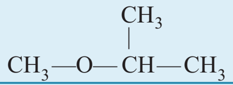
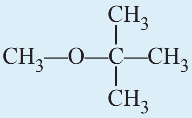
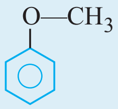
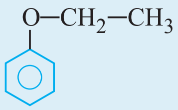
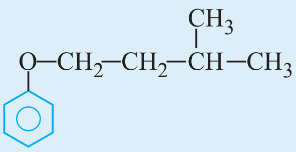
10. Ethers:

Ethers: Ethers are the compounds with general formula of $C_nH_{2n+2}O$ (same as monohydric alcohols). These are represented by general structure, R—O—R′.

The groups R and R′ in ether may either be same or different. In case these groups are same, the compounds are known as simple ethers or symmetrical ethers. On the other hand, if R and R′ groups are different, the compounds are called mixed ether or unsymmetrical ethers.

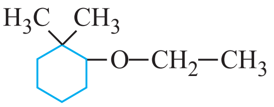
Nomenclature: According to IUPAC system, ethers are named as alkoxyalkanes. The larger alkyl group forms the part of parent chain while smaller alkyl group constitutes the alkoxy group.

Table 11.2: Common and IUPAC Names of Some Ethers

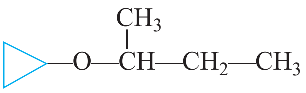
Common Name	Structural Formula	IUPAC Name
Dimethyl ether	$CH_3—O—CH_3$	Methoxymethane
Diethyl ether	$CH_3—CH_2—O—CH_2—CH_3$	Ethoxyethane
Methyl isopropyl ether	 $CH_3—O—\overset{\overset{\displaystyle CH_3}{\vert}}{CH}—CH_3$	2-Methoxypropane
Methyl tert.-butyl ether	 $CH_3—O—\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}—CH_3$	2-Methoxy-2-methyl propane
Anisole		Methoxybenzene
Phenetole		Ethoxybenzene
Phenyl isopentyl ether		3-Methyl-butoxybenzene

$$CH_3—O—CH_2—CH_2—O—CH_3$$

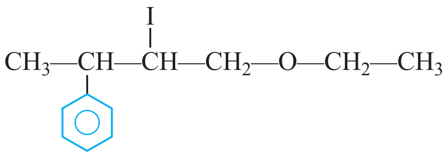
1, 2-Dimethoxyethane



2-Ethoxy-1, 1-dimethylcyclohexane

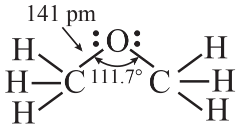


2-Cyclopropoxybutane



1-Ethoxy -2-iodo-3-phenylbutane

Structure of ROR: In ethers, the four electron pairs, *i.e.*, the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (—R) groups. The C—O bond length (141 pm) is almost the same as in alcohols.



Structure of Methoxymethane

11. Preparation of Ethers:

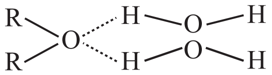
By dehydration of alcohols

$$\underset{\text{(excess)}}{2CH_3—CH_2—OH} \xrightarrow[\text{413 K}]{\text{conc. } H_2SO_4} \underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} + H_2O$$

This method is suitable for the preparation of ethers having primary alkyl groups only.

12. Physical Properties:

1. **Boiling points:** Ethers have much lower boiling points as compared to isomeric alcohols. Unlike alcohols, ether molecules are not associated by hydrogen bonds. The interparticle forces existing in their liquid states are weak dipole–dipole forces.
2. **Solubility:** The solubility of ethers is comparable to those of corresponding alcohols. The solubility of ethers is due to the ability of their molecules to form hydrogen bond with water molecules.



However, solubility of ethers in water decreases from lower members to higher members. This is because of the relative increase in the hydrocarbon portion of the molecule which decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone, etc.

13. Chemical Reactions:

Chemical Reactions: Ethers are relatively inert compounds in spite of the presence of oxygen atom carrying two lone pairs of electrons in their molecules. It is because of this reason that these are used as solvents. They undergo chemical reactions under specific conditions. Some of the reactions of ethers are being described as follows:

(*a*) **Cleavage of C—O bond:** Carbon oxygen bond in ethers can be cleaved by the use of reagents like halogen acids, sulphuric acid and phosphorus pentachloride, etc.

Cleavage with halogen acid: Ethers can be cleaved by the use of hydroiodic acid or hydrobromic acid to give alkyl halide and alcohol.

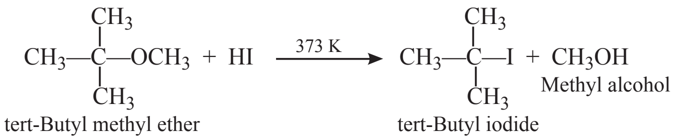
$$\underset{\text{Ether}}{R—O—R} + HX \xrightarrow{\text{373 K}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX} \quad (X = Br, I)$$

$$\underset{\text{Diethylether}}{C_2H_5OC_2H_5} + HI \xrightarrow{\text{373 K}} \underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Ethyliodide}}{C_2H_5I}$$

In case excess of HI is used, the alcohol formed reacts further with HI to form alkyl iodide. The overall reaction can be written as

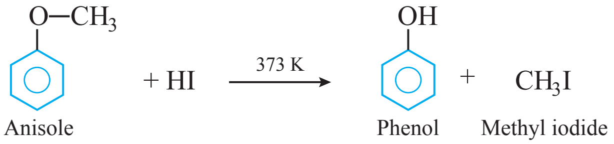
$$C_2H_5OC_2H_5 + \underset{\text{(Excess)}}{2HI} \xrightarrow{\text{373 K}} 2C_2H_5I + H_2O$$

If one group is methyl and other group is tertiary alkyl group, the main product is methyl alcohol and tertiary alkyl halide. It is because the departure of leaving group (CH_3—OH) creates a more stable tertiary carbocation.



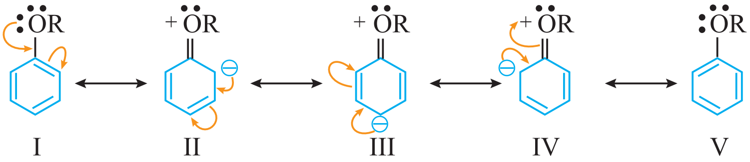
$$\underset{\text{tert-Butyl methyl ether}}{CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OCH_3} + HI \xrightarrow{\text{373 K}} \underset{\text{tert-Butyl iodide}}{CH_3—\overset{CH_3}{\underset{CH_3}{C}}—I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

In case of anisole, the products formed are phenol and methyl iodide.

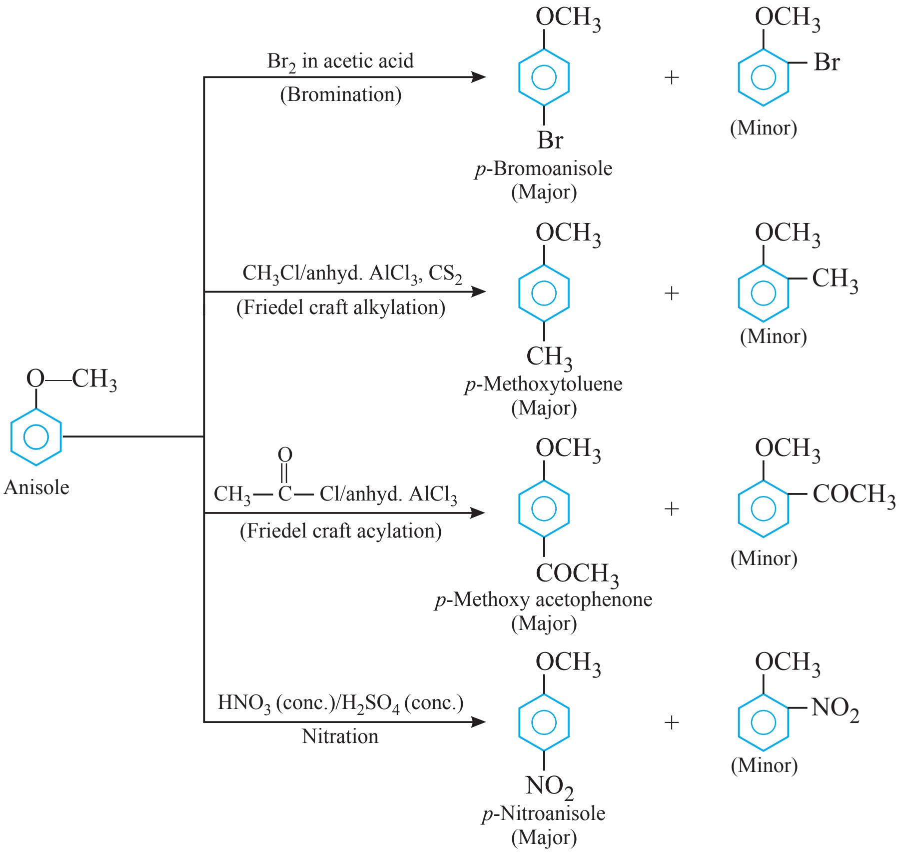


The bond between O—CH_3 is weaker than the bond between O—C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore, the attack of I^- ion breaks O—CH_3 bond to form CH_3I.

(*b*) **Ring substitution in aromatic ethers:** The alkoxy group (—OR) attached to aromatic ring activates the ring towards electrophilic substitution and directs the incoming electrophile to ortho and para positions.



The presence of negative charge at ortho and para positions indicates that electron density is more at these positions. Therefore, electrophile is likely to attack on these positions resulting in the formation of ortho and para substituted products.



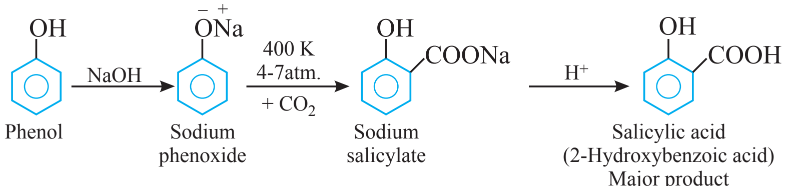
14. Uses of Ethers

Ethers are used in several ways:

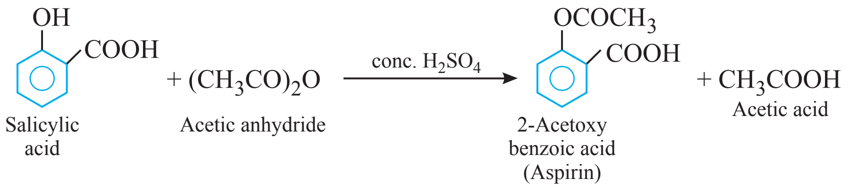
1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethyl ether is used as a solvent for organic reactions and also as an industrial solvent for oils, gums, resins, etc. It is also used as an extracting solvent.

15. Some Important Name Reactions

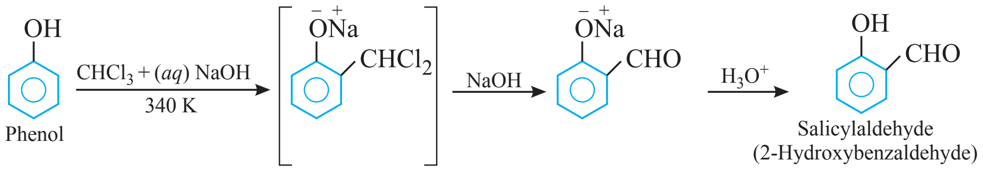
(*i*) **Kolbe's reaction:** When sodium phenoxide is heated with CO_2 at 400 K under a pressure of 4 –7 atm, the resulting product on acidification yields salicylic acid.



Salicylic acid is the starting material for the manufacture of 2-acetoxybenzoic acid (aspirin).



(*ii*) **Reimer–Tiemann reaction:** Treatment of phenol with chloroform in the presence of sodium hydroxide followed by hydrolysis of resulting product gives *o*-hydroxybenzaldehyde (salicylaldehyde) as a major product.

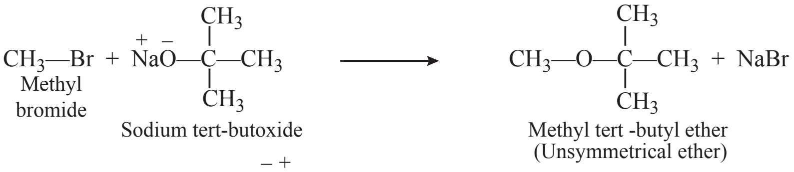


(*iii*) **Williamson synthesis:** It consists of reacting an alkyl halide with sodium alkoxide or sodium phenoxide to form ether.

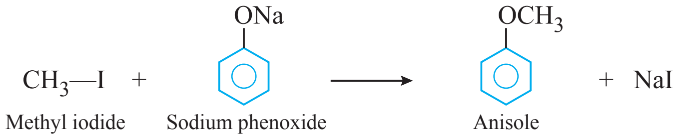
$$\underset{\text{Alkyl halide}}{R—X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}—\overset{-}{O}—R'} \longrightarrow \underset{\text{Ether}}{R—O—R'} + NaX$$

It is a convenient method for the preparation of symmetrical as well as unsymmetrical ethers.

$$\underset{\text{Ethyl iodide}}{CH_3—CH_2—I} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}—\overset{-}{O}—CH_2—CH_3} \longrightarrow \underset{\substack{\text{Diethyl ether}\\\text{(Symmetrical ether)}}}{CH_3—CH_2—O—CH_2—CH_3} + NaI$$



$$\underset{\substack{\text{Methyl}\\\text{bromide}}}{CH_3—Br} + \underset{\text{Sodium tert-butoxide}}{\overset{+}{Na}\overset{-}{O}—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—CH_3} \longrightarrow \underset{\substack{\text{Methyl tert -butyl ether}\\\text{(Unsymmetrical ether)}}}{CH_3—O—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—CH_3} + NaBr$$



16. Distinction between Primary, Secondary and Tertiary Alcohols

(*a*) **Lucas test:** In this test, the alcohol is treated with Lucas reagent which is an equimolar mixture of HCl and $ZnCl_2$. Alcohols are soluble in Lucas reagent and form a clear solution. On reaction, alkyl chlorides are formed which being insoluble result in turbidity in the solution.

$$\text{Alcohol} \xrightarrow[ZnCl_2]{HCl} \text{Alkyl chloride} + H_2O$$

If turbidity appears immediately, tertiary alcohol is indicated.

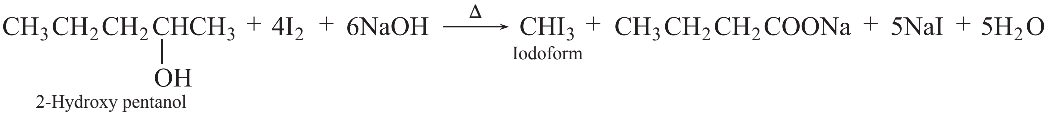
If turbidity appears within five minutes, secondary alcohol is indicated.

If turbidity appears only upon heating, primary alcohol is indicated.

(*b*) **Iodoform test:** When ethyl alcohol or any alcohol containing the group $\boxed{CH_3-\overset{\overset{OH}{|}}{C}H-}$ or $CH_3-\overset{\overset{O}{\|}}{C}-$ group is heated with iodine and aqueous NaOH or Na_2CO_3 solution at 333–343 K, a yellow precipitate of iodoform is obtained.

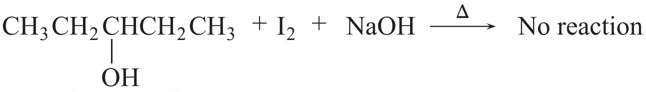
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

$$\underset{\text{Methanol}}{CH_3OH} + I_2 + NaOH \xrightarrow{\Delta} \text{No reaction}$$



$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + CH_3CH_2CH_2COONa + 5NaI + 5H_2O$$

2-Hydroxy pentanol



$$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3 + I_2 + NaOH \xrightarrow{\Delta} \text{No reaction}$$

3-Hydroxy pentanol

(*c*) **Ferric chloride test for phenols:** Phenol gives a violet-coloured water soluble complex with ferric chloride.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \xrightarrow{373\text{ K}} \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

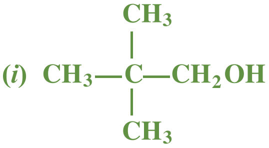
In general, all compounds containing enolic group ($=\overset{|}{C}-OH$) respond to this test.

However, the colours of complexes are different such as green, blue, violet, etc., and depend upon the structure of phenols.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Classify the following as primary, secondary and tertiary alcohols:

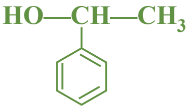


(*i*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$

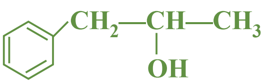
(*ii*) $H_2C=CH-CH_2OH$

(*iii*) $CH_3-CH_2-CH_2-OH$

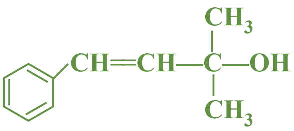
(*iv*)



(*v*)



(*vi*)



Ans. (*i*) Primary (*ii*) Primary

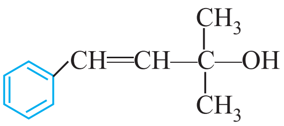
(*iii*) Primary (*iv*) Secondary

(*v*) Secondary (*vi*) Tertiary

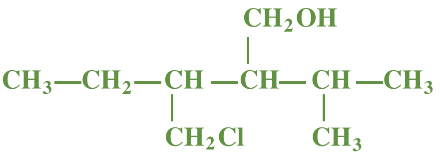
Q. 2. Identify allylic alcohols in the above examples.

Ans. (*ii*) $H_2C=CH-CH_2OH$

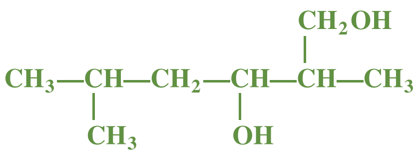
(*vi*)



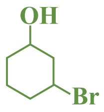
Q. 3. Name the following compounds according to IUPAC system.

(*i*) 

$$CH_3-CH_2-\underset{\substack{|\\ CH_2Cl}}{CH}-\overset{\substack{CH_2OH\\ |}}{CH}-\underset{\substack{|\\ CH_3}}{CH}-CH_3$$

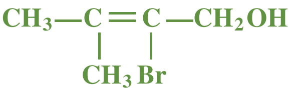
(*ii*) 

$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ OH}}{CH}-\overset{\substack{CH_2OH\\ |}}{CH}-CH_3$$

(*iii*) 

(*iv*) 

$$H_2C=CH-\underset{\substack{|\\ OH}}{CH}-CH_2-CH_2-CH_3$$

(*v*) 

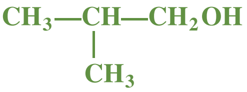
$$CH_3-\underset{\substack{|\\ CH_3}}{C}=\underset{\substack{|\\ Br}}{C}-CH_2OH$$

Ans. (*i*) 3-Chloromethyl-2-isopropylpentan-1-ol (*ii*) 2, 5-Dimethylhexane-1,3-diol

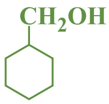
(*iii*) 3-Bromocyclohexanol (*iv*) Hex-1-en-3-ol

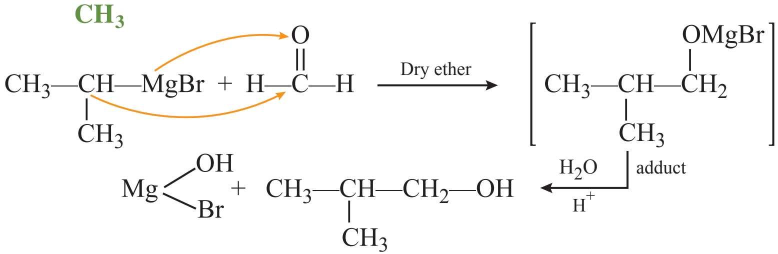
(*v*) 2-Bromo-3-methylbut-2-en-1-ol

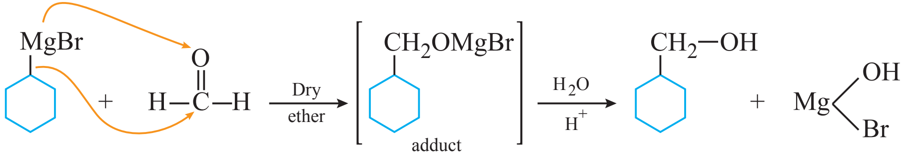
Q. 4. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal.

(*i*) 

$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2OH$$

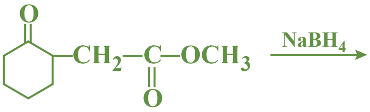
(*ii*) 

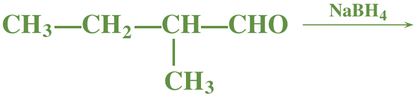
Ans. (*i*) 

(*ii*) 

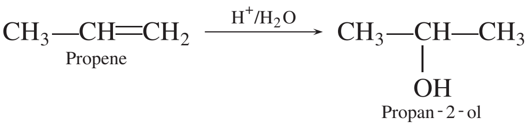
Q. 5. Write structures of the products of the following reactions.

(*i*) $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$

(*ii*) 

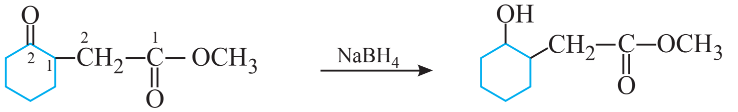
(*iii*) 

$$CH_3-CH_2-\underset{\substack{|\\ CH_3}}{CH}-CHO \xrightarrow{NaBH_4}$$

Ans. (*i*) 

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{H^+/H_2O} \underset{\text{Propan-2-ol}}{CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3}$$

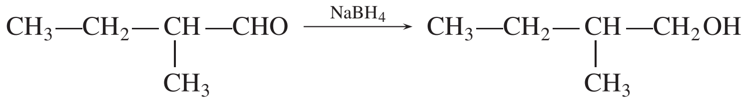
(*ii*) $NaBH_4$ is a weak reducing agent, it reduces the aldehydes/ketones and not the esters.



Methyl (2-oxocyclohexyl) ethanoate

Methyl (2-hydroxycyclohexyl) ethanoate

(*iii*)



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO \xrightarrow{NaBH_4} CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$$

2-Methylbutanal 2-Methylbutan-1-ol

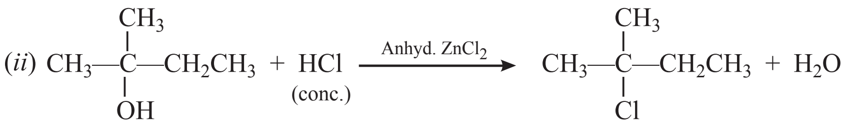
Q. 6. Give structures of the products you would expect when each of the following alcohol reacts with (*a*) HCl–$ZnCl_2$, (*b*) HBr and (*c*) $SOCl_2$.

(*i*) Butan-1-ol (*ii*) 2-Methylbutan-2-ol

Ans. **(*a*) With HCl–$ZnCl_2$ (Lucas reagent):**

(*i*) $\underset{\text{Butan-1-ol}(1°)}{CH_3CH_2CH_2CH_2-OH} + \underset{\text{(conc.)}}{HCl} \xrightarrow{\text{Anhyd.}ZnCl_2}$ No reaction at room temperature

(*ii*)



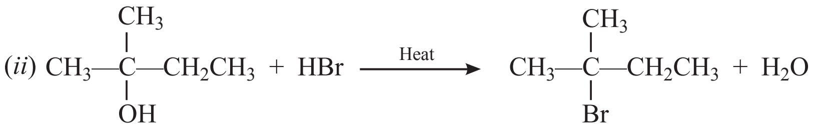
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_2CH_3 + \underset{\text{(conc.)}}{HCl} \xrightarrow{\text{Anhyd. }ZnCl_2} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_2CH_3 + H_2O$$

2-Methylbutan-2-ol 2-Chloro-2-methylbutane

(*b*) With HBr:

(*i*) $$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + HBr \xrightarrow{\text{Heat}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} + H_2O$$

(*ii*)



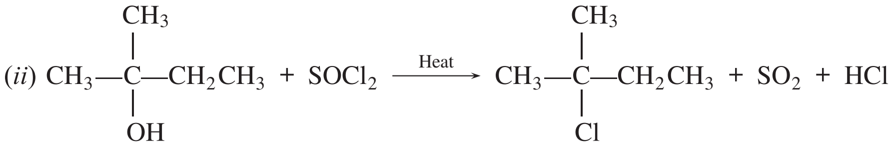
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_2CH_3 + HBr \xrightarrow{\text{Heat}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_2CH_3 + H_2O$$

2-Methylbutan-2-ol 2-Bromo-2-methylbutane

(*c*) With $SOCl_2$:

(*i*) $$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + SOCl_2 \xrightarrow{\text{Heat}} \underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + SO_2 + HCl$$

(*ii*)

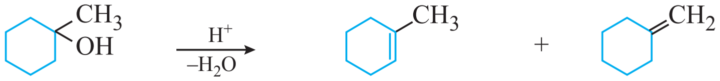


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_2CH_3 + SOCl_2 \xrightarrow{\text{Heat}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_2CH_3 + SO_2 + HCl$$

2-Methylbutan-2-ol 2-Chloro-2-methylbutane

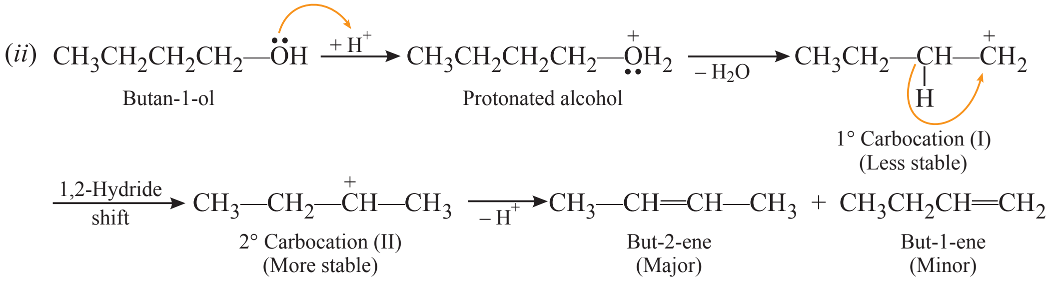
Q. 7. Predict the major product of acid catalysed dehydration of (*i*) 1-methylcyclohexanol and (*ii*) butan-1-ol.

Ans. (*i*) Acid catalysed dehydration of 1-methylcyclohexanol can give two products, I and II. Since product (I) is more substituted, according to Saytzeff rule, it is the major product.



I
1-Methylcyclohexene
(Major product)

II
Methylenecyclohexane
(Minor product)

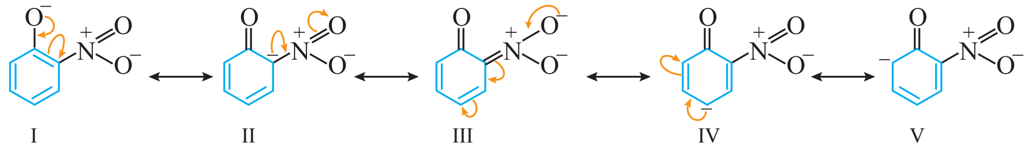


(*ii*) $$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2-\ddot{O}H} \xrightarrow{+H^+} \underset{\text{Protonated alcohol}}{CH_3CH_2CH_2CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2} \xrightarrow[-H_2O]{} \underset{\substack{1°\text{ Carbocation (I)}\\ \text{(Less stable)}}}{CH_3CH_2-\underset{\displaystyle H}{\underset{|}{CH}}-\overset{+}{C}H_2}$$

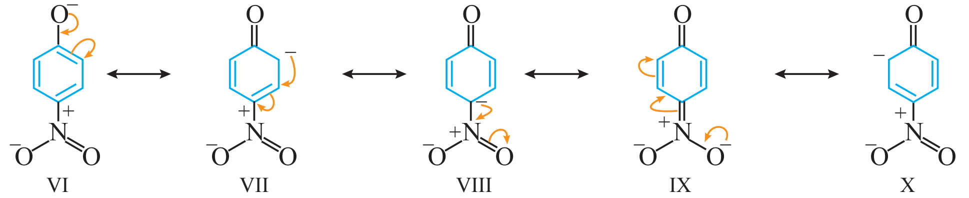
$$\xrightarrow[\text{shift}]{\text{1,2-Hydride}} \underset{\substack{2°\text{ Carbocation (II)}\\ \text{(More stable)}}}{CH_3-CH_2-\overset{+}{C}H-CH_3} \xrightarrow[-H^+]{} \underset{\substack{\text{But-2-ene}\\ \text{(Major)}}}{CH_3-CH{=}CH-CH_3} + \underset{\substack{\text{But-1-ene}\\ \text{(Minor)}}}{CH_3CH_2CH{=}CH_2}$$

Q. 8. *Ortho* and *para*-nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions. ***[CBSE (AI) 2009]***

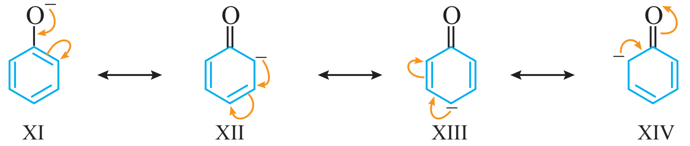
Ans. The resonance structures of *o*- and *p*-nitrophenoxide ions and phenoxide ion are given as follows:



Resonance structures of *o*-nitrophenoxide ion



Resonance structures of *p*-nitrophenoxide ion



Resonance structures of phenoxide ion

It is clear from the above structures that due to –R-effect of NO_2 group, *o*-and *p*-nitrophenoxide ions are more stable than phenoxide ion. Consequently, *o*- and *p*-nitrophenols are more acidic than phenol.

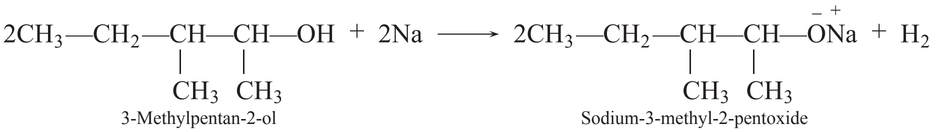
Q. 9. Write the equations involved in the following reactions:

(*i*) Reimer–Tiemann reaction **(*ii*) Kolbe's reaction**

Ans. Refer to Basic Concepts Point 15.

Q. 10. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol. ***[HOTS]***

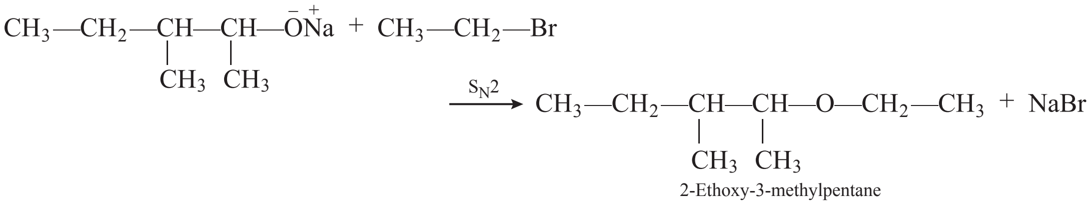
Ans.



$$2CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}\underset{CH_3}{\underset{|}{CH}}{-}OH + 2Na \longrightarrow 2CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}\underset{CH_3}{\underset{|}{CH}}{-}\overset{-}{O}\overset{+}{Na} + H_2$$

3-Methylpentan-2-ol Sodium-3-methyl-2-pentoxide

$$\underset{\text{Ethanol}}{CH_3{-}CH_2{-}OH} + HBr \xrightarrow{\Delta} \underset{\text{Bromoethane}}{CH_3{-}CH_2{-}Br} + H_2O$$

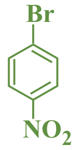


$$CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}\underset{CH_3}{\underset{|}{CH}}{-}\overset{-}{O}\overset{+}{Na} + CH_3{-}CH_2{-}Br \xrightarrow{S_N2} CH_3{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}\underset{CH_3}{\underset{|}{CH}}{-}O{-}CH_2{-}CH_3 + NaBr$$

2-Ethoxy-3-methylpentane

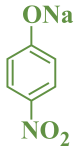
Q. 11. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(*i*)



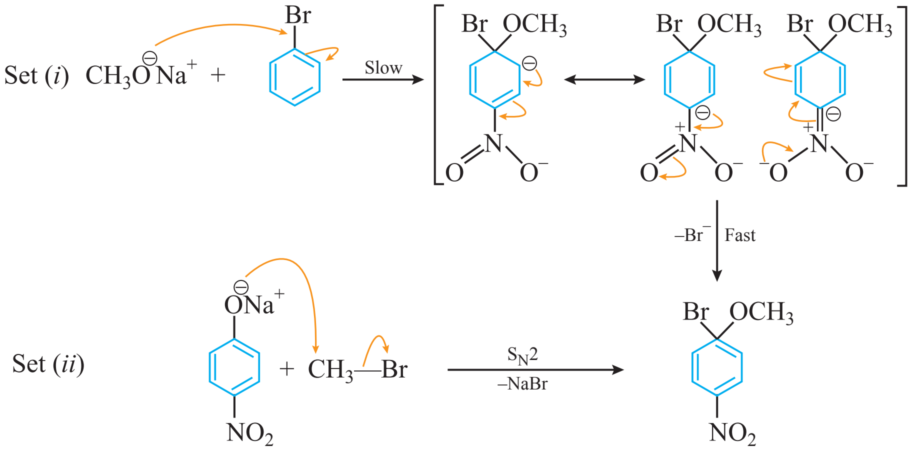
+ CH_3ONa

(*ii*)



+ CH_3Br

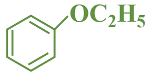
Ans. Chemically both sets are equally probable. In set (*i*), the Br atom is activated by the electron withdrawing effect of —NO_2 group. Therefore, nucleophilic attack by $CH_3O^-Na^+$ followed by elimination of NaBr gives desired ether, while in set (*ii*) nucleophilic attack by 4-nitrophenoxide ion on methyl bromide gives the desired ether.

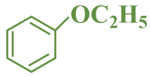


1-Methoxy-4-nitrobenzene

Q. 12. Predict the products of the following reactions:

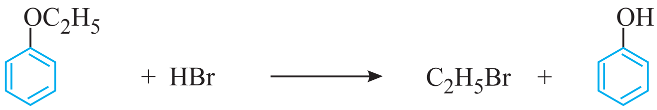
(i) $CH_3—CH_2—CH_2—O—CH_3 + HBr \longrightarrow$

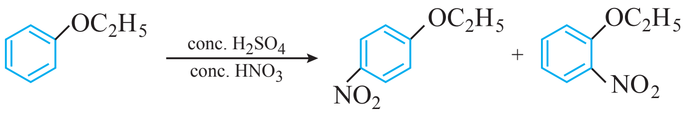
(ii)  $+ HBr \longrightarrow$

(iii)  $\xrightarrow[\text{Conc. HNO}_3]{\text{Conc. H}_2\text{SO}_4}$

(iv) $(CH_3)_3C—OC_2H_5 \xrightarrow{HI}$ **[*CBSE (F) 2012*]**

Ans. (i) $CH_3—CH_2—CH_2—O—CH_3 + H—Br \longrightarrow CH_3—Br + CH_3—CH_2—CH_2—OH$

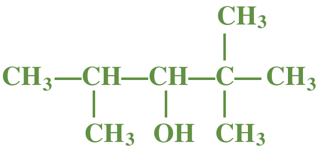
(ii) 

(iii) 

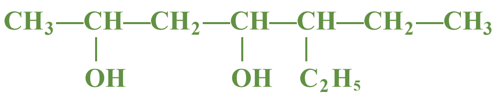
(iv) $(CH_3)_3C—OC_2H_5 + HI \longrightarrow (CH_3)_3C—I + C_2H_5—OH$

NCERT Textbook Exercises

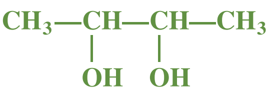
Q. 1. Write the IUPAC names of the following compounds:

(i) 

$CH_3—\underset{CH_3}{CH}—\underset{OH}{CH}—\overset{CH_3}{\underset{CH_3}{C}}—CH_3$

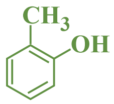
(ii) 

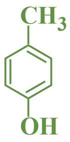
$CH_3—\underset{OH}{CH}—CH_2—\underset{OH}{CH}—\underset{C_2H_5}{CH}—CH_2—CH_3$

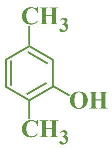
(iii) 

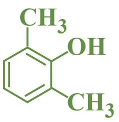
$CH_3—\underset{OH}{CH}—\underset{OH}{CH}—CH_3$

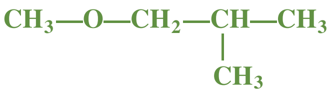
(iv) $HOCH_2—CHOH—CH_2OH$

(v) 

(vi) 

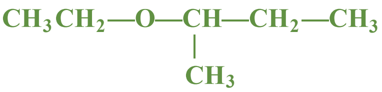
(vii) 

(viii) 

(*ix*) 
$CH_3-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(*x*) $C_6H_5-O-C_2H_5$

(*xi*) $C_6H_5-O-C_7H_{15}$ (*n*–)

(*xii*) 
$CH_3CH_2-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

Ans. (*i*) 2, 2, 4-Trimethylpentan-3-ol

(*ii*) 5-Ethylheptane-2, 4-diol

(*iii*) Butane-2, 3-diol

(*iv*) Propane-1, 2, 3-triol

(*v*) 2-Methylphenol

(*vi*) 4-Methylphenol

(*vii*) 2, 5-Dimethylphenol

(*viii*) 2, 6-Dimethylphenol

(*ix*) 1-Methoxy-2-methylpropane

(*x*) Ethoxybenzene

(*xi*) 1-Phenoxyheptane

(*xii*) 2-Ethoxybutane

Q. 2. Write the structures of the compounds whose IUPAC names are as follows:

(*i*) 2-Methylbutan-2-ol

(*ii*) 1-Phenylpropan-2-ol

(*iii*) 3, 5-Dimethylhexane-1, 3, 5-triol

(*iv*) 2, 3-Diethylphenol

(*v*) 1-Ethoxypropane

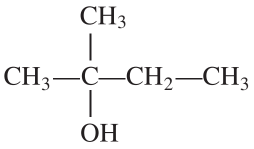
(*vi*) 2-Ethoxy-3-methylpentane

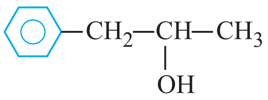
(*vii*) Cyclohexylmethanol

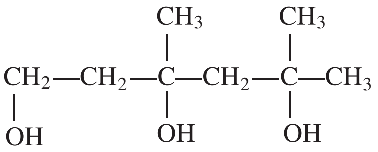
(*viii*) 3-Cyclohexylpentan-3-ol

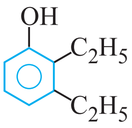
(*ix*) Cyclopent-3-en-1-ol

(*x*) 4-Chloro-3-ethylbutan-1-ol

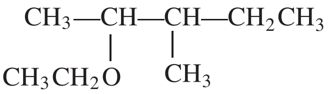
Ans. (*i*) 
$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_3$

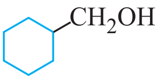
(*ii*) 

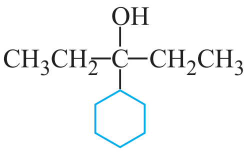
(*iii*) 
$\underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

(*iv*) 

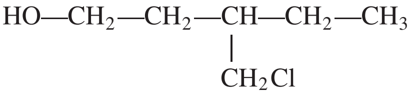
(*v*) $CH_3CH_2O-CH_2CH_2CH_3$

(*vi*) 
$CH_3-\underset{CH_3CH_2O}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_3$

(*vii*) 

(*viii*) 

(*ix*) 

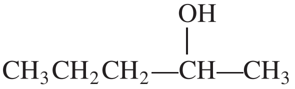
(*x*) 
$HO-CH_2-CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-CH_2-CH_3$

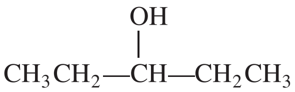
Q. 3. (*a*) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.

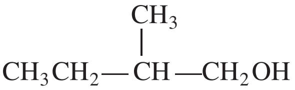
(*b*) Classify the isomers in Q. 3(*a*) into primary, secondary and tertiary alcohols.

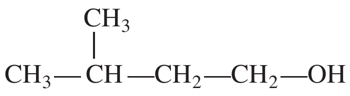
Ans. Eight isomers are possible. These are:

(*i*) $CH_3CH_2CH_2CH_2CH_2OH$
Pentan-1-ol(1°)

(*ii*) 
$CH_3CH_2CH_2-\overset{OH}{\overset{|}{CH}}-CH_3$
Pentan-2-ol(2°)

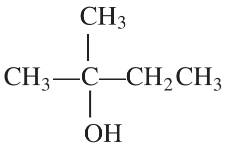
(*iii*) 
$CH_3CH_2-\overset{OH}{\overset{|}{CH}}-CH_2CH_3$
Pentan-3-ol(2°)

(*iv*) 
$CH_3CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2OH$
2-Methylbutan-1-ol(1°)

(*v*) 

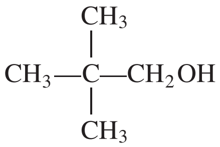
$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_2-OH$$

3-Methylbutan-1-ol(1°)

(*vi*) 

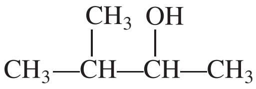
$$CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2CH_3$$

2-Methylbutan-2-ol (3°)

(*vii*) 

$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH$$

2,2-Dimethylpropan-1-ol(1°)

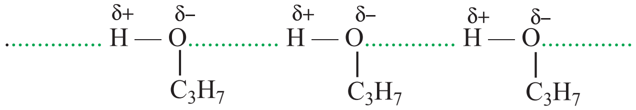
(*viii*) 

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

3-Methylbutan-2-ol(2°)

Q. 4. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

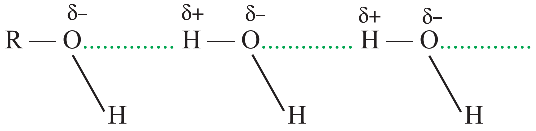
Ans. The molecules of butane are held together by weak van der Waal's forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonds.



Hence, the boiling point of propanol is much higher than that of butane.

Q. 5. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

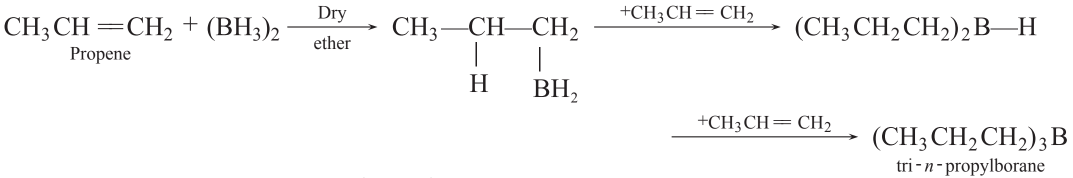
Ans. Alcohols can form H-bonds with water and break the H-bonds already existing between water molecules. Hence, they are soluble in water.



In contrast, hydrocarbons cannot form H-bonds with water and hence are insoluble in water.

Q. 6. What is meant by hydroboration–oxidation reaction? Illustrate it with an example.

Ans. The addition of diborane to alkenes to form trialkylboranes followed by their oxidation with alkaline hydrogen peroxide to form alcohols is called hydroboration–oxidation reaction.



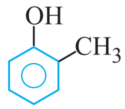
$$\underset{\text{Propene}}{CH_3CH=CH_2} + (BH_3)_2 \xrightarrow[\text{ether}]{\text{Dry}} CH_3-\underset{H}{\underset{|}{C}H}-\underset{BH_2}{\underset{|}{C}H_2} \xrightarrow{+CH_3CH=CH_2} (CH_3CH_2CH_2)_2B-H \xrightarrow{+CH_3CH=CH_2} \underset{\text{tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B}$$

$$\underset{\text{tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B} + 3H_2O_2 \xrightarrow{OH^-,\ H_2O} \underset{n\text{-Propylalcohol}}{3CH_3CH_2CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

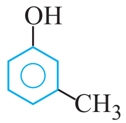
The alcohols obtained by this process is contrary to the Markovnikov's rule.

Q. 7. Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.

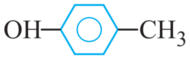
Ans. The three isomers are given as follows:



2-Methylphenol
or *o*-Cresol



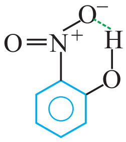
3-Methylphenol
or *m*-Cresol



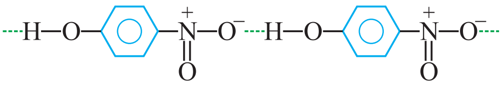
4-Methylphenol
or *p*-Cresol

Q. 8. While separating a mixture of *ortho* and *para*-nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reasons.

Ans. *o*-Nitrophenol is steam volatile as it exists as discrete molecules due to intramolecular H-bonding and hence can be separated by steam distillation from *p*-nitrophenol which is less volatile as it exists as associated molecules because of intermolecular H-bonding.



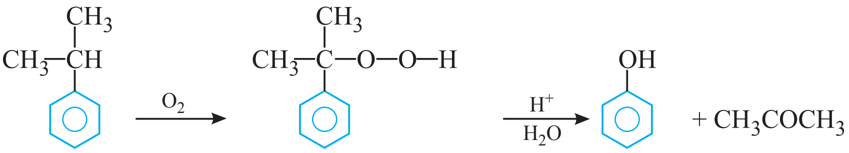
o-Nitrophenol



p-Nitrophenol

Q. 9. Give the equations of reactions for the preparation of phenol from cumene. ***[CBSE 2020 (56/3/2)]***

Ans.

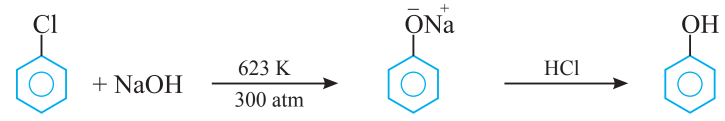


Cumene

Cumene hydroperoxide

Q. 10. Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans.



Chlorobenzene

Sodium phenoxide

Phenol

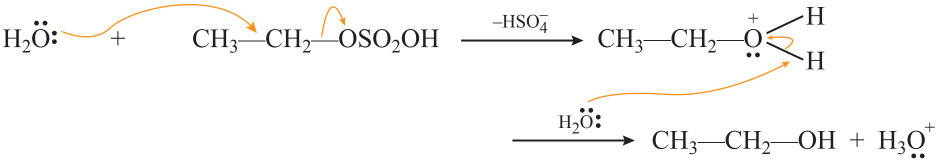
Q. 11. Write the mechanism of hydration of ethene to form ethanol. ***[CBSE 2019 (56/4/2), 2020 (56/5/1)]***

Ans. Direct addition of H_2O to ethene in presence of an acid does not occur. Ethene is first passed through conc. H_2SO_4, when ethyl hydrogen sulphate is formed.

$$H_2SO_4 \longrightarrow H^+ + {}^-OSO_2OH$$

$$\underset{\text{Ethene}}{CH_2=CH_2} + H^+ \longrightarrow \underset{\text{Ethyl carbocation}}{CH_3-\overset{+}{C}H_2} \xrightarrow[\text{Fast}]{{}^-OSO_2OH} \underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-OSO_2OH}$$

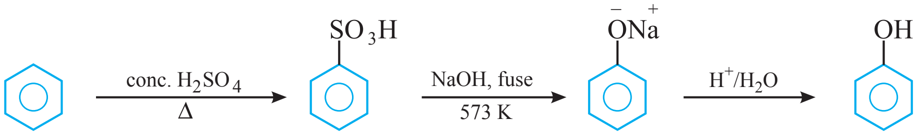
Ethyl hydrogen sulphate when boiled with water undergoes hydrolysis to form ethanol.



Ethanol

Q. 12. You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

Ans.



Benzene

Benzene sulphonic acid

Sodium phenoxide

Phenol

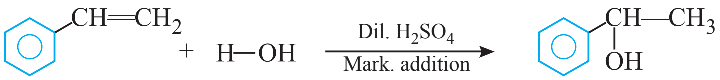
Q. 13. Show how will you synthesise:

(*i*) 1-phenylethanol from a suitable alkene?

(*ii*) cyclohexylmethanol using an alkyl halide by an S_N2 reaction?

(*iii*) pentan-1-ol using a suitable alkyl halide?

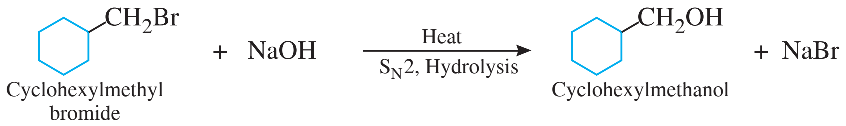
Ans. (*i*) Addition of H_2O to ethenylbenzene in presence of dil. H_2SO_4 gives 1-phenylethanol.



Phenylethene

1-Phenylethanol

(*ii*) Hydrolysis of cyclohexylmethyl bromide by aqueous NaOH gives cyclohexylmethanol.



(*iii*) Hydrolysis of 1-bromopentane by aqueous NaOH gives pentan-1-ol.

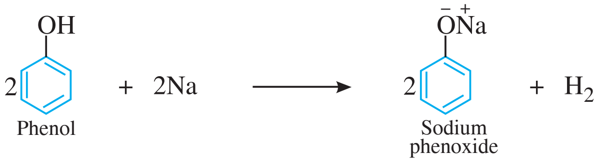
$$\underset{\text{1-bromopentane}}{CH_3—CH_2—CH_2—CH_2—CH_2—Br} + NaOH \xrightarrow[S_N2,\ \text{Hydrolysis}]{\text{Heat}}$$

$$\underset{\text{Pentan-1-ol}}{CH_3CH_2—CH_2—CH_2—CH_2—OH} + NaBr$$

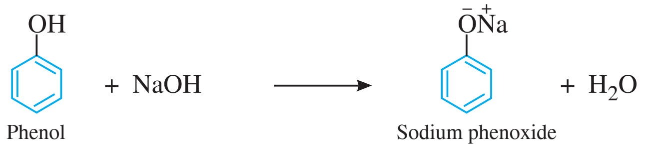
Q. 14. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol. **[*CBSE (AI) 2009*]**

Ans. The reactions showing acidic nature of phenol are:

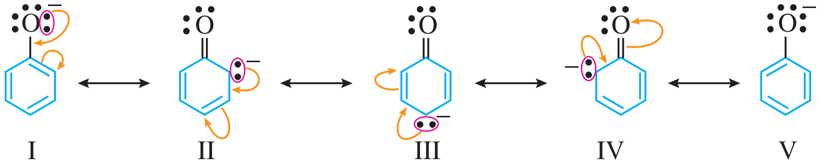
(*i*) **Reaction with sodium:** Phenol reacts with active metals like sodium to liberate H_2 gas.



(*ii*) **Reaction with NaOH:** Phenol dissolves in NaOH to form sodium phenoxide and water.

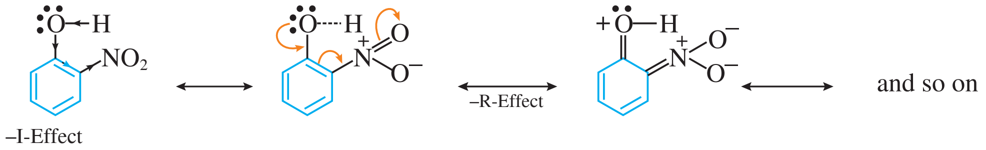


Comparison of acidic character of phenol and ethanol: Phenol is more acidic than ethanol. This is due to the reason that phenoxide ion left after the loss of a proton from phenol is stabilised by resonance while ethoxide ion left after loss of a proton from ethanol is not stabilised by resonance.

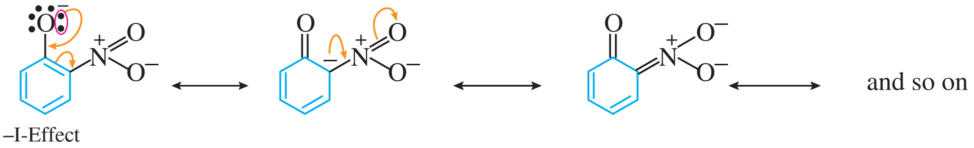


Q. 15. Explain why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol. **[*HOTS*]**

Ans. Due to strong –R and –I-effect of the NO_2 group, electron density in the O—H bond decreases and hence the loss of a proton becomes easy.

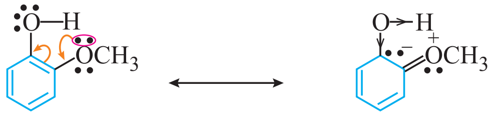


Moreover, after the loss of a proton, the *o*-nitrophenoxide ion left behind is stabilised by resonance.

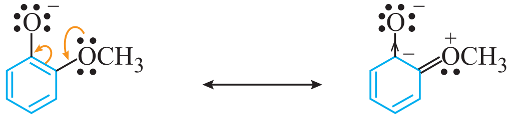


This makes *o*-nitrophenol a stronger acid.

In contrast, due to +R effect, OCH_3 group increases the electron-density in the O—H bond thereby making the loss of proton difficult.



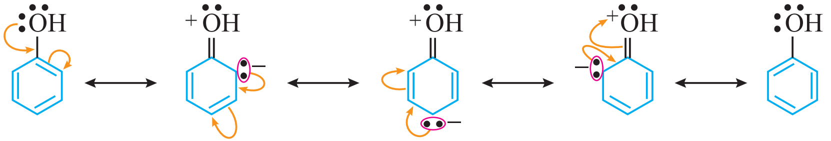
Moreover, the *o*-methoxyphenoxide ion left after the loss of a proton is destabilised by resonance as the two negative charges repel each other thereby making *o*-methoxyphenol a weaker acid.



Hence, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

Q. 16. Explain how does —OH group attached to a carbon of benzene ring activate it towards electrophilic substitution.

Ans. Phenol may be regarded as a resonance hybrid of following structures:



I II III IV V

Thus, due to +R-effect of the —OH group, the electron density in the benzene ring increases thereby facilitating the attack of an electrophile. In other words, presence of —OH group, activates the benzene ring towards electrophilic substitution reactions. Now, since the electron density is relatively higher at the two *o*- and one *p*-position, electrophilic substitution occurs mainly at *o*- and *p*-positions.

Q. 17. Give equations of the following reactions:

(*i*) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

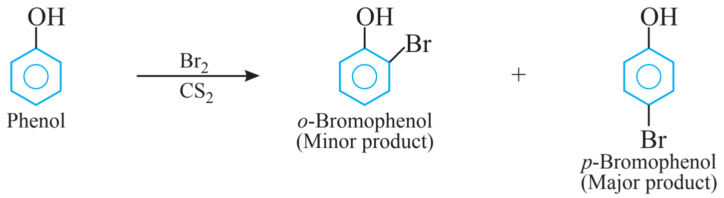
(*ii*) Bromine in CS_2 with phenol.

(*iii*) Dilute HNO_3 with phenol.

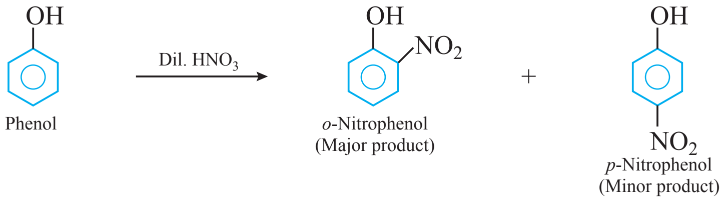
(*iv*) Treating phenol with chloroform in presence of aqueous NaOH.

Ans. (*i*) $$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + 2[O] \xrightarrow[H^+/H_2O]{\text{Alk. KMnO}_4\text{ (Oxidation)}} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

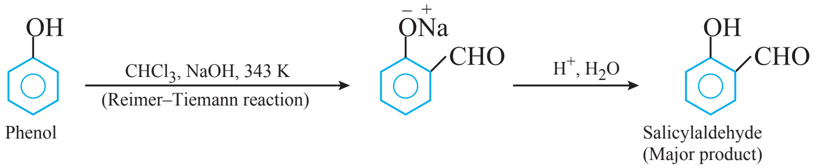
(*ii*)



(*iii*)



(*iv*)



A small amount of *p*-hydroxybenzaldehyde is also formed.

Q. 18. Explain the following with an example:

(*i*) Kolbe's reaction **(*ii*) Reimer–Tiemann reaction**

(*iii*) Williamson ether synthesis **(*iv*) Unsymmetrical ether**

Ans. (*i*) Refer to Basic Concepts Point 15 (*i*).

(*ii*) Refer to Basic Concepts Point 15 (*ii*).

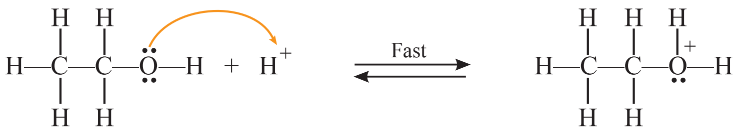
(*iii*) Refer to Basic Concepts Point 15(*v*).

(*iv*) **Unsymmetrical ether:** If the alkyl or aryl groups attached to the oxygen atom are different, ethers are called unsymmetrical ethers. For example, ethyl methyl ether, methyl phenyl ether, etc.

Q. 19. Write the mechanism of acid catalysed dehydration of ethanol to yield ethene. **[*CBSE 2019 (56/4/1)*]**

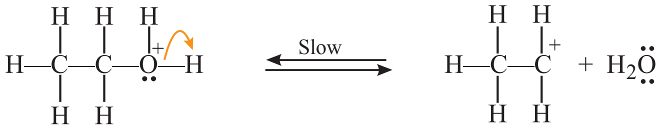
Ans. The mechanism of dehydration of ethanol involves the following steps:

Step 1: Formation of protonated alcohol

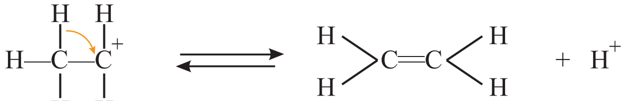


Ethanol Ethyl oxonium ion

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



Step 3: Formation of ethane by elimination of a proton



Ethene

The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

Q. 20. How are the following conversions carried out?

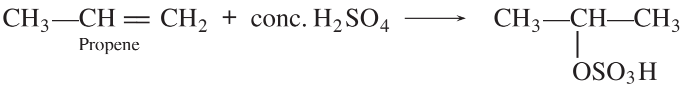
(*i*) Propene $\longrightarrow$ Propan-2-ol

(*ii*) Benzyl chloride $\longrightarrow$ Benzyl alcohol

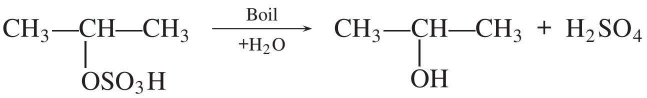
(*iii*) Ethyl magnesium chloride $\longrightarrow$ Propan-1-ol

(*iv*) Methyl magnesium bromide $\longrightarrow$ 2-Methylpropan-2-ol

Ans. (*i*) Propan-2-ol can be prepared from propene by hydration as shown below:

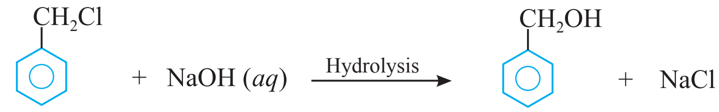


$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + \text{conc. } H_2SO_4 \longrightarrow \underset{\text{Isopropyl hydrogen sulphate}}{CH_3{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}{-}CH_3}$$

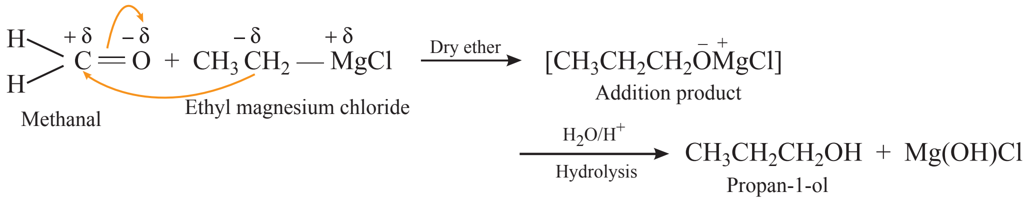


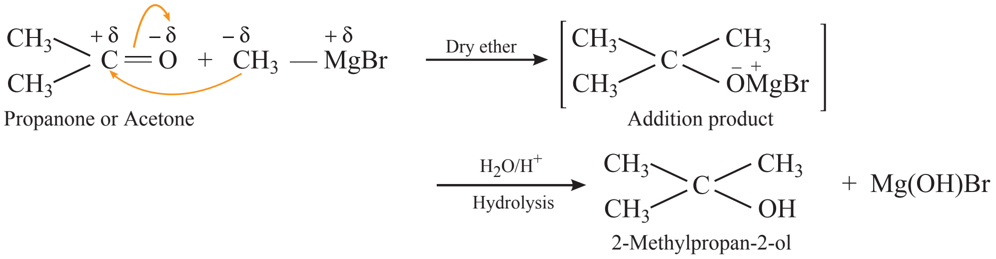
$$CH_3{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}{-}CH_3 \xrightarrow[+H_2O]{\text{Boil}} \underset{\text{Propan-2-ol}}{CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3} + H_2SO_4$$

(*ii*)



Benzyl chloride Benzyl alcohol

(*iii*) 

(*iv*) 

Q. 21. Name the reagents used in the following reactions: **[*CBSE (F) 2014*]**

(*i*) **Oxidation of primary alcohol to carboxylic acid**

(*ii*) **Oxidation of a primary alcohol to aldehyde.**

(*iii*) **Bromination of phenol to 2, 4, 6-tribromophenol**

(*iv*) **Benzyl alcohol to benzoic acid.**

(*v*) **Dehydration of propan-2-ol to propene.**

(*vi*) **Butan-2-one to butan-2-ol**

Ans. (*i*) Acidified potassium dichromate solution ($K_2Cr_2O_7/H_2SO_4$) or alkaline potassium permanganate solution ($KMnO_4/OH^-$) followed by hydrolysis with dil. H_2SO_4.

(*ii*) Pyridinium chlorochromate (PCC), $C_5H_5\overset{+}{N}HClCrO_3^-$ in CH_2Cl_2

(*iii*) Aqueous bromine (Br_2/H_2O)

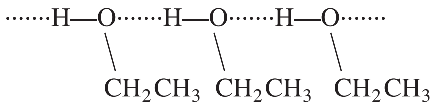
(*iv*) Acidified or alkaline potassium permanganate.

(*v*) Conc. H_2SO_4 at 433–443 K.

(*vi*) Lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$)

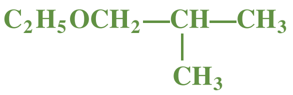
Q. 22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Ans. Ethanol undergoes intermolecular H-bonding due to the presence of a hydrogen attached to the electronegative oxygen atom. As a result, ethanol exists as associated molecules.



Consequently, a large amount of energy is required to break these hydrogen bonds. Therefore, the boiling point of ethanol is higher than that of methoxymethane which does not form H-bonds.

Q. 23. Give the IUPAC names of the following ethers:

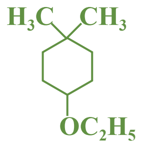
(*i*) 

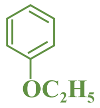
$C_2H_5OCH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(*ii*) $CH_3OCH_2CH_2Cl$

(*iii*) $O_2N-C_6H_4-OCH_3$ (*p*)

(*iv*) $CH_3CH_2CH_2OCH_3$

(*v*) 

(*vi*) 

Ans. (*i*) 1-Ethoxy-2-methylpropane

(*ii*) 2-Chloro-1-methoxyethane

(*iii*) 4-Nitroanisole

(*iv*) 1-Methoxypropane

(*v*) 4-Ethoxy-1, 1-dimethylcyclohexane

(*vi*) Ethoxybenzene

Q. 24. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

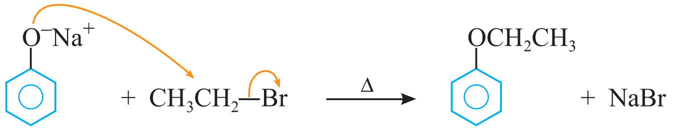
(*i*) 1-Propoxypropane **(*ii*) Ethoxybenzene**

(*iii*) 2-methoxy-2-methylpropane **[*CBSE 2020 (56/4/2)*]**

(*iv*) 1-Methoxyethane

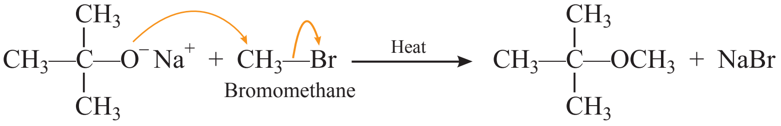
Ans. (*i*) $\underset{\text{Sodium propoxide}}{CH_3CH_2CH_2O^-Na^+} + \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2—Br} \xrightarrow{\text{Heat}} \underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} + NaBr$

(*ii*)



Sodium phenoxide Bromoethane Ethoxybenzene

(*iii*)



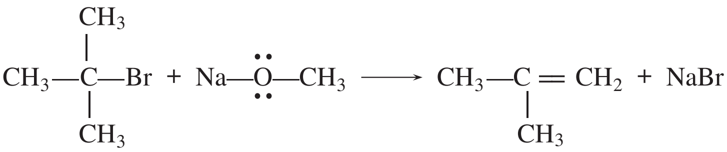
$$CH_3—\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}—O^-Na^+ + CH_3—Br \xrightarrow{\text{Heat}} CH_3—\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}—OCH_3 + NaBr$$

Bromomethane 2-Methoxy-2-methylpropane

(*iv*) $\underset{\text{Sodium ethoxide}}{CH_3CH_2O^-Na^+} + \underset{\text{Bromomethane}}{CH_3—Br} \xrightarrow{\text{Heat}} \underset{\text{1-Methoxyethane}}{CH_3—CH_2—O—CH_3} + NaBr$

Q. 25. Illustrate with examples the limitations of Williamson synthesis for the preparation of certain type of ethers.

Ans. (*i*) Williamson's synthesis cannot be employed for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of CH_3ONa with $(CH_3)_3C—Br$ gives exclusively 2-methylpropene.



$$CH_3—\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}—Br + Na—\ddot{\underset{..}{O}}—CH_3 \longrightarrow CH_3—\underset{CH_3}{\underset{|}{C}} = CH_2 + NaBr$$

(*ii*) Aryl halides and vinyl halides cannot be used as substrates because of their low reactivity in nucleophilic substitution.

Q. 26. How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

Ans. The following method can be used:

Williamson's synthesis

(*i*) $\underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH} + PBr_3 \longrightarrow \underset{\text{1-Bromopropane}}{3CH_3CH_2CH_2Br} + H_3PO_3$

(*ii*) $\underset{\text{Propan-1-ol}}{2CH_3CH_2CH_2OH} + 2Na \longrightarrow \underset{\text{Sodium propoxide}}{2CH_3CH_2CH_2O^-Na^+} + H_2$

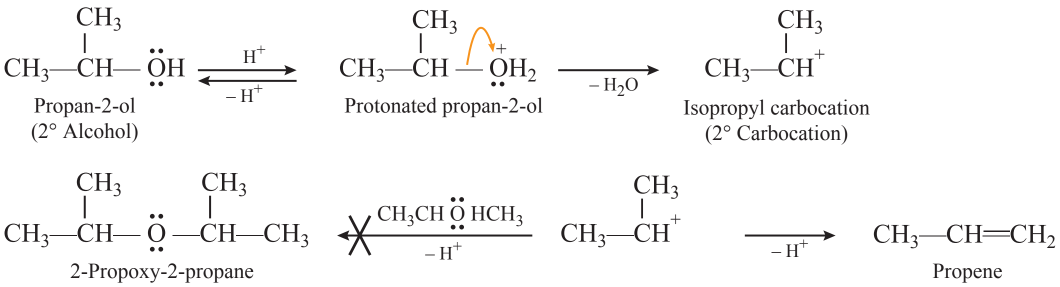
Mechanism: $CH_3CH_2CH_2O^-Na^+ + CH_3CH_2CH_2—Br \xrightarrow[\text{Heat}]{\text{Dry ether}} \underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} + NaBr$

Q. 27. Preparation of ethers by acid-catalysed dehydration of secondary and tertiary alcohols is not a suitable method. Give reason.

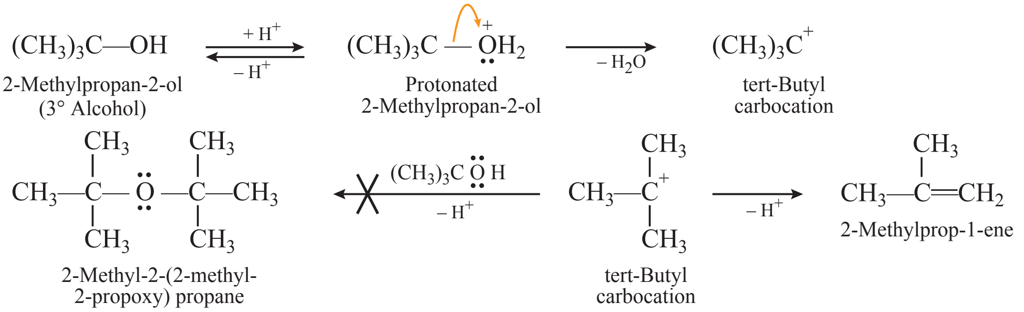
Ans. Acid-catalysed dehydration of primary alcohols to ethers occurs by S_N2 reaction involving nucleophilic attack of the alcohol molecule on the protonated alcohol molecule.

$$CH_3CH_2CH_2\ddot{\underset{..}{O}}H + CH_3CH_2CH_2—\overset{+}{O}H_2 \xrightarrow[-H_2O]{S_N2} CH_3CH_2CH_2—\ddot{\underset{..}{O}}—CH_2CH_2CH_3$$

Under these conditions, secondary and tertiary alcohols, however, give alkenes rather than ethers. This is because due to steric hindrance, nucleophilic attack of the alcohol molecule on the protonated alcohol molecule does not occur. Instead, protonated secondary and tertiary alcohols lose a molecule of water to form stable secondary and tertiary carbocations. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.



Similarly, tertiary alcohols give alkenes rather than ethers.

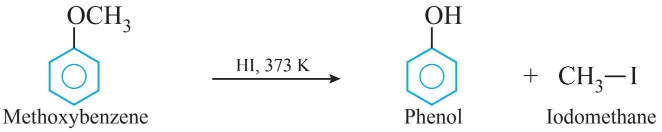


Q. 28. Write the equation for the reaction of hydrogen iodide with

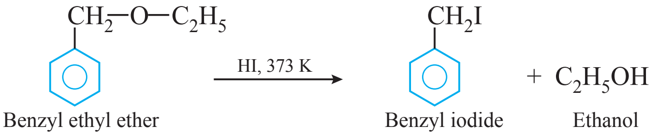
(*i*) 1-propoxypropane (*ii*) methoxybenzene (*iii*) benzyl ethyl ether

Ans. (*i*) $$\underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3} \xrightarrow[373\,K]{HI} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2{-}OH} + \underset{\text{Iodopropane}}{CH_3CH_2CH_2{-}I}$$

(*ii*)

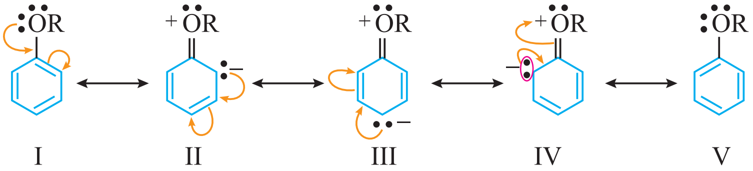


(*iii*)

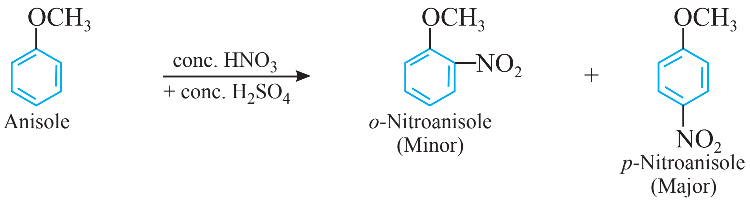


Q. 29. Explain the fact that in aryl alkyl ethers (*i*) the alkoxy group activates the benzene ring towards electrophilic substitution and (*ii*) it directs the incoming substituents to ortho and para positions in benzene ring.

Ans. **Electrophilic substitution reactions:** In aryl alkyl ethers, the +R-effect of the alkoxy group (OR) increases the electron density in the benzene ring thereby activating the benzene ring towards electrophilic substitution reactions.

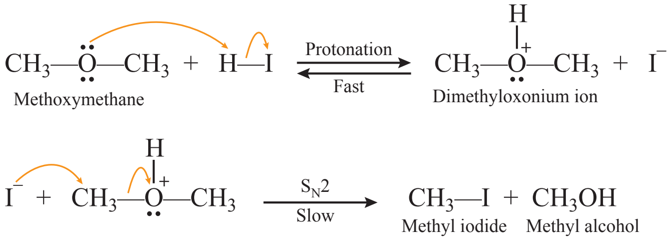


Since the electron density increase more at the two ortho and one para position as compared to *m*-positions, electrophilic substitution reactions mainly occur at *o*-and *p*-positions. For example,



Q. 30. Write mechanism of the reaction of HI with methoxymethane.

Ans. With equimolar amounts of HI and methoxymethane, a mixture of methyl alcohol and methyl iodide are formed by the following mechanism:



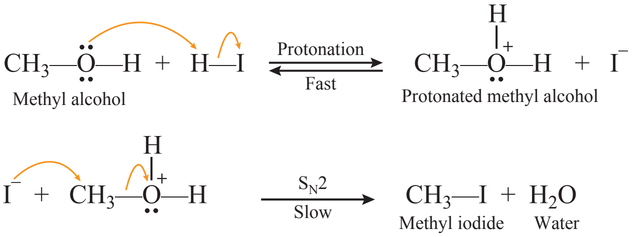
Step I: $$CH_3-\ddot{\underset{\cdot\cdot}{O}}-CH_3 + H-I \underset{\text{Fast}}{\overset{\text{Protonation}}{\rightleftharpoons}} CH_3-\overset{H}{\overset{|+}{\underset{\cdot\cdot}{O}}}-CH_3 + I^-$$

Methoxymethane Dimethyloxonium ion

Step II: $$I^- + CH_3-\overset{H}{\overset{|+}{\underset{\cdot\cdot}{O}}}-CH_3 \xrightarrow[\text{Slow}]{S_N2} CH_3-I + CH_3OH$$

Methyl iodide Methyl alcohol

If excess of HI is used, methyl alcohol formed in step II is also converted into methyl iodide by the following mechanism:



Step III: $$CH_3-\ddot{\underset{\cdot\cdot}{O}}-H + H-I \underset{\text{Fast}}{\overset{\text{Protonation}}{\rightleftharpoons}} CH_3-\overset{H}{\overset{|+}{\underset{\cdot\cdot}{O}}}-H + I^-$$

Methyl alcohol Protonated methyl alcohol

Step IV: $$I^- + CH_3-\overset{H}{\overset{|+}{\underset{\cdot\cdot}{O}}}-H \xrightarrow[\text{Slow}]{S_N2} CH_3-I + H_2O$$

Methyl iodide Water

Q. 31. Write equations of the following reactions:

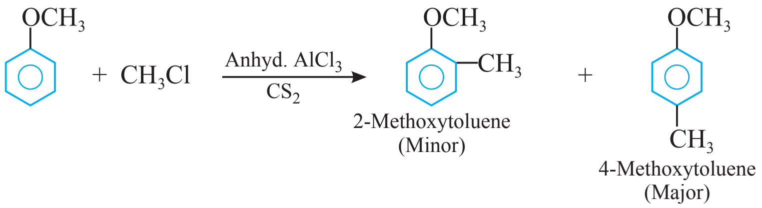
(*i*) Friedel–Crafts reaction—alkylation of anisole

(*ii*) Nitration of anisole

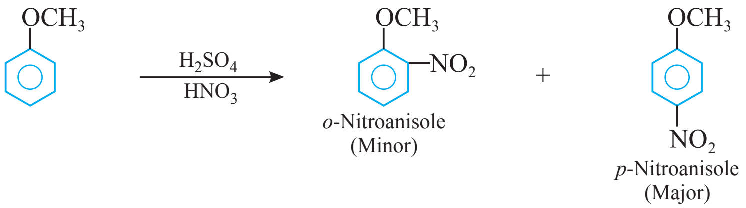
(*iii*) Bromination of anisole in ethanoic acid medium

(*iv*) Friedel–Crafts acetylation of anisole.

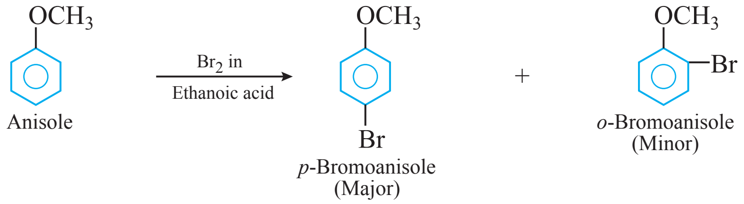
Ans. **(*i*) Friedel–Crafts reaction (Alkylation):**



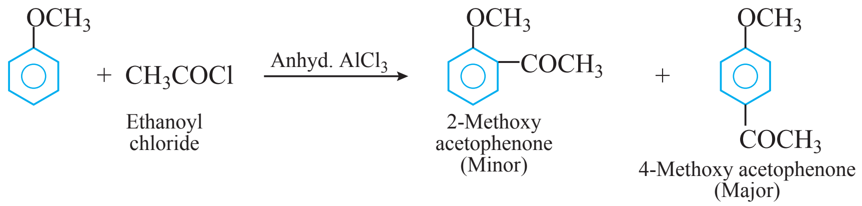
(*ii*) Nitration of anisole: Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



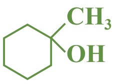
(*iii*) Halogenation:



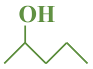
(*iv*) Friedel–Crafts acetylation of anisole:

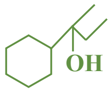


Q. 32. Show how would you synthesise the following alcohols from appropriate alkenes? **[*HOTS*]**

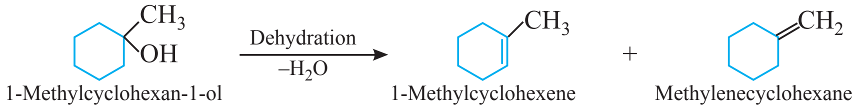
(*i*)


(*ii*)

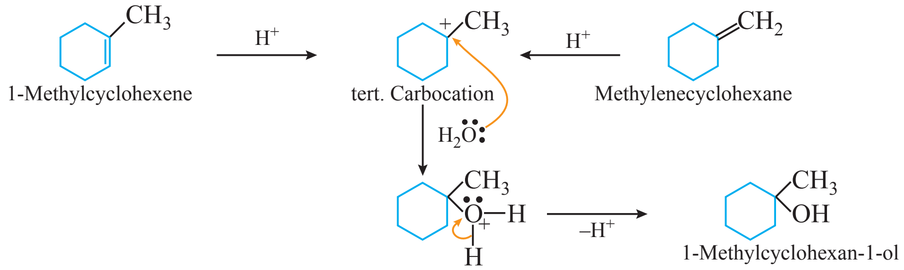

(*iii*)


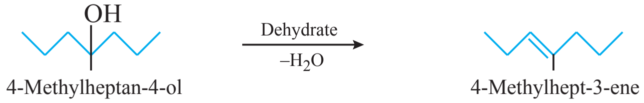
(*iv*)


Ans. As addition and elimination are opposite to each other, the general strategy is to first dehydrate alcohol to give either a single alkene or a mixture of alkenes. If a mixture of alkenes is possible, then find out which of the alkenes will give the desired product.

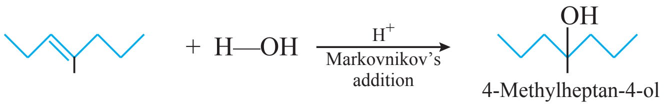
(*i*)


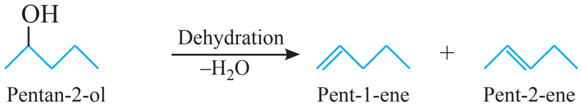
Addition of H_2O to both these alkenes gives 1-methyl cylohexan-1-ol.



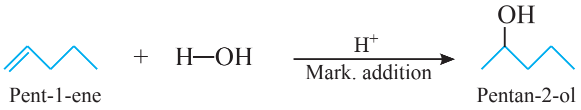
(*ii*)


Addition of H_2O to 4-methylhept-3-ene in presence of an acid gives the desired alcohol.

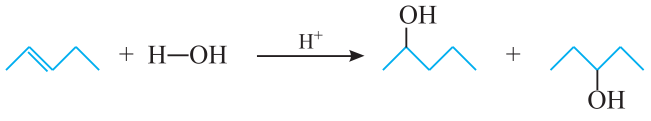


(*iii*)


Addition of H_2O to pent-1-ene gives pentan-2-ol.



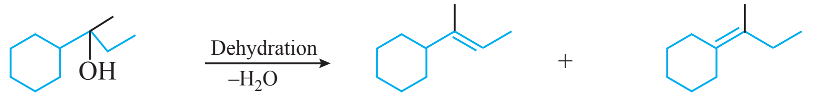
Now, addition of H_2O to pent-2-ene gives a mixture of pentan-2-ol, pentan-3-ol.



Pent-2-ene Pentan-2-ol Pentan-3-ol

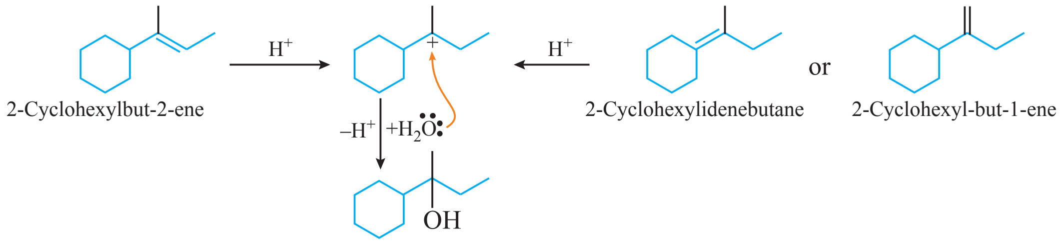
Hence, the desired alkene is pent-1-ene and not pent-2-ene.

(*iv*)



2-Cyclohexylbutan-2-ol 2-Cyclohexylbut-2-ene 2-Cyclohexylidenebutane

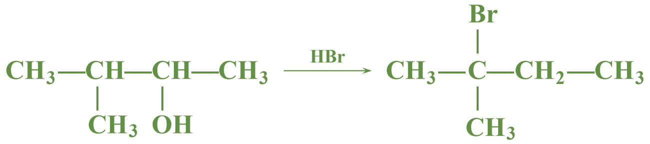
Now addition of H_2O to both 2-cyclohexylbut-2-ene and 2-cyclohexylidenebutane in presence of an acid gives 2-cyclohexylbutan-2-ol.



2-Cyclohexylbut-2-ene 2-Cyclohexylidenebutane 2-Cyclohexyl-but-1-ene

2-Cyclohexylbutan-2-ol

Q. 33. When 3-methyl butan-2-ol is treated with HBr, the following reaction takes place.

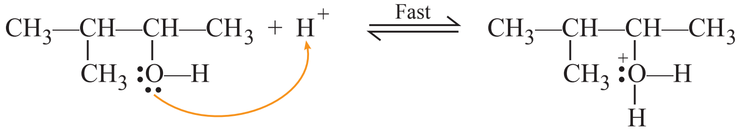


$$\underset{\substack{|\\CH_3}}{CH_3-CH}-\underset{\substack{|\\OH}}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{\substack{Br\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_3$$

Give a mechanism for this reaction.

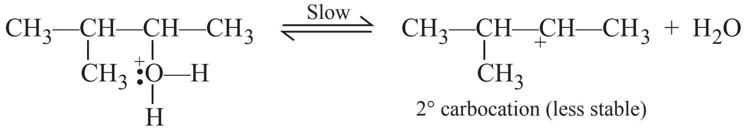
Ans. Mechanism: The reaction takes place through the following mechanism:

Step I: Formation of protonated alcohol.



$$CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\:\ddot{O}-H}}{CH}-CH_3 + H^+ \xrightleftharpoons{Fast} CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\:\overset{+}{O}-H\\|\\H}}{CH}-CH_3$$

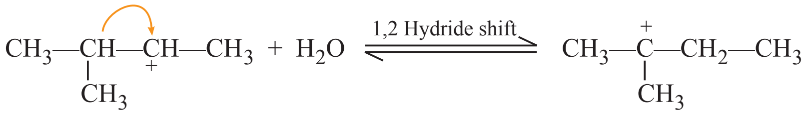
Step II: Formation of carbocation.



$$CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\:\overset{+}{O}-H\\|\\H}}{CH}-CH_3 \xrightleftharpoons{Slow} CH_3-\underset{\substack{|\\CH_3}}{CH}-\overset{+}{C}H-CH_3 + H_2O$$

2° carbocation (less stable)

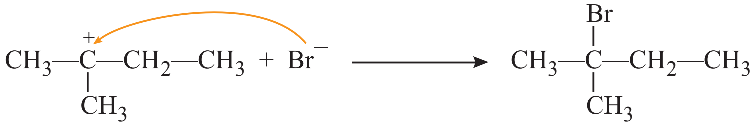
2° carbocation being less stable undergoes 1, 2 hydride shift to form more stable 3° carbocation.



$$CH_3-\underset{\substack{|\\CH_3}}{CH}-\overset{+}{C}H-CH_3 + H_2O \xrightleftharpoons{\text{1,2 Hydride shift}} CH_3-\underset{\substack{|\\CH_3}}{\overset{+}{C}}-CH_2-CH_3$$

2° carbocation 3° carbocation (more stable)

Step III: Attack of nucleophile



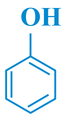
$$CH_3-\underset{\substack{|\\CH_3}}{\overset{+}{C}}-CH_2-CH_3 + Br^- \longrightarrow CH_3-\overset{\substack{Br\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_3$$

2-Bromo-2-methylbutane

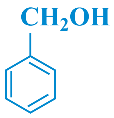
Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

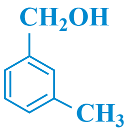
1. Which of the following compounds is aromatic alcohol? *[NCERT Exemplar]*



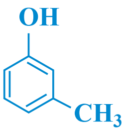
(A)



(B)



(C)



(D)

(*a*) A, B, C, D (*b*) A, D (*c*) B, C (*d*) A

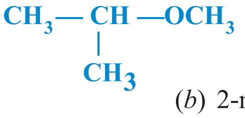
2. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature? *[NCERT Exemplar]*

(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 4

3. IUPAC name of *m*-cresol is ________________. *[NCERT Exemplar]*

(*a*) 3-methylphenol (*b*) 3-chlorophenol (*c*) 3-methoxyphenol (*d*) benzene-1, 3-diol

4. IUPAC name of the compound



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OCH_3$

is ________________. *[NCERT Exemplar]*

(*a*) 1-methoxy-1-methylethane (*b*) 2-methoxy-2-methylethane

(*c*) 2-methoxypropane (*d*) isopropylmethyl ether

5. The C—O bond length in phenol is less than that in methanol due to

(*a*) partial double bond character in aromatic ring (*b*) sp^2 hybridised carbon

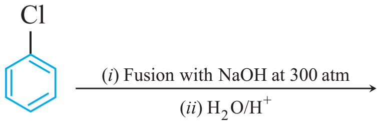
(*c*) sp^3 hybridised carbon (*d*) both (*a*) and (*b*)

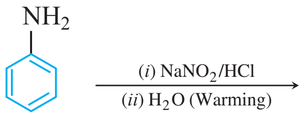
6. Which of the following are used to convert RCHO into RCH_2OH? *[NCERT Exemplar]*

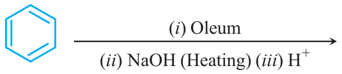
(*a*) H_2/Pd (*b*) $LiAlH_4$

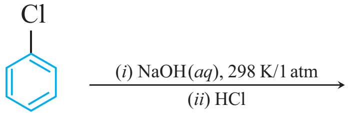
(*c*) $NaBH_4$ (*d*) Reaction with RMgX followed by hydrolysis

7. Which of the following reactions will yield phenol? *[NCERT Exemplar]*

(*a*)


(*b*)


(*c*)


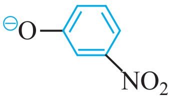
(*d*)


8. The order of reactivity of the alkenes, (*i*) $(CH_3)_2C{=}CH_2$, (*ii*) $CH_3CH{=}CH_2$, (*iii*) $CH_2{=}CH_2$, when subjected to acid catalysed hydration is:

(*a*) (*i*) > (*iii*) > (*ii*) (*b*) (*i*) > (*ii*) > (*iii*) (*c*) (*ii*) > (*i*) > (*iii*) (*d*) (*iii*) > (*ii*) > (*i*)

9. Which of the following species can act as the strongest base? *[NCERT Exemplar]*

(*a*) $^{\ominus}OH$ (*b*) $^{\ominus}OR$ (*c*) $^{\ominus}OC_6H_5$ (*d*)



10. Phenol is less acidic than ________________. *[NCERT Exemplar]*

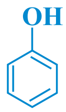
(*a*) ethanol (*b*) *o*-nitrophenol (*c*) *o*-methylphenol (*d*) *o*-methoxyphenol

11. Which is the correct order of acid strength of the following?

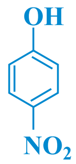
(*a*) $C_6H_5OH > H_2O > ROH > HC{\equiv}CH$ (*b*) $C_6H_5OH > ROH > H_2O > HC{\equiv}CH$

(*c*) $C_6H_5OH > HC{\equiv}CH > H_2O > ROH$ (*d*) $C_6H_5OH > H_2O > HC{\equiv}CH > ROH$

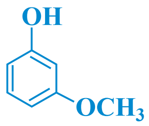
12. Mark the correct order of decreasing acid strength of the following compounds. [*NCERT Exemplar*]



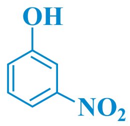
(*i*)



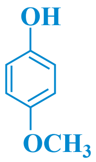
(*ii*)



(*iii*)



(*iv*)



(*v*)

(*a*) (*v*) > (*iv*) > (*ii*) > (*i*) > (*iii*)   (*b*) (*ii*) > (*iv*) > (*i*) > (*iii*) > (*v*)

(*c*) (*iv*) > (*v*) > (*iii*) > (*ii*) > (*i*)   (*d*) (*v*) > (*iv*) > (*iii*) > (*ii*) > (*i*)

13. In the reaction given below, X is:

$$\text{Neopentyl alcohol} \xrightarrow{H_2SO_4} X$$

(*a*) 2-methylpent-2-ene   (*b*) 2-methylpentane

(*c*) 2-methylbut-2-ene   (*d*) neopentane

14. Tertiary alcohols on reaction with $KMnO_4$ at elevated temperature form

(*a*) aldehyde

(*b*) ketone

(*c*) mixture of carboxylic acids containing lesser number of carbon atoms

(*d*) mixture of carboxylic acids containing more number of carbon atoms

15. What is the correct order of reactivity of alcohols in the following reaction?

$$R—OH + HCl \xrightarrow{ZnCl_2} R—Cl + H_2O$$

[*NCERT Exemplar*]

(*a*) 1° > 2° > 3°   (*b*) 1° < 2° > 3°   (*c*) 3° > 2° > 1°   (*d*) 3° > 1° > 2°

16. The compound that reacts fastest with Lucas reagent at room temperature is

(*a*) butan-1-ol   (*b*) butan-2-ol

(*c*) 2 methylpropan-1-ol   (*d*) 2-methylpropan-2-ol

17. CH_3CH_2OH can be converted into CH_3CHO by ______________. [*NCERT Exemplar*]

(*a*) catalytic hydrogenation   (*b*) treatment with $LiAlH_4$

(*c*) treatment with pyridinium chlorochromate   (*d*) treatment with $KMnO_4$

18. An alcohol on oxidation is found to give CH_3COOH and CH_3CH_2COOH. The structure of the alcohol is:

(*a*) $CH_3CH_2CH_2OH$ (*b*) $(CH_3)_2C(OH)CH_2—CH_3$

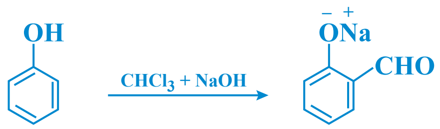
(*c*) $CH_3(CH_2)_3CH_2OH$ (*d*) $CH_3CHOHCH_2CH_2CH_3$

19. Which of the following compounds will react with sodium hydroxide solution in water?

[*NCERT Exemplar*]

(*a*) C_6H_5OH (*b*) $C_6H_5CH_2OH$ (*c*) $(CH_3)_3$ COH   (*d*) C_2H_5OH

20.



The electrophile involved in the above reaction is:

(*a*) ^{+}CHO (*b*) $^{+}CHCl_2$ (*c*) $^{-}CCl_3$ (*d*) $:CCl_2$

21. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields.

[*NCERT Exemplar*]

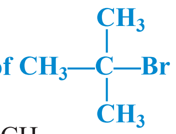
(*a*) *o*-Cresol   (*b*) *m*-Cresol

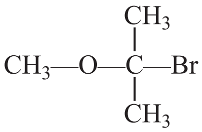
(*c*) 2, 4-Dihydroxytoluene   (*d*) Benzyl alcohol

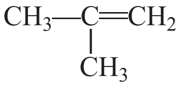
22. Which of the following compounds is oxidised to methyl ethyl ketone?

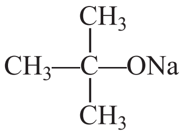
(*a*) 2-Propanol   (*b*) 1-Butanol

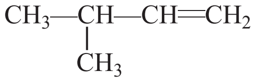
(*c*) 2-Butanol   (*d*) *tert*. Butyl alcohol

23. The reaction of  $CH_3-C(CH_3)_2-Br$ **with $NaOCH_3$ forms the product,**

(*a*)  $CH_3-O-C(CH_3)_2-Br$

(*b*)  $CH_3-C(CH_3)=CH_2$

(*c*)  $CH_3-C(CH_3)_2-ONa$

(*d*)  $CH_3-CH(CH_3)-CH=CH_2$

Answers

1. (*c*) **2.** (*a*) **3.** (*a*) **4.** (*c*) **5.** (*d*) **6.** (*a*, *b*, *c*) **7.** (*a*, *b*, *c*) **8.** (*b*) **9.** (*b*) **10.** (*b*)
11. (*a*) **12.** (*b*) **13.** (*c*) **14.** (*c*) **15.** (*c*) **16.** (*d*) **17.** (*c*) **18.** (*d*) **19.** (*a*) **20.** (*d*)
21. (*d*) **22.** (*c*) **23.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

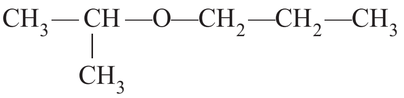
(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion (*A*) :** IUPAC name of the compound

 $CH_3-CH(CH_3)-O-CH_2-CH_2-CH_3$ is 2-Ethoxy-2-methylethane.

Reason (*R*) : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group].

2. **Assertion (*A*) :** The boiling point of ethanol is higher than methoxymethane.

Reason (*R*) : There is intramolecular hydrogen bonding in ethanol.

3. **Assertion (*A*) :** Ethanol is a weaker acid than phenol.

Reason (*R*) : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

4. **Assertion (*A*) :** *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason (*R*) : *m*- and *p*- Nitrophenols exist as associated molecules.

5. **Assertion (*A*) :** *p*-nitrophenol is more acidic than phenol.

Reason (*R*) : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

6. **Assertion (*A*) :** In lucas test, 3° alcohols react immediately.

Reason (*R*) : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

7. **Assertion (*A*) :** Phenol on oxidation with chromic acid gives benzoquinone.

Reason (*R*) : Pure phenol is colourless but turn pink due to oxidation to phenoquinone.

8. **Assertion (*A*) :** Phenol is more reactive than benzene towards electrophilic substitution reaction.

Reason (*R*) : In the case of phenol, the intermediate carbocation is more resonance stabilized.

9. **Assertion (*A*) :** Phenols give *o*- and *p*-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

Reason (*R*) : —OH group in phenol is *o*–, *p*– directing.

10. **Assertion (*A*) :** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason (*R*) : Lewis acid polarises the bromine molecule.

11. **Assertion (*A*) :** The reaction of phenol with acid chloride to form ether occurs in the presence of pyridine.

Reason (*R*) : Pyridine is a base so it neutralises the HCl formed and proceeds the reaction.

12. **Assertion (*A*) :** Bond angle in ethers is slightly less than the tetrahedral angle.

Reason (*R*) : There is a repulsion between the two bulky (—R) groups.

Answers

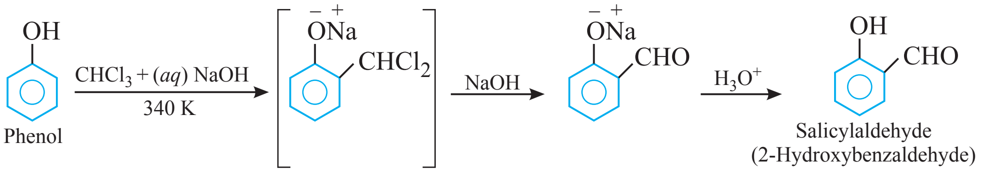
1. (*d*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*a*) **6.** (*b*) **7.** (*b*) **8.** (*a*) **9.** (*d*) **10.** (*d*)
11. (*a*) **12.** (*d*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

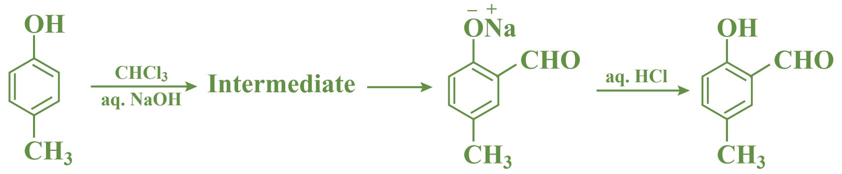
Phenols undergo electrophilic substitution reactions readily due to the strong activating effect of OH group attached to the benzene ring. Since, the OH group increases the electron density more at *o*- and *p*-positions therefore OH group is *ortho*, *para*-directing. Reimer-Tiemann reaction is one of the examples of electrophilic substitution reaction. Riemer-Tiemann reaction introduces an aldehyde group on the aromatic ring of phenol, ortho to the hydroxyl group. This is a general method for the synthesis of substituted salicylaldehydes. In this reaction, treatment of phenol with chloroform in presence of aqueous sodium or potassium hydroxide at 340 K followed by hydrolysis of the reacting product gives 2-hydroxybenzaldehyde as the major product.



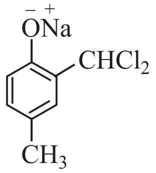
1. What is the electrophile used in Reimer-Tiemann reaction?

Ans. :CCl_2

2. Draw the structure of the intermediate in the following reaction:



Ans.



3. Write the IUPAC name of the product formed in the equation given in above question.

Ans. 2-hydroxy-5-methylbenzaldehyde

4. Which is more reactive, phenol or benzene towards electrophilic substitution?

Ans. Phenol is more reactive than benzene towards electrophilic substitution reaction because in case of phenol, the intermediate carbocation is more resonance stabilized.

5. **What happens when carbon tetrachloride is used in the reaction instead of chloroform?**

Ans. Salicylic acid is formed as the major product.

PASSAGE–2

Williamson synthesis is one of the best methods for the preparation of ethers. It involves the treatment of an alkyl halide with a suitable sodium alkoxide. Williamson's synthesis involves nucleophilic substitution of the halogen atom of an alkyl halide by an alkoxide group as shown below:

$$R{-}O^{-}Na^{+} + R'X \longrightarrow R{-}O{-}R' + NaX$$

When alkyl halide used in the reaction is primary, Williamson's synthesis proceeds via S_N2 mechanism leading to the formation of an ether. This method is a versatile method for the synthesis of both symmetrical and unsymmetrical ethers.

1. **Why is Williamson's synthesis not applicable when the alkyl halide used is tertiary?**

Ans. This is because 3° alkyl halides are highly susceptible to dehydrohalogenation in the presence of sodium alkoxides and elimination reaction occurs.

2. **How would you obtain allyl phenyl ether?**

Ans. Allyl phenyl ether can be obtained by heating

$$CH_2{=}CHCH_2Br \text{ and } C_6H_5{-}\overset{-}{O}\overset{+}{Na}$$

3. **What happens when benzyl ethyl ether reacts with HI?**

Ans. Benzyl iodide and ethyl alcohol will be formed after the reaction of benzyl ethyl ether with HI.

4. **Name the alkyl halide and sodium alkoxide used to synthesise tert-butyl ethyl ether.**

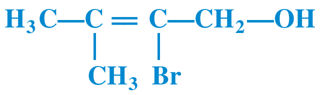
Ans. Ethyl bromide and sodium tert-butoxide.

5. **$(CH_3)_3C{-}O{-}CH_3$ on reaction with HI gives $(CH_3)_3C{-}I$ and $CH_3{-}OH$ as the main products and not $(CH_3)_3C{-}OH$ and $CH_3{-}I$. Give reason.**

Ans. The reaction between $(CH_3)_3COCH_3$ and HI follows S_N1 mechanism. For an S_N1 reaction, the formation of product is controlled by stability of the carbocation formed in the slowest step. Since tert.butyl carbonium ion $(CH_3)_3\overset{\oplus}{C}$ formed after the cleavage of C—O bond in the slowest step is more stable than methyl carbonium ion $(\overset{\oplus}{C}H_3)$ therefore $(CH_3)_3C{-}I$ and CH_3OH are the main products.

Very Short Answer Questions [1 mark]

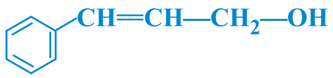
Q. 1. Write the IUPAC name of the following compound: [*CBSE (AI) 2017*]



$$H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}\underset{\displaystyle Br}{\underset{|}{C}}{-}CH_2{-}OH$$

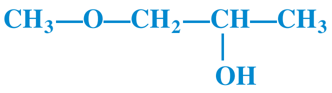
Ans. 2-Bromo-3-methylbut-2-en-1-ol

Q. 2. Write the IUPAC name of the following compound: [*CBSE (AI) 2017*]



Ans. 3-phenylprop-2-en-1-ol

Q. 3. Write the IUPAC name of the following compound: [*CBSE Chennai 2015*]



$$CH_3{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

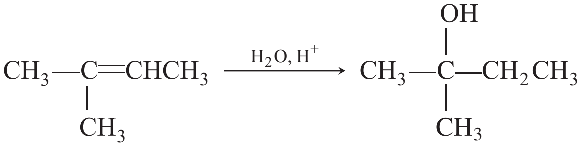
Ans. 1-methoxypropan-2-ol.

Q. 4. How would you convert ethanol to ethene? [*CBSE (AI) 2011*]

Ans. $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[443\text{ K}]{\text{conc.}H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2O$$

Q. 5. **How will you synthesise the following alcohol from appropriate alkene:** *[CBSE 2019 (56/4/1)]*

Ans.



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH_3 \xrightarrow{H_2O,\ H^+} CH_3—\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}—CH_2CH_3$$

Q. 6. ***o*-Nitrophenol has lower boiling point than *p*-nitrophenol. Explain.**

Ans. Due to intramolecular H-bonding *o*-nitrophenol exists as a discrete molecule whereas due to intermolecular H-bonding *p*-nitrophenol exists as associated molecules. As a result of this *p*-nitrophenol has higher boiling point than *o*-nitrophenol.

Q. 7. **Of the two hydroxy organic compounds ROH and R′OH, the first one is basic and the other is acidic in behaviour. How is R different from R′?**

Ans. R is an alkyl group whereas R′ is an aryl group.

Q. 8. **Arrange the following compounds in the increasing order of their acid strengths:**

4-nitrophenol, phenol, 2,4,6-trinitrophenol *[CBSE (F) 2013]*

Ans. Phenol < 4-nitrophenol < 2,4,6-trinitrophenol

Q. 9. **Phenol is an acid but does not react with sodium bicarbonate solution. Why?** *[HOTS]*

Ans. Phenol is a weaker acid than carbonic acid (H_2CO_3) and hence does not liberate CO_2 from sodium bicarbonate.

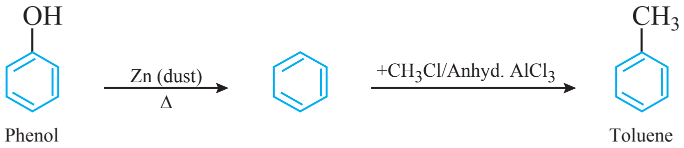
Q. 10. **Suggest a reagent for conversion of ethanol to ethanoic acid.** *[NCERT Exemplar]*

Ans. (*i*) $CrO_3 – H_2SO_4$ (*ii*) $KMnO_4/OH^–$,

(*iii*) H_3O^+ (*iv*) Acidified $KMnO_4$ or $K_2Cr_2O_7$

Q. 11. **How is toluene obtained from phenol?** *[CBSE Delhi 2013C]*

Ans.



Q. 12. **Suggest a reagent for the following conversion:**

[NCERT Exemplar]

Ans. CrO_3, Pyridine and HCl (Pyridinium chlorochromate)

Q. 13. **What is denatured alcohol?** *[NCERT Exemplar]*

Ans. Alcohol is made unfit for drinking by mixing some copper sulphate and pyridine in it. This is called denatured alcohol.

Q. 14. **Explain why sodium metal can be used for drying diethyl ether but not ethyl alcohol.** *[HOTS]*

Ans. Due to presence of an active hydrogen atom, ethyl alcohol reacts with sodium metal.

$$2CH_3—CH_2—OH + 2Na \longrightarrow 2CH_3—CH_2—\overset{-}{O}\overset{+}{Na} + H_2$$

Diethyl ether, on the other hand, does not have replaceable hydrogen atom therefore does not react with sodium metal hence can be dried by metallic sodium.

Q. 15. **What is the order of dehydration of primary, secondary and tertiary alcohols?**

Ans. Tertiary alcohols > Secondary alcohols > Primary alcohols.

Q. 16. **Name the reagents used in the following reactions:** *[CBSE (F) 2014]*

Friedel–Crafts alkylation of anisole

Ans. Anhydrous aluminium chloride (anhyd. $AlCl_3$)

Short Answer Questions–I [2 marks]

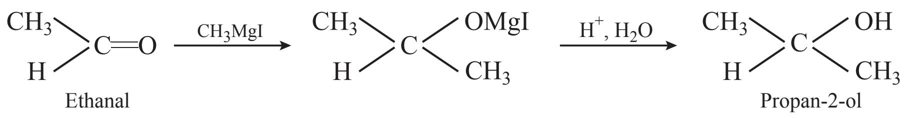
Q. 1. How will you convert:

(*i*) Propene to Propan-1-ol?

(*ii*) Ethanal to Propan-2-o1? ***[CBSE Delhi 2013]***

Ans. (*i*) $\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br \xrightarrow[\Delta]{\text{KOH }(aq)} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$

(*ii*)



Q. 2. Which is a stronger acid—phenol or cresol? Explain.

Ans. All the cresols are weaker acids than phenols. Methyl group has +I effect (positive inductive effect) as well as hyperconjugation effect but the hyperconjugation effect predominates over the +I effect. Since both these effects increase the electron density on the O—H bond and hence all the cresols are weaker acids than phenols.

As hyperconjugation effect can operate only through *ortho* and *para* positions and not through meta positions, therefore, meta-cresol is stronger acid than *ortho* and *para*-cresols. However, due to stronger +I effect at *ortho* position than at *para* position (+I effect decreases with distance), *ortho*-cresol is a weaker acid than *para*-cresol. Thus, the order of acidic strength in increasing order is:

ortho-cresol < *para*-cresol < *meta*-cresol < phenol

Q. 3. Arrange: water, ethanol and phenol in increasing order of acidity and give reason for your answer. ***[NCERT Exemplar]***

Ans. Increasing order of acidity is ethanol < water < phenol. The phenoxide ion obtained after the removal of a proton is stabilised by resonance whereas the ethoxide ion obtained after the removal of a proton is destabilised by +I effect of $—C_2H_5$ group. Therefore, phenol is stronger acid than ethanol. On the other hand, ethanol is weaker acid than water because electron releasing $—C_2H_5$ group in ethanol increases the electron density on oxygen and hence the polarity of O—H bond in ethanol decreases which results in the decreasing acidic strength. Hence, acidic strength increases in the order given above.

Q. 4. Answer the following questions.

(*i*) Among HI, HBr, HCl, HI is most reactive towards alcohols. Why?

(*ii*) Of the two alcohols; (*a*) $CH_2{=}CH—CH_2OH$ and (*b*) $CH_2{=}CH—CH_2—CH_2OH$, which one will react more easily with conc. HCl in the presence of $ZnCl_2$? ***[CBSE (F) 2012]***

Ans. (*i*) HI has the lowest bond dissociation energy due to longer bond length that is why it is most reactive.

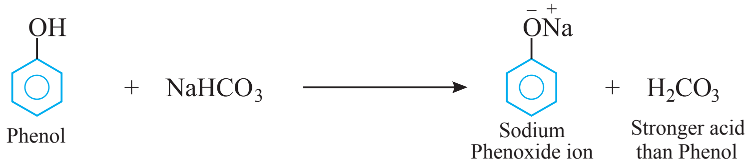
(*ii*) $CH_2{=}CH—CH_2OH$

Q. 5. Account for the following:

(*i*) Phenol does not react with $NaHCO_3$ whereas carboxylic acids react.

(*ii*) Phenol is more easily nitrated than benzene. ***[HOTS]***

Ans. (*i*) $RCOOH + NaHCO_3 \longrightarrow RCOONa + \underset{\substack{\text{Weaker acid}\\ \text{than RCOOH}}}{H_2CO_3}$



Such acid–base reaction takes place only if the acid formed is weaker than the reacting acid. In other words, phenol is not a strong enough acid to react with $NaHCO_3$.

(*ii*) Nitration involves attack of electrophile nitronium ion ($\overset{+}{N}O_2$) on benzene ring. Due to +R effect of —OH group electron density on benzene increases. Therefore, phenol is more easily nitrated as compared to benzene.

Q. 6. Answer the following questions:

(*i*) Dipole moment of phenol is smaller that of methanol. Why?

(*ii*) In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

[*NCERT Exemplar*]

Ans. (*i*) In phenol, C—O bond is less polar due to electron-withdrawing effect of benzene ring whereas in methanol, C—O bond is more polar due to electron-releasing effect of $-CH_3$ group.

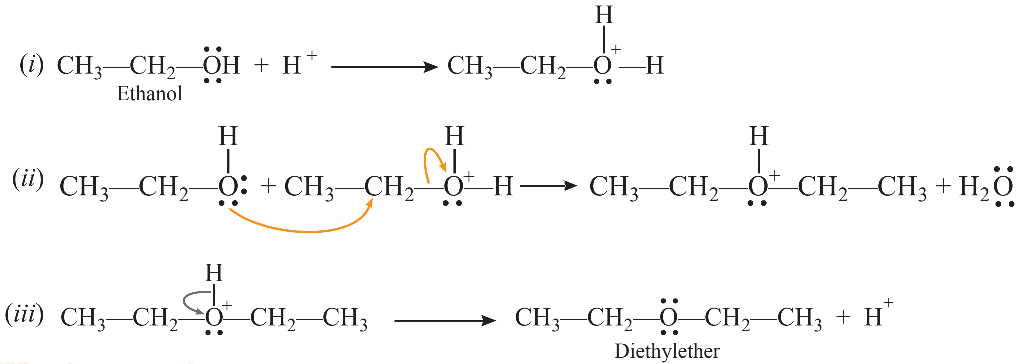
(*ii*) Phenoxide ion is more reactive than phenol towards electrophilic aromatic substitution and hence undergoes electrophilic substitution with carbon dioxide which is a weak electrophile.

Q. 7. Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow[413\ K]{conc.\ H_2SO_4} CH_3-CH_2-O-CH_2-CH_3$$

[*CBSE Delhi 2016, 2019 (56/4/3), 2020 (56/3/2)*] [*HOTS*]

Ans. The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on protonated alcohol as shown below:



$$(i)\ \underset{\text{Ethanol}}{CH_3-CH_2-\ddot{O}H} + H^+ \longrightarrow CH_3-CH_2-\overset{\overset{H}{|}}{\ddot{O}^+}-H$$

$$(ii)\ CH_3-CH_2-\overset{\overset{H}{|}}{\ddot{O}}: + CH_3-CH_2-\overset{\overset{H}{|}}{\ddot{O}^+}-H \longrightarrow CH_3-CH_2-\overset{\overset{H}{|}}{\ddot{O}^+}-CH_2-CH_3 + H_2\ddot{O}$$

$$(iii)\ CH_3-CH_2-\overset{\overset{H}{|}}{\ddot{O}^+}-CH_2-CH_3 \longrightarrow \underset{\text{Diethylether}}{CH_3-CH_2-\ddot{O}-CH_2-CH_3} + H^+$$

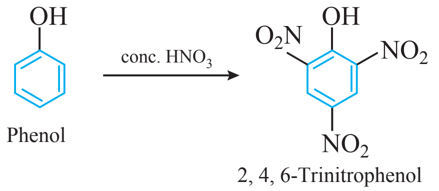
Q. 8. What happens when

(*i*) Phenol reacts with Conc. HNO_3?

(*ii*) Ethyl chloride reacts with $NaOC_2H_5$?

Write the chemical equations involved in the above reactions. **[*CBSE 2019 (56/4/3)*]**

Ans. (*i*)



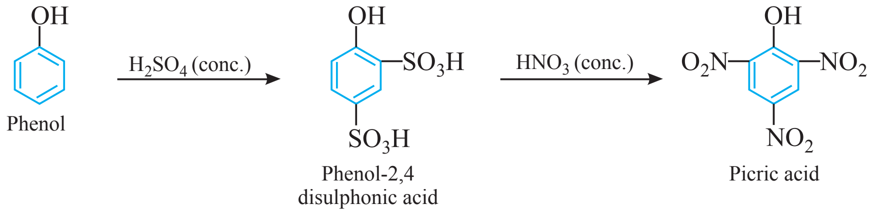
(*ii*)
$$\underset{\text{Ethyl chloride}}{CH_3CH_2-Cl} + \underset{\text{Sodium ethoxide}}{CH_3-CH_2\overset{-}{O}\overset{+}{Na}} \longrightarrow \underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2-CH_3} + NaCl$$

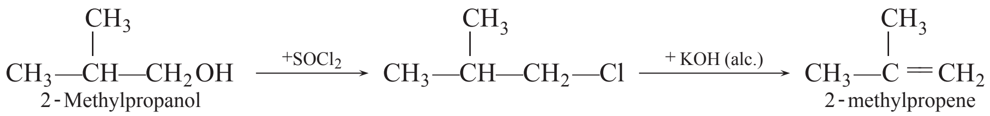
Q. 9. How would you obtain

(*i*) picric acid (2, 4, 6-trinitrophenol) from phenol?

(*ii*) 2-Methylpropene from 2-Methylpropanol? **[*CBSE Delhi 2011*]**

Ans. (*i*)



(*ii*) 

$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2OH} \xrightarrow{+SOCl_2} \mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-Cl} \xrightarrow{+\,KOH\,(alc.)} \mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2}$$

2-Methylpropanol → 2-methylpropene

Short Answer Questions–II [3 marks]

Q. 1. Explain the mechanism of the following reactions:

(*i*) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.

(*ii*) Acid catalysed dehydration of an alcohol forming an alkene.

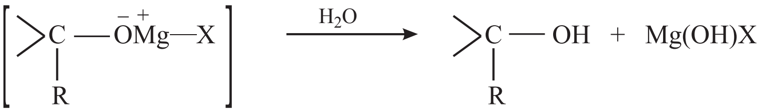
OR

Give the mechanism for the formation of ethene from ethanol. ***[CBSE 2020 (56/1/2)]***

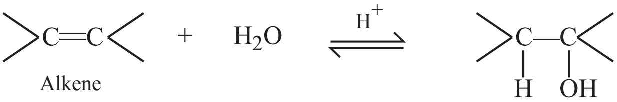
(*iii*) Acid catalysed hydration of an alkene forming an alcohol. ***[HOTS]***

Ans. (*i*) **Step I:** Nucleophilic addition of Grignard reagent to carbonyl group.

Step II: Hydrolysis

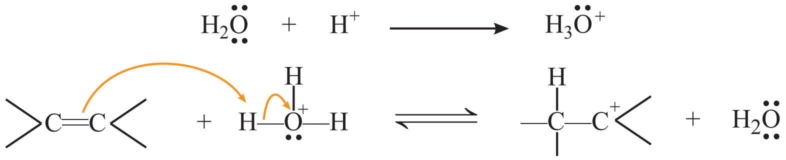


(*ii*) Refer to NCERT Textbook Exercises, Q. 19.

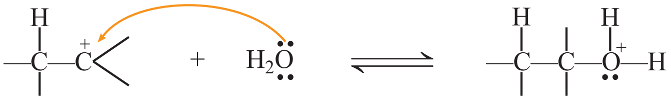
(*iii*) 

Mechanism:

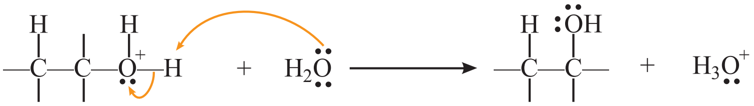
Step I: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.



Step II: Nucleophilic attack of water on carbocation.



Step III: Deprotonation to form an alcohol



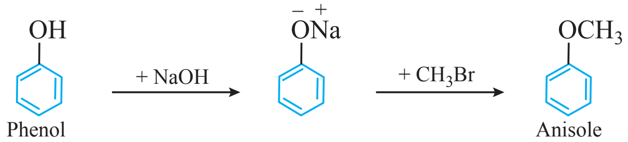
Q. 2. How do you convert the following:

(*i*) Phenol to anisole

(*ii*) Propan-2-ol to 2-methylpropan-2-ol

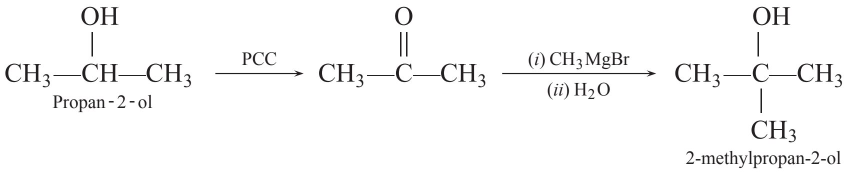
(*iii*) Aniline to phenol **[*CBSE Delhi 2015*]**

Ans. (*i*)



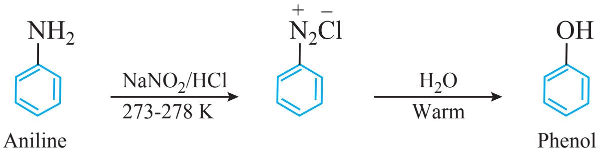
Phenol → Anisole

(*ii*)



$$\underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow{PCC} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} \underset{\text{2-methylpropan-2-ol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

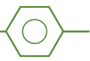
(*iii*)



Aniline → Phenol

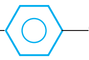
Q. 3. Arrange the following compounds in decreasing order of acidity. **[*NCERT Exemplar*]**

(*i*) H_2O, ROH, HC≡CH

(*ii*) CH_3O—**—OH, O_2N—****—OH, C_6H_5OH**

(*iii*) CH_3OH, H_2O, C_6H_5OH

Ans. (*i*) $H_2O > ROH > HC\equiv CH$

(*ii*) O_2N——OH $> C_6H_5OH >$ CH_3O——OH

(*iii*) $C_6H_5OH > H_2O > CH_3OH$

Q. 4. Give one chemical test to distinguish between the following: **[*CBSE 2019 (56/5/1)*]**

(*i*) Phenol and propan-1-ol

(*ii*) Ethanol and dimethyl ether

(*iii*) propan-1-ol and 2-Methyl-propan-2-ol

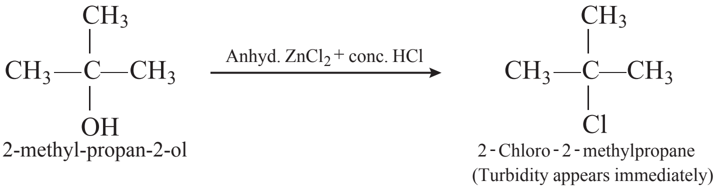
Ans. (*i*) Phenol gives a violet coloration with neutral $FeCl_3$ solution while propan-1-ol does not.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{3+} + 3H^+ + 3HCl$$

(*ii*) Ethanol gives yellow precipitate of iodoform when warmed with NaOI ($NaOH/I_2$) while dimethylether does not.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3\downarrow} + HCOONa + 5NaI + 5H_2O$$

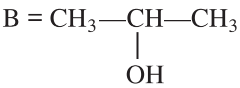
(*iii*) Propan-1-ol being a 1° alcohol does not produce turbidity at room temperature on treatment with Lucas reagent (anhyd. $ZnCl_2$ + conc. HCl) whereas 2-methylpropan-2-ol being a 3° alcohol gives turbidity immediately at room temperature on treatment with Lucas reagent.

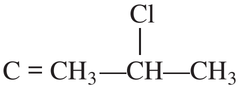


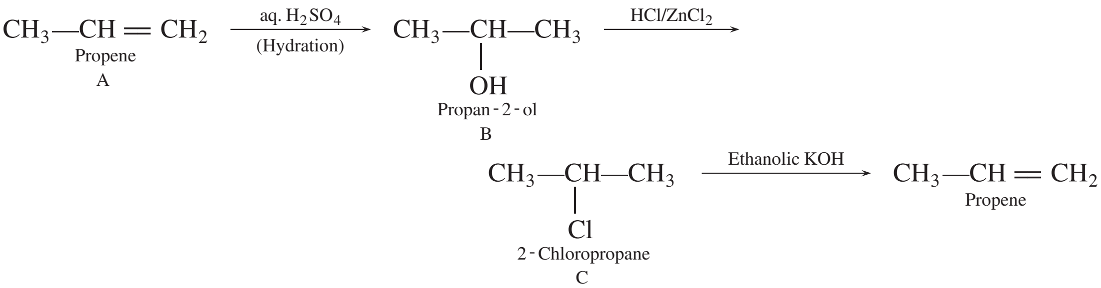
$$\underset{\text{2-methyl-propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3} \xrightarrow{\text{Anhyd. } ZnCl_2 + \text{conc. HCl}} \underset{\substack{\text{2-Chloro-2-methylpropane}\\ \text{(Turbidity appears immediately)}}}{CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

Q. 5. An organic compound 'A' having molecular formula C_3H_6 on treatment with aqueous H_2SO_4 gives 'B' which on treatment with HCl/$ZnCl_2$ gives 'C'. The compound C on treatment with ethanolic KOH gives back the compound 'A'. Identify the compounds A, B, C. [*HOTS*]

Ans. A = $CH_3—CH = CH_2$
Propene

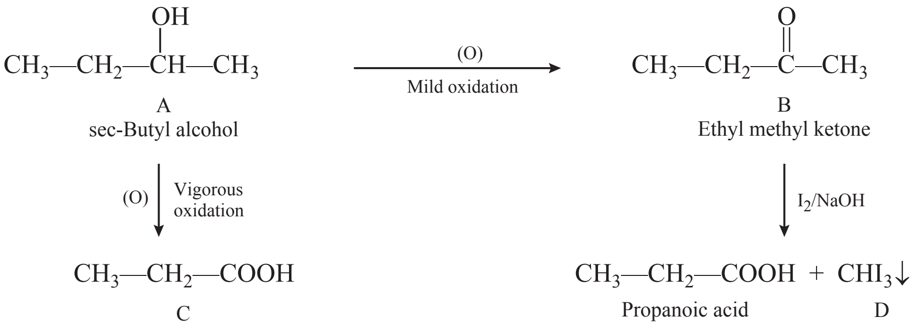

$$B = CH_3—\underset{\substack{|\\ OH}}{CH}—CH_3$$
Propan-2-ol


$$C = CH_3—\overset{\substack{Cl\\ |}}{CH}—CH_3$$
2-chloropropane


$$\underset{\substack{\text{Propene}\\ \text{A}}}{CH_3—CH = CH_2} \xrightarrow[\text{(Hydration)}]{\text{aq. } H_2SO_4} \underset{\substack{\text{Propan-2-ol}\\ \text{B}}}{CH_3—\underset{\substack{|\\ OH}}{CH}—CH_3} \xrightarrow{HCl/ZnCl_2}$$
$$\underset{\substack{\text{2-Chloropropane}\\ \text{C}}}{CH_3—\underset{\substack{|\\ Cl}}{CH}—CH_3} \xrightarrow{\text{Ethanolic KOH}} \underset{\text{Propene}}{CH_3—CH = CH_2}$$

Q. 6. A compound 'A' is optically active. On mild oxidation, it gives a compound 'B' but on vigorous oxidation gives another compound 'C'. C along with D is also formed from B by reaction with iodine and alkali. Deduce the structures of A, B, C, D. [*HOTS*]

Ans.


$$\underset{\substack{\text{A}\\ \text{sec-Butyl alcohol}}}{CH_3—CH_2—\overset{\substack{OH\\ |}}{CH}—CH_3} \xrightarrow[\text{Mild oxidation}]{(O)} \underset{\substack{\text{B}\\ \text{Ethyl methyl ketone}}}{CH_3—CH_2—\overset{\substack{O\\ \|}}{C}—CH_3}$$
$$\text{A} \xrightarrow[\text{Vigorous oxidation}]{(O)} \underset{\text{C}}{CH_3—CH_2—COOH}$$
$$\text{B} \xrightarrow{I_2/NaOH} \underset{\text{Propanoic acid}}{CH_3—CH_2—COOH} + \underset{\text{D}}{CHI_3\downarrow}$$

Q. 7. Account for the following:

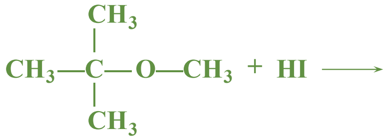
(*i*) Rectified spirit cannot be converted into absolute alcohol by simple distillation.
(*ii*) Diethyl ether does not react with sodium.
(*iii*) Phenols do not undergo substitution of the —OH group like alcohols.

Ans. (*i*) Rectified spirit containing 95% ethyl alcohol and 5% water forms an azeotropic mixture which distils at a constant temperature of 351.13 K.

(*ii*) Since diethyl ether does not contain an active hydrogen attached to oxygen like alcohols and phenols, it does not react with sodium.

(*iii*) The C—O bond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by nucleophile. In contrast, the C—O bond in alcohols is a pure single bond and hence can be easily cleaved by nucleophile.

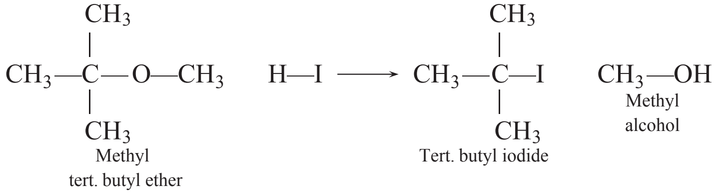
Q. 8. Write the main product(s) in each of the following reactions: [*CBSE Delhi 2016*]

(*i*)

$$CH_3—\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}—O—CH_3 + HI \longrightarrow$$

(*ii*) $CH_3—CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6}$

(*iii*) $C_6H_5—OH \xrightarrow[(ii)\ CO_2,\ H^+]{(i)\ \text{aq. NaOH}}$

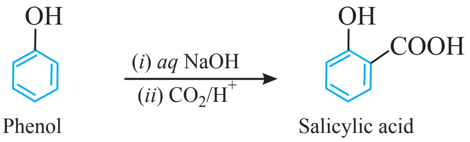
Ans. (*i*)



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3 \quad H-I \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-I \quad CH_3-OH$$

(*ii*) $$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} \underset{n\text{-propyl alcohol}}{CH_3-CH_2-CH_2-OH}$$

(*iii*)



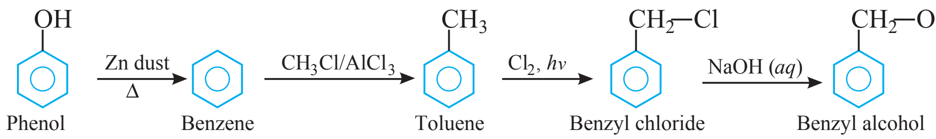
Q. 9. How will you bring the following conversions?

(*i*) Phenol to benzyl alcohol

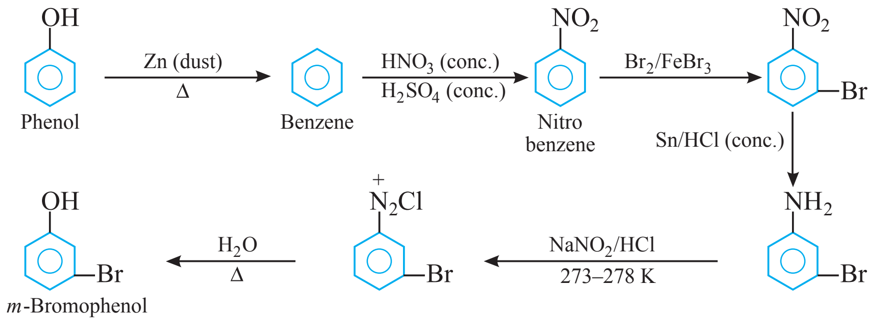
(*ii*) Phenol to *m*-bromophenol

(*iii*) Phenol to aspirin. **[*HOTS*]**

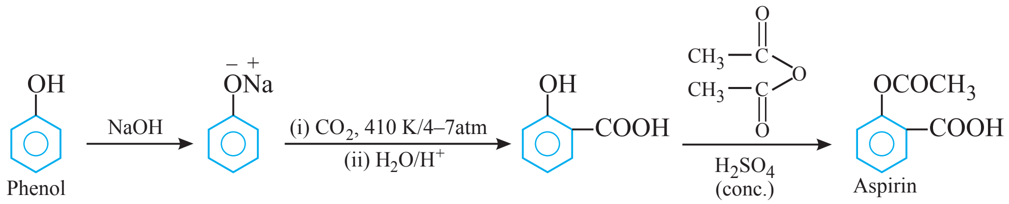
Ans. (*i*)



(*ii*)



(*iii*)



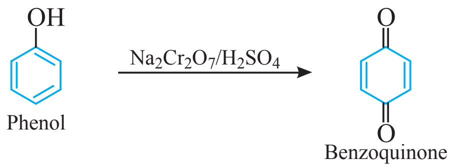
Q. 10. How would you obtain the following?

(*i*) Benzoquinone from phenol **[*CBSE 2020 (56/1/2)*]**

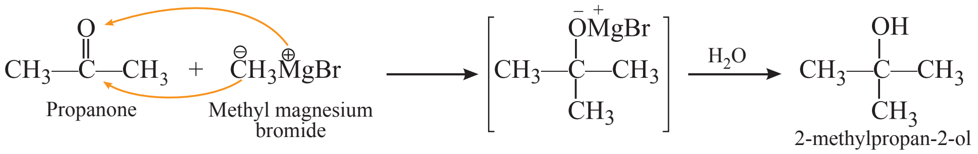
(*ii*) 2-Methylpropan-2-ol from methylmagnesium bromide

(*iii*) Propan-2-ol from propene **[*CBSE (AI) 2011, (F) 2011*]**

Ans. (*i*)

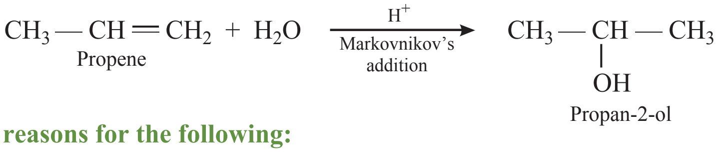


(*ii*)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \overset{\ominus}{C}H_3\overset{\oplus}{M}gBr \longrightarrow \left[CH_3-\underset{CH_3}{\overset{\overset{-\ +}{O}MgBr}{C}}-CH_3\right] \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

(*iii*)



$$CH_3-CH=CH_2 + H_2O \xrightarrow[\text{Markovnikov's addition}]{H^+} CH_3-\underset{OH}{CH}-CH_3$$

Q. 11. Give reasons for the following:

(*i*) Phenol is more acidic than methanol.

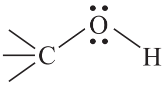
(*ii*) The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle (109°28′).

(*iii*) $(CH_3)_3C-O-CH_3$ on reaction with HI gives $(CH_3)_3C-I$ and CH_3-OH as the main products and not $(CH_3)_3C-OH$ and CH_3-I. ***[CBSE Allahabad 2015]*** **[*HOTS*]**

Ans. (*i*) In phenol, the phenoxide ion obtained after the removal of a proton is stabilised by resonance whereas there is no resonance in the alkoxide ion of methanol.

Moreover, due to +*I* effect of CH_3 group the electron density in O—H bond increases which makes release of H^+ difficult.

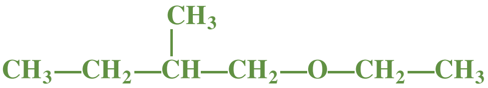
(*ii*) It is due to the repulsion between the lone pair of electrons on oxygen atoms,



(*iii*) The reaction between $(CH_3)_3COCH_3$ and HI follows S_N1 mechanism. For an S_N1 reaction, the formation of product is controlled by stability of the carbocation formed in the slowest step. Since tert.butyl carbonium ion $(CH_3)_3\overset{\oplus}{C}$) formed after the cleavage of C—O bond in the slowest step is more stable than methyl carbonium ion ($\overset{\oplus}{C}H_3$) therefore $(CH_3)_3C-I$) and CH_3OH are the main products.

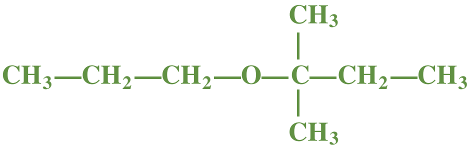
Q. 12. Give the major products that are formed by heating each of the following ethers with HI.

(*i*)



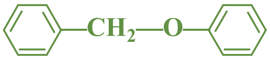
$$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-O-CH_2-CH_3$$

(*ii*)



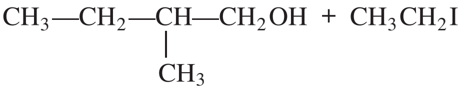
$$CH_3-CH_2-CH_2-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$$

(*iii*)



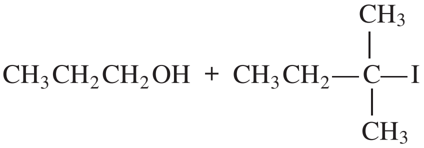
[*HOTS*]

Ans. (*i*)



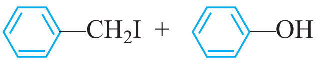
$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2OH + CH_3CH_2I$$

(*ii*)



$$CH_3CH_2CH_2OH + CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-I$$

(*iii*)



Q. 13. The following is not an appropriate reaction for the preparation of tert.-butyl ethyl ether:

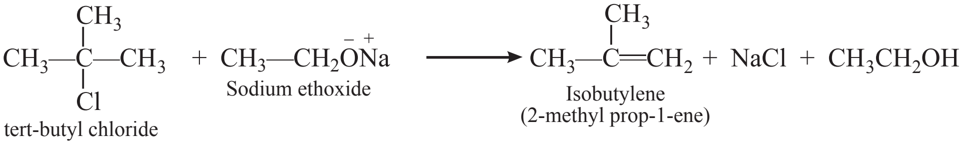
$$C_2H_5\overset{-}{O}\overset{+}{Na} + (CH_3)_3C—Cl \longrightarrow (CH_3)_3C—OC_2H_5$$

(*i*) What would be the major product of the given reaction?

(*ii*) Write a suitable reaction for the preparation of tert-butyl ethyl ether, specifying the names of reagents used.

Justify your answer in both cases. [*CBSE Sample Paper 2016*] [*HOTS*]

Ans. (*i*) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide ($CH_3—CH_2\overset{-}{O}\,\overset{+}{Na}$) is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution reaction.



$$CH_3—\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3 + CH_3—CH_2\overset{-}{O}\overset{+}{Na} \longrightarrow CH_3—\overset{\overset{CH_3}{|}}{C}=CH_2 + NaCl + CH_3CH_2OH$$

tert-butyl chloride

Sodium ethoxide

Isobutylene (2-methyl prop-1-ene)

(*ii*) To prepare tertiary butylethyl ether, the alkyl halide should be primary, *i.e.*, ethyl chloride and the nucleophile should be tertiary, *i.e.*, tertiary butoxide ion. It is because the reaction occurs by S_N2 mechanism and primary alkyl halides are most reactive in S_N2 reactions.

$$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—\ddot{\overset{-}{O}}\overset{+}{Na} + CH_3CH_2Cl \longrightarrow CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OC_2H_5 + NaCl$$

Sodium-tert-butoxide

Ethyl chloride

tert-Butyl ethyl ether

Q. 14. Answer the following questions:

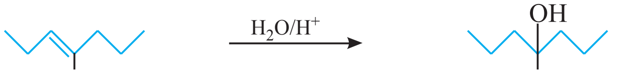
(*i*) Why are ethers insoluble in water?

(*ii*) Complete the reaction equation:

(*iii*) How will you know whether a given OH group is alcoholic or phenolic in nature?

Ans. (*i*) Ethers are insoluble in water because due to the bigger size of the alkyl groups, the oxygen atom in ethers fails to form intermolecular H-bonds with water.

(*ii*)



4-Methylhept-3-ene

4-Methylheptan-4-ol

(*iii*) Phenolic OH group gives blue or violet colouration with neutral $FeCl_3$, while alcoholic OH group does not.

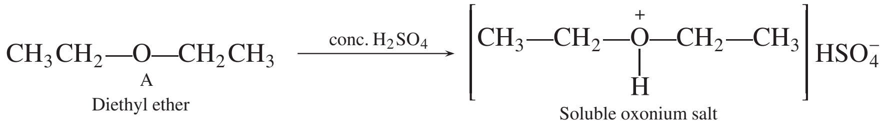
Q. 15. A compound 'A' having molecular formula $C_4H_{10}O$ is found to be soluble in concentrated sulphuric acid. It does not react with sodium metal or potassium permanganate. On heating with excess of HI, it gives a single alkyl halide. Deduce the structure of compound A and explain all the reactions. [*HOTS*]

Ans. (*i*) As compound A does not react with sodium metal or potassium permanganate, it cannot be an alcohol.

(*ii*) As compound A dissolves in conc. H_2SO_4, it may be an ether.

(*iii*) As compound A on heating with excess of HI gives a single alkyl halide, therefore, compound A must be a symmetrical ether.

(*iv*) The only symmetrical ether having molecular formula $C_4H_{10}O$ is diethyl ether. Thus compound 'A' is diethylether, $CH_3—CH_2—O—CH_2—CH_3$.

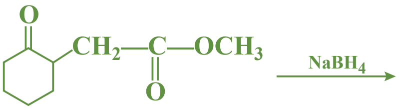


$$\underset{\substack{\text{A}\\\text{Diethyl ether}}}{CH_3CH_2—O—CH_2CH_3} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{Soluble oxonium salt}}{\left[CH_3—CH_2—\overset{+}{\underset{H}{O}}—CH_2—CH_3\right]HSO_4^-}$$

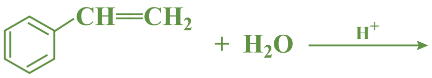
$$\underset{\substack{\text{A}\\\text{Diethyl ether}}}{CH_3CH_2OCH_2CH_3} \xrightarrow[\Delta]{HI} \underset{\text{Ethyl iodide}}{2CH_3CH_2—I}$$

Q. 16. Write the structures of the main products in the following reactions:

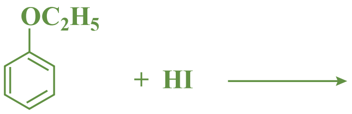
(*i*)



(*ii*)

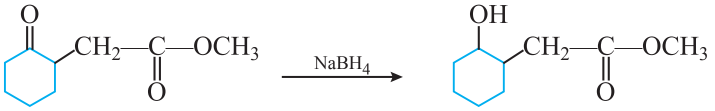


(*iii*)



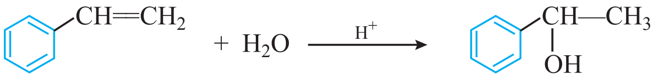
[*CBSE 2018*]

Ans. (*i*)



Methyl (2-oxocyclohexyl) ethanoate → Methyl (2-hydroxycyclohexyl) ethanoate

(*ii*)



Ethenyl benzene → 1-Phenylethanol

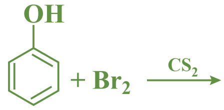
(*iii*)

Ethoxy benzene → Phenol + Iodoethane

Q. 17. Write the products of the following reactions:

(*i*) $CH_3—CH_2—O—CH_3 + HI \longrightarrow$

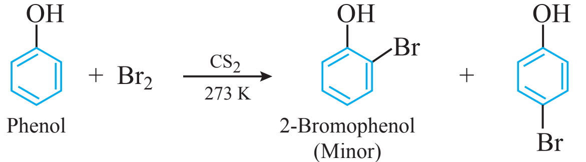
(*ii*)

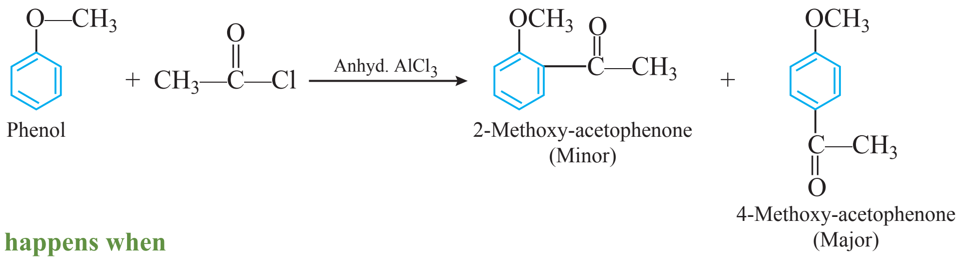


(*iii*)

Ans. (*i*) $\underset{\text{Ethyl methyl ether}}{CH_3—CH_2—O—CH_3} + HI \longrightarrow \underset{\text{Methyl iodide}}{CH_3—I} + \underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH}$

(*ii*)



Phenol → 2-Bromophenol (Minor) + 4-Bromophenol (Major) (*iii*) 

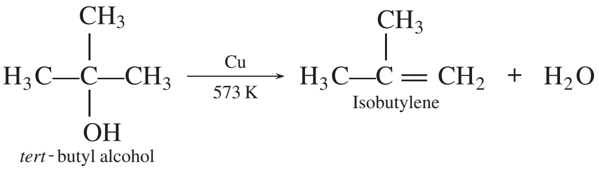
Q. 18. What happens when

(*i*) $(CH_3)_3C—OH$ is treated with Cu at 573 K,

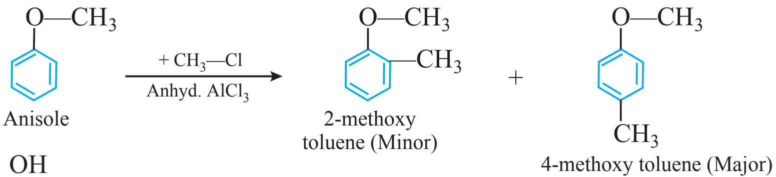
(*ii*) Anisole is treated with CH_3Cl/anhydrous $AlCl_3$,

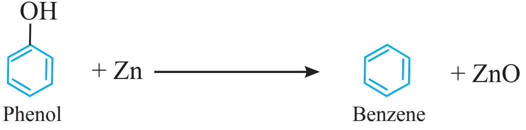
(*iii*) Phenol is treated with Zn dust?

Write chemical equations in support of your answer. **[*CBSE (F) 2017*]**

Ans. (*i*) 

$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_3 \xrightarrow[573\,K]{Cu} H_3C-\overset{\displaystyle CH_3}{C}=CH_2 + H_2O$$

(*ii*) 

(*iii*) 

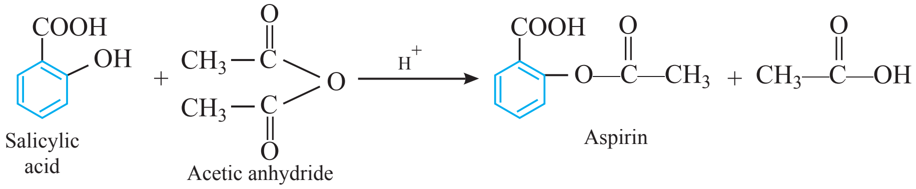
Q. 19. What happens when

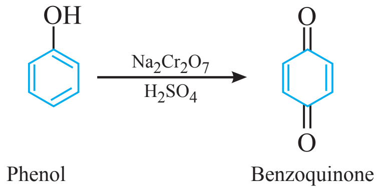
(*i*) Salicylic acid is treated with $(CH_3CO)_2O/H^+$?

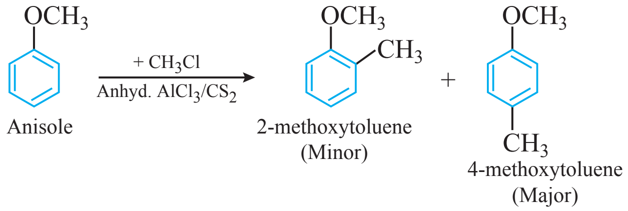
(*ii*) Phenol is oxidised with $Na_2Cr_2O_7/H^+$?

(*iii*) Anisole is treated with CH_3Cl/anhydrous $AlCl_3$?

Write chemical equation in support of your answer. **[*CBSE 2019 (56/3/1)*]**

Ans. (*i*) 

(*ii*) 

(*iii*) 

Long Answer Questions [5 marks]

Q. 1. **(*i*) Write the formula of reagents used in the following reactions:**

(*a*) Bromination of phenol to 2, 4, 6-tribromophenol

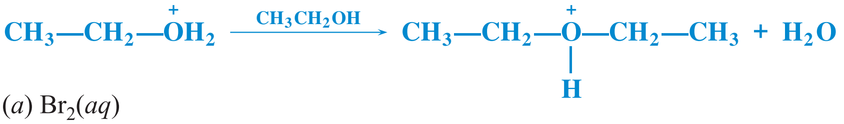
(*b*) Hydroboration of propene and then oxidation to propanol.

(*ii*) Arrange the following compound groups in the increasing order of their property indicated:

(*a*) *p*-nitrophenol, ethanol, phenol (acidic character)

(*b*) Propanol, propane, propanal (boiling point)

(*iii*) Write the mechanism (using curved arrow notation) of the following reaction:



$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3 + H_2O$$

[CBSE Delhi 2017]

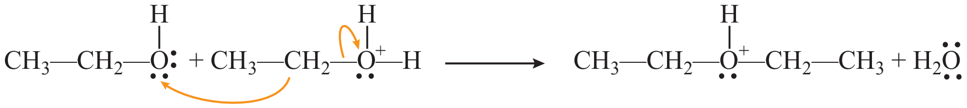
Ans. (*i*) (*a*) $Br_2(aq)$

(*b*) B_2H_6, H_2O, H_2O_2 and OH^-

(*ii*) (*a*) Ethanol < Phenol < *p*-nitrophenol

(*b*) Propane < Propanal < Propanol

(*iii*)



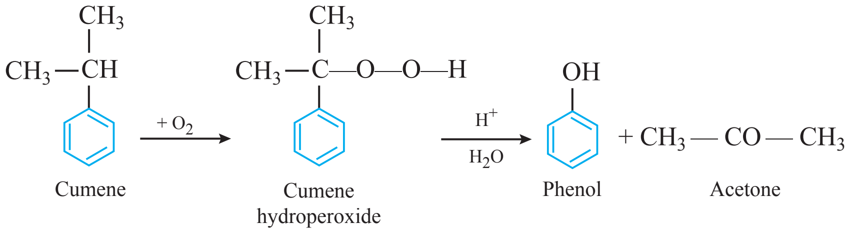
$$CH_3-CH_2-\overset{\overset{H}{|}}{\ddot{O}}: + CH_3-CH_2-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{\overset{+}{O}}}-H \longrightarrow CH_3-CH_2-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{\overset{+}{O}}}-CH_2-CH_3 + H_2\ddot{O}$$

Q. 2. **(*i*) How can you obtain phenol from (*a*) Cumene, (*b*) Benzene sulphonic acid, (*c*) Benzene diazonium chloride?**

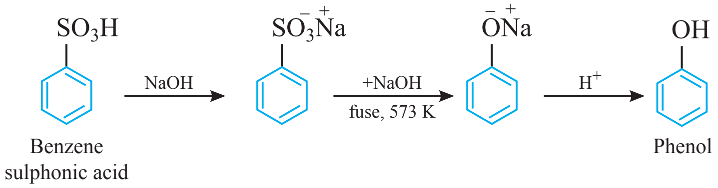
(*ii*) Write the structure of the major product obtained from dinitration of 3-methylphenol.

(*iii*) Write the reaction involved in Kolbe's reaction. ***[CBSE 2019 (56/2/1)]***

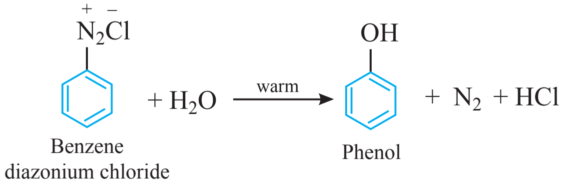
Ans. (*i*) (*a*)



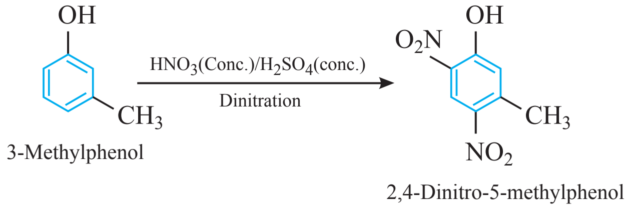
(*b*)



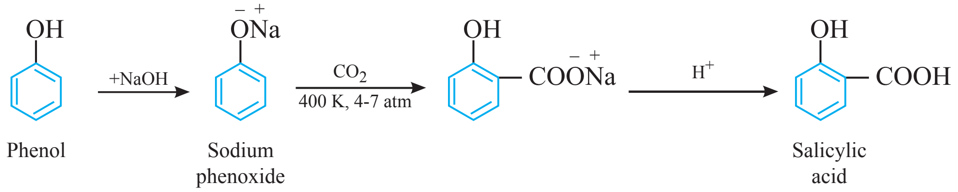
(*c*)



(*ii*)

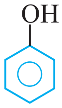


(*iii*) Kolbe's reaction:



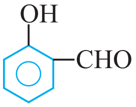
Q. 3. An aromatic compound 'A' on treatment with $CHCl_3$/KOH gives two compounds 'B' and 'C'. Both B and C give the same product 'D' when distilled with zinc dust. Oxidation of D gives E having molecular formula $C_7H_6O_2$. The sodium salt of E on heating with sodalime gives F which may also be obtained by distilling A with zinc dust. Identify A to F. **[*HOTS*]**

Ans. A =



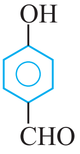
Phenol

B =



o-Hydroxy benzaldehyde

C =

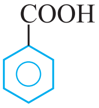


p-Hydroxy benzaldehyde

D =

Benzaldehyde

E =

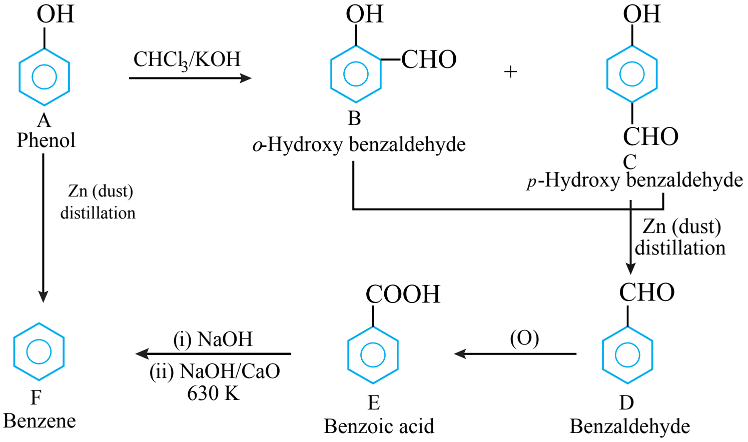


Benzoic acid

F =

Benzene

Reactions involved:



Q. 4. (*i*) Give equations of the following reactions:

(*a*) Phenol is treated with conc. HNO_3.

(*b*) Propene is treated with B_2H_6 followed by H_2O_2/OH^-.

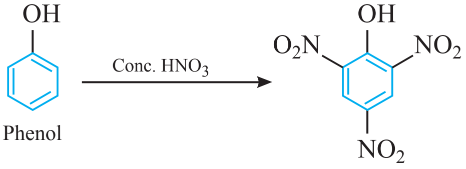
(*c*) Sodium *t*-butoxide is treated with CH_3Cl.

(*ii*) How will you distinguish between butan-1-ol and butan-2-ol?

(*iii*) Arrange the following in increasing order of acidity:

Phenol, ethanol, water **[*CBSE 2019 (56/2/1)*]**

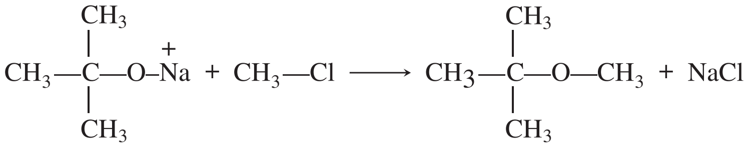
Ans. (*i*) (*a*)



2, 4, 6-Trinitrophenol

(*b*) $CH_3{-}CH{=}CH_2 \xrightarrow[(ii)\ H_2O_2/\overline{O}H]{(i)\ B_2H_6} CH_3CH_2CH_2OH$

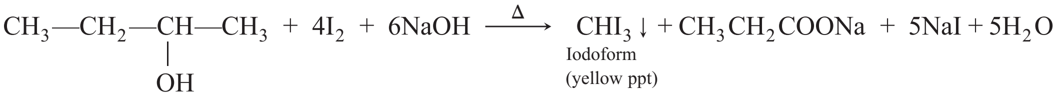
Propene — Propanol

(*c*) 

$$CH_3{-}C(CH_3)_2{-}O^{-}\overset{+}{Na} + CH_3{-}Cl \longrightarrow CH_3{-}C(CH_3)_2{-}O{-}CH_3 + NaCl$$

Sodium tert.butoxide — Methyl tert. butyl ether

(*ii*) Butan-2-ol when warmed with I_2 in NaOH (NaOI) gives yellow precipitate of iodoform while butan-1-ol does not respond to this test.



$$CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3\downarrow + CH_3CH_2COONa + 5NaI + 5H_2O$$

Butan-2-ol — Iodoform (yellow ppt)

(*iii*) Ethanol < water < phenol

Q. 5. (*i*) What happens when

(*a*) phenol reacts with bromine water?

(*b*) ethanol reacts with CH_3COCl/pyridine?

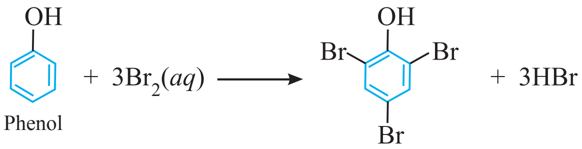
(*c*) anisole reacts with HI?

Write the chemical equations involved in the above reactions.

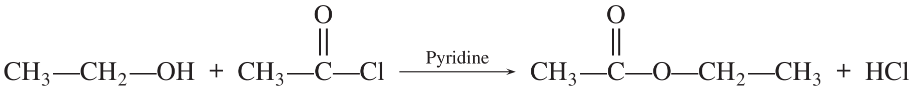
(*ii*) Distinguish between:

(*a*) Ethanol and phenol

(*b*) Propan-2-ol and 2-methylpropan-2-ol ***[CBSE (F) 2016]***

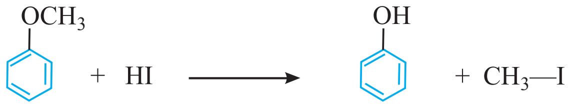
Ans. (*i*) (*a*) 

Phenol — 2,4,6-Tribromophenol

(*b*) 

$$CH_3{-}CH_2{-}OH + CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl \xrightarrow{\text{Pyridine}} CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3 + HCl$$

Ethanol — Ethanoyl chloride — Ethyl ethanoate

(*c*) 

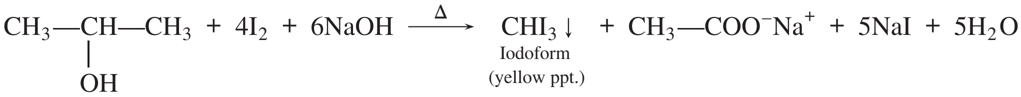
Anisole — Phenol — Methyl iodide

(*ii*) (*a*) Phenol gives violet colouration with $FeCl_3$ solution but ethanol does not.

$$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{3-} + 3H^+ + 3HCl$$

Phenol — Violet colouration complex

(*b*) Propan-2-ol when warmed with I_2 in NaOH gives yellow precipitate of iodoform while 2-methylpropan-2-ol does not respond to this test.



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3\downarrow + CH_3{-}COO^-Na^+ + 5NaI + 5H_2O$$

Propan-2-ol — Iodoform (yellow ppt.)

Q. 6. **(*i*) Write equations of the following reactions:**

(*a*) Bromine in CS_2 with phenol

(*b*) Treating phenol with chloroform in the presence of aq. NaOH

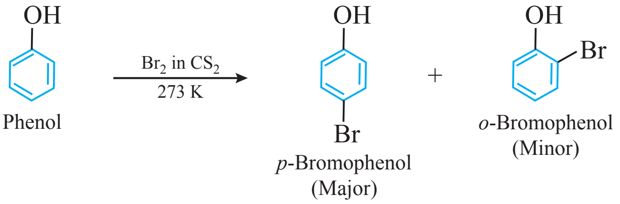
(*c*) Anisole reacts with HI

(*ii*) Distinguish between

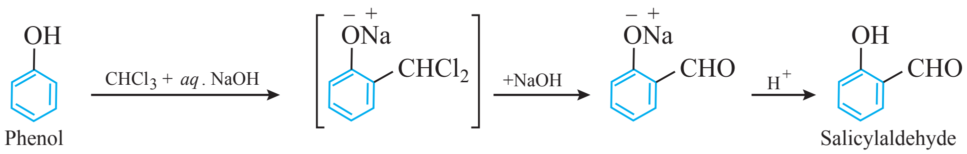
(*a*) Ethanol and Diethyl ether

(*b*) Propanol and *t*-butyl alcohol **[*CBSE South 2016*]**

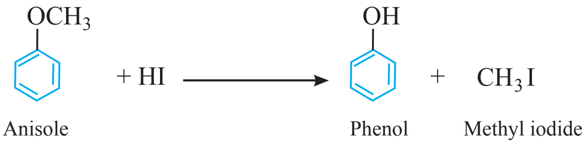
Ans. (*i*) (*a*)



(*b*)



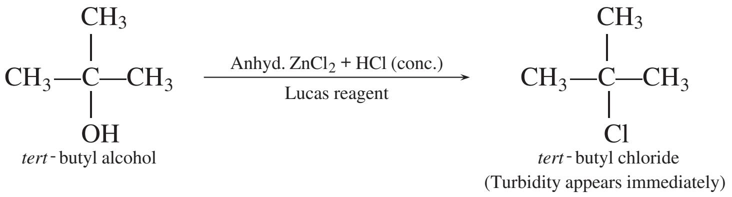
(*c*)



(*ii*) (*a*) Ethanol when warmed with I_2 in NaOH gives yellow precipitate of iodoform while diethyl ether does not.

$$CH_3—CH_2—OH + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform} \\ \text{(yellow ppt.)}}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

(*b*) *tert*-butyl alcohol on treatment with the Lucas reagent immediately gives turbidity while propanol does not produce turbidity at room temperature.



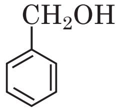
$$\underset{\textit{tert}\text{-butyl alcohol}}{CH_3—\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}—CH_3} \xrightarrow[\text{Lucas reagent}]{\text{Anhyd. } ZnCl_2 + HCl \text{ (conc.)}} \underset{\substack{\textit{tert}\text{-butyl chloride} \\ \text{(Turbidity appears immediately)}}}{CH_3—\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large Cl}{|}}{C}}—CH_3}$$

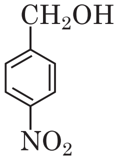
Self-Assessment Test

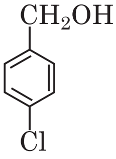
Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. **Which of the following reagents cannot be used to distinguish phenol and benzyl alcohol?**
   (*a*) NaOH (*b*) $NaHCO_3$
   (*c*) Br_2/CCl_4 (*d*) $FeCl_3$
2. **Alcohols are soluble in water because**
   (*a*) alcohol forms ionic bond with water
   (*b*) alcohol forms hydrogen bond with water
   (*c*) alcohol forms covalent bond with water
   (*d*) alcohol forms interstitial compound with water
3. **Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.**


(*i*)


(*ii*)


(*iii*)

   (*a*) (*i*) < (*ii*) < (*iii*) (*b*) (*ii*) < (*i*) < (*iii*)
   (*c*) (*ii*) < (*iii*) < (*i*) (*d*) (*iii*) < (*ii*) < (*i*)

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. **Assertion (A)** : Phenol is more reactive than benzene towards electrophilic substitution reaction.
   Reason (R) : In the case of phenol, the intermediate carbocation is more resonance stablized.
5. **Assertion (A)** : Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol.
   Reason (R) : Addition of water in acidic medium proceeds through the formation of primary carbocation.
6. **Assertion (A)** : Ethers behave as bases in the presence of mineral acids.
   Reason (R) : Due to the presence of lone pairs of electrons on oxygen.

Answer the following questions:

7. While separating a mixture of ortho and para-nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reasons. **(1)**
8. Give a chemical test to distinguish between ethyl alcohol and methyl alcohol. **(1)**
9. (*i*) Arrange the following compounds in the increasing order of their acid strength:
   p-cresol, *p*-nitrophenol, phenol
   (*ii*) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_2{=}CH_2 \xrightarrow{H_3O^+} CH_3{-}\overset{+}{C}H_2 + H_2O$$

[*CBSE (AI) 2017*] (2)

10. Give reasons for the following:

(*i*) Anisole reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol.

(*ii*) *o*-Nitrophenol is less soluble in water than *p*-nitrophenol. **(2)**

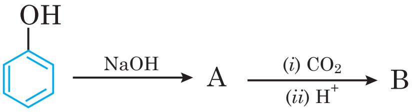
11. Write the structures of the products when Butan-2-ol reacts with the following:

(*i*) CrO_3 (*ii*) $SOCl_2$ ***[CBSE (AI) 2017]*** **(2)**

12. Alcohols react both as nucleophiles as well as electrophiles. Write one reaction of each type and describe its mechanism. **(2)**

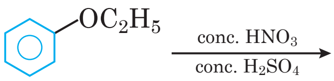
13. (*i*) Write mechanism of the reaction of HI with methoxymethane.

(*ii*) Identify A and B in the following reactions:

(*a*)


(*b*) $C_2H_5OH \xrightarrow[H_3O^+]{Cu,\ 573\ K} A \xrightarrow[H_2O/H^+]{CH_3MgBr} B$

(*iii*) Give the structure and the IUPAC name of the major product obtained in the following reaction:



[CBSE Sample Paper 2015] **(3)**

14. (*i*) Arrange the following sets of compounds in order of their increasing boiling points:

(*a*)Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol

(*b*)Pentan-1-ol, *n*-butane, pentanal, ethoxyethane.

(*ii*) Arrange the following compounds in increasing order of acidity and give a suitable explanation.

Phenol, *o*-nitrophenol, *o*-cresol ***[NCERT Exemplar]*** **(3)**

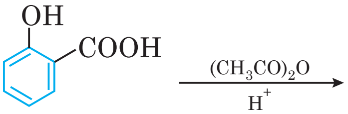
15. Name the reagents which are used in the following conversions:

(*i*) A primary alcohol to aldehyde

(*ii*) Butan-2-one to butan-2-ol

(*iii*) Benzyl alcohol to benzoic acid **(3)**

16. (*i*) Write the product(s) in the following reactions:

(*a*)


(*b*) $CH_3—CH_2—O—CH_2—CH_3 \xrightarrow{HI} ?$

(*c*) $CH_3—CH=CH—CH_2—OH \xrightarrow{PCC} ?$

(*ii*) Give simple chemical tests to distinguish between the following pairs of compounds:

(*a*) Ethanol and Phenol

(*b*) Pentan-2-ol and pentan-3-ol **(5)**

Answers

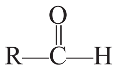
1. (*b*) **2.** (*b*) **3.** (*c*) **4.** (*a*) **5.** (*c*) **6.** (*a*)

Chapter–12

Aldehydes, Ketones and Carboxylic Acids

basic concepts

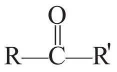
1. **The Carbonyl Group, $>C{=}O$:** The functional group $>C{=}O$ is called carbonyl group. Organic compounds containing carbonyl group are aldehydes, ketones, carboxylic acids and their derivatives. The general formulae of these compounds are given below:



$R-\overset{\overset{\Large O}{\|}}{C}-H$

Aldehyde

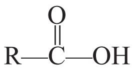
(where R may be H or any alkyl, aryl or aralkyl group)



$R-\overset{\overset{\Large O}{\|}}{C}-R'$

Ketone

(where R and R' may be same or different alkyl, aryl or aralkyl group)

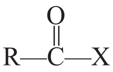


$R-\overset{\overset{\Large O}{\|}}{C}-OH$

Carboxylic acid

(where R may be H or any alkyl, aryl or aralkyl group)

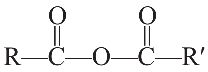
Derivatives of Carboxylic Acids:



$R-\overset{\overset{\Large O}{\|}}{C}-X$

Acyl halide

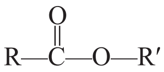
X = Halogen



$R-\overset{\overset{\Large O}{\|}}{C}-O-\overset{\overset{\Large O}{\|}}{C}-R'$

Acid anhydride

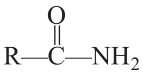
(where R and R′ may be same or different groups)



$R-\overset{\overset{\Large O}{\|}}{C}-O-R'$

Ester

(where R and R′ may be same or different groups)



$R-\overset{\overset{\Large O}{\|}}{C}-NH_2$

Acid amide

(where R may be H or any group)

The carbon atom of the carbonyl group is sp^2 hybridised. The structure of carbonyl group is shown in Fig. 12.1.

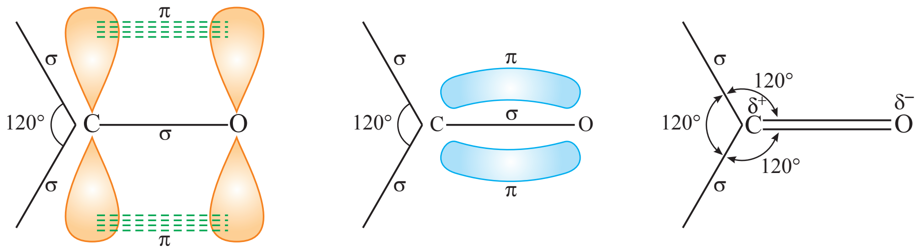


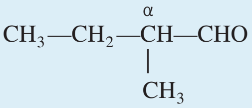
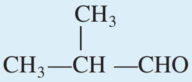
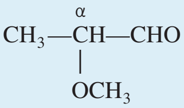
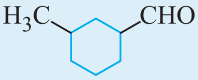
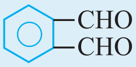
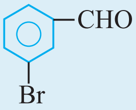
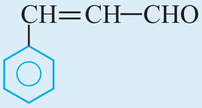
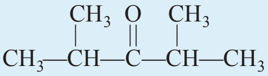
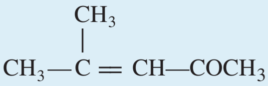
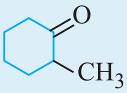
Fig. 12.1 Structure of Carbonyl Group ($>C{=}O$)

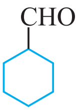
The $>\overset{\delta^+}{C}{=}\overset{\delta^-}{O}$ bond is polar due to higher electronegativity of oxygen atom as compared to carbon.

2. **Common and IUPAC Names of Some Aldehydes and Ketones:**

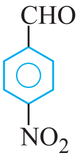
Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Common Name	Structural Formula	IUPAC Name
Formaldehyde	HCHO	Methanal
Acetaldehyde	CH_3—CHO	Ethanal

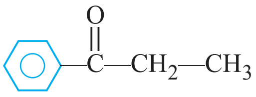
α-Methylbutyraldehyde	 $CH_3-CH_2-\underset{CH_3}{\underset{\vert}{\overset{\alpha}{C}H}}-CHO$	2-Methylbutanal
Isobutyraldehyde	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CHO$	2-Methylpropanal
Valeraldehyde	$CH_3-CH_2-CH_2-CH_2-CHO$	Pentanal
Acrolein	$CH_2=CH-CHO$	Prop-2-enal
α-Methoxypropionaldehyde	 $CH_3-\underset{OCH_3}{\underset{\vert}{\overset{\alpha}{C}H}}-CHO$	2-Methoxypropanal
γ-Methylcyclohexane		3-Methylcyclohexanecarbaldehyde
Phthaldehyde		Benzene-1, 2-dicarbaldehyde
m-Bromobenzaldehyde		3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Crotonaldehyde	$CH_3-CH=CH-CHO$	But-2-enal
Cinnamaldehyde		3-Phenyl prop-2-enal
Acetone	CH_3COCH_3	Propanone
Diisopropyl ketone	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-\overset{O}{\overset{\Vert}{C}}-\overset{CH_3}{\overset{\vert}{C}H}-CH_3$	2, 4-Dimethylpentan-3-one
Mesityl oxide	 $CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH-COCH_3$	4-Methylpent-3-en-2-one
α-Methylcyclohexanone		2-Methylcyclohexanone



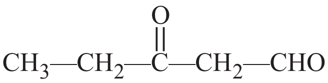
Cyclohexanecarbaldehyde



4-Nitrobenzenecarbaldehyde
or 4-Nitrobenzaldehyde

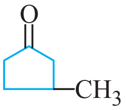


1-Phenyl propanone

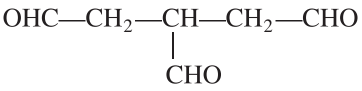


$$CH_3-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_2-CHO$$

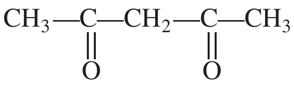
3-Oxopentanal



3-Methylcyclopentanone



$$\underset{\text{Propane-1,2,3-tricarbaldehyde}}{OHC{-}CH_2{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}CH_2{-}CHO}$$



$$\underset{\text{Pentane-2,4-dione}}{CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3}$$

3. Preparation of Aldehydes

(*a*) By oxidation of primary alcohols

$$\underset{\text{1° Alcohol}}{R{-}CH_2{-}OH} + [O] \xrightarrow[\text{or } KMnO_4]{K_2Cr_2O_7/H_2SO_4} \underset{\substack{\text{Aldehyde}\\ \text{(distilled out as soon}\\ \text{as formed)}}}{R{-}CHO} + H_2O$$

$$\underset{\text{1° Alcohol}}{R{-}CH_2{-}OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{Aldehyde}}{R{-}CHO}$$

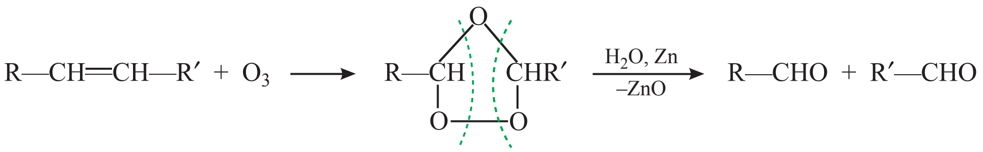
$$\underset{\text{But-2-en-1-ol}}{CH_3{-}CH{=}CH{-}CH_2{-}OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{But-2-en-1-al}}{CH_3{-}CH{=}CH{-}CHO}$$

(*b*) By dehydrogenation of primary alcohols

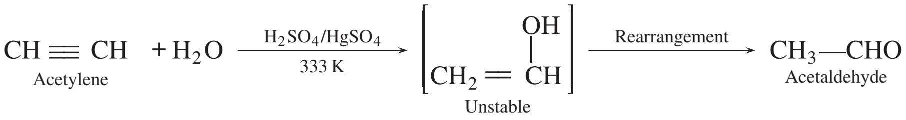
$$\underset{\text{1° Alcohol}}{R{-}CH_2{-}OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{R{-}CHO} + H_2$$

(*c*) From hydrocarbons

(*i*) By ozonolysis of alkenes

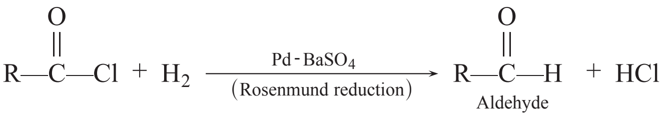


(*ii*) By hydration of alkynes

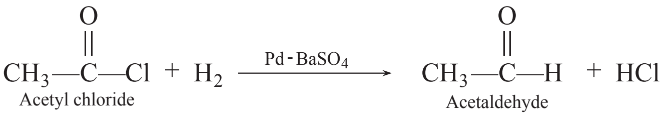


$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[333\text{ K}]{H_2SO_4/HgSO_4} \underset{\text{Unstable}}{\left[CH_2=\overset{\displaystyle OH}{\overset{|}{CH}}\right]} \xrightarrow{\text{Rearrangement}} \underset{\text{Acetaldehyde}}{CH_3{-}CHO}$$

(*d*) From acyl chloride



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl + H_2 \xrightarrow[\text{(Rosenmund reduction)}]{Pd\text{-}BaSO_4} \underset{\text{Aldehyde}}{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H} + HCl$$



$$\underset{\text{Acetyl chloride}}{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl} + H_2 \xrightarrow{Pd\text{-}BaSO_4} \underset{\text{Acetaldehyde}}{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H} + HCl$$

(*e*) From nitriles and esters

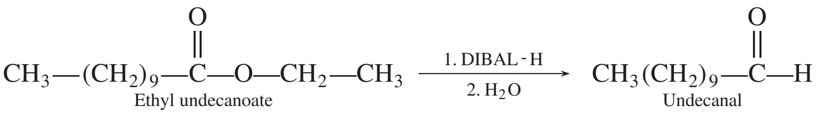
$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

$$R{-}C\equiv N + HCl + 2[H] \longrightarrow R{-}CH=NH.HCl \xrightarrow[-\,NH_4Cl]{+H_2O} \underset{\text{Aldehyde}}{R{-}CHO}$$

This reaction is called **Stephen reaction**

$$R{-}CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} \underset{\text{Aldehyde}}{R{-}CHO}$$

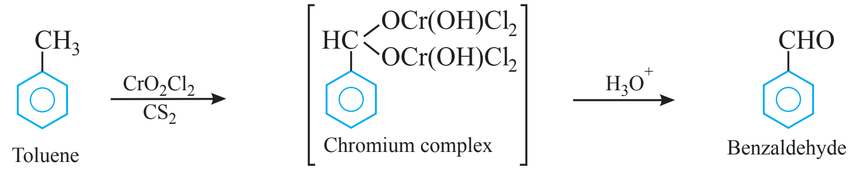
$$\underset{\text{Hex-4-enenitrile}}{CH_3{-}CH=CH{-}CH_2{-}CH_2{-}CN} \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} \underset{\text{Hex-4-en-1-al}}{CH_3{-}CH=CH{-}CH_2{-}CH_2{-}CHO}$$



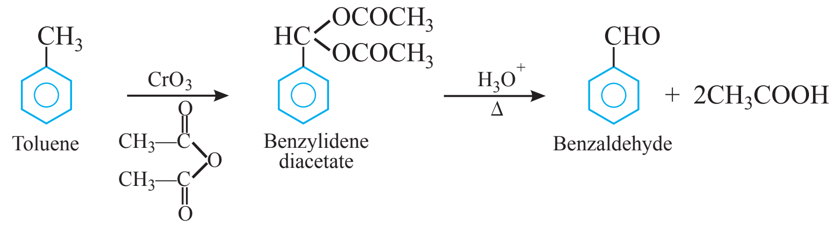
$$\underset{\text{Ethyl undecanoate}}{CH_3{-}(CH_2)_9{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3} \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} \underset{\text{Undecanal}}{CH_3(CH_2)_9{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H}$$

4. Preparation of Benzaldehyde

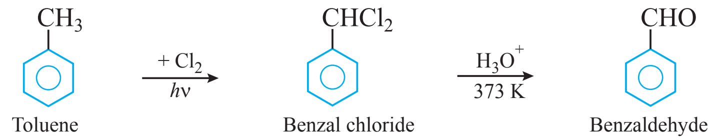
(*a*) By oxidation of toluene



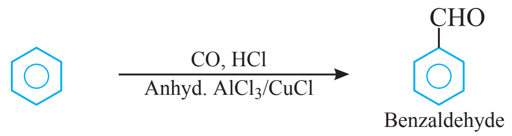
This reaction is called **Etard reaction**.



(*b*) By side chain chlorination followed by hydrolysis

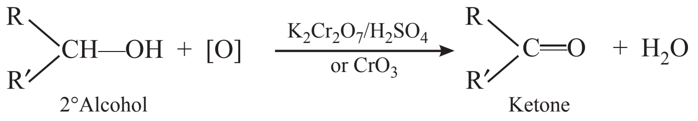


(*c*) By Gatterman–Koch reaction

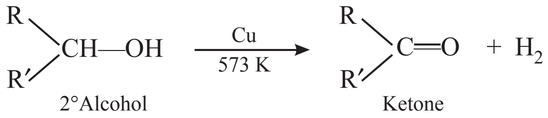


5. Preparation of Ketones

(*a*) By oxidation of secondary alcohols

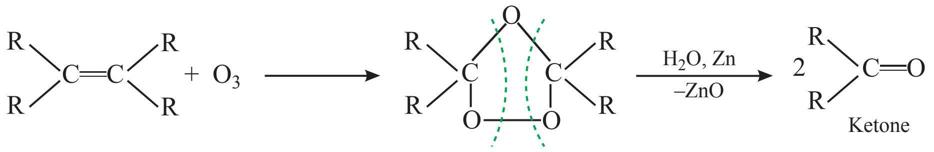


(*b*) By dehydrogenation of secondary alcohols

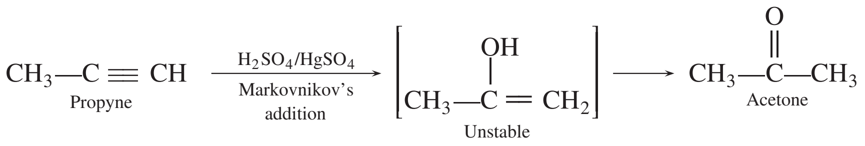


(*c*) From hydrocarbons

(*i*) By ozonolysis of alkenes



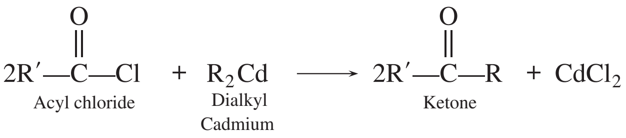
(*ii*) By hydration of alkynes



$$\underset{\text{Propyne}}{CH_3—C \equiv CH} \xrightarrow[\text{Markovnikov's addition}]{H_2SO_4/HgSO_4} \underset{\text{Unstable}}{\left[CH_3—\overset{\overset{\large OH}{|}}{C} = CH_2\right]} \longrightarrow \underset{\text{Acetone}}{CH_3—\overset{\overset{\large O}{\|}}{C}—CH_3}$$

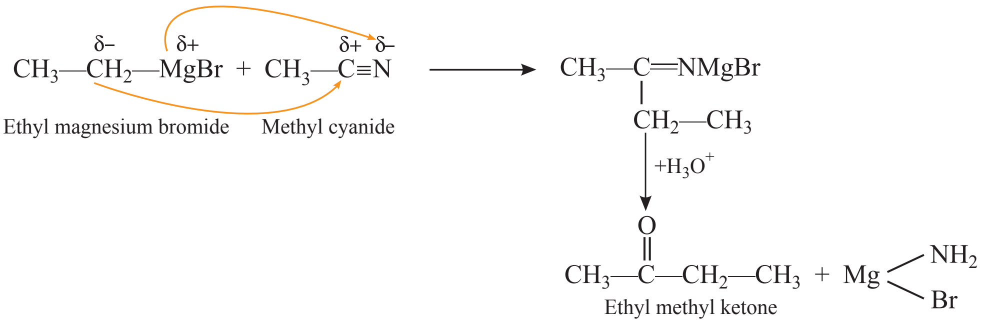
(*d*) From acyl chlorides

$$2R{-}MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$



$$\underset{\text{Acyl chloride}}{2R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl} + \underset{\text{Dialkyl Cadmium}}{R_2Cd} \longrightarrow \underset{\text{Ketone}}{2R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R} + CdCl_2$$

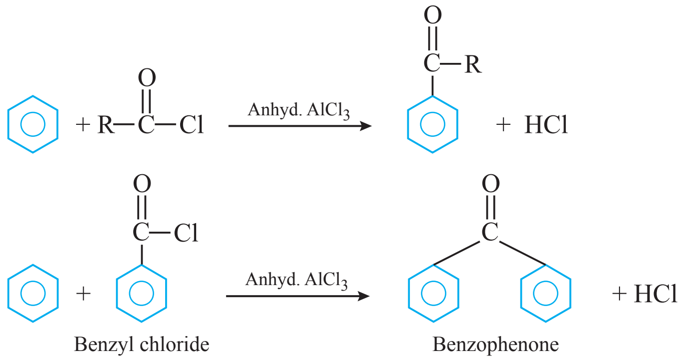
(*e*) From nitriles



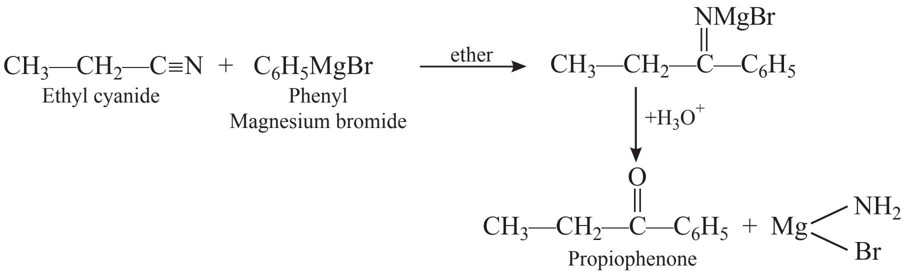
$$\underset{\text{Ethyl magnesium bromide}}{CH_3{-}\overset{\delta-}{C}H_2{-}\overset{\delta+}{Mg}Br} + \underset{\text{Methyl cyanide}}{CH_3{-}\overset{\delta+}{C}{\equiv}\overset{\delta-}{N}} \longrightarrow CH_3{-}\underset{\underset{\displaystyle CH_2{-}CH_3}{|}}{C}{=}NMgBr \xrightarrow{+H_3O^+} \underset{\text{Ethyl methyl ketone}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3} + Mg\begin{matrix}NH_2\\Br\end{matrix}$$

6. Preparation of Aromatic Ketones

(*a*) By Friedel-Crafts acylation



(*b*) From nitriles



$$\underset{\text{Ethyl cyanide}}{CH_3{-}CH_2{-}C{\equiv}N} + \underset{\text{Phenyl Magnesium bromide}}{C_6H_5MgBr} \xrightarrow{\text{ether}} CH_3{-}CH_2{-}\overset{\overset{\displaystyle NMgBr}{\|}}{C}{-}C_6H_5 \xrightarrow{+H_3O^+} \underset{\text{Propiophenone}}{CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_6H_5} + Mg\begin{matrix}NH_2\\Br\end{matrix}$$

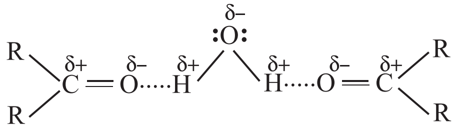
7. Physical Properties of Aldehydes and Ketones

(*a*) **Physical state:** Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell. The higher members are colourless solids. Aromatic ketones are usually solids with a pleasant smell.

(*b*) **Boiling points:** Aldehydes and ketones have relatively high boiling points as compared to hydrocarbons of comparable molecular masses. It is due to the reason that aldehydes and ketones contain polar carbonyl group and therefore, they have stronger dipole–dipole interactions between the opposite ends of C$=$O dipoles.

These dipole–dipole interactions are however, weaker than intermolecular H-bonding in alcohols. Consequently, boiling points of aldehydes and ketones are relatively lower than the alcohols of comparable molecular masses.

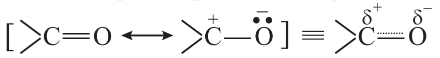
(*c*) **Solubility:** The lower members of aldehydes and ketones (up to four carbon atoms) are soluble in water. It is due to their capability to form hydrogen bonds with water molecules. The solubility of these compounds in water decreases with the increase in the size of alkyl group. It is because of the increase in the magnitude of non-polar part in the molecule. However, higher homologues are soluble in organic solvents.



8. Chemical Properties

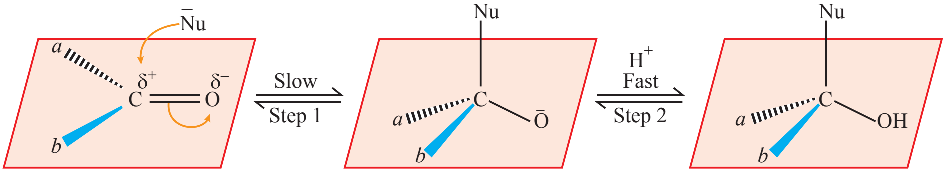
Aldehydes and ketones are highly reactive compounds. Both aldehydes and ketones undergo nucleophilic addition reactions.

Explanation: The reactive nature of aldehydes and ketones is because of the presence of a polar carbonyl group. As the oxygen atom is more electronegative, therefore, it pulls the electron around itself acquiring a partial negative charge (δ^-) whereas a partial positive charge (δ^+) is developed on the carbon atom.



Resonating forms

The positively charged carbon atom of carbonyl group is then readily attacked by the nucleophilic species for initiation of the reaction. This leads to the formation of an intermediate anion which further undergoes the attack of (H^+) ion or other positively charged species to form the final product. The nucleophilic reactions may be catalysed by acids or bases. The reaction in general, may be represented as:

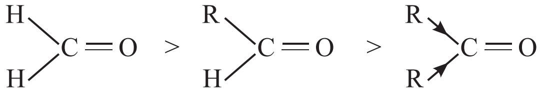


Planar   Tetrahedral intermediate   Addition product

Relative Reactivity of Aldehydes and Ketones

In general, ketones are less reactive than aldehydes on account of the following facts:

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

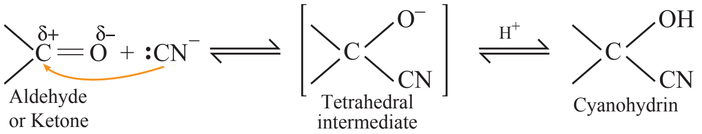


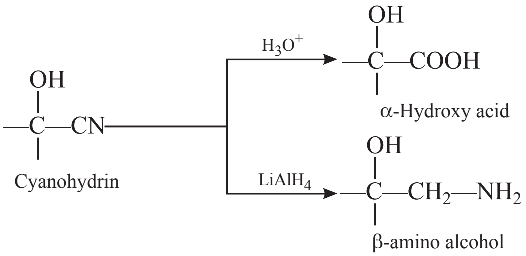
Formaldehyde   Aldehyde   Ketone

Some Important Nucleophilic Addition Reactions

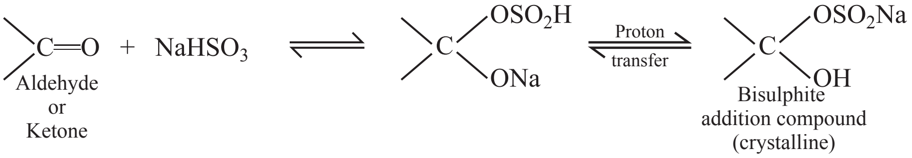
(*a*) (*i*) **Addition of hydrogen cyanide (HCN)**

$$HCN + OH^- \rightleftharpoons :CN^- + H_2O$$



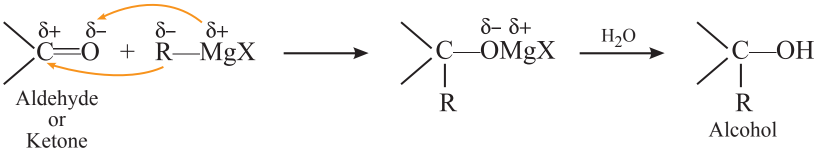


(*ii*) Addition of sodium hydrogensulphite ($NaHSO_3$)

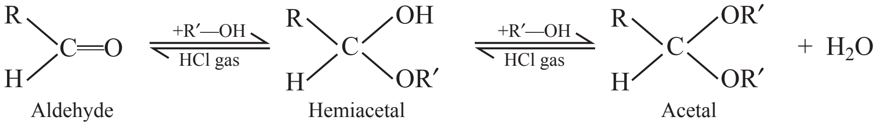


This reaction is useful for separation and purification of aldehydes and ketones.

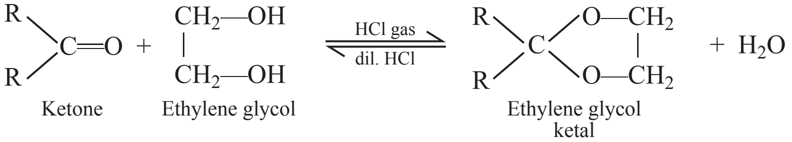
(*iii*) Addition of Grignard reagent



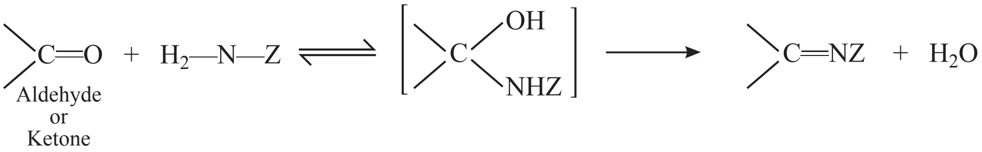
(*iv*) Addition of alcohols

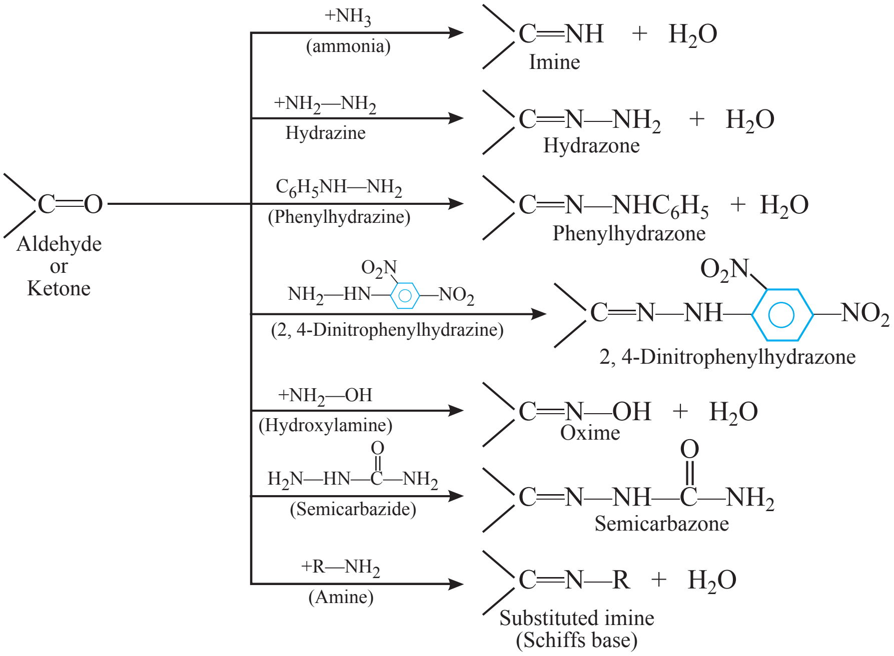


Ketones do not react with monohydric alcohols but react with dihydric alcohols to give ketals.



(*b*) Addition of ammonia and its derivatives

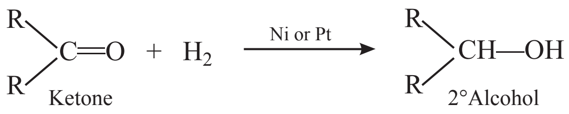




(*c*) Reduction

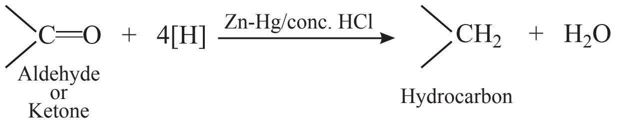
(*i*) Reduction to alcohols: Aldehydes and ketones are reduced to primary and secondary alcohols, respectively, by $LiAlH_4$ or $NaBH_4$ or H_2 in the presence of Ni or Pt.

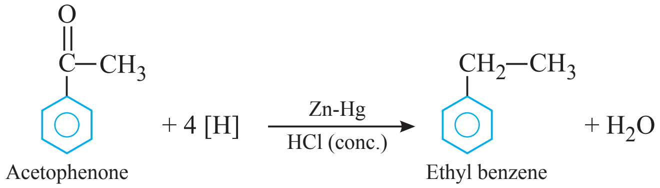
$$R{-}CHO + 2[H] \xrightarrow[\text{or NaBH}_4]{\text{LiAlH}_4} \underset{1^\circ\ \text{Alcohol}}{R{-}CH_2{-}OH}$$



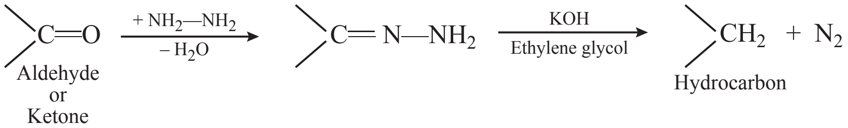
(*ii*) Reduction to hydrocarbons

(Clemmensen reduction)





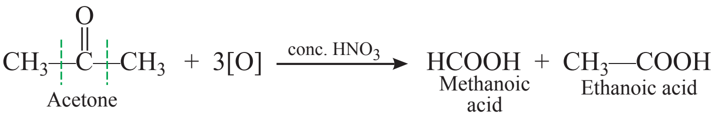
(Wolff–Kishner reduction)



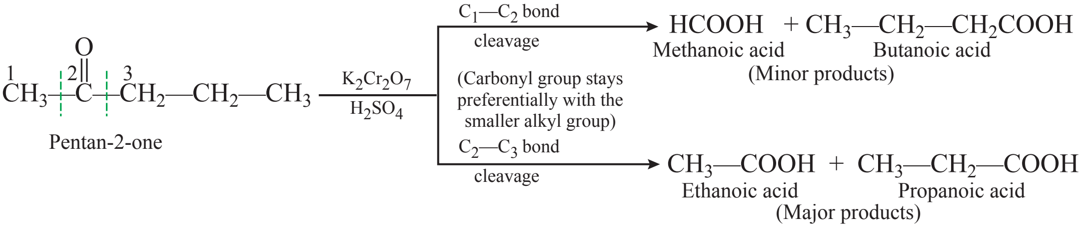
(*d*) Oxidation: Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents or mild oxidising agent like Tollens' reagent or Fehling's solution.

$$\underset{\text{Aldehyde}}{R{-}CHO} + [O] \xrightarrow[\text{or } KMnO_4/H_2SO_4]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Carboxylic acid}}{R{-}COOH}$$

Ketones undergo oxidation under vigorous conditions with cleavage of carbon–carbon bond.



$$\underset{\text{Acetone}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + 3[O] \xrightarrow{\text{conc. } HNO_3} \underset{\text{Methanoic acid}}{HCOOH} + \underset{\text{Ethanoic acid}}{CH_3{-}COOH}$$

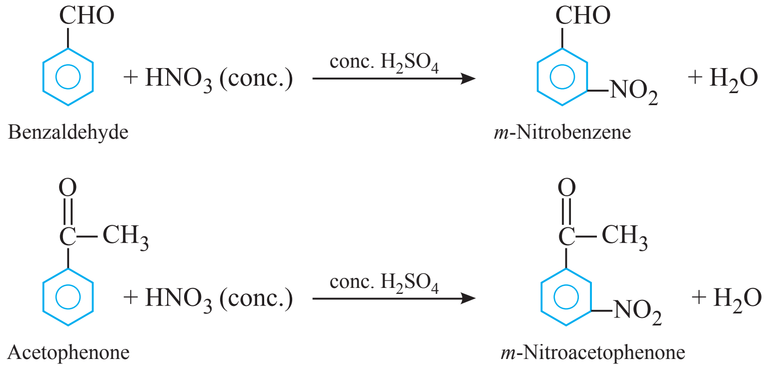


As ketones are not oxidised by mild oxidising agents such as Tollens' reagent and Fehling's solution, these reagents are used to distinguish aldehydes from ketones.

Electrophilic substitution reactions:

As, $-\overset{\overset{O}{\|}}{C}-H$ or $-\overset{\overset{O}{\|}}{C}-R$ group are electron-withdrawing and, therefore they are deactivating and *m*-directing.

Nitration:



9. Uses of Aldehydes and Ketones

(*i*) A 40% aqueous solution of formaldehyde is known as formalin and is used to preserve biological specimens and to prepare bakelite.

(*ii*) Acetaldehydes are used as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.

(*iii*) Benzaldehyde is used in perfumery and in dye industries.

(*iv*) Acetone and ethyl methyl ketone are common industrial solvents.

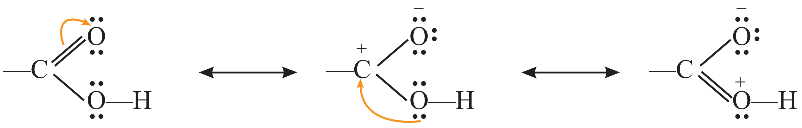
10. Carboxylic Acid

Organic compounds containing carboxyl group $-C\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$ possess sufficient acidic character and are called carboxylic acids. The carboxyl group is made up of carbonyl, $>C=O$ and hydroxyl, —OH group, hence, its name is carboxyl group (carb from carbonyl and oxyl from hydroxyl). Carboxylic acids may be aliphatic (R—COOH) or aromatic (Ar—COOH) depending upon whether —COOH group is attached to aliphatic alkyl chain or aryl groups, respectively.

Aliphatic monocarboxylic acids are known as fatty acids because some of their higher members (C_{12}—C_{18}) like palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) exist in natural fats as esters of glycerol and are obtained by their hydrolysis.

Structure of Carboxyl Group

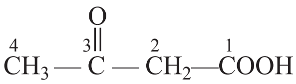
In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



11. In IUPAC system, the name of carboxylic acid is derived by replacing terminal **e** of the alkane with **oic acid**. For example,

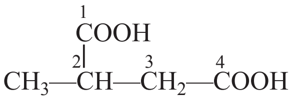
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}OOH$

Propanoic acid



$\overset{4}{C}H_3-\overset{\overset{O}{\|}}{\overset{3}{C}}-\overset{2}{C}H_2-\overset{1}{C}OOH$

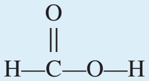
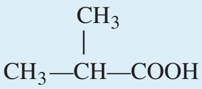
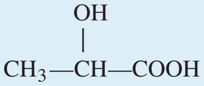
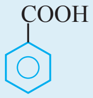
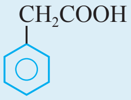
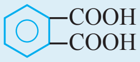
3-Oxobutanoic acid

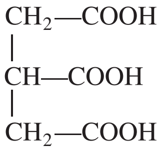


$CH_3-\underset{2}{C}H(\overset{1}{C}OOH)-\overset{3}{C}H_2-\overset{4}{C}OOH$

2-Methyl butane-1, 4-dioic acid

Table 12.2: Common and IUPAC Names of Some Carboxylic Acids

Common Name	Structural Formula	IUPAC Name
Formic acid	 $H-\overset{\overset{O}{\parallel}}{C}-O-H$	Methanoic acid
Acetic acid	CH_3-COOH	Ethanoic acid
Isobutyric acid	 $CH_3-\overset{\overset{CH_3}{\vert}}{C}H-COOH$	2-Methyl propanoic acid
Oxalic acid	$HOOC-COOH$	Ethanedioic acid
Malonic acid	$HOO\overset{3}{C}-\overset{2}{C}H_2-\overset{1}{C}OOH$	Propane-1, 3-dioic acid
Succinic acid	$HOOC-(CH_2)_2-COOH$	Butane-1, 4-dioic acid
Glutaric acid	$HOOC-(CH_2)_3-COOH$	Pentane-1, 5-dioic acid
Adipic acid	$HOOC-(CH_2)_4-COOH$	Hexane-1, 6-dioic acid
Lactic acid	 $CH_3-\overset{\overset{OH}{\vert}}{C}H-COOH$	2-Hydroxy propanoic acid
Acrylic acid	$CH_2{=}CH-COOH$	Prop-2-enoic acid
Crotonic acid	$CH_3-CH{=}CH-COOH$	But-2-enoic acid
Benzoic acid		Benzene carboxylic acid(Benzoic acid)
Phenyl acetic acid		2-Phenylethanoic acid
Phthalic acid		Benzene-1, 2-dicarboxylic acid



$$\begin{array}{l} CH_2-COOH \\ \vert \\ CH-COOH \\ \vert \\ CH_2-COOH \end{array}$$

Propane - 1, 2, 3 - tricarboxylic acid

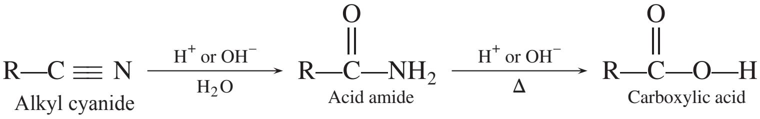
12. Methods of Preparation of Carboxylic Acids

(*a*) By oxidation of primary alcohols and aldehydes.

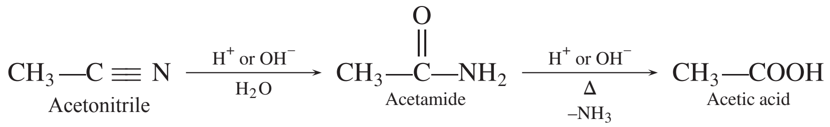
$$\underset{1°\text{ Alcohol}}{R-CH_2-OH} \xrightarrow[(ii)\ H_3O^+]{(i)\text{ Alk. }KMnO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

$$\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow[\substack{\text{or} \\ CrO_3/H_2SO_4 \\ \text{(Jones reagent)}}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

(*b*) From alkyl cyanides and amides.

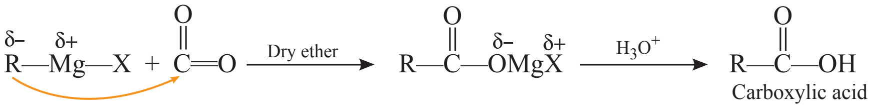


$$\underset{\text{Alkyl cyanide}}{R-C\equiv N} \xrightarrow[H_2O]{H^+\text{ or }OH^-} \underset{\text{Acid amide}}{R-\overset{\overset{O}{\parallel}}{C}-NH_2} \xrightarrow[\Delta]{H^+\text{ or }OH^-} \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{\parallel}}{C}-O-H}$$

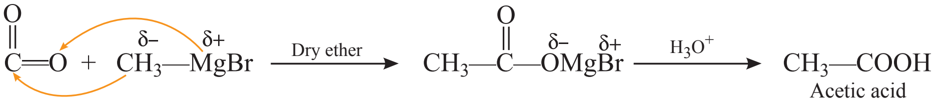


$$\underset{\text{Acetonitrile}}{CH_3-C\equiv N} \xrightarrow[H_2O]{H^+ \text{ or } OH^-} \underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[\substack{\Delta\\ -NH_3}]{H^+ \text{ or } OH^-} \underset{\text{Acetic acid}}{CH_3-COOH}$$

(*c*) From Grignard reagent

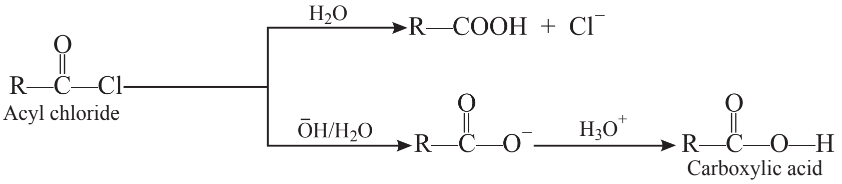


$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-X + \overset{O}{\overset{\|}{C}}=O \xrightarrow{\text{Dry ether}} R-\overset{O}{\overset{\|}{C}}-\overset{\delta-}{O}\overset{\delta+}{MgX} \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH}$$



$$\overset{O}{\overset{\|}{C}}=O + \overset{\delta-}{CH_3}-\overset{\delta+}{MgBr} \xrightarrow{\text{Dry ether}} CH_3-\overset{O}{\overset{\|}{C}}-\overset{\delta-}{O}\overset{\delta+}{MgBr} \xrightarrow{H_3O^+} \underset{\text{Acetic acid}}{CH_3-COOH}$$

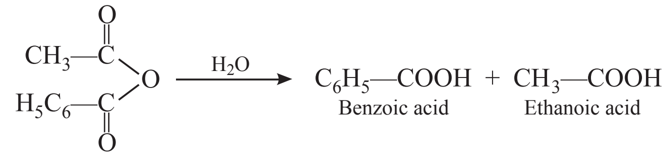
(*d*) By hydrolysis of acyl halides and acid anhydrides



$$\underset{\text{Acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow{H_2O} R-COOH + Cl^-$$

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\bar{O}H/H_2O} R-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-O-H}$$

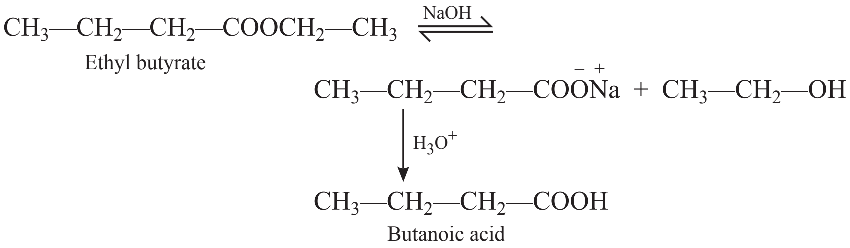
$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2C_6H_5-COOH}$$



$$CH_3-CO-O-CO-C_6H_5 \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5-COOH} + \underset{\text{Ethanoic acid}}{CH_3-COOH}$$

Benzoic ethanoic anhydride

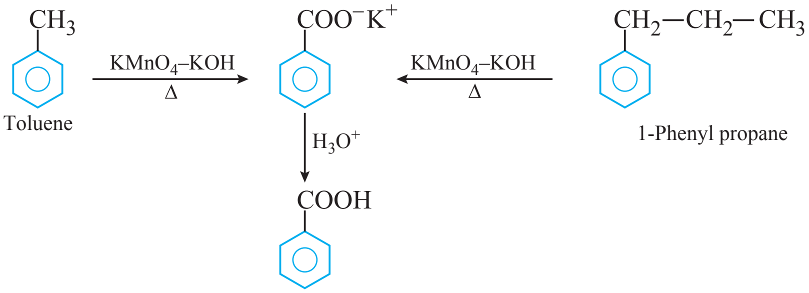
(*e*) By hydrolysis of esters



$$\underset{\text{Ethyl butyrate}}{CH_3-CH_2-CH_2-COOCH_2-CH_3} \overset{NaOH}{\rightleftharpoons} CH_3-CH_2-CH_2-CO\overset{-}{O}\overset{+}{Na} + CH_3-CH_2-OH \xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3-CH_2-CH_2-COOH}$$

Preparation of benzoic acid

(*i*) From alkyl benzene

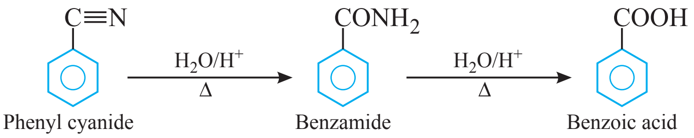


Toluene

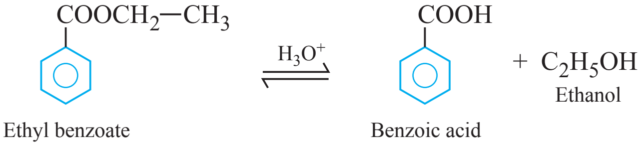
1-Phenyl propane

Benzoic acid

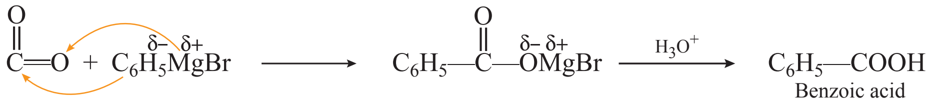
(*ii*) From nitriles and amides



(*iii*) By hydrolysis of esters



(*iv*) From Grignard reagent



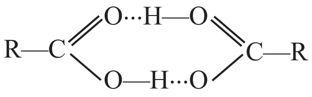
13. Physical Properties of Carboxylic Acids

(*a*) **Physical state:** The first three aliphatic acids are colourless liquids with pungent smell. The next six are oily liquids with an odour of rancid butter while the higher members are colourless, odourless, waxy solids. Benzoic acid is a crystalline solid.

(*b*) **Solubility:** Carboxylic acid molecules are polar, like alcohols, and can form intermolecular hydrogen bonds. The first four acids are miscible with water, the $C_5H_{11}COOH$ is partly soluble and the higher acids are insoluble. It is because of the increase in the magnitude of non-polar part in the molecule. Benzoic acid is practically insoluble in water.

Carboxylic acids are soluble in less polar solvents like ether, benzene, alcohol, etc.

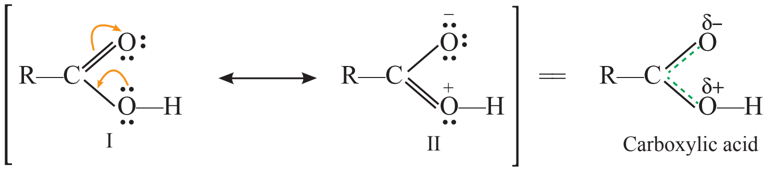
(*c*) **Boiling points:** Because of their ability to form intermolecular hydrogen bonding, carboxylic acids have high boiling points. The hydrogen bonds formed by the carboxylic acids are stronger than those in alcohols because O—H bond in COOH is strongly polarised due to the presence of electron-withdrawing carbonyl group in adjacent position than the O—H bond of alcohols. Therefore, the boiling points of carboxylic acids particularly lower members are higher than alcohols of comparable molecular masses.



Intermolecular hydrogen bonding in carboxylic acids

14. Chemical Properties of Carboxylic Acids

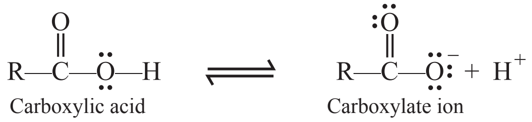
Carboxylic acids are resonance hybrid of the following structures:



From these structures, it is clear that the carbonyl parts of the carboxyl group have a reduced double bond character. Thus, it does not give the reactions of the carbonyl group. Also it is evident that the two contributing structures of carboxylic acid are not equivalent, therefore, they are less resonance stabilized. Moreover, oxygen atom of —OH group has positive charge in structure II, this indicates its electron deficient nature. Hence, the shared pair of electrons of O—H bond will be strongly pulled towards oxygen and this makes the O—H bond quite polar. Thus, the reactions of carboxylic acids are characteristic of the carboxyl group and alkyl group.

Acidic Nature

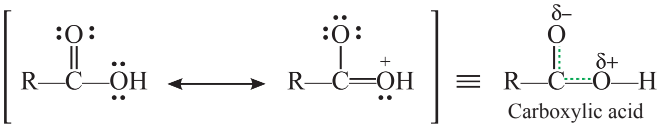
Carboxylic acids are quite strong acids because of the presence of polar O—H group. They ionise to give hydrogen ions and hence behave as acids.



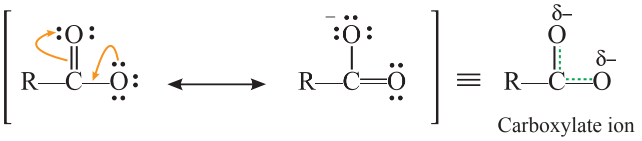
$$R-\overset{\overset{O}{\|}}{C}-\ddot{O}-H \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^{-} + H^{+}$$

Carboxylic acids behave as fairly strong acids: This can be explained as follows:

Carboxylic acids as well as carboxylate ion both are stabilised by resonance. However, carboxylate ion is more stabilised by resonance because its contributing structures are exactly identical. On the other hand, the contributing structures of carboxylic acid involve charge separation. Since carboxylate ion is more stabilised by resonance than carboxylic acid, therefore, equilibrium lies very much in forward direction, *i.e.*, in favour of ionised form. Hence, carboxylic acids behave as fairly strong acids.



Less stabilised



More stabilised

Acidity of carboxylic acids: Both carboxylic acid and carboxylate ion are resonance stabilised but stabilisation is far greater for the carboxylate ion than for the acid. Thus, carboxylic acids get ionised due to gain in the stability in going from carboxylic acid to the more stable carboxylate ion. Any factor that stabilises the carboxylate ion more would facilitate the release of protons and increase the acidity. Thus, electron-withdrawing substituents (Cl, NO_2, CN, etc.) in a carboxylic acid would disperse the negative charge of the COO^-, stabilise it and thus enhance the acid strength. On the other hand, the presence of an electron-donating substituent such as alkyl group, would intensify the negative charge on the COO^- ion and thus destabilise it, making the carboxylic acid less acidic.

The effect of some substituents is as follows:

(*i*) Effect of electron withdrawing substituents: The electron withdrawing substituents decrease the electron density on the O—H bond thus facilitating the release of H^+ ions and also stabilise the carboxylate anion by dispersal of negative charge. Thus, an electron-withdrawing group increases the strength of the acid.

(*ii*) Effect of electron releasing substituents—alkyl groups: The presence of electron releasing substituent intensifies the electron density in O—H bond. As a result, it adversely affects the release of H^+ ions and thus decreases the acidic character.

(*iii*) Acidity decreases with larger alkyl groups as the +I effect of the alkyl group increases with size of alkyl group. For example, Formic acid > Acetic acid > Propanoic acid.

(*iv*) Acidity increases with increasing number of electron-withdrawing substituents on the α-carbon. For example, Acetic acid < Chloroacetic acid < Dichloroacetic acid (Cl_2CH—COOH) < Trichloroacetic acid (Cl_3C—COOH).

(*v*) Acidity increases with increasing electronegativity of substituents. Thus,

Iodoacetic acid (ICH_2—COOH) < Bromoacetic acid ($BrCH_2$—COOH) < Chloroacetic acid ($ClCH_2$—COOH) < Fluoroacetic acid (FCH_2—COOH).

(*vi*) Acidity declines with increasing distance between electron-withdrawing group and COOH group. For example, 2-Chlorobutanoic acid > 3-Chlorobutanoic acid > 4-Chlorobutanoic acid.

(*vii*) Unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aliphatic carboxylic acids. Benzoic acid is a stronger acid than acetic acid. Further, since formic acid does not contain any alkyl group, therefore, it is a stronger acid than benzoic acid. Thus,

Formic acid > Benzoic acid > Acetic acid

Effect of substituents on the acidic strength of benzoic acid.

(*i*) The electron-releasing groups such as, —CH_3, —OH, —NH_2, etc., tend to decrease the acid strength of benzoic acid. The electron-withdrawing groups such as —Cl, —NO_2, etc., tend to increase the strength of benzoic acid.

(*ii*) Ortho isomer of benzoic acid is the strongest of all the isomers irrespective of the nature of the substituent. This is called ortho effect. This effect may be due to a combination of steric and electronic factors.

(*iii*) The acid-strengthening effect of electron-withdrawing group (*e.g.*, —Cl, —NO_2, etc.) is more pronounced at *p*-position than at *m*-position.

(*iv*) The acid-weakening effect of an electron-releasing substituent (*e.g.*, —OH, —CH_3, —NH_2, etc.) is more pronounced at *p*-position than at *m*-position.

15. Chemical Reactions

The reaction of carboxylic acids are classified as follows:

(*a*) Reactions involving cleavage of O—H bond: Reaction with metals and alkalis.

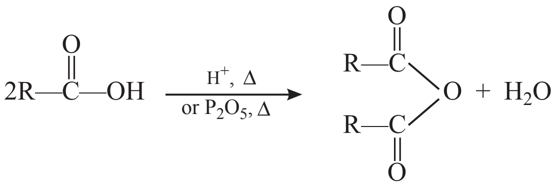
$$2R\text{—}COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R\text{—}CO\overset{-}{O}\overset{+}{Na}} + H_2$$

$$R\text{—}COOH + NaOH \longrightarrow R\text{—}CO\overset{-}{O}\overset{+}{Na} + H_2O$$

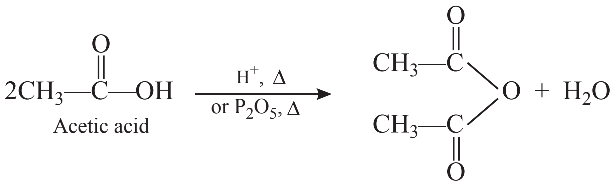
$$R\text{—}COOH + NaHCO_3 \longrightarrow R\text{—}CO\overset{-}{O}\overset{+}{Na} + H_2O + CO_2\uparrow$$

(*b*) Reactions involving cleavage of C—OH bond

(*i*) Formation of anhydride



Acid anhydride



Acetic anhydride

(*ii*) Esterification:

$$R\text{—}COOH + R'\text{—}OH \xrightleftharpoons{H^+} R\text{—}COOR' + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3\text{—}COOH} + CH_3\text{—}CH_2\text{—}OH \xrightleftharpoons{H^+} \underset{\text{Ethyl acetate}}{CH_3\text{—}COOCH_2\text{—}CH_3} + H_2O$$

(*iii*) Reactions with PCl_5, PCl_3 and $SOCl_2$

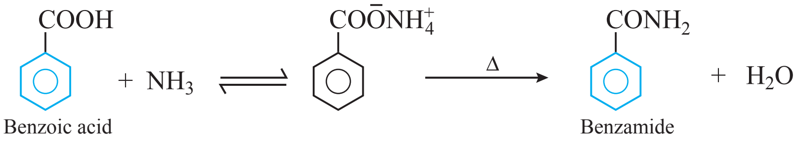
$$\underset{}{R{-}COOH} + PCl_5 \longrightarrow \underset{\text{Acyl chloride}}{RCOCl} + POCl_3 + HCl$$

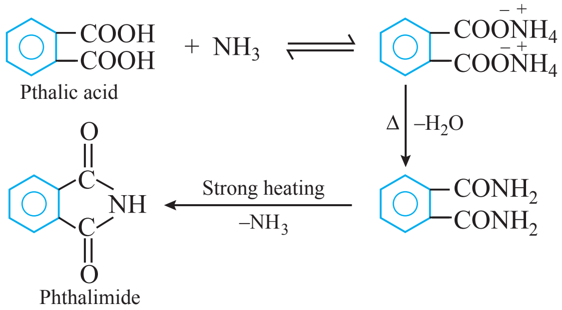
$$3R{-}COOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$R{-}COOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

(*iv*) Reaction with ammonia:

$$R{-}COOH + NH_3 \rightleftharpoons R{-}COO^-\overset{+}{N}H_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Acid amide}}{R{-}CONH_2}$$





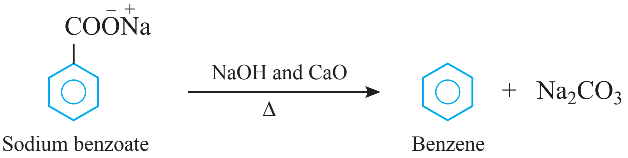
(*c*) Reaction involving —COOH group

(*i*) Reduction:

$$R{-}COOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/\text{ether or } B_2H_6} \underset{1^\circ\ \text{Alcohol}}{R{-}CH_2{-}OH}$$

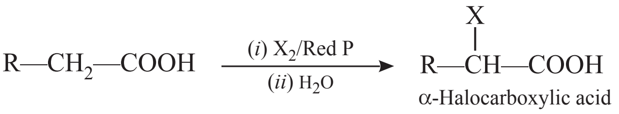
(*ii*) Decarboxylation:

$$\underset{\text{Sodium carboxylate}}{R{-}CO\overset{-}{O}\overset{+}{N}a} \xrightarrow[\Delta]{\text{NaOH and CaO}} R{-}H + Na_2CO_3$$



(*iii*) Halogenation:

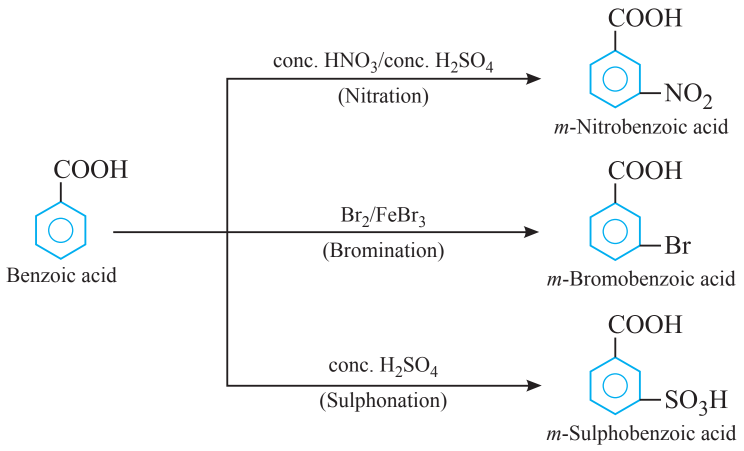
(Hell-Volhard Zelinsky reaction)



$$R{-}CH_2{-}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} \underset{\alpha\text{-Halocarboxylic acid}}{R{-}\overset{\overset{\displaystyle X}{|}}{C}H{-}COOH}$$

(X = Cl, Br)

(*d*) **Ring substitution reaction:** Aromatic carboxylic acids undergo electrophilic substitution reactions in which —COOH group acts as a deactivating and meta-directing group. They however do not undergo Friedel–Crafts reaction because the carboxyl group is deactivating and the catalyst $AlCl_3$ (Lewis acid) gets bonded to the carboxyl group.



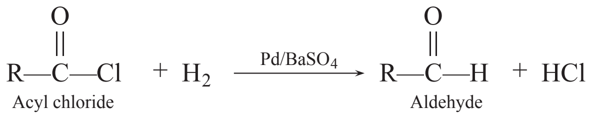
16. Uses of Carboxylic acids:

(*i*) Formic acid is used in rubber, textile, dyeing, leather and electroplating industry.
(*ii*) Acetic acid is used as solvent and as vinegar in food industry.
(*iii*) Adipic acid is used in the manufacture of nylon-6, 6.
(*iv*) Sodium benzoate is used as preservative.
(*v*) Higher fatty acids are used for the manufacture of soaps and detergents.
(*vi*) Esters of benzoic acid are used in perfumery.

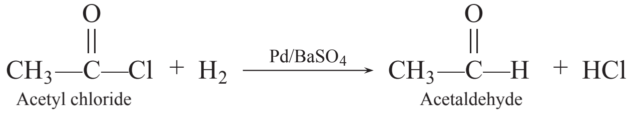
17. Some Important Name Reactions

(*a*) Rosenmund Reduction:

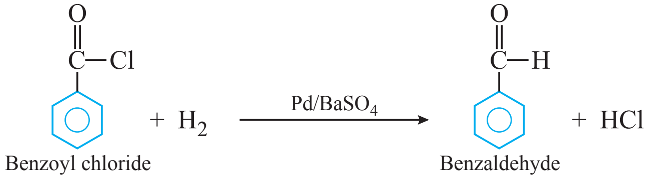
Acid chloride are converted to corresponding aldehydes by catalytic reduction. The reaction is carried out by passing H_2 gas through a hot solution of acid chloride in the presence of Pd deposited over $BaSO_4$ (partially poisoned with sulphur or quinoline).



$$\underset{\text{Acyl chloride}}{R{-}\overset{\overset{\Large O}{\|}}{C}{-}Cl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{Aldehyde}}{R{-}\overset{\overset{\Large O}{\|}}{C}{-}H} + HCl$$



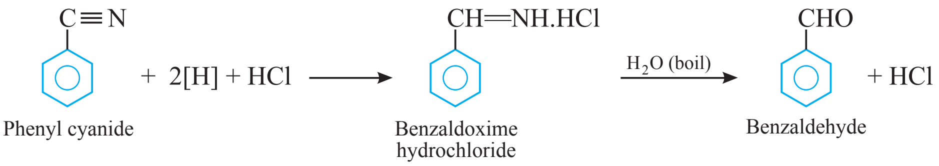
$$\underset{\text{Acetyl chloride}}{CH_3{-}\overset{\overset{\Large O}{\|}}{C}{-}Cl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{CH_3{-}\overset{\overset{\Large O}{\|}}{C}{-}H} + HCl$$



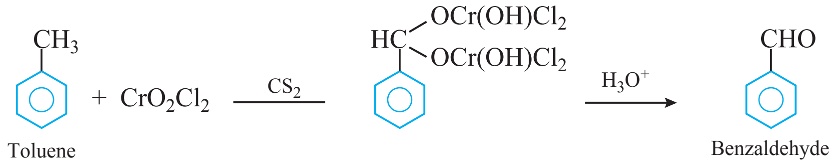
(*b*) Stephen reaction: Nitriles are reduced to corresponding imines with $SnCl_2$ in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

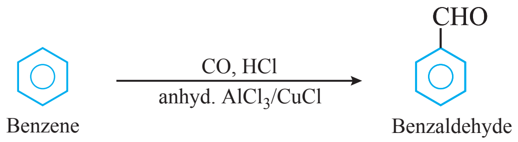
$$\underset{\text{Ethanenitrile}}{CH_3{-}C{\equiv}N} + 2[H] + HCl \longrightarrow \underset{\text{Acetaldoxime hydrochloride}}{CH_3{-}CH{=}NH.HCl} \xrightarrow{H_2O\text{ (boil)}} \underset{\text{Acetaldehyde}}{CH_3{-}CHO} + NH_4Cl$$



(*c*) **Etard reaction:** Chromyl chloride oxidises toluene to chromium complex which on hydrolysis gives benzaldehyde.

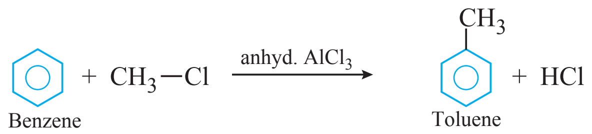


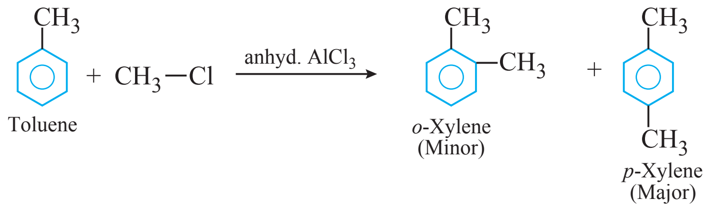
(*d*) **Gatterman–Koch reaction:** When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous $AlCl_3$ and CuCl, it gives benzaldehyde or substituted benzaldehyde.



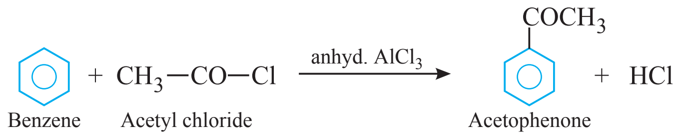
(*e*) **Friedel–Crafts reactions:**

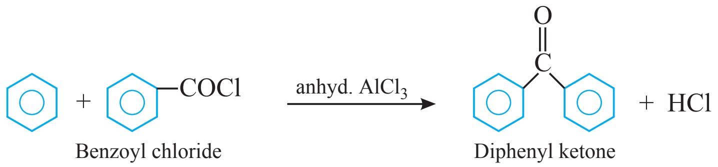
Friedel–Crafts alkylation: Benzene and other aromatic compounds react with alkyl halides in the presence of anhydrous $AlCl_3$ to form alkyl benzenes.

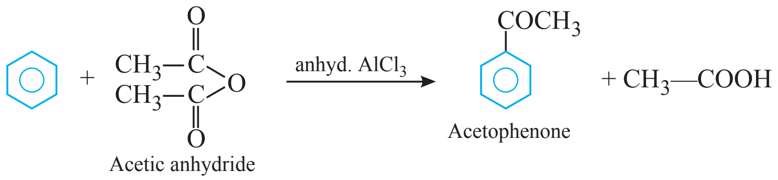




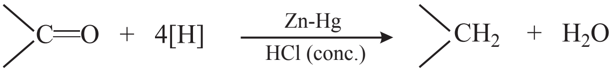
Friedel–Crafts acylation: Benzene and other aromatic compounds react with acylchlorides or acid anhydrides in the presence of anhyd. $AlCl_3$ to form aromatic ketone.





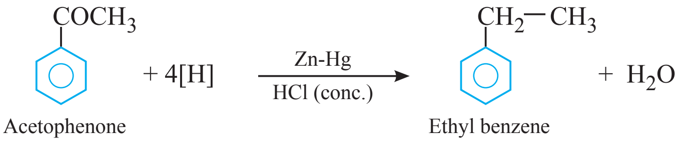


(*f*) **Clemmensen reduction:** The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.

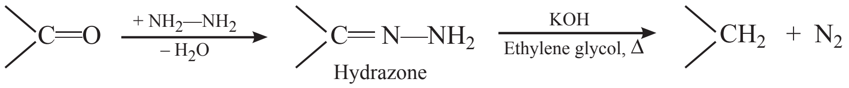


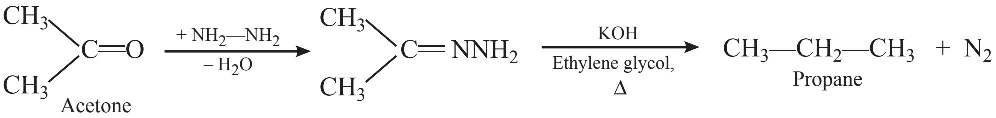
$$>C=O + 4[H] \xrightarrow[\text{HCl (conc.)}]{\text{Zn-Hg}} >CH_2 + H_2O$$

$$\underset{\text{Butyraldehyde}}{CH_3-CH_2-CH_2-CHO} + [H] \xrightarrow[\text{HCl (conc.)}]{\text{Zn-Hg}} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} + H_2O$$

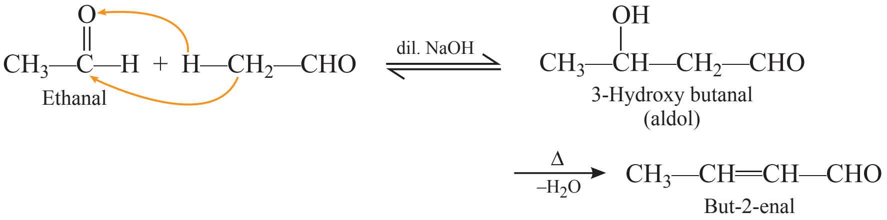


(*g*) **Wolff–Kishner reduction:** The carbonyl group of aldehydes and ketones is reduced to $—CH_2$ group on treatment with hydrazine followed by heating with potassium or sodium hydroxide in a high boiling solvent such as ethylene glycol.



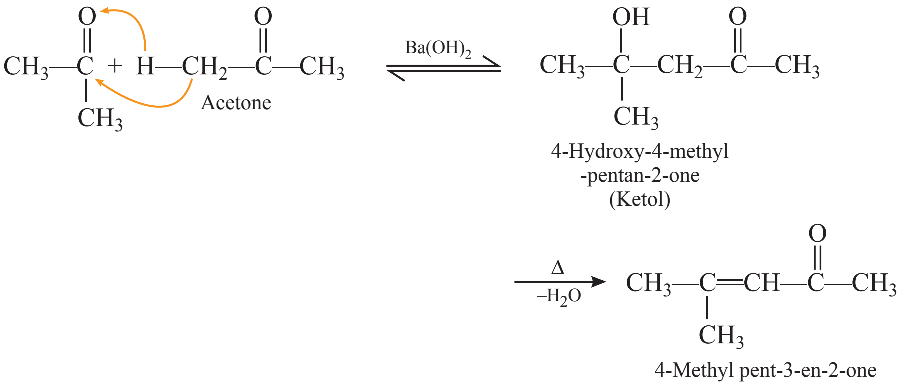


(*h*) **Aldol condensation:** Two molecules of aldehydes or ketones containing at least one α-hydrogen atom on treatment with dilute alkali undergo condensation to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (Ketol).



$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H-CH_2-CHO \xrightleftharpoons{\text{dil. NaOH}} \underset{\substack{\text{3-Hydroxy butanal}\\ \text{(aldol)}}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-CHO}$$

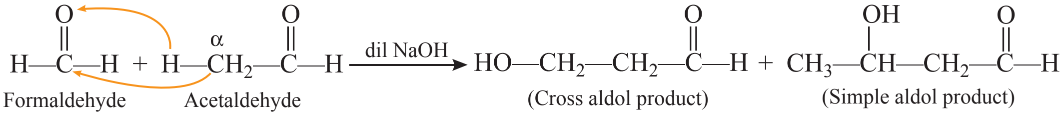
$$\xrightarrow[-H_2O]{\Delta} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$



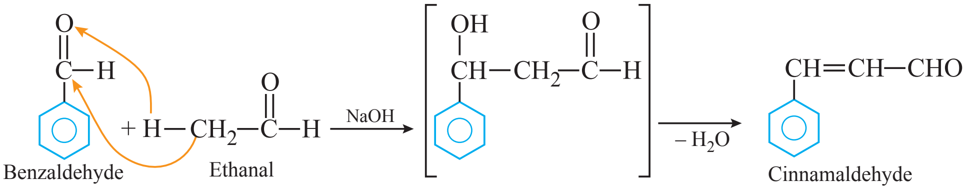
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + \underset{\text{Acetone}}{H-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightleftharpoons{Ba(OH)_2} \underset{\substack{\text{4-Hydroxy-4-methyl}\\ \text{-pentan-2-one}\\ \text{(Ketol)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

$$\xrightarrow[-H_2O]{\Delta} \underset{\text{4-Methyl pent-3-en-2-one}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

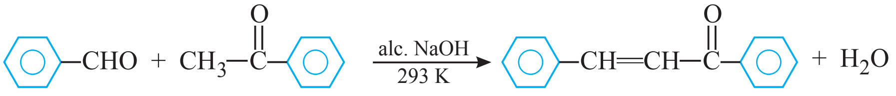
(*i*) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation.



$$\underset{\text{Formaldehyde}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-H} + \underset{\text{Acetaldehyde}}{H-\overset{\alpha}{CH_2}-\overset{\overset{\displaystyle O}{\|}}{C}-H} \xrightarrow{\text{dil NaOH}} \underset{\text{(Cross aldol product)}}{HO-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H} + \underset{\text{(Simple aldol product)}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$



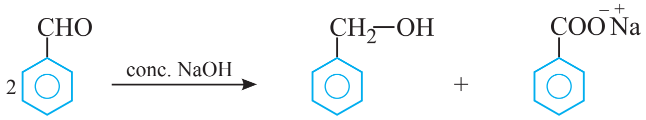
Benzaldehyde Ethanal Cinnamaldehyde



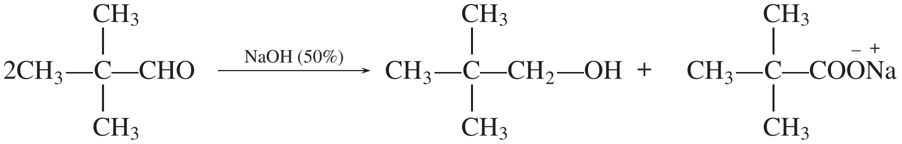
Benzaldehyde Acetophenone Benzalacetophenone (1, 3-Diphenyl prop-2-en-1-one) (Major product)

(*j*) **Cannizzaro reaction:** Aldehydes which do not have an α-hydrogen, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

$$\underset{\text{Formaldehyde}}{2HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{Methyl alcohol}}{CH_3—OH} + \underset{\text{Potassium formate}}{HCOO^-K^+}$$

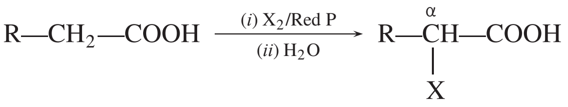


Benzaldehyde Benzyl alcohol Sodium benzoate

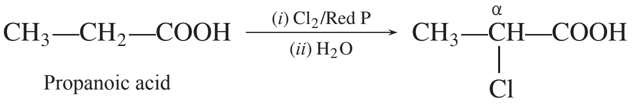


$$\underset{\text{2,2-Dimethylpropanal}}{2CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—CHO} \xrightarrow{\text{NaOH (50\%)}} \underset{\text{2,2-Dimethylpropanol}}{CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—CH_2—OH} + \underset{\text{Sodium 2, 2-dimethylpropanoate}}{CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—\overset{-\ +}{COONa}}$$

(*k*) **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 red phosphorus to give α-halocarboxylic acids.



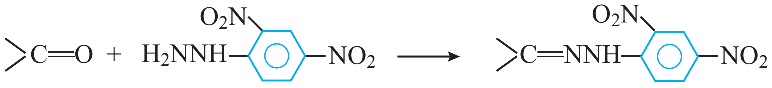
$$R—CH_2—COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} \underset{\alpha\text{-Halocarboxylic acid}}{R—\overset{\alpha}{\underset{\displaystyle X}{CH}}—COOH} \qquad (X = Cl, Br)$$



$$\underset{\text{Propanoic acid}}{CH_3—CH_2—COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/\text{Red P}} \underset{\text{2-Chloropropanoic acid}}{CH_3—\overset{\alpha}{\underset{\displaystyle Cl}{CH}}—COOH}$$

18. Chemical Tests for Aldehydes and Ketones

(*a*) **Test for carbonyl group (2, 4-Dinitrophenyl hydrazine test):** Both aldehydes and ketones contain carbonyl group. Hence, they react with 2, 4-dinitrophenyl hydrazine to form yellow, or orange precipitate of 2, 4-dinitrophenyl hydrazone.



2, 4-Dinitrophenylhydrazine 2, 4-DNP-derivative (Yellow, orange ppt.)

(*b*) (*i*) **Tollens' test:** When aldehydes are heated with Tollens' reagent (ammoniacal silver nitrate solution), they form silver mirror on the inner side of the test tube. Ketones do not respond to this test.

$$R{-}CHO + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow R{-}COO^- + \underset{\text{(Silver mirror)}}{2Ag\downarrow} + 2H_2O + 4NH_3$$

(*ii*) **Fehling's test:** Aliphatic aldehydes when warmed with a few drops of Fehling's solution give a reddish brown precipitate of cuprous oxide. Ketones do not respond to this test.

$$R{-}CHO + \underset{\text{Fehling solution}}{2Cu^{2+}} + 5OH^- \longrightarrow R{-}COO^- + \underset{\text{Red brown ppt.}}{Cu_2O\downarrow} + 3H_2O$$

(*iii*) **Iodoform test:** Acetaldehyde, acetone or any ketone having at least one $-CH_3$ group when heated with alkaline solution of iodine form yellow coloured precipitate of iodoform.

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$

$$R{-}COCH_3 \xrightarrow[-NaOH]{+3NaOI} R{-}COCI_3 \xrightarrow{NaOH} R{-}COO^-\overset{+}{Na} + \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3\downarrow}$$

(*c*) Tests for Carboxylic Acids

(*i*) **Litmus test:** Aqueous solutions of carboxylic acids turn blue litmus red. Phenols also give this test. Alcohols do not respond to this test.

(*ii*) **Sodium bicarbonate test:** When carboxylic acid is added to an aqueous solution of sodium bicarbonate, brisk effervescence of CO_2 is evolved.

$$\underset{\text{Carboxylic acid}}{RCOOH} + NaHCO_3 \longrightarrow \underset{\substack{\text{Sodium}\\ \text{carboxylate}}}{RCOONa} + H_2O + CO_2\uparrow$$

Phenols and alcohols do not give this test.

(*iii*) **Ester formation test:** On warming carboxylic acids with an alcohol (*e.g.*, ethanol) in presence of a small amount of sulphuric acid, a fruity smell of ester is obtained.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xrightarrow{H_2SO_4} \underset{\substack{\text{Ester}\\ \text{(Fruity smell)}}}{RCOOR'} + H_2O$$

(*iv*) **Distinction between formic acid and acetic acid.**

Tollens' reagent test: Formic acid reduces Tollens' reagent to metallic silver but acetic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow \underset{\substack{\text{(Silver}\\ \text{mirror)}}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$$

$HgCl_2$ test: Formic acid reduces $HgCl_2$ to give white ppt. of Hg_2Cl_2 while acetic acid does not give this test.

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\substack{\text{Mercuric}\\ \text{chloride}}}{2HgCl_2} \longrightarrow \underset{\substack{\text{Mercurous}\\ \text{chloride}\\ \text{(white ppt.)}}}{Hg_2Cl_2\downarrow} + 2HCl + CO_2\uparrow$$

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Write the structures of the following compounds:

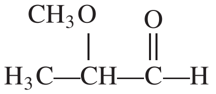
(*i*) α-Methoxypropionaldehyde **(*ii*) 3-Hydroxybutanal**

(*iii*) 2-Hydroxycyclopentane carbaldehyde

(*iv*) 4-oxopentanal **(*v*) Di-sec. butyl ketone**

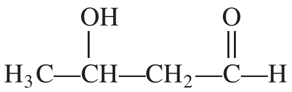
(*vi*) 4-Fluoroacetophenone

Ans. (*i*)



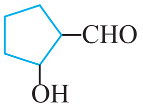
$$H_3C-\overset{\overset{CH_3O}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$$

(*ii*)

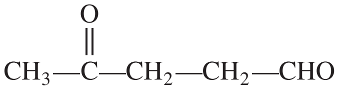


$$H_3C-\overset{\overset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

(*iii*)

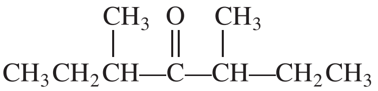


(*iv*)



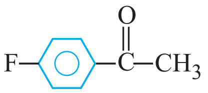
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CHO$$

(*v*)



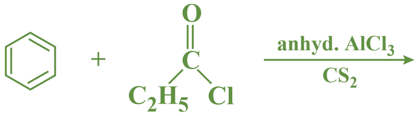
$$CH_3CH_2\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$$

(*vi*)



Q. 2. Write the structures of products of the following reactions:

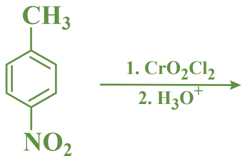
(*i*)



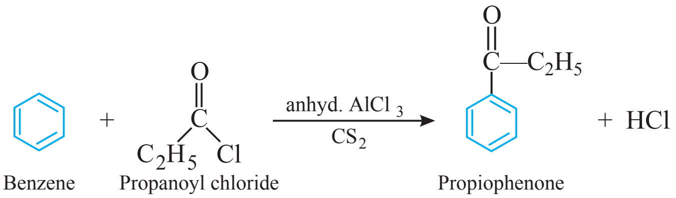
(*ii*) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

(*iii*) $H_3C-C \equiv C-H \xrightarrow{Hg^{2+}, H_2SO_4}$

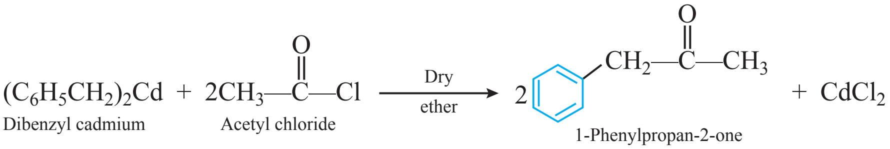
(*iv*)



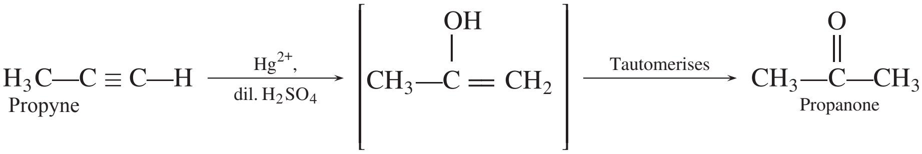
Ans. (*i*)



(*ii*)

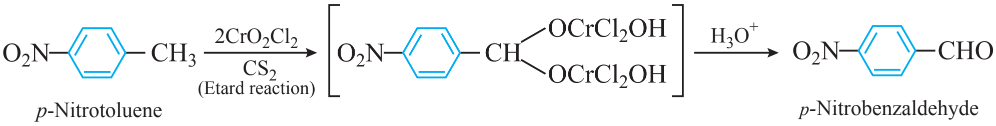


(*iii*)



$$\underset{\text{Propyne}}{H_3C-C \equiv C-H} \xrightarrow[\text{dil. } H_2SO_4]{Hg^{2+},} \left[CH_3-\overset{\overset{OH}{|}}{C}=CH_2\right] \xrightarrow{\text{Tautomerises}} \underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

(*iv*)



Q. 3. Arrange the following compounds in increasing order of their boiling points.

$CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

Q. 4. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(*i*) Ethanal, Propanal, Propanone, Butanone

(*ii*) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone

Ans. (*i*) The reactivity in nucleophilic addition reactions increases in the order:

Butanone < Propanone < Propanal < Ethanal

(*ii*) Acetophenone is a ketone. All the other three compounds are aldehydes. Hence, acetophenone is least reactive.

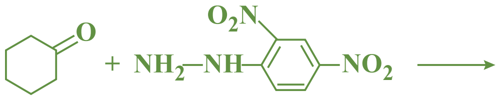
p-Tolualdehyde has an electron-donating methyl group at the para position of the benzene ring whereas *p*-nitrobenzaldehyde has an electron-withdrawing nitro group at the para position. Thus, *p*-tolualdehyde is less reactive and *p*-nitrobenzaldehyde is more reactive than benzaldehyde.

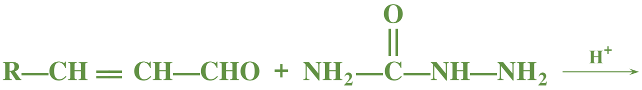
Therefore, the required order is as follows:

Acetophenone < *p*-Tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde

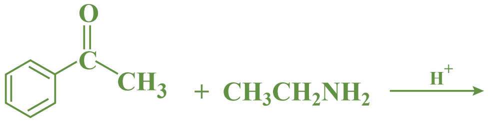
Q. 5. Predict the products of the following reactions:

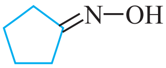
(*i*)

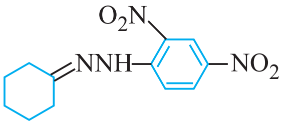

(*ii*)


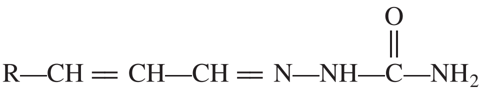
(*iii*)


$$R—CH = CH—CHO + NH_2—\overset{\overset{\Large O}{\|}}{C}—NH—NH_2 \xrightarrow{H^+}$$

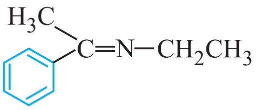
(*iv*)


Ans. (*i*)


(*ii*)


(*iii*)


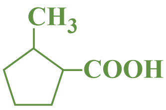
$$R—CH = CH—CH = N—NH—\overset{\overset{\Large O}{\|}}{C}—NH_2$$

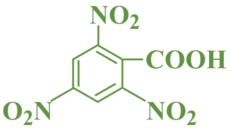
(*iv*)


Q. 6. Give the IUPAC names of the following compounds:

(*i*) $PhCH_2CH_2COOH$

(*ii*) $(CH_3)_2C{=}CHCOOH$

(*iii*)


(*iv*)


Ans. (*i*) 3-Phenylpropanoic acid

(*ii*) 3-Methylbut-2-enoic acid

(*iii*) 2-Methylcyclopentanecarboxylic acid

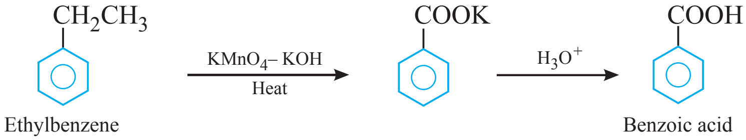
(*iv*) 2, 4, 6-Trinitrobenzoic acid.

Q. 7. Show how each of the following compounds can be converted to benzoic acid:

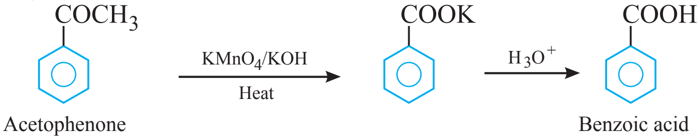
(*i*) Ethylbenzene **(*ii*) Acetophenone**

(*iii*) Bromobenzene **(*iv*) Phenylethene (Styrene)**

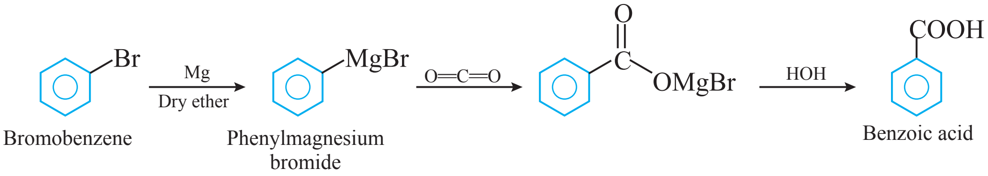
Ans. (*i*)



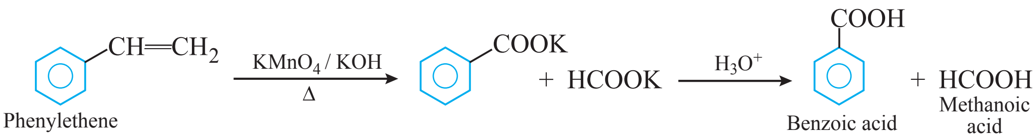
(*ii*)



(*iii*)



(*iv*)

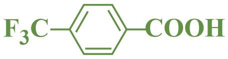


Q. 8. Which acid of each pair shown here would you expect to be stronger?

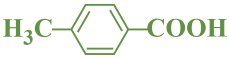
(*i*) CH_3CO_2H or CH_2FCO_2H **(*ii*) CH_2FCO_2H or CH_2ClCO_2H**

(*iii*) $CH_2FCH_2CH_2CO_2H$ or CH_3—CHF—CH_2CO_2H

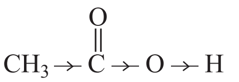
(*iv*)



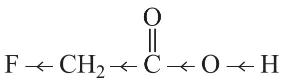
or



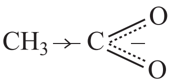
Ans. (*i*)


$CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow O \rightarrow H$

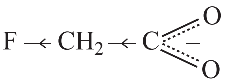
The release of a proton is difficult because +I-effect of CH_3 group increases the electron density in the O—H bond.


$F \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

The release of a proton is easier because –I-effect of F decreases the electron density in the O—H bond.



By intensifying the negative charge , +I-effect destabilises the carboxylate ion.

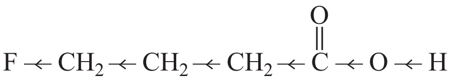


By dispersing the negative charge, –I-effect stabilises the carboxylate ion.

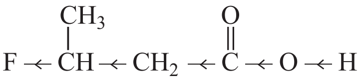
Therefore, due to lesser electron density in the O—H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion, FCH_2COOH is a stronger acid than CH_3COOH.

(*ii*) The FCH_2COO^- ion is much more stable than $ClCH_2COO^-$ ion due to much stronger –I effect of F than Cl and thus FCH_2COOH is a stronger acid than $ClCH_2COOH$.

(*iii*)


$F \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

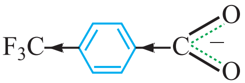
4-Fluorobutanoic acid


$F \leftarrow \overset{\overset{CH_3}{|}}{CH} \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$

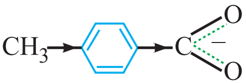
3-Fluorobutanoic acid

Inductive effect decreases with distance, therefore, –I effect of F is somewhat stronger in 3-fluorobutanoic acid than in 4-fluorobutanoic acid. Hence, CH_3CHFCH_2COOH is a stronger acid than $FCH_2CH_2CH_2COOH$.

(*iv*)



CF_3 has a strong –I-effect, it stabilises the carboxylate ion by dispersing the –ve charge



CH_3 has a weak +I-effect, it destabilises the carboxylate ion by intensifying the –ve charge

Hence, due to greater stability of F_3C—C_6H_4—COO^- (*p*) ion than CH_3—$C_6H_4COO^-$ (*p*) ion, F_3C—C_6H_4—COOH (*p*) is a much stronger acid than CH_3—C_6H_4—COOH (*p*).

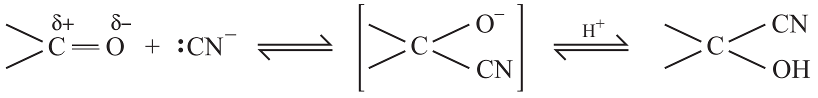
NCERT Textbook Exercises

Q. 1. What is meant by the following terms? Give an example of the reaction in each case.

(*i*) Cyanohydrin **(*ii*) Acetal** **(*iii*) Semicarbazone**
(*iv*) Aldol **(*v*) Hemiacetal** **(*vi*) Oxime**
(*vii*) Ketal **(*viii*) Imine** **(*ix*) 2, 4-DNP derivative**
(*x*) Schiff's base

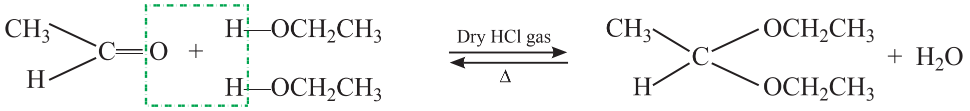
Ans. (*i*) gem-Hydroxynitriles, *i.e.*, compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. It is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

$$HCN + OH^- \rightleftharpoons :CN^- + H_2O$$



Tetrahedral intermediate Cyanohydrin

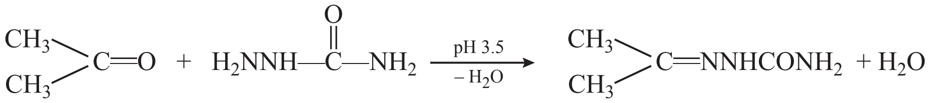
(*ii*) gem-Dialkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in the presence of dry HCl gas.



Acetaldehyde Ethyl alcohol Acetaldehyde diethyl acetal

These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehydic group in organic synthesis.

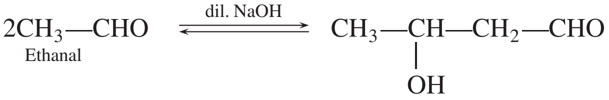
(*iii*) Semicarbazones are derivatives of aldehydes and ketones and are produced by the action of semicarbazide on them in weak acidic medium.



Acetone Semicarbazide Acetone semicarbazone

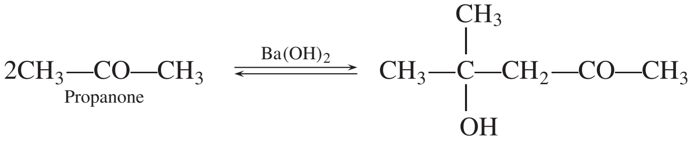
These are used for identification and characterisation of aldehydes and ketones.

(*iv*) Aldols are β-hydroxy aldehydes or ketones and are produced by the condensation two same or different molecules of aldehyde or ketones.



$$2CH_3\text{—}CHO \overset{\text{dil. NaOH}}{\rightleftharpoons} CH_3\text{—}\underset{\substack{|\\ OH}}{CH}\text{—}CH_2\text{—}CHO$$

Ethanal 3-Hydroxybutanal (Aldol)

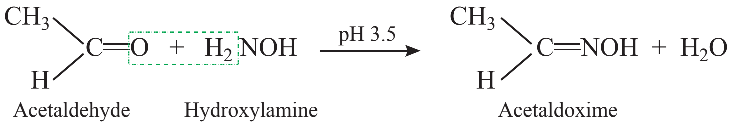


$$2CH_3\text{—}CO\text{—}CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3\text{—}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ OH}}{C}}\text{—}CH_2\text{—}CO\text{—}CH_3$$

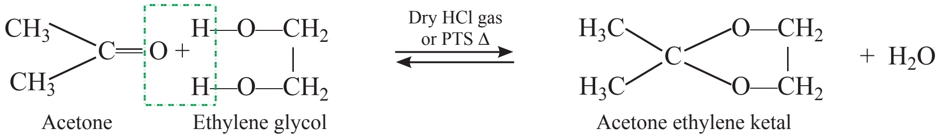
Propanone 4-Hydroxy-4-methylpentan-2-one

(*v*) gem-Alkoxyalcohols are called hemiacetals. These are produced by addition of one molecule of a monohydric alcohol to an aldehyde in presence of dry HCl gas.

Ethanal Methyl alcohol 1-Hydroxy-1-methoxyethane (A hemiacetal) (*vi*) Oximes are produced when aldehydes or ketones react with hydroxylamine in weak acidic medium.



(*vii*) gem-Dialkoxyalkanes are called ketals. In ketals, the two alkoxy groups are present on the same carbon within the chain. These are produced when a ketone is heated with ethylene glycol in presence of dry HCl gas or *p*-toluenesulphonic acid (PTS).



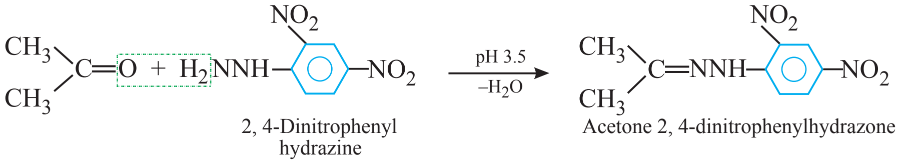
These are easily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore, ketals are used for protection of keto groups in organic synthesis.

(*viii*) Compounds containing $>C=N-$ group are called imines. These are produced when aldehydes and ketones react with ammonia derivatives.

$$\underset{\text{Aldehyde/Ketone}}{>C=O} + \underset{\text{Ammonia derivative}}{H_2N-Z} \longrightarrow \underset{\text{Imines}}{>C=N-Z} + H_2O$$

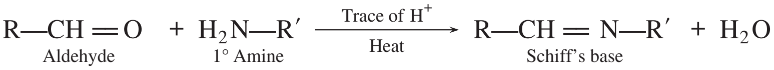
$Z = H$, Alkyl, aryl, $-NH_2$, $-OH$, $-C_6H_5NH$, $-NHCONH_2$, etc.

(*ix*) 2, 4-Dinitrophenylhydrazones (2, 4-DNP derivatives) are produced when aldehydes or ketones react with 2, 4-dinitrophenylhydrazine in weakly acidic medium.



2, 4-DNP derivatives are used for identification and characterisation of aldehydes and ketones.

(*x*) Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or Schiff's bases.



$$\underset{\text{Aldehyde}}{R-CH=O} + \underset{1^\circ \text{ Amine}}{H_2N-R'} \xrightarrow[\text{Heat}]{\text{Trace of } H^+} \underset{\text{Schiff's base}}{R-CH=N-R'} + H_2O$$

Q. 2. Name the following compounds according to IUPAC system of nomenclature.

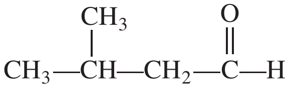
(*i*) $CH_3CH(CH_3)CH_2CH_2CHO$
(*ii*) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
(*iii*) $CH_3CH{=}CHCHO$ [***CBSE 2019(56/5/2)***]
(*iv*) $CH_3COCH_2COCH_3$
(*v*) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$
(*vi*) $(CH_3)_3CCH_2COOH$
(*vii*) $OHCC_6H_4CHO$-*p*

Ans. (*i*) 4-Methylpentanal
(*ii*) 6-Chloro-4-ethylhexan-3-one
(*iii*) But-2-en-1-al
(*iv*) Pentane-2, 4-dione
(*v*) 3, 3, 5-Trimethylhexan-2-one
(*vi*) 3, 3-Dimethylbutanoic acid
(*vii*) Benzene-1, 4-dicarbaldehyde

Q. 3. Draw the structures of the following compounds:

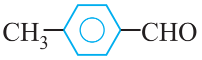
(*i*) 3-Methylbutanal
(*ii*) *p*-Nitropropiophenone
(*iii*) *p*-Methylbenzaldehyde
(*iv*) 4-Methylpent-3-en-2-one
(*v*) 4-Chloropentan-2-one
(*vi*) 3-Bromo-4-phenylpentanoic acid
(*vii*) *p-p*′-Dihydroxybenzophenone
(*viii*) Hex-2-en-4-ynoic acid

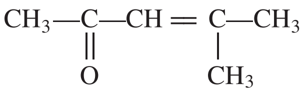
Ans. (*i*)



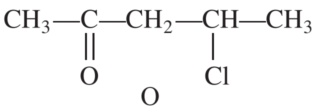
$$CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CH_2-\overset{\overset{\large O}{||}}{C}-H$$

(*ii*)

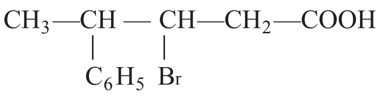
(*iii*) 

(*iv*) 

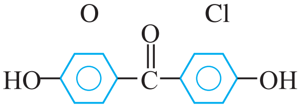
$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$

(*v*) 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

(*vi*) 

$CH_3-\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_2-COOH$

(*vii*) 

(*viii*) $CH_3-C\equiv C-CH=CH-COOH$

Q. 4. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

(*i*) $CH_3CO(CH_2)_4CH_3$

(*ii*) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$

(*iii*) $CH_3(CH_2)_5CHO$

(*iv*) Ph—CH=CH—CHO

(*v*) 

(*vi*) PhCOPh

Ans.

S.No.	IUPAC Name	Common Name
(*i*)	Heptan-2-one	Methyl *n*-pentyl ketone
(*ii*)	4-Bromo-2-methylhexanal	γ-Bromo-α-methylcaproaldehyde
(*iii*)	Heptanal	—
(*iv*)	3-Phenylprop-2-enal	β-Phenylacrolein
(*v*)	Cyclopentanecarbaldehyde	Cyclopentanecarbaldehyde
(*vi*)	Diphenylmethanone	Benzophenone

Q. 5. Draw structures of the following derivatives:

(*i*) The 2, 4-dinitrophenylhydrazone of benzaldehyde

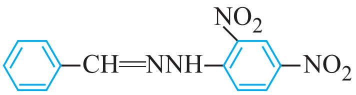
(*ii*) Cyclopropanone oxime

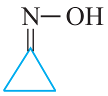
(*iii*) Acetaldehydedimethylacetal

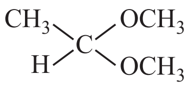
(*iv*) The semicarbazone of cyclobutanone

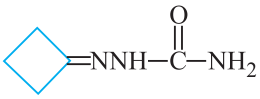
(*v*) The ethylene ketal of hexan-3-one

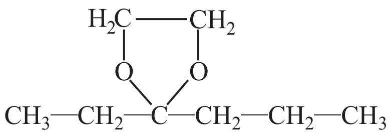
(*vi*) The methyl hemiacetal of formaldehyde.

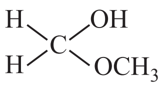
Ans. (*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

Q. 6. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents:

(*i*) PhMgBr and then H_3O^+

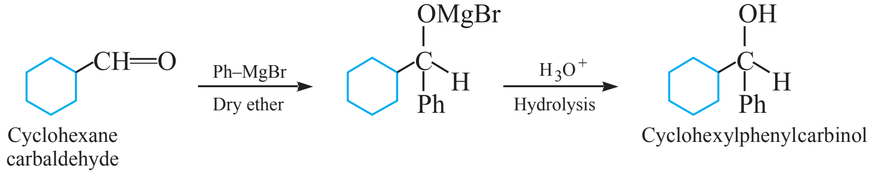
(*ii*) Tollens' reagent

(*iii*) Semicarbazide and weak acid

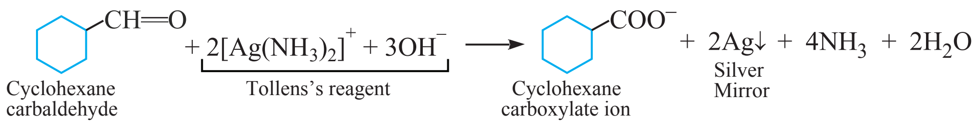
(*iv*) Excess ethanol and acid

(*v*) Zinc amalgam and dilute hydrochloric acid.

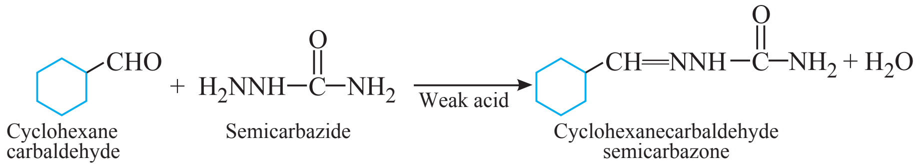
Ans. (*i*)



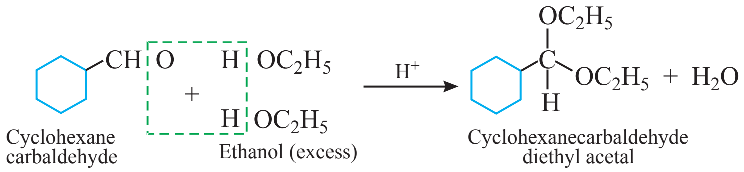
(*ii*)



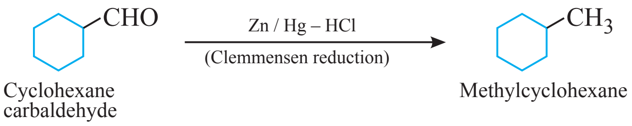
(*iii*)



(*iv*)



(*v*)



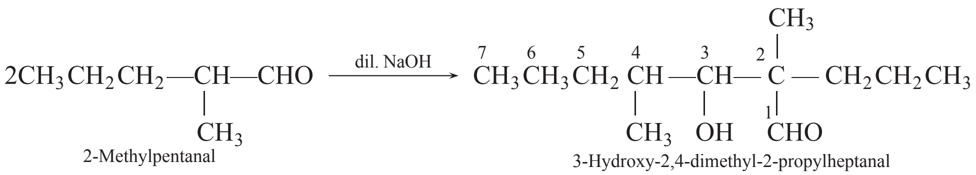
Q. 7. Which of the following compounds will undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(*i*) Methanal	**(*ii*) 2-Methylpentanal**
(*iii*) Benzaldehyde	**(*iv*) Benzophenone**
(*v*) Cyclohexanone	**(*vi*) 1-Phenylpropanone**
(*vii*) Phenylacetaldehyde	**(*viii*) Butan-1-ol**
(*ix*) 2, 2-Dimethylbutanal.	

Ans. (*i*) Methanal does not contain α-hydrogen and hence undergoes cannizzaro reaction.

$$\underset{\text{Methanal}}{2HCHO} \xrightarrow{\text{conc. NaOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sodium methanoate}}{HCOONa}$$

(*ii*) 2-Methylpentanal, contains α-hydrogens and hence undergo aldol condensation.

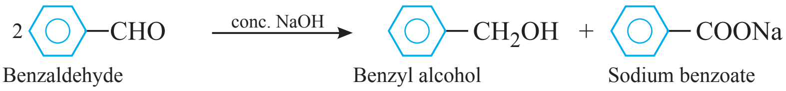


$$2CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{\text{dil. NaOH}} \overset{7}{C}H_3\overset{6}{C}H_3\overset{5}{C}H_2\,\underset{\underset{CH_3}{|}}{\overset{4}{C}H}-\underset{\underset{OH}{|}}{\overset{3}{C}H}-\underset{\underset{CHO}{|^1}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-CH_2CH_2CH_3$$

2-Methylpentanal

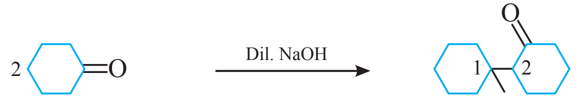
3-Hydroxy-2,4-dimethyl-2-propylheptanal

(*iii*) Benzaldehyde does not contain α-hydrogen and hence undergoes cannizzaro reaction.



(*iv*) Benzophenone is a ketone having no α-hydrogen. It neither undergoes aldol condensation nor Cannizzaro reaction.

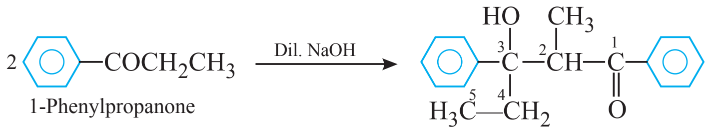
(*v*) Cyclohexanone contains α-hydrogens and hence undergo aldol condensation.



Cyclohexanone

2-(1-Hydroxy-1-cyclohexyl) cyclohexan-1-one

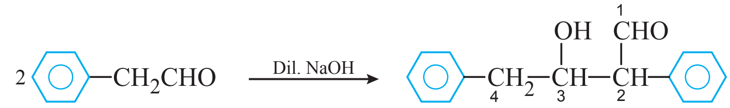
(*vi*) 1-Phenylpropanone contains α-hydrogens and hence undergo aldol condensation.



1-Phenylpropanone

3-Hydroxy-2-methyl-1,3-diphenylpentan-1-one

(*vii*) Phenylacetaldehyde contains α-hydrogen and hence undergoes aldol condensation.

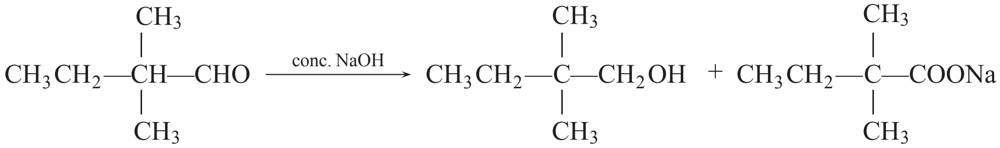


Phenylacetaldehyde

3-Hydroxy-2, 4-diphenylbutanal

(*viii*) Butan-1-ol is an alcohol, so it neither undergoes aldol condensation nor Cannizzaro reaction.

(*ix*) 2, 2-dimethylbutanal does not contain α-hydrogen and hence undergo Cannizzaro reaction.



$$\underset{\text{2, 2-Dimethylbutanal}}{CH_3CH_2-\overset{CH_3}{\underset{CH_3}{CH}}-CHO} \xrightarrow{\text{conc. NaOH}} \underset{\text{2, 2-Dimethylbutan-1-ol}}{CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH} + \underset{\text{Sodium 2, 2-Dimethylbutanonate}}{CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-COONa}$$

Q. 8. How will you convert ethanal into the following compounds?

(*i*) Butane-1, 3-diol (*ii*) But-2-enal (*iii*) But-2-enoic acid.

Ans. (*i*)

$$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{\overset{4}{C}H_3\overset{3}{C}HOH-\overset{2}{C}H_2-\overset{1}{C}HO} \xrightarrow[\text{(Reduction)}]{NaBH_4} \underset{\text{Butane-1. 3-diol}}{\overset{4}{C}H_3-\overset{3}{C}HOH-\overset{2}{C}H_2\overset{1}{C}H_2OH}$$

(*ii*)

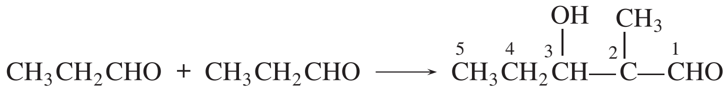
$$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{\overset{4}{C}H_3-\overset{3}{C}HOH-\overset{2}{C}H_2-\overset{1}{C}HO} \xrightarrow[-H_2O]{H_3O^+/\text{Heat}} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$

(*iii*)

$$\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow[(ii)\ H^+,\Delta]{(i)\ \text{dil. NaOH}} \underset{\text{But-2-enal}}{CH_3CH=CHCHO} \xrightarrow[\text{Tollens' reagent}]{[Ag(NH_3)_2]^+OH^-} \underset{\text{But-2-enoic acid}}{CH_3CH=CHCO_2H}$$

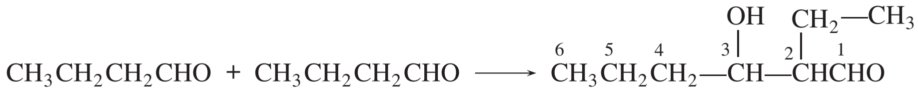
Q. 9. Write structural formula and names of four possible aldol condensation products from propanal and butanal. In each case indicate which aldehyde acts as nucleophile and which as electrophile.

Ans. (*i*) Propanal serves as nucleophile and also as electrophile.



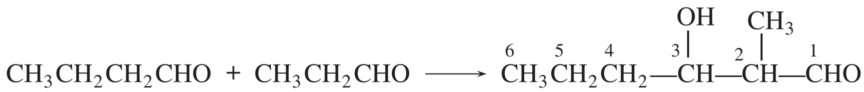
$$\underset{\text{(Nucleophile)}}{\underset{\text{Propanal}}{CH_3CH_2CHO}} + \underset{\text{(Electrophile)}}{\underset{\text{Propanal}}{CH_3CH_2CHO}} \longrightarrow \underset{\text{3-Hydroxy-2-methylpentanal}}{CH_3CH_2\overset{OH}{CH}-\overset{CH_3}{C}-CHO}$$

(*ii*) Butanal serves both as nucleophile and an electrophile.



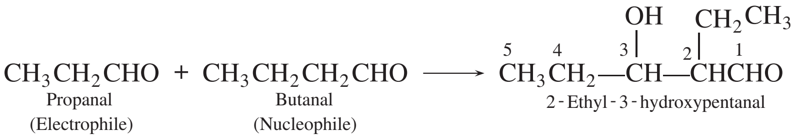
$$\underset{\text{(Electrophile)}}{\underset{\text{Butanal}}{CH_3CH_2CH_2CHO}} + \underset{\text{(Nucleophile)}}{\underset{\text{Butanal}}{CH_3CH_2CH_2CHO}} \longrightarrow \underset{\text{2-Ethyl-3-hydroxyhexanal}}{CH_3CH_2CH_2-\overset{OH}{CH}-\overset{CH_2-CH_3}{C}HCHO}$$

(*iii*) Butanal as electrophile and propanal as nucleophile.



$$\underset{\text{(Electrophile)}}{\underset{\text{Butanal}}{CH_3CH_2CH_2CHO}} + \underset{\text{(Nucleophile)}}{\underset{\text{Propanal}}{CH_3CH_2CHO}} \longrightarrow \underset{\text{3-Hydroxy-2-methylhexanal}}{CH_3CH_2CH_2-\overset{OH}{CH}-\overset{CH_3}{CH}-CHO}$$

(*iv*) Propanal as electrophile and butanal as nucleophile.



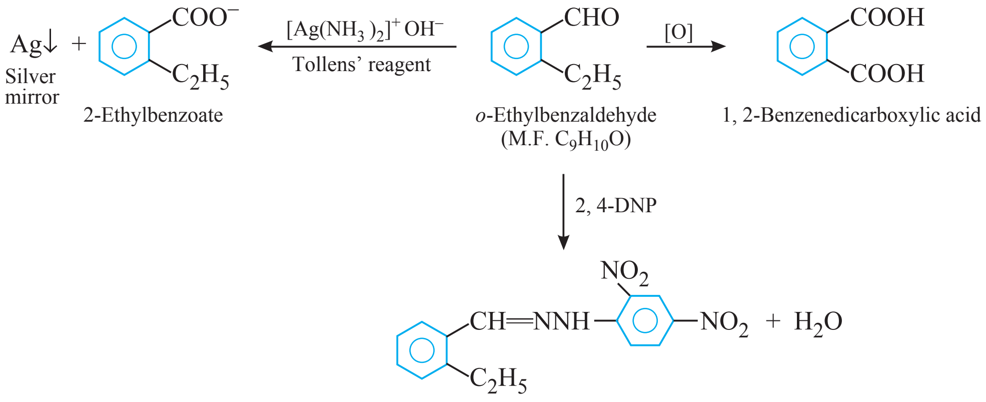
$$\underset{\substack{\text{Propanal}\\\text{(Electrophile)}}}{CH_3CH_2CHO} + \underset{\substack{\text{Butanal}\\\text{(Nucleophile)}}}{CH_3CH_2CH_2CHO} \longrightarrow \underset{\text{2-Ethyl-3-hydroxypentanal}}{\overset{5}{C}H_3\overset{4}{C}H_2-\overset{\overset{OH}{|}}{\overset{3}{C}H}-\overset{\overset{CH_2CH_3}{|}}{\overset{2}{C}H}\overset{1}{C}HO}$$

Q. 10. An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound. ***[HOTS]***

Ans. (*i*) The given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Tollens' reagent, it must be an aldehyde.

(*ii*) As it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to the benzene ring.

(*iii*) On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde. The only *o*-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is *o*-ethylbenzaldehyde. All the reactions can be explained on the basis of this structure.



2, 4-DNP derivative

Q. 11. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved. ***[CBSE Delhi 2010; (AI) 2009] [HOTS]***

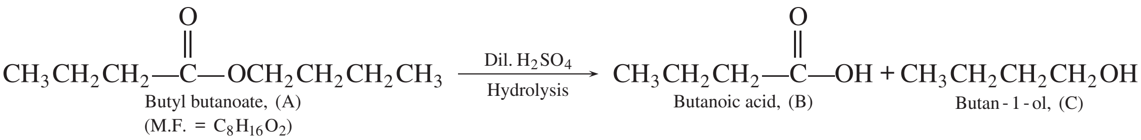
Ans. As the organic compound (*A*) with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid (*B*) and the alcohol (*C*) therefore (*A*) must be an ester and oxidation of (*C*) with chromic acid produces the acid (*B*), therefore, both the carboxylic acid (*B*) and alcohol (*C*) must contain the same number of carbon atoms.

Now ester (*A*) contains eight carbon atoms, therefore, both the carboxylic acid (B) and the alcohol (C) must contain four carbon atoms each.

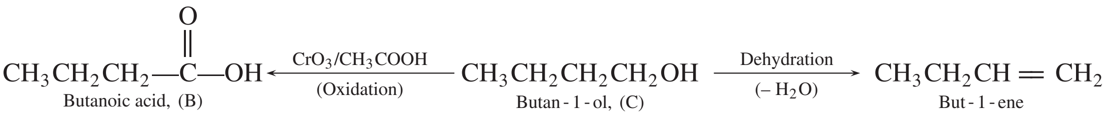
As the alcohol (*C*) on dehydration gives but-1-ene, therefore, (*C*) must be a straight chain alcohol, *i.e.*, butan-1-ol.

If *C* is butan-1-ol, then the acid (*B*) which it gives on oxidation must be butanoic acid and the ester (*A*) must be butyl butanoate.

The relevant equations for all the reactions involved may be explained as follows:



$$\underset{\substack{\text{Butyl butanoate, (A)}\\\text{(M.F. = }C_8H_{16}O_2)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3} \xrightarrow[\text{Hydrolysis}]{\text{Dil. }H_2SO_4} \underset{\text{Butanoic acid, (B)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Butan-1-ol, (C)}}{CH_3CH_2CH_2CH_2OH}$$



$$\underset{\text{Butanoic acid, (B)}}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH} \xleftarrow[\text{(Oxidation)}]{CrO_3/CH_3COOH} \underset{\text{Butan-1-ol, (C)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[(-\,H_2O)]{\text{Dehydration}} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

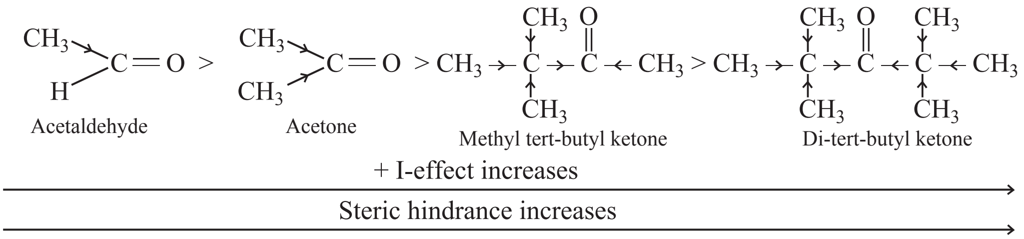
Q. 12. Arrange the following compounds in increasing order of their property as indicated:

(*i*) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN).

(*ii*) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength).

(*iii*) Benzoic acid, 4-nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid (acid strength).

Ans. (*i*) The reactivity towards HCN addition decreases as the +I-effect of the alkyl group/s increases and/or the steric hindrance to the nucleophilic attack by CN^- at the carbonyl carbon increases. Hence, the reactivity decreases in the order:

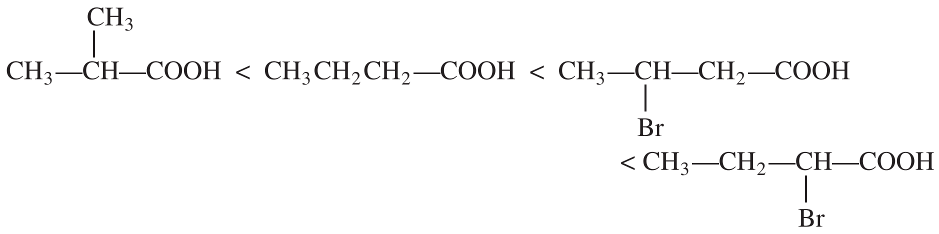


Thus, di-tert-butyl ketone < methyl tert-butyl ketone < Acetone < Acetaldehyde.

(*ii*) As we know + I-effect decreases while – I-effect increases the acid strength of carboxylic acids. As +I-effect of isopropyl group is more than that of *n*-propyl group, therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$.

Now –I-effect decreases with distance, therefore, $CH_3CH_2CH(Br)COOH$ is a stronger acid than $CH_3CH(Br)CH_2COOH$.

Therefore, the overall acid strength increases in the order:



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-COOH < CH_3CH_2CH_2-COOH < CH_3-\underset{\underset{\displaystyle Br}{|}}{C}H-CH_2-COOH < CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{C}H-COOH$$

(*iii*) As electron-donating groups decrease the acid strength, therefore 4-methoxybenzoic acid is a weaker acid than benzoic acid.

Now electron-withdrawing groups increase the acid strength, therefore, both 4-nitrobenzoic acid and 3, 4-dinitrobenzoic acids are stronger acids than benzoic acid. Further due to the presence of an additional NO_2 groups at *m*-position w.r.t. COOH group, 3, 4-dinitrobenzoic acid is a little stronger acid than 4-nitrobenzoic acid. Therefore, the overall acid strength increases in the following order:

4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3, 4-dinitrobenzoic acid.

Q. 13. Give simple chemical tests to distinguish between the following pairs of compounds:

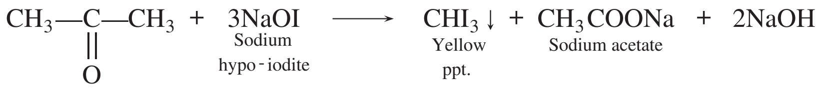
[*CBSE 2019*(*56/2/1*)]

(*i*) Propanal and Propanone
(*ii*) Acetophenone and Benzophenone
(*iii*) Phenol and Benzoic acid
(*iv*) Benzoic acid and Ethyl benzoate
(*v*) Pentan-2-one and Pentan-3-one
(*vi*) Benzaldehyde and Acetophenone
(*vii*) Ethanal and Propanal

Ans. (*i*) **Propanal and propanone:**

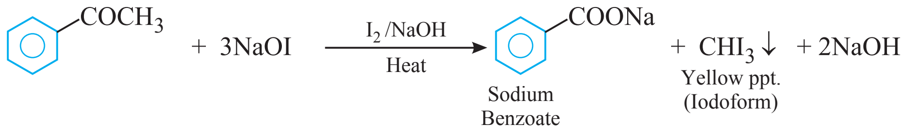
Iodoform test: This test is given by propanone and not by propanal. Propanone on reacting with hot $NaOH/I_2$ gives a yellow precipitate of CHI_3 while propanal does not.

$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$

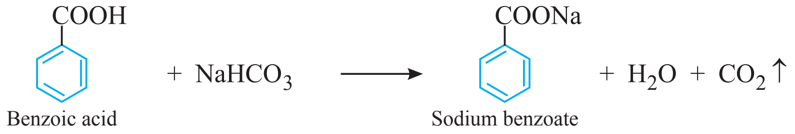


$$CH_3-\underset{\underset{\displaystyle O}{||}}{C}-CH_3 + \underset{\text{Sodium hypo-iodite}}{3NaOI} \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + \underset{\text{Sodium acetate}}{CH_3COONa} + 2NaOH$$

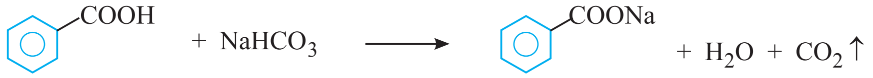
(*ii*) **Acetophenone and benzophenone:** Acetophenone responds to iodoform test, but benzophenone does not.



(*iii*) **Phenol and benzoic acid:** Benzoic acid reacts with $NaHCO_3$ giving CO_2 gas with effervescence, whereas phenol does not.



(*iv*) **Benzoic acid and ethyl benzoate:** Benzoic acid on reaction with sodium hydrogencarbonate gives out CO_2 gas with effervescence, while ethyl benzoate does not.



(*v*) **Pentan-2-one and Pentan-3-one:** Pentan-2-one when treated with NaOI (I_2/NaOH) gives yellow precipitate of iodoform but pentan-3-one does not give this test.

$$\underset{\text{Pentan-2-one}}{CH_3—CH_2—CH_2—COCH_3} + \underset{\text{Sodium hypoiodite}}{3NaOI} \longrightarrow CH_3CH_2CH_2COONa + \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$$

(*vi*) **Benzaldehyde and Acetophenone:** Benzaldehyde being an aldehyde gives silver mirror with Tollens' reagent but acetophenone being a ketone does not give this test.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow C_6H_5COO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

(*vii*) **Ethanal (CH_3CHO) and propanal (CH_3CH_2CHO):** Ethanal responds to iodoform test, while propanal does not.

$$CH_3CHO + 3NaOI \xrightarrow[\Delta]{NaOH/I_2} \underset{\text{(Yellow ppt.)}}{CHI_3\downarrow} + HCOONa + 2NaOH$$

Q. 14. How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

(*i*) Methyl benzoate

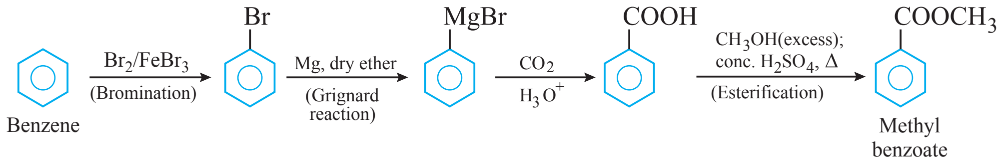
(*ii*) *m*-nitrobenzoic acid

(*iii*) *p*-nitrobenzoic acid

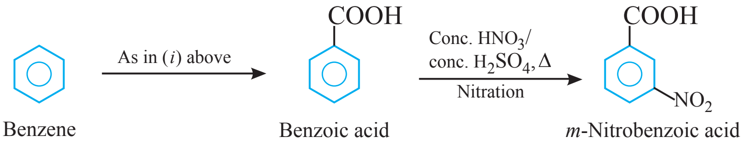
(*iv*) Phenylacetic acid

(*v*) *p*-nitrobenzaldehyde

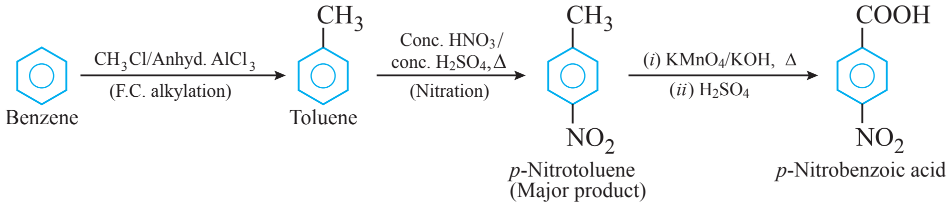
Ans. (*i*)



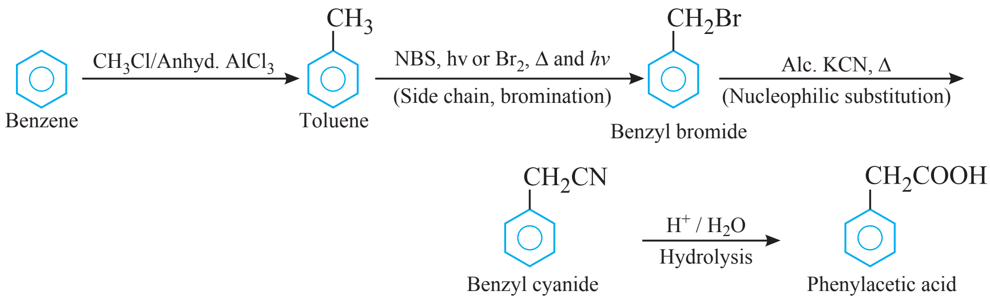
(*ii*)



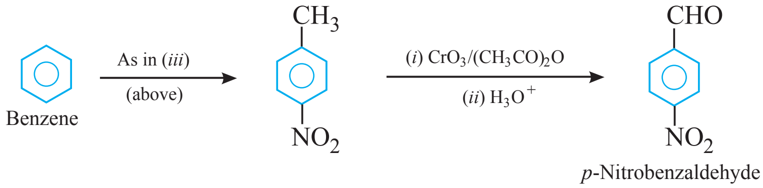
(*iii*)



(*iv*)



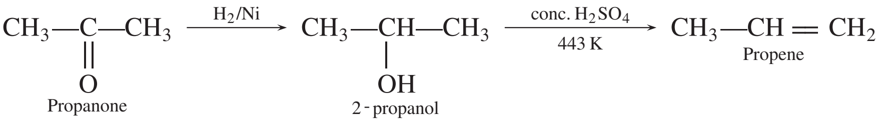
(*v*)



Q. 15. How will you bring about the following conversions in not more than two steps?

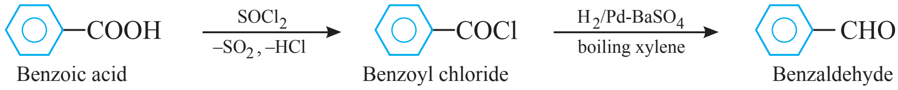
(*i*) Propanone to Propene
(*ii*) Benzoic acid to Benzaldehyde
(*iii*) Ethanol to 3-Hydroxybutanal
(*iv*) Benzene to *m*-Nitroacetophenone
(*v*) Benzaldehyde to Benzophenone
(*vi*) Bromobenzene to 1-Phenylethanol
(*vii*) Benzaldehyde to 3-Phenylpropan-1-ol
(*viii*) Benzaldehyde to α-Hydroxyphenylacetic acid
(*ix*) Benzoic acid to *m*-Nitrobenzyl alcohol

Ans. **(*i*) Propanone to Propene**

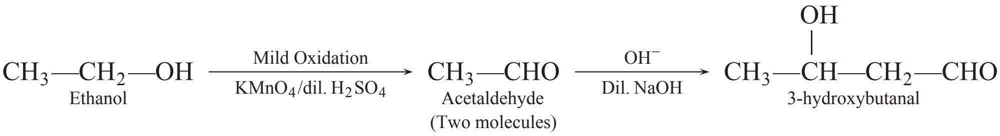


$$\underset{\text{Propanone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow{H_2/Ni} \underset{\text{2 - propanol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[443\text{ K}]{\text{conc. }H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

(*ii*) Benzoic acid to Benzaldehyde

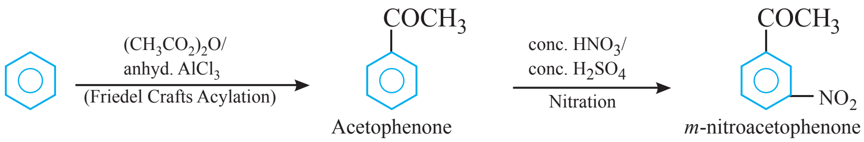


(*iii*) Ethanol to 3-Hydroxybutanal

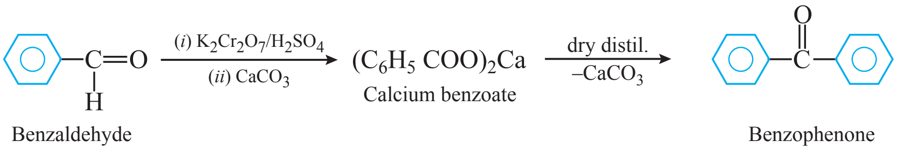


$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[\text{KMnO}_4/\text{dil. }H_2SO_4]{\text{Mild Oxidation}} \underset{\substack{\text{Acetaldehyde}\\ \text{(Two molecules)}}}{CH_3-CHO} \xrightarrow[\text{Dil. NaOH}]{OH^-} \underset{\text{3-hydroxybutanal}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO}$$

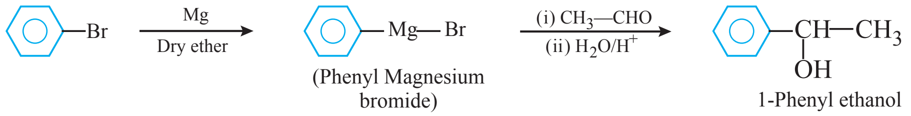
(*iv*) Benzene to *m*-Nitroacetophenone



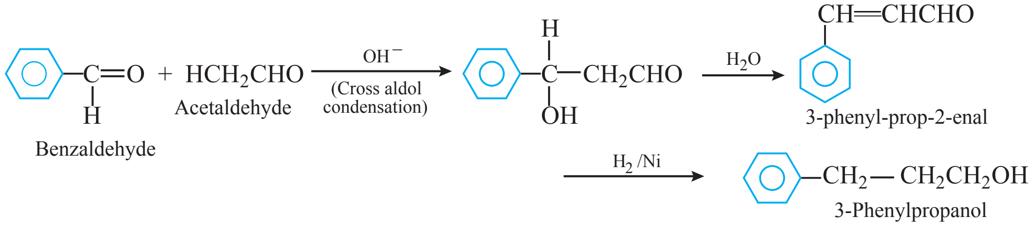
(*v*) Benzaldehyde to Benzophenone



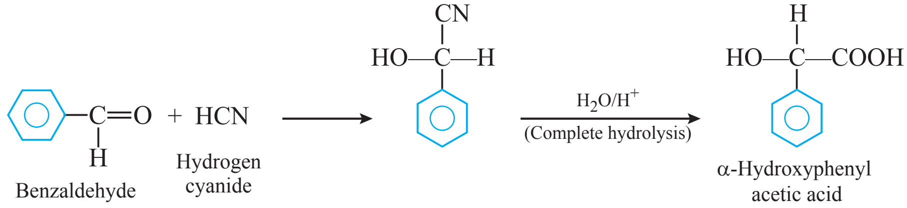
(*vi*) Bromobenzene to 1-phenylethanol:



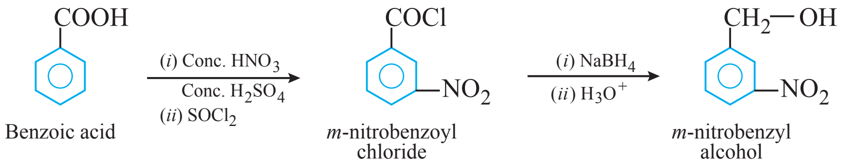
(*vii*) Benzaldehyde to 3-phenylpropan-1-ol:



(*viii*) Benzaldehyde to α-Hydroxyphenylacetic acid



(*ix*) Benzoic acid to *m*-nitrobenzyl alcohol:

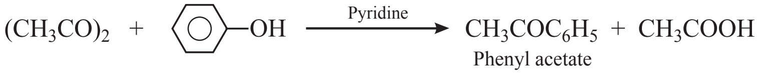


Q. 16. Describe the following:

(*i*) **Acetylation**
(*ii*) **Cannizzaro reaction**
(*iii*) **Cross aldol condensation**
(*iv*) **Decarboxylation**

Ans. (*i*) **Acetylation:** The replacement of an active hydrogen of alcohols, phenols or amines with an acyl (RCO) group to form the corresponding esters or amides is called acetylation. This replacement is carried out by using acid chloride or an acid anhydride in the presence of a base like pyridine or dimethylaniline.

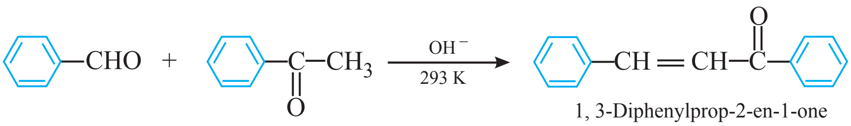
$$CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



$$CH_3COCl + C_2H_5NH_2 \longrightarrow \underset{\text{N-Ethylacetamide}}{CH_3CONHC_2H_5} + HCl$$

(*ii*) **Cannizzaro reaction:** Refer to Basic Concepts Point 17(*j*).

(*iii*) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of benzaldehyde and acetophenone.

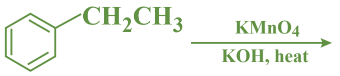


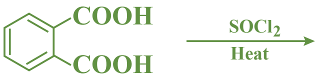
1, 3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

(*iv*) **Decarboxylation:** Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1). The reaction is known as decarboxylation.

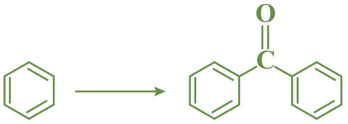
$$R—COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R—H + Na_2CO_3$$

Q. 17. Complete each synthesis by giving missing starting material, reagent or products.

(*i*)


(*ii*)


(*iii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(*iv*)


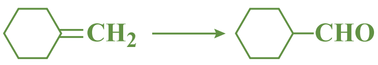
(*v*)

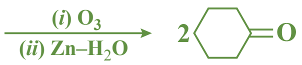

(*vi*)

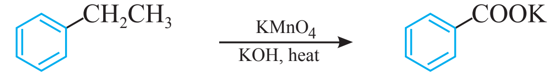

(*vii*) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow[\Delta]{\text{dil. NaOH}}$

(*viii*) $CH_3COCH_2COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$

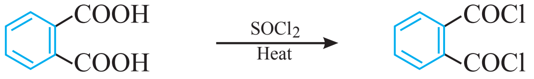
(*ix*)


(*x*)


(*xi*)


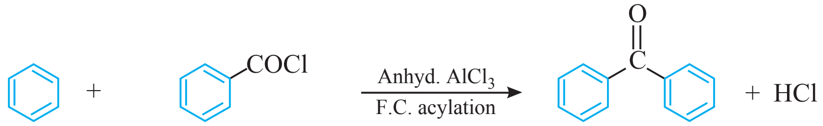
Ans. (*i*)


Ethylbenzene Potassium benzoate

(*ii*)


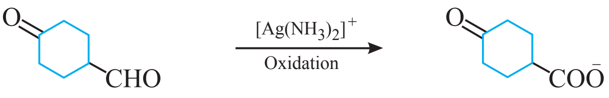
Phthalic acid Phthaloyl chloride

(*iii*) $\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Semicarbazide}}{H_2NNHCONH_2} \longrightarrow \underset{\text{Benzaldehyde semicarbazone}}{C_6H_5CH = NNHCONH_2} + H_2O$

(*iv*)


Benzene Benzoyl chloride Benzophenone

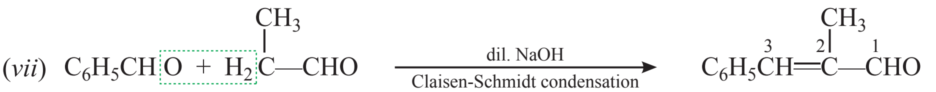
(*v*) Only aldehydes are oxidised by Tollens' reagent.



4-Oxocyclohexanecarbaldehyde 4-Oxocyclohexanecarboxylate anion

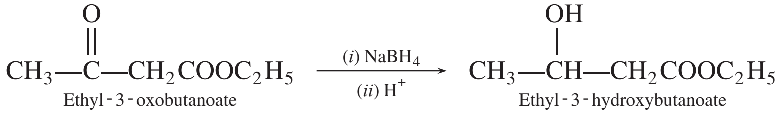
(*vi*) Cyanohydrin formation occurs at the aldehyde group

2-Formylbenzoic acid 2-[1-Hydroxycyanomethyl] benzoic acid

(*vii*)


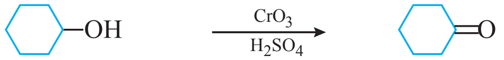
$$\underset{\text{Benzaldehyde}}{C_6H_5CH}\boxed{O + \underset{\text{Propanal}}{H_2}}\overset{CH_3}{\overset{|}{C}}—CHO \xrightarrow[\text{Claisen-Schmidt condensation}]{\text{dil. NaOH}} \underset{\text{2-Methyl-3-phenyl-prop-2-enal}}{C_6H_5\overset{3}{C}H = \overset{CH_3}{\overset{2|}{C}}—\overset{1}{C}HO}$$

(*viii*) Only keto group is reduced by $NaBH_4$.

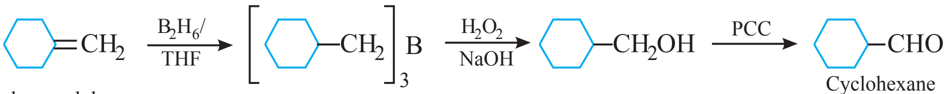


$$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4} CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_2COOC_2H_5$$

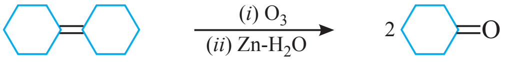
Ethyl-3-oxobutanoate Ethyl-3-hydroxybutanoate

(*ix*) 

Cyclohexanol Cyclohexanone

(*x*) 

Methylenecyclohexane Cyclohexane carbaldehyde

(*xi*) 

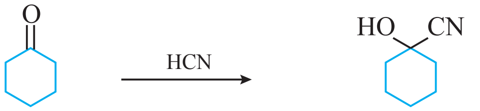
Cyclohexylidenecyclohexane Cyclohexanone

Q. 18. Give plausible explanation for each of the following:

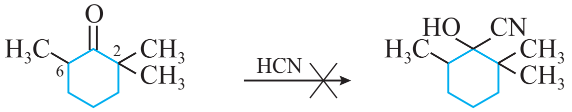
(*i*) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

(*ii*) There are two —NH_2 groups in semicarbazide, only one is involved in the formation of semicarbazone.

(*iii*) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

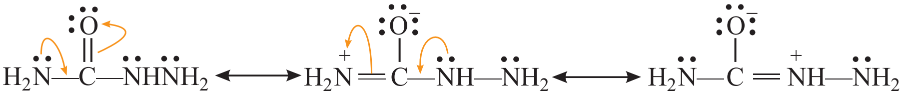
Ans. (*i*) 

Cyclohexanone Cyclohexanone cyanohydrin



2,2,6-trimethylcyclohexanone

Due to the presence of three methyl groups at α-position with respect to the C═O group, the nucleophilic attack by the CN^- ion does not occur due to steric hindrance. As there is no such steric hindrance in cyclohexanone, hence, nucleophilic attack by the CN^- ion occurs readily and hence cyclohexanone cyanohydrin is obtained in good yield.

(*ii*) 

$$H_2\ddot{N}-\overset{\overset{:\ddot{O}}{\|}}{C}-\ddot{N}H\ddot{N}H_2 \longleftrightarrow H_2\overset{+}{N}=\overset{\overset{:\ddot{O}:^-}{|}}{C}-\ddot{N}H-\ddot{N}H_2 \longleftrightarrow H_2\ddot{N}-\overset{\overset{:\ddot{O}:^-}{|}}{C}=\overset{+}{N}H-\ddot{N}H_2$$

Semicarbazide

Semicarbazide has two –NH_2 groups but one of them (*i.e.*, directly attached to C═O) is involved in resonance as shown above. Thus, electron density on this NH_2 group decreases hence it does not act as a nucleophile. In contrast, the lone pair of electrons on the other NH_2 group (*i.e.*, attached to —NH) is not involved in resonance and hence is available for nucleophilic attack on the C═O group of aldehydes and ketones.

(*iii*) The formation of esters from a carboxylic acid and an alcohol in presence of an acid catalyst is a reversible reaction.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

To shift the equilibrium in the forward direction, the water or the ester formed should be removed as fast as it is formed.

Q. 19. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an additional compound with sodium hydrogensulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acid. Write the possible structure of the compound.

[CBSE Delhi 2009; (AI) 2009] [*HOTS*]

Ans.

Element	Percentage	Atomic mass	No. of moles	Simplest molar ratio
C	69.77	12	$\frac{69.77}{12} = 5.81$	$\frac{5.81}{1.16} = 5$
H	11.63	1	$\frac{11.63}{1} = 11.63$	$\frac{11.63}{1.16} = 10$
O	(100 – 81.4) = 18.60	16	$\frac{18.60}{16} = 1.16$	$\frac{1.16}{1.16} = 1$

Empirical formula of the compound *A* = $C_5H_{10}O$

Molecular formula of the compound *A* = *n* (Empirical formula)

$$n = \frac{\text{Molecular mass of compound A}}{\text{Empirical formula mass of compound A}}$$

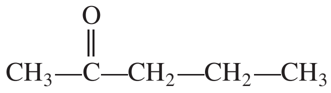
Molecular mass of compound *A* = 86

Empirical formula mass of compound *A* = 5 × 12 + 1 × 10 + 1 × 16 = 60 + 10 + 16 = 86

$$n = \frac{86}{86} = 1$$

Molecular formula of the compound A = 1 ($C_5H_{10}O$) = $C_5H_{10}O$

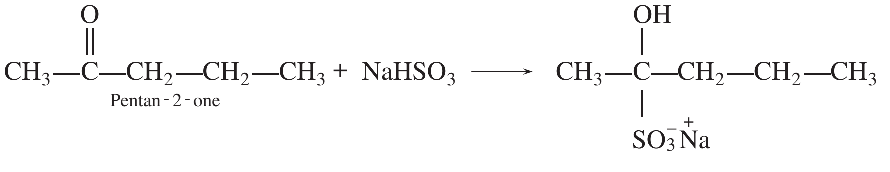
As the compound *A* forms addition compound with $NaHSO_3$ therefore it must be either an aldehyde or ketone. As it does not reduce Tollens' reagent and give positive iodoform test therefore it must be a methyl ketone. As on oxidation the compound A gives a mixture of ethanoic acid and propanoic acid, therefore compound A is



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

Pentan-2-one

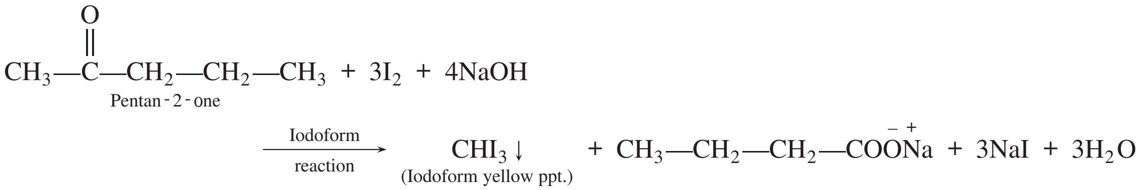
The chemical reactions are:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 + NaHSO_3 \longrightarrow CH_3-\underset{\underset{SO_3^-\overset{+}{Na}}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_2-CH_3$$

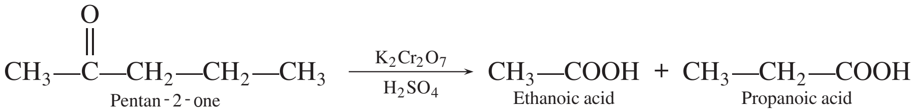
Pentan-2-one

Sodium hydrogen sulphite (addition product)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 + 3I_2 + 4NaOH \xrightarrow[\text{reaction}]{\text{Iodoform}} \underset{\text{(Iodoform yellow ppt.)}}{CHI_3\downarrow} + CH_3-CH_2-CH_2-CO\overset{-}{O}\overset{+}{Na} + 3NaI + 3H_2O$$

Pentan-2-one

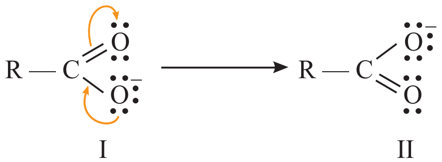


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Ethanoic acid}}{CH_3-COOH} + \underset{\text{Propanoic acid}}{CH_3-CH_2-COOH}$$

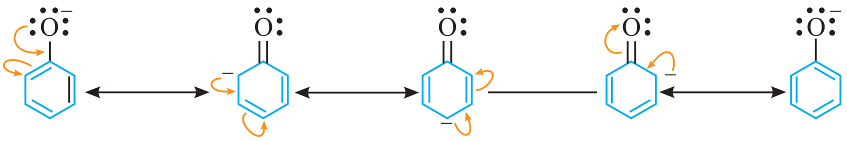
Pentan-2-one

Q. 20. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is stronger acid than phenol. Why?

Ans. Consider the resonating structures of carboxylate ion and phenoxide ion.



I II



III IV V VI VII

In the resonating structures IV, V, VI of phenoxide ion carry a negative charge on the less electronegative carbon atom. Therefore, their contribution towards the resonance stabilisation of phenoxide ion is very small and hence can be rejected.

In structures I and II of carboxylate ion the negative charge on the carboxylate ion is delocalised over two electronegative oxygen atoms while in structures III and VII of phenoxide ion, the negative charge on electronegative oxygen atom remains localised while the electrons of the benzene ring only are delocalised. As the delocalisation of benzene electrons contributes little towards the stability of phenoxide ion, therefore, carboxylate ion is much more resonance stabilised than phenoxide ion. Thus, the release of proton from carboxylic acid is much easier than from phenol. Hence, carboxylic acid is a stronger acid than phenol.

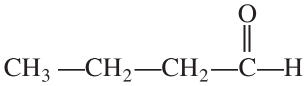
Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

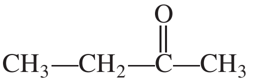
1. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution? *[NCERT Exemplar]*

(*a*) Butan-1-ol (*b*) Butan-2-ol (*c*) Both of these (*d*) None of these

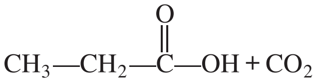
2. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these condition? *[NCERT Exemplar]*

(*a*) 

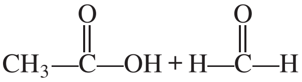
$CH_3—CH_2—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—H$

(*b*) 

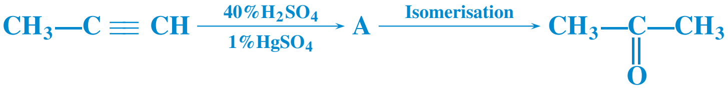
$CH_3—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$

(*c*) 

$CH_3—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—OH + CO_2$

(*d*) 

$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—OH + H—\overset{\overset{\displaystyle O}{\|}}{C}—H$

3. 

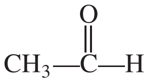
$CH_3—C \equiv CH \xrightarrow[1\% HgSO_4]{40\% H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3—\underset{\underset{\displaystyle O}{\|}}{C}—CH_3$

Structure of 'A' and type of isomerism in the above reaction are respectively. *[NCERT Exemplar]*

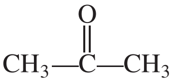
(*a*) Prop–1–en–2–ol, metamerism (*b*) Prop–1–en–1–ol, tautomerism

(*c*) Prop–2–en–2–ol, geometrical isomerism (*d*) Prop–1–en–2–ol, tautomerism

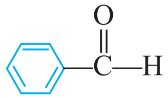
4. Which of the following compounds is most reactive towards nucleophilic addition reactions? *[NCERT Exemplar]*

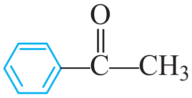
(*a*) 

$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—H$

(*b*) 

$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$

(*c*) 

(*d*) 

5. The formation of cyanohydrin from propanone is which type of reaction?

(*a*) Electrophilic substitution (*b*) Nucleophilic substitution

(*c*) Electrophilic addition (*d*) Nucleophilic addition

6. Compounds A and C in the following reaction are ______________. *[NCERT Exemplar]*

$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} (A) \xrightarrow{H_2SO_4, \Delta} (B) \xrightarrow{\text{Hydroboration oxidation}} (C)$

(*a*) identical (*b*) positional isomers (*c*) functional isomers (*d*) optical isomers

7. The reagent which does not react with both, acetone and benzaldehyde is *[NCERT Exemplar]*

(*a*) Sodium hydrogensulphite (*b*) Phenyl hydrazine

(*c*) Fehling's solution (*d*) Grignard reagent

8. Which is the most suitable reagent for the following conversion? *[NCERT Exemplar]*

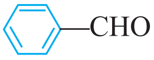
$$CH_3-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow CH_3-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

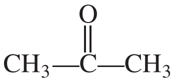
(*a*) Tollens' reagent (*b*) Benzoyl peroxide

(*c*) I_2 and NaOH solution (*d*) Sn and NaOH solution

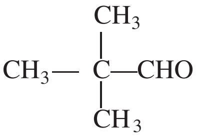
9. Which of the following compounds do not undergo aldol condensation?

(*a*) CH_3-CHO

(*b*) 

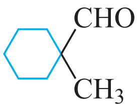
(*c*) 

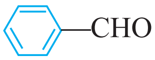
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(*d*) 

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CHO$

10. Cannizzaro's reaction is not given by _____________. *[NCERT Exemplar]*

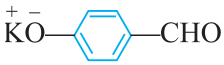
(*a*) 

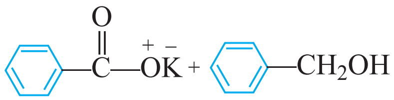
(*b*) 

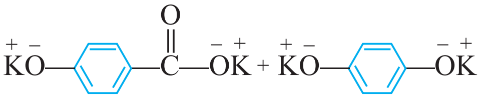
(*c*) HCHO

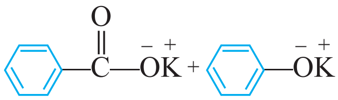
(*d*) CH_3CHO

11. Which product is formed when the compound  **is treated with concentrated aqueous KOH solution?** *[NCERT Exemplar]*

(*a*) 

(*b*) 

(*c*) 

(*d*) 

12. Which of the following reactions will not result in the formation of carbon-carbon bond?

(*a*) Friedel-Crafts acylation (*b*) Wurtz reaction

(*c*) Cannizzaro reaction (*d*) Reimer-Tiemann reaction

13. An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests.

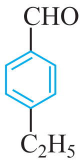
(*i*) Forms 2, 4-DNP derivative

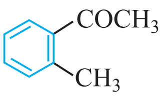
(*ii*) Reduces Tollens' reagent

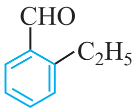
(*iii*) Undergoes Cannizzaro reaction

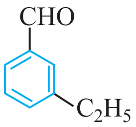
(*iv*) On vigorous oxidation, 1-2-benzenedicarboxylic acid is obtained.

X is:

(*a*) 

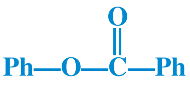
(*b*) 

(*c*) 

(*d*) 

14. The acid formed when propyl magnesium bromide is treated with CO_2 is :

(*a*) C_3H_7COOH (*b*) C_2H_5COOH (*c*) both (*d*) None of these

15. Treatment of compound  $Ph-O-\overset{\overset{\displaystyle O}{\|}}{C}-Ph$ **with NaOH solution yields** *[NCERT Exemplar]*

(*a*) Phenol (*b*) Sodium phenoxide (*c*) Sodium benzoate (*d*) Benzophenone

16. Which of the following compounds will give brisk effervescence of CO_2 on treatment with $NaHCO_3$?

(*a*) Phenol (*b*) Acetic acid (*c*) both (*d*) None of these

17. The correct order of increasing acidic strength is _____________. *[NCERT Exemplar]*

(*a*) Phenol < Ethanol < Chloroacetic acid < Acetic acid

(*b*) Ethanol < Phenol < Chloroacetic acid < Acetic acid

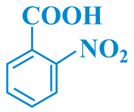
(*c*) Ethanol < Phenol < Acetic acid < Chloroacetic acid

(*d*) Chloroacetic acid < Acetic acid < Phenol < Ethanol

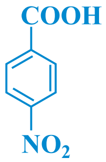
18. The weakest acid among the following is:

(*a*) $CHCl_2COOH$ (*b*) CH_3COOH (*c*) $CH_2ClCOOH$ (*d*) CCl_3COOH

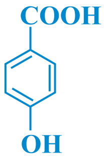
19. Arrange the following acids in order of the increasing acidity.



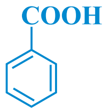
(A)



(B)



(C)



(D)

(*a*) B < C < A < D (*b*) A < B < C < D (*c*) C < B < D < A (*d*) C < D < B < A

20. Which one of the following reagents is used for the conversion of ethanoic acid to ethanoic anhydride?

(*a*) P_2O_5, Δ (*b*) $SOCl_2$, Δ (*c*) PCl_3, Δ (*d*) both (*a*) and (*b*)

Answers

1. (*b*) **2.** (*b*) **3.** (*d*) **4.** (*a*) **5.** (*d*) **6.** (*b*) **7.** (*c*) **8.** (*c*) **9.** (*b*, *d*) **10.** (*d*)

11. (*b*) **12.** (*c*) **13.** (*c*) **14.** (*a*) **15.** (*b*, *c*) **16.** (*b*) **17.** (*c*) **18.** (*b*) **19.** (*d*) **20.** (*a*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- ***(a)*** *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- ***(b)*** *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- ***(c)*** *Assertion (A) is correct, but Reason (R) is incorrect statement.*
- ***(d)*** *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. Assertion (*A*) : Formaldehyde is a planar molecule.
Reason (*R*) : It contains sp^2 hybridised carbon atom.

2. Assertion (*A*) : The solubility of aldehydes and ketones in water decreases with increase in the size of alkyl group.
Reason (*R*) : Alkyl groups are electron-repelling groups.

3. Assertion (*A*) : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.
Reason (*R*) : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

4. Assertion (*A*) : Aldehydes and ketones, both react with Tollens' reagent to form silver mirror.
Reason (*R*) : Both, aldehydes and ketones contain a carbonyl group.

5. Assertion (*A*) : The α-hydrogen atom in carbonyl compounds is less acidic.
Reason (*R*) : The anion formed after the loss of α-hydrogen atom is resonance stabilised.

6. Assertion (*A*) : Acetaldehyde undergoes aldol condensation with dil. NaOH.
Reason (*R*) : Aldehydes which do not contain α-hydrogen undergoes aldol condensation.

7. Assertion (*A*) : Benzoic acid does not undergo Friedel-crafts reaction.
Reason (*R*) : The carboxyl group is activating and undergo electrophilic substitution reaction.
[*CBSE 2020(56/4/2)*]

8. Assertion (*A*) : A carboxylate ion ($RCOO^-$) is stabilised by resonance to a greater extent as compared to the acid (RCOOH).
Reason (*R*) : The contributing structures of $RCOO^-$ are equivalent while those of RCOOH are not.

9. Assertion (*A*) : CH_3^- adds to $>C=O$ group irrevesibly but CN^- ion adds reversibly.

Reason (*R*) : CH_3^- ion is much stronger nucleophile than CN^- ion.

10. Assertion (*A*) : Aromatic acids do not undergo Friedel-Crafts reaction.

Reason (*R*) : —COOH group is a *m*-directing group.

Answers

1. (*a*)	**2.** (*b*)	**3.** (*b*)	**4.** (*d*)	**5.** (*d*)	**6.** (*c*)	**7.** (*c*)	**8.** (*a*)	**9.** (*b*)	**10.** (*b*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

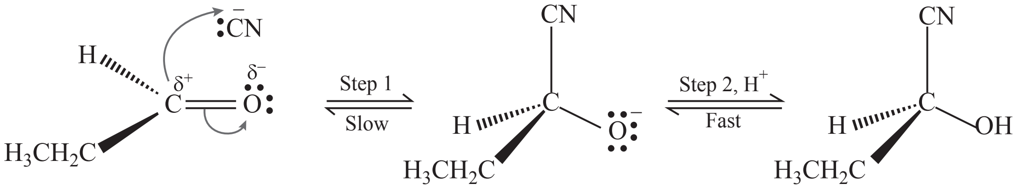
PASSAGE–1

Aldehydes and ketones are highly reactive compounds. Since both these classes of organic compounds have the same functional group, *i.e.*, polarized carbonyl group, they show a number of common reactions. However, the presence of a H-atom on the carbonyl group of aldehydes make them much more reactive than ketones. At the same time, this H-atom is responsible for many reactions in which aldehydes differ from ketones. The carbonyl group $\left(>C{=}O\right)$ undergoes nucleophilic addition reactions due to electronegativity difference between carbon and oxygen atoms. Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. Further aldehydes and ketones having atleast one α-H atom in the presence of dilute alkali as a catalyst form β-hydroxy aldehyde (aldol) or β-hydroxy ketones (ketol). This reaction is known as aldol condensation. Aldehydes which do not have an α-hydrogen undergo disproportionation reaction in the presence of concentrated alkali giving a mixture of alcohol and salt of carboxylic acid. This reaction is called Cannizzaro reaction. Cannizzaro reaction involves a hydride ion shift from the carbonyl carbon that is attacked by the base to another carbonyl carbon. Since, there is no hydrogen attached to the carbonyl carbon in a ketone therefore it does not undergo Cannizzaro reaction.

1. Propose the mechanism for the following reaction:

$$CH_3{-}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}H + HCN \xrightarrow{H^+} CH_3{-}CH_2{-}\overset{\overset{\large OH}{|}}{CH}{-}CN$$

Ans. The reaction proceeds through the nucleophilic attack of CN^- ion as follows.

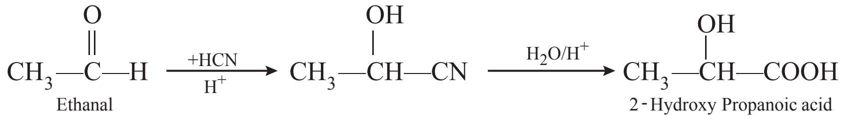


2. Propanone is less reactive than ethanal towards nucleophilic addition reactions. Why?

Ans. The methyl group due to its +I effect reduces the magnitude of positive charge on carbonyl carbon atom. Moreover, it also hinders the approach of the nucleophile. Since in propanone, there are two methyl groups while in acetaldehyde there is one methyl group, therefore, propanone is less reactive than acetaldehyde towards nucleophilic addition reactions.

3. How will you convert ethanal to 2-hydroxy propanoic acid?

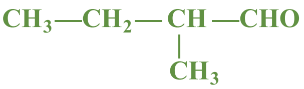
Ans.



$$\underset{\text{Ethanal}}{CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}H} \xrightarrow[H^+]{+HCN} CH_3{-}\overset{\overset{\large OH}{|}}{CH}{-}CN \xrightarrow{H_2O/H^+} \underset{\text{2-Hydroxy Propanoic acid}}{CH_3{-}\overset{\overset{\large OH}{|}}{CH}{-}COOH}$$

4. **Which of the following compounds will undergo Cannizzaro reaction?**

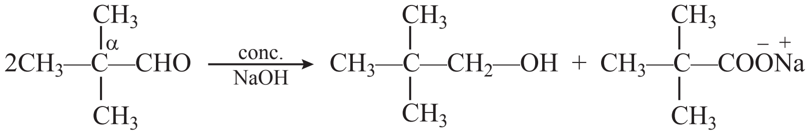
(*i*) $(CH_3)_3$—C—CHO **(*ii*)**



$CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CHO$

Write the structures of expected product of the Cannizzaro reaction.

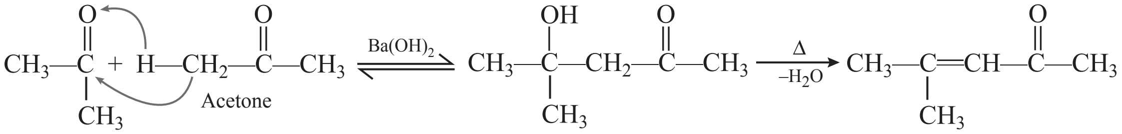
Ans. (*i*) will undergo Cannizzaro reaction as it does not contain α-hydrogen.



2,2-Dimethyl propanal 2, 2-Dimethyl propan-1-ol Sodium-2,2-dimethylpropanoate

5. **What happens when acetone undergoes aldol condensation? Write the reaction and name of the products.**

Ans.



4-Hydroxy-4-methyl-pentan-2-one (Ketol) 4-Methyl pent-3-en-2-one

PASSAGE–2

Carboxylic acids are the most acidic amongst all the organic compounds studied so far. However,carboxylic acids are much weaker acids than the mineral acids.

Carboxylic acids are more acidic than alcohols and phenols due to the less electrophilic nature of carboxyl carbon which puts a partial positive charge on the hydroxyl O-atom. The value of K_a is a measure of the acidic strength of an acid. Greater the value of K_a, greater is the tendency of the acid to ionize and hence stronger is the acid. The acidic strength of saturated aliphatic carboxylic acids depends mainly upon the inductive effect of the substituent and its position with respect to —COOH group. Electron-donating substituents tend to decrease whereas electron-withdrawing substituents tend to increase the acidic strength. The acidic strength of aromatic carboxylic acids, on the other hand depends upon both the inductive and the resonance effect of the substituents.

1. **What is meant by 'acidity constant' K_a? How is it expressed?**

Ans. Acidity constant K_a is a measure of the strength of the acid. It is expressed as,

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

2. **What makes ethanoic acid a stronger acid than ethanol?**

Ans. Ethanoate ion obtained by loss of a proton from ethanoic acid is stabilized by resonance but ethoxide ion obtained by loss of a proton from ethanol does not.

3. **Why is pK_a of chloroacetic acid lower than pK_a of acetic acid?**

Ans. Due to –I effect of Cl atom and +I effect of CH_3 group the electron density in the O—H bond in chloroacetic acid is much weaker than in acetic acid and hence loses a proton more easily than acetic acid.

4. **Arrange the following in the decreasing order of their acidic character:**

CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

Ans. $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

5. **Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.**

Ans.
- Resonating structures of carboxylate ion are more stable than phenoxide ion.
- Negative charge is dispersing on two electronegative oxygens in carboxylate ion whereas it is on one oxygen atom in phenoxide ion.

Very Short Answer Questions [1 mark]

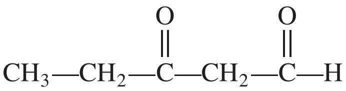
Q. 1. Give IUPAC name of the following compound: *[CBSE (F) 2010]*

$(CH_3)_2C{=}CHCOCH_3$

Ans. 4-Methyl-pent-3-en-2-one

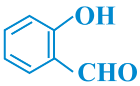
Q. 2. Write the structure of the following compound : 3-oxopentanal. *[CBSE (F) 2011]*

Ans.



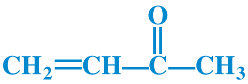
$$CH_3{-}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}H$$

Q. 3. Write the IUPAC name of the following compound: *[CBSE (F) 2014]*



Ans. 2-hydroxybenzaldehyde

Q. 4. Write the IUPAC name of the following compound: *[CBSE 2019(56/3/2)]*



$$CH_2{=}CH{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3$$

Ans. But-3-en-2-one

Q. 5. Give the name of the reagent that bring the following transformation: But-2-ene to ethanal.

Ans. O_3/H_2O—Zn dust

Q. 6. Arrange the following in increasing order of their boiling point:

CH_3CH_2OH, CH_3CHO, $CH_3{-}O{-}CH_3$ *[CBSE 2019(56/3/2)]*

Ans. $CH_3{-}O{-}CH_3 < CH_3CHO < CH_3{-}CH_2{-}OH$

Q. 7. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions: ethanal, propanal, propanone, butanone. *[CBSE Delhi 2012]*

Ans. Butanone < Propanone < Propanal < Ethanal

Q. 8. What is Tollens' reagent? Write one usefulness of this reagent. *[CBSE (AI) 2010]*

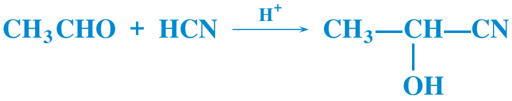
Ans. Ammonical silver nitrate ($AgNO_3 + NH_4OH$) solution is known as Tollens' reagent. It is used to detect the presence of —CHO group in an organic compound.

Q. 9. What do you mean by Schiff's base? Give an example.

Ans. Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or Schiff's bases.

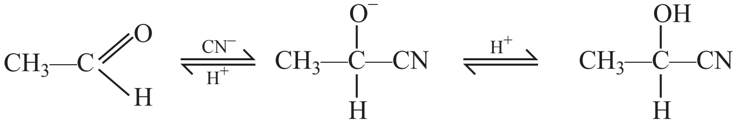
$$\underset{\text{Aldehyde}}{R{-}CH{=}O} + \underset{1^\circ\text{ Amine}}{H_2N{-}R'} \xrightarrow[\text{Heat}]{\text{Trace of }H^+} \underset{\text{Schiff's base}}{R{-}CH{=}N{-}R'} + H_2O$$

Q. 10. Propose the mechanism for the following reaction: *[HOTS]*



$$CH_3CHO + HCN \xrightarrow{H^+} CH_3{-}\underset{\underset{\large OH}{|}}{CH}{-}CN$$

Ans. The reaction proceeds through the nucleophilic attack of CN^- ion as follows:



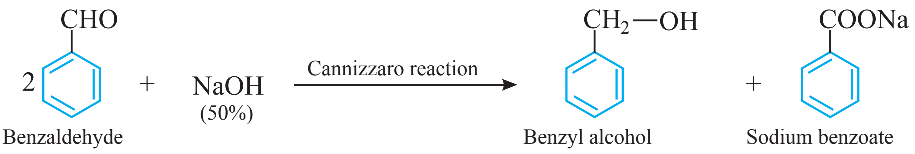
Acetaldehyde Intermediate Acetaldehyde cyanohydrin

Q. 11. Name the aldehyde which does not give Fehling's solution test.

Ans. Benzaldehyde

Q. 12. How will you prepare benzyl alcohol from benzaldehyde without using a reducing agent? [*HOTS*]

Ans.



Here, a concentrated solution of NaOH is used which is not a reducing agent.

Q. 13. Write two important uses of formalin. [*CBSE Sample Paper 2011*]

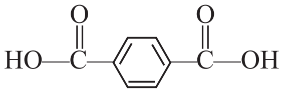
Ans. Formalin is used in the

(*i*) preservation of biological specimens.

(*ii*) manufacture of bakelite.

Q. 14. Write the structural formula and IUPAC name of terephthalic acid.

Ans.

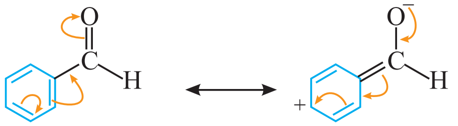


Benzene-1, 4-dicarboxylic acid

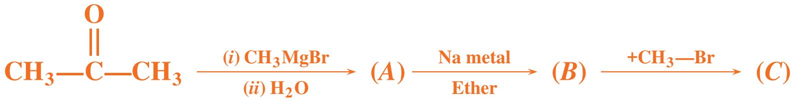
Short Answer Questions–I [2 marks]

Q. 1. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Ans. The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

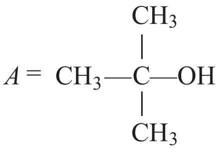


Q. 2. Complete the following reaction sequence: [*NCERT Exemplar*]



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} (A) \xrightarrow[\text{Ether}]{\text{Na metal}} (B) \xrightarrow{+CH_3-Br} (C)$$

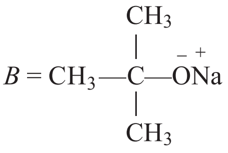
Ans.



$$A = CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$

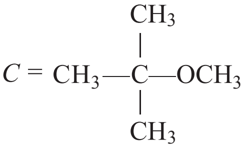
2-methyl propan-2-ol

,



$$B = CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{-}{O}\overset{+}{Na}$$

Sodium tert. butoxide



$$C = CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OCH_3$$

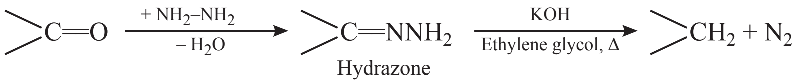
2-methoxy-2-methylpropane

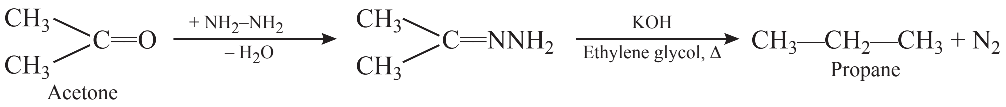
Q. 3. Write the equations involved in the following reactions:

(*i*) Wolff-Kishner reduction

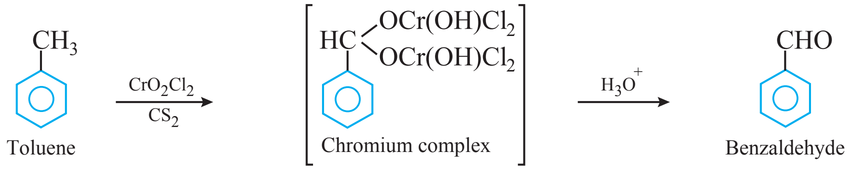
(*ii*) Etard reaction **[*CBSE Delhi 2017*]**

Ans. (*i*) **Wolff–Kishner reduction:**





(*ii*) **Etard reaction:**

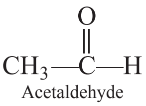


Q. 4. Write structures of main compounds *A* and *B* in each of the following reactions. [*CBSE 2019(56/2/3)*]

(*i*) $CH_3CH_2OH \xrightarrow{PCC} A \xrightarrow{CH_3OH/dry\ HCl(g)} B$

(*ii*) $C_6H_5COCH_3 \xrightarrow{NaOI} A + B$

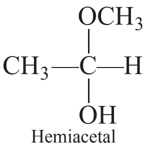
Ans. (*i*) $A =$



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

Acetaldehyde

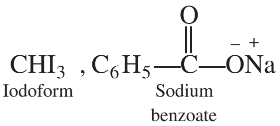
$B =$



$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OCH_3}{|}}{C}}-H$

Hemiacetal

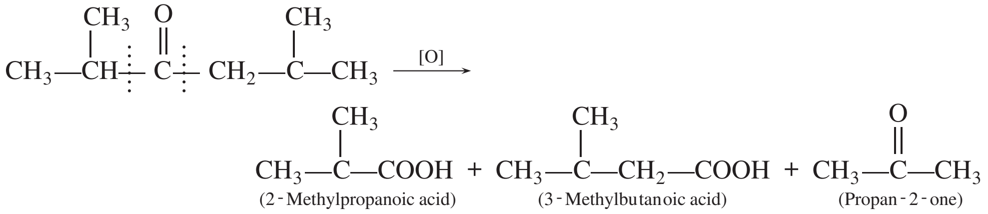
(*ii*) A and $B =$



$\underset{\text{Iodoform}}{CHI_3}\ ,\ \underset{\text{Sodium benzoate}}{C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}}$

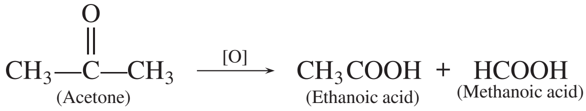
Q. 5. Oxidation of ketones involves carbon–carbon bond cleavage. Name the products formed on oxidation of 2, 5-dimethylhexan-3-one. [*NCERT Exemplar*]

Ans.



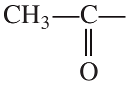
$$CH_3-\overset{\overset{CH_3}{|}}{CH}\vdots\overset{\overset{O}{\|}}{C}\vdots CH_2-\overset{\overset{CH_3}{|}}{C}-CH_3 \xrightarrow{[O]}$$

$$\underset{\text{(2-Methylpropanoic acid)}}{CH_3-\overset{\overset{CH_3}{|}}{C}-COOH} + \underset{\text{(3-Methylbutanoic acid)}}{CH_3-\overset{\overset{CH_3}{|}}{C}-CH_2-COOH} + \underset{\text{(Propan-2-one)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$



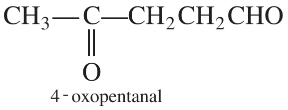
$$\underset{\text{(Acetone)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{[O]} \underset{\text{(Ethanoic acid)}}{CH_3COOH} + \underset{\text{(Methanoic acid)}}{HCOOH}$$

Q. 6. An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane on treatment with Zn–Hg/HCl. 'A' forms a dioxime with hydroxylamine and gives a positive Iodoform test and Tollens' test. Identify the compound A and deduce its structure. [*HOTS*]



Ans. As '*A*' gives positive iodoform test, so it has $CH_3-\underset{\underset{O}{\|}}{C}-$ group.

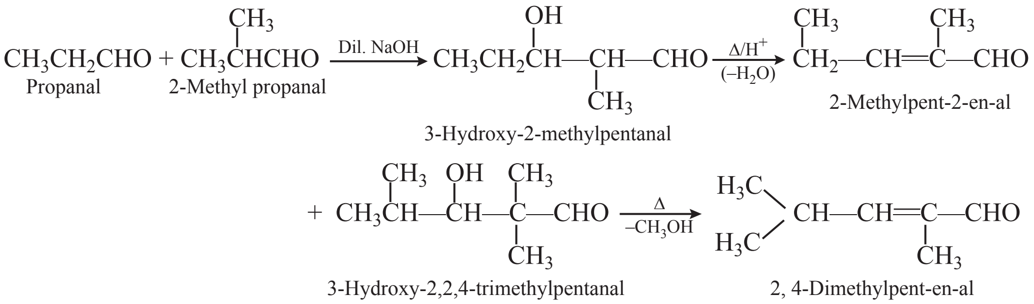
As '*A*' gives positive Tollens' test, so it must have —CHO group.



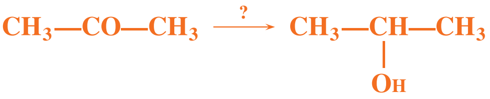
So '*A*' is $\underset{\text{4-oxopentanal}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2CHO}$

Q. 7. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? Write the name of the reaction also. **[*NCERT Exemplar*] [*HOTS*]**

Ans. The reaction taking place is cross aldol condensation.



Q. 8. Name the reagents used in the following reactions: **[*CBSE Delhi 2015*]**



(*i*) $CH_3-CO-CH_3 \xrightarrow{?} CH_3-\underset{OH}{\underset{|}{C}H}-CH_3$

(*ii*) $C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$

Ans. (*i*) Sodium borohydride ($NaBH_4$) or Lithium aluminium hydride ($LiAlH_4$)

(*ii*) Alkaline potassium permanganate ($KMnO_4$—KOH)

Q. 9. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous $AlCl_3$. Name the reaction also. **[*NCERT Exemplar*]**

Ans. $C_6H_5\overset{\oplus}{C}O$ (Benzoylinium cation)

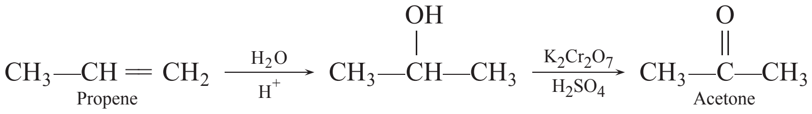
Friedel–Crafts acylation reaction

Q. 10. Do the following conversions in not more than two steps: **[*CBSE (F) 2017*]**

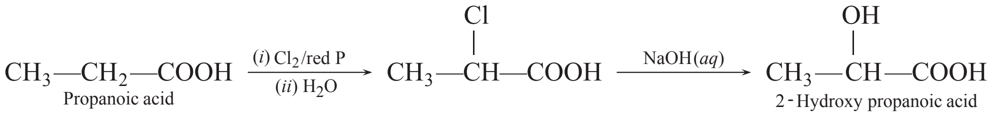
(*i*) Propene to Acetone

(*ii*) Propanoic acid to 2-hydroxypropanoic acid

Ans.



(*i*) $\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[H^+]{H_2O} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$



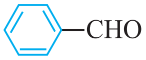
(*ii*) $\underset{\text{Propanoic acid}}{CH_3-CH_2-COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/\text{red P}} CH_3-\overset{Cl}{\overset{|}{C}H}-COOH \xrightarrow{NaOH(aq)} \underset{\text{2-Hydroxy propanoic acid}}{CH_3-\overset{OH}{\overset{|}{C}H}-COOH}$

Q. 11. An aromatic compound 'A' on treatment with $CHCl_3$ and KOH gives two compounds, both of which give same product 'B' when distilled with zinc dust. Oxidation of 'B' gives 'C' with molecular formula $C_7H_6O_2$. Sodium salt of 'C' on heating with soda lime gives 'D' which may also be obtained by distilling 'A' with zinc dust. Identify 'A', 'B', 'C' and 'D'. **[*CBSE 2019(56/5/2)*]**

Ans. A =

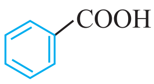
Phenol

, B =



Benzaldehyde

, C =



Benzoic acid

, D =

Benzene

Q. 12. Write the reagents used in the following reactions: **[*CBSE Ajmer 2015*]**

(*i*) $C_6H_5-CO-CH_3 \xrightarrow{?} C_6H_5-CH_2-CH_3$

(*ii*) $CH_3COOH \xrightarrow{?} CH_3-COCl$

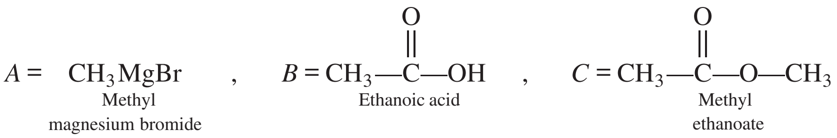
Ans. (*i*) Zn—Hg, conc. HCl or H_2NNH_2 and KOH/ethylene glycol, Heat

(*ii*) PCl_5 or $SOCl_2$

Q. 13. Identify the compounds *A*, *B* and *C* in the following reaction: **[*NCERT Exemplar*]**

$$CH_3—Br \xrightarrow{Mg/Ether} (A) \xrightarrow[(ii)\ Water]{(i)\ CO_2} (B) \xrightarrow[\Delta]{CH_3OH/H^+} (C)$$

Ans.



$$A = \underset{\text{Methyl magnesium bromide}}{CH_3MgBr}, \quad B = \underset{\text{Ethanoic acid}}{CH_3—\overset{\overset{O}{\|}}{C}—OH}, \quad C = \underset{\text{Methyl ethanoate}}{CH_3—\overset{\overset{O}{\|}}{C}—O—CH_3}$$

Q. 14. Arrange the following compounds in increasing order of their property as indicated:

(*i*) CH_3COCH_3, $C_6H_5—CO—C_6H_5$, CH_3CHO (reactivity towards nucleophilic addition reaction)

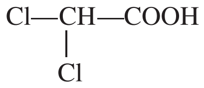
(*ii*)

$Cl—\underset{\underset{Cl}{|}}{CH}—COOH$, $Cl—CH_2—COOH$, $CCl_3—COOH$ (acidic character)

[*CBSE Bhubaneshwar 2015*]

Ans. (*i*) $C_6H_5COC_6H_5 < CH_3COCH_3 < CH_3CHO$

(*ii*)



$Cl—CH_2—COOH < Cl—\underset{\underset{Cl}{|}}{CH}—COOH < CCl_3—COOH$

Q. 15. Give reasons:

(*i*) Oxidation of aldehydes is easier than ketones. **[*CBSE 2019 (51/5/2)*]**

OR

Oxidation of propanal is easier than propanone. **[*CBSE 2020 (56/4/3)*]**

(*ii*) $CH_2{=}CH—COOH$ is more acidic than $CH_3CH_2—COOH$. **[*CBSE East 2016*]**

Ans. (*i*) As aldehydes contain H atom on the carbonyl group but ketones do not. Cleavage of C—H bond in aldehydes is easier than cleavage of C—C bond in ketones.

(*ii*) This is because in $CH_2{=}CH—COOH$, the carbonyl group attached to sp^2 hybridised carbon atom which is more electronegative and makes release of H^+ ion easy.

Q. 16. (*i*) Give reason: **[*CBSE 2019(56/2/1)*]**

(*a*) Benzoic acid is a stronger acid than acetic acid.

(*b*) Methanal is more reactive towards nucleophilic addition reaction than ethanal.

(*ii*) Give a simple chemical test to distinguish between propanal and propanone.

Ans. (*i*) (*a*) This is because of greater electronegativity of sp^2 hybridised carbonyl to which carboxyl carbon is attached in benzoic acid.

$\overset{sp^2}{C_6H_5}—COOH$ Benzoic acid

$\overset{sp^3}{CH_3}—COOH$ Acetic acid

(*b*) The methyl group due to its +ve I effect reduces the positive charge on carbonyl carbon atom. Moreover it also hinders the approach of the nucleophile. Since in ethanal there is one methyl group while in methanal there is no methyl group on carbonyl carbon atom therefore methanal is more reactive towards nucleophilic addition reaction than ethanal.

(*ii*) Propanal being an aldehyde gives silver mirror with Tollens' reagent while propanone being a ketone does not give this test.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow CH_3CH_2COO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

Q. 17. Arrange the following in the decreasing order of their acidic character.

(*i*) C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH

(*ii*) CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

Ans. (*i*) $NO_2CH_2COOH > FCH_2COOH > C_6H_5COOH$

(*ii*) $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

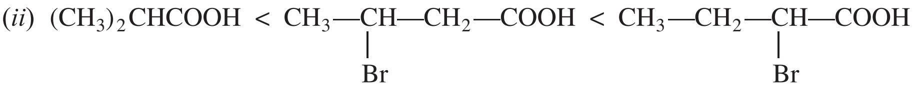
Q. 18. Arrange the following in order of property indicated for each set.

(*i*) CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ (increasing order of boiling points)

(*ii*) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ (increasing order of their acid strengths)

Ans. (*i*) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

(*ii*)

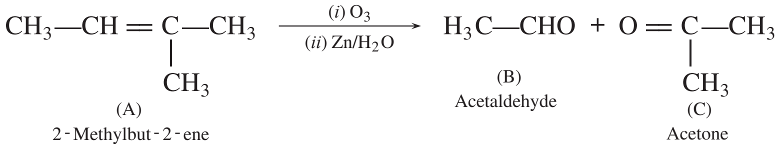


$(CH_3)_2CHCOOH < CH_3-CH(Br)-CH_2-COOH < CH_3-CH_2-CH(Br)-COOH$

Short Answer Questions–II [3 marks]

Q. 1. An alkene 'A' molecular formula (C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling's test but forms iodoforms. Identify the compounds 'A', 'B' and 'C' giving suitable explanation and write the reactions of ozonolysis and iodoform formation from either 'B' or 'C'. [*NCERT Exemplar*] [*HOTS*]

Ans. Compound 'B' gives both Fehling's test and iodoform test and therefore it must be an aldehyde with $-COCH_3$ group. Moreover, compound 'C' doesn't give Fehling's test but give positive iodoform test and therefore it must be a ketone with $-COCH_3$ group. Thus, the compound A, B and C are as follows:



$$CH_3-CH=C(CH_3)-CH_3 \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} H_3C-CHO + O=C(CH_3)-CH_3$$

(A) 2-Methylbut-2-ene; (B) Acetaldehyde; (C) Acetone

$$CH_3-CHO + 3I_2 + 4NaOH \xrightarrow[\text{reaction}]{\text{Iodoform}} HCOONa + CHI_3\downarrow + 3NaI + 3H_2O$$

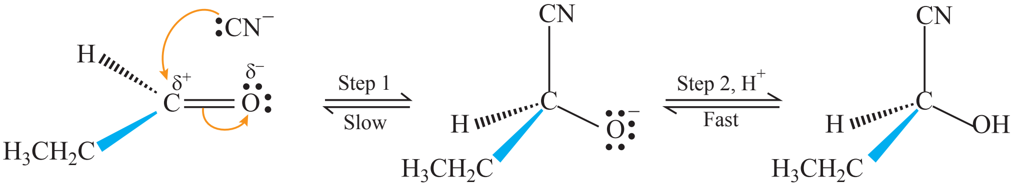
Other isomers of 'A' will not give products corresponding to the given test.

Q. 2. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why? [*NCERT Exemplar*] [*HOTS*]

Ans. CH_3CH_2CHO (I) CH_3COCH_3 (II)

(*a*) Compound I will react faster with HCN due to less steric hinderance and electronic reasons than II.

Mechanism: Nucleophilic addition reaction:



(*b*) No, it is a reversible reaction. Hence, equilibrium is established.

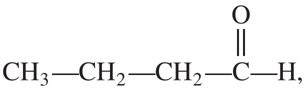
(*c*) Addition of acid inhibits the reaction because the formation of CN^- ions is prevented.

Q. 3. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/conc. HCl give the same product (D).

(*i*) Write the structures of (A), (B), (C) and (D).

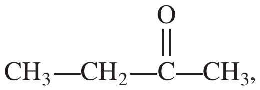
(*ii*) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?

[*CBSE 2018*]

Ans. (*i*) $A =$ 

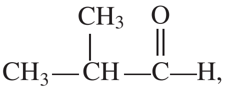
$CH_3{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$,

Butanal

$B =$ 

$CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$,

Butanone

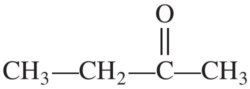
$C =$ 

$CH_3{-}\underset{}{\overset{CH_3}{\overset{|}{CH}}}{-}\overset{O}{\overset{\|}{C}}{-}H$,

2-Methylpropanal

$D = CH_3{-}CH_2{-}CH_2{-}CH_3$

Butane

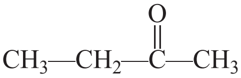
(*ii*) 

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

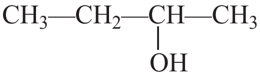
Butanone (*B*)

Q. 4. An organic compound (A) having molecular formula C_4H_8O gives orange red precipitate with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow precipitate of iodoform on heating with NaOH and I_2. Compound (A) on reduction with $NaBH_4$ gives compound (B) which undergoes dehydration reaction on heating with conc. H_2SO_4 to form compound (C). Compound (C) on Ozonolysis gives two molecules of ethanal.

Identify (A), (B) and (C) and write their structures. Write the reactions of compound (A) with (*i*) NaOH/I_2 and (*ii*) $NaBH_4$ and explain the reactions. **[*HOTS*] [*CBSE 2020 (56/4/3)*]**

Ans. A = Butan-2-one; 

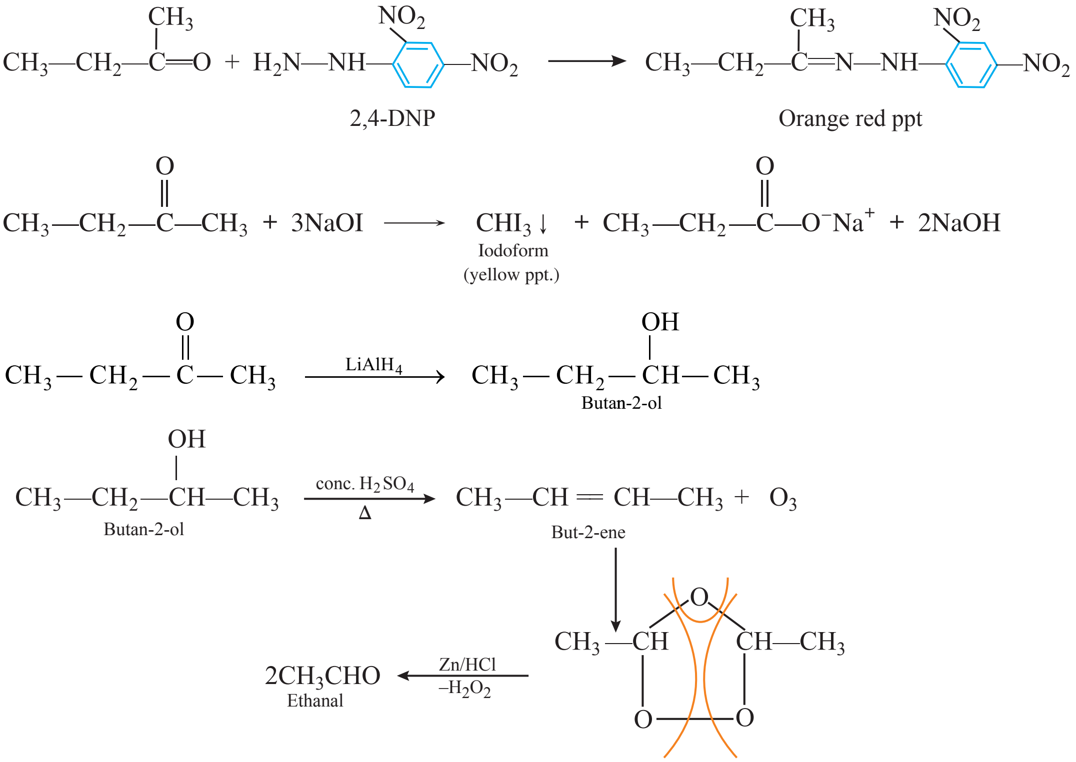
$CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

B = Butan-2-ol ; 

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

C = But-2-ene ; $CH_3{-}CH{=}HC{-}CH_3$

Reactions involved:



Q. 5. An unknown aldehyde 'A' on reacting with alkali gives a β-hydroxy aldehyde, which loses water to form an unsaturated aldehyde, But-2-enal. Another aldehyde 'B' undergoes disproportionation reaction in the presence of conc. alkali to form products C and D. C is an arylalcohol with the formula, C_7H_8O.

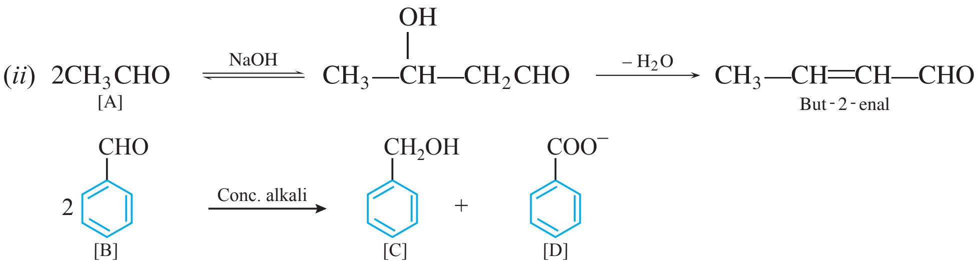
(*i*) Identify A and B.

(*ii*) Write the sequence of reactions involved.

(*iii*) Name the product, when 'B' reacts with zinc amalgam and hydrochloric acid. ***[HOTS]***

Ans. (*i*) A is CH_3CHO (ethanal) and B is C_6H_5CHO (benzaldehyde).

(*ii*)



$$\underset{[A]}{2CH_3CHO} \xrightleftharpoons{NaOH} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2CHO \xrightarrow{-H_2O} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$$

(*iii*) Toluene.

Q. 6. (*i*) Account for the following:

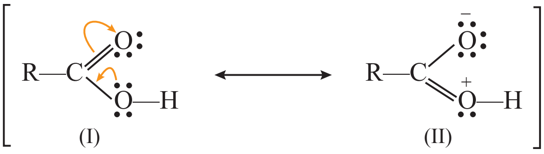
(*a*) $Cl-CH_2COOH$ is a stronger acid than CH_3COOH.

(*b*) Carboxylic acids do not give reactions of carbonyl group.

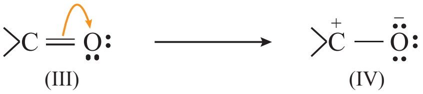
(*ii*) Out of $CH_3CH_2-CO-CH_2-CH_3$ and $CH_3CH_2-CH_2-CO-CH_3$, which gives iodoform test? ***[CBSE (AI) 2014]***

Ans. (*i*) (*a*) Because of –I effect of Cl atom in $ClCH_2COOH$ and +I effect of CH_3 group in CH_3COOH the electron density in the O—H bond in $ClCH_2COOH$ is much lower than CH_3COOH. As a result O—H bond in $ClCH_2COOH$ is much weaker than in CH_3COOH therefore loses a proton more easily than CH_3COOH. Hence $ClCH_2COOH$ acid is stronger acid than CH_3COOH.

(*b*) Carboxylic acids are resonance hybrid of the following structures:



Similarly, a carbonyl group of aldehydes and ketones may regarded as resonance hybrid of following structures.



Because of contribution of structure (IV), the carbonyl carbon in aldehydes and ketones is electrophilic. On the other hand, electrophilic character of carboxyl carbon is reduced due to contribution of structure (II). As carbonyl carbon of carboxyl group is less electropositive than carbonyl carbon in aldehydes and ketones, therefore, carboxylic acids do not give nucleophilic addition reactions of aldehydes and ketones.

(*ii*) $CH_3-CH_2-CH_2-COCH_3$

Q. 7. Arrange the following compounds in increasing order of their property as indicated:

(*i*) Acetaldehyde, Acetone, Methyl tert-butyl ketone (reactivity towards HCN)

(*ii*) Benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

(*iii*) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$ (acid strength) ***[CBSE (AI) 2012]***

Ans. (*i*) Methyl tert-butyl ketone < Acetone < Acetaldehyde

(*ii*) 4-Methoxy benzoic acid < Benzoic acid < 3,4-Dinitrobenzoic acid

(*iii*) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

Q. 8. Complete each synthesis by giving missing reagents or products in the following:

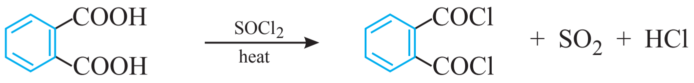
(*i*)

(*ii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(*iii*)

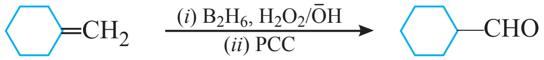
[*CBSE (AI) 2011*]

Ans. (*i*)



(*ii*) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2} C_6H_5CH = NNHCONH_2 + H_2O$

(*iii*)



Q. 9. Write structures of compounds *A, B* and *C* in each of the following reactions:

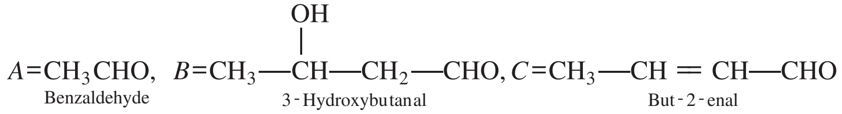
(*i*) $C_6H_5Br \xrightarrow{\text{Mg/dryether}} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_2(g)} B \xrightarrow{PCl_5} C$

(*ii*) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$

[*CBSE Delhi 2017*]

Ans. (*i*) $A = C_6H_5MgBr$ (Phenyl magnesium bromide), $B = C_6H_5COOH$ (Benzoic acid), $C = C_6H_5COCl$ (Benzoyl chloride)

(*ii*)



$A = \underset{\text{Benzaldehyde}}{CH_3CHO}$, $B = \underset{\text{3-Hydroxybutanal}}{CH_3—\overset{\overset{\large OH}{|}}{C}H—CH_2—CHO}$, $C = \underset{\text{But-2-enal}}{CH_3—CH = CH—CHO}$

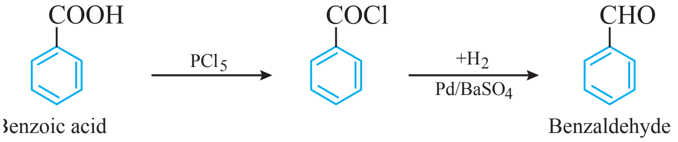
Q. 10. Do the following conversions in not more than two steps: **[*CBSE Delhi 2017*]**

(*i*) **Benzoic acid to Benzaldehyde**

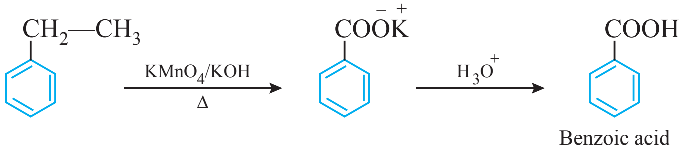
(*ii*) **Ethyl benzene to Benzoic acid**

(*iii*) **Propanone to Propene**

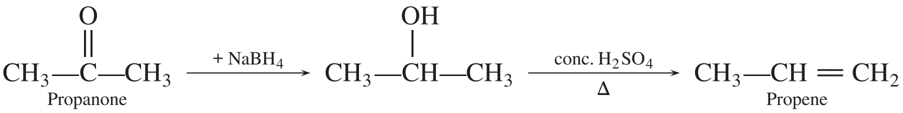
Ans. (*i*) **Benzoic acid to Benzaldehyde**



(*ii*) **Ethyl benzene to Benzoic acid**

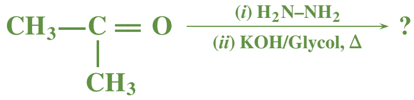


(*iii*) **Propanone to Propene**



$$\underset{\text{Propanone}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_3} \xrightarrow{+NaBH_4} CH_3—\overset{\overset{OH}{|}}{C}H—CH_3 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} \underset{\text{Propene}}{CH_3—CH = CH_2}$$

Q. 11. Predict the products of the following reactions: **[*CBSE Delhi 2015*]**

(*i*) 

$$CH_3-\underset{\substack{|\\CH_3}}{C}=O \xrightarrow[(ii)\ KOH/Glycol,\ \Delta]{(i)\ H_2N-NH_2} ?$$

(*ii*) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(*iii*) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$

Ans. (*i*) $CH_3-CH_2-CH_3$ (Propane)

(*ii*) $C_6H_5COO^-Na^+$ (Sodium benzoate) and CHI_3 (Iodoform)

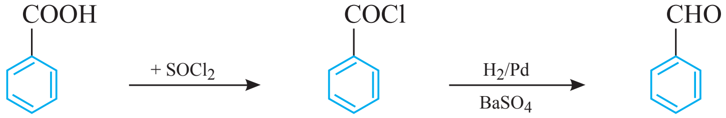
(*iii*) CH_4 (Methane)

Q. 12. How do you convert the following?

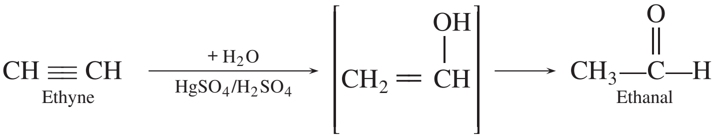
(*i*) Benzoic acid to Benzaldehyde

(*ii*) Ethyne to Ethanal

(*iii*) Acetic acid to Methane **[*CBSE (F) 2015*]**

Ans. (*i*) 

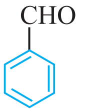
Benzoic acid Benzaldehyde

(*ii*) 

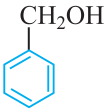
$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[HgSO_4/H_2SO_4]{+H_2O} \left[CH_2=\overset{\substack{OH\\|}}{CH}\right] \longrightarrow \underset{\text{Ethanal}}{CH_3-\overset{\substack{O\\\|}}{C}-H}$$

(*iii*) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{+NaOH} CH_3CO\overset{-}{O}\overset{+}{Na} \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4}$

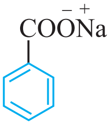
Q. 13. An organic compound (*A*) has characteristic odour. On treatment with NaOH, it forms compounds (*B*) and (*C*). Compound (*B*) has molecular formula C_7H_8O which on oxidation gives back (*A*). The compound (*C*) is a sodium salt of an acid. When (*C*) is treated with soda-lime, it yields an aromatic compound (*D*). Deduce the structures of (*A*), (*B*), (*C*) and (*D*). Write the sequence of reactions involved. **[*CBSE Sample Paper 2015*]**

Ans. *A* = 

Benzaldehyde

; *B* = 

Benzyl alcohol

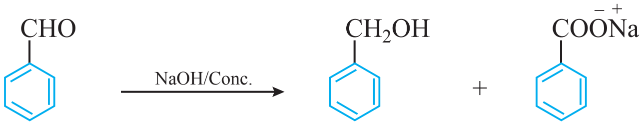
; *C* = 

Sodium benzoate

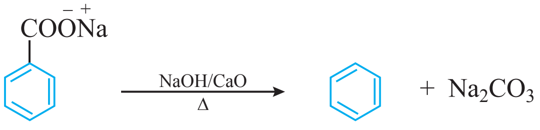
; *D* = 

Benzene

Reaction involved are:



(*A*) (*B*) (*C*)



(*C*) (*D*)

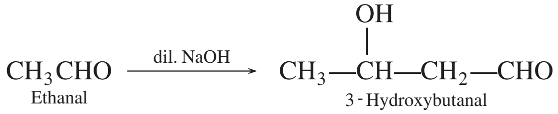
Q. 14. How would you bring about the following conversions? Write the complete equation in each case.

(*i*) Ethanal to 3-hydroxybutanal

(*ii*) Benzoic acid to *m*-nitrobenzyl alcohol

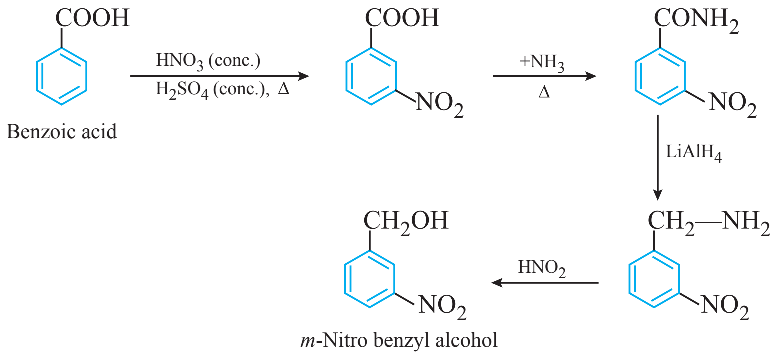
(*iii*) Benzaldehyde to benzophenone **[*CBSE (AI) 2011*]**

Ans. (*i*)

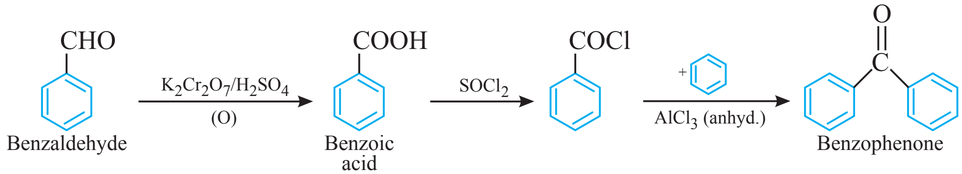


$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{\text{dil. NaOH}} \underset{\text{3-Hydroxybutanal}}{CH_3—\overset{\overset{OH}{|}}{C}H—CH_2—CHO}$$

(*ii*)



(*iii*)



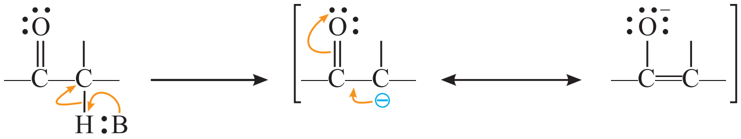
Q. 15. Give reasons:

(*i*) The α-hydrogen of aldehydes and ketones are acidic in nature. **[*CBSE 2020 (56/4/3)*]**

(*ii*) Propanone is less reactive than ethanal towards addition of HCN.

(*iii*) Benzoic acid does not give Friedel-Crafts reaction. **[*CBSE (F) 2016*]**

Ans. (*i*) The acidity of α-hydrogen atom of carbonyl carbon is due to the strong withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



(*ii*) This is due to steric and electronic reasons. Sterically, the presence of two methyl groups in propanone hinders more the approach of nucleophile to carbonyl carbon than in ethanal having one methyl group. Electronically two methyl groups reduce the positivity of the carbonyl carbon more effectively in propanone than in ethanal.

(*iii*) Benzoic acid does not give Friedel Craft reaction because:

(*a*) the carboxyl group is strongly deactivating.

(*b*)the catalyst $AlCl_3$ which is a lewis acid gets bonded to the carboxyl group strongly.

Long Answer Questions [5 marks]

Q. 1. Give names of the reagents that bring about the following transformations:

(*i*) Hexan-1-ol to hexanal

(*ii*) *p*-Fluorotoluene to *p*-fluorobenzaldehyde

(*iii*) Ethanenitrile to ethanol

(*iv*) Allyl alcohol to propenal

(*v*) Ethanoic acid to ethanol

Ans. (*i*) $[C_5H_5NH]^+[CrO_3Cl]^-$ (PCC)

(*ii*) CrO_3 in the presence of acetic anhydride/1. CrO_2Cl_2 2. H_3O^+

(*iii*) Diisobutyl aluminium hydride (DIBAL-H)

(*iv*) PCC

(*v*) $LiAlH_4$

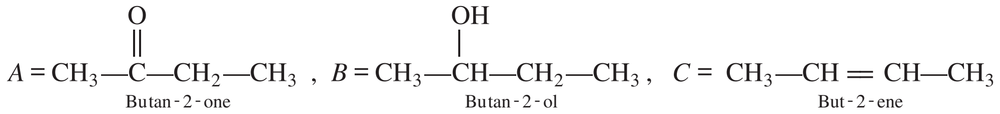
Q. 2. **(*i*) A ketone *A* which undergoes haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms mono-ozonide *D*. The compound *D* on hydrolysis in presence of zinc dust gives only acetaldehyde. Write the structures and IUPAC names of *A, B* and *C*. Write down the reactions involved.**

(*ii*) Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.

(*a*) PhMgBr and then H_3O^+

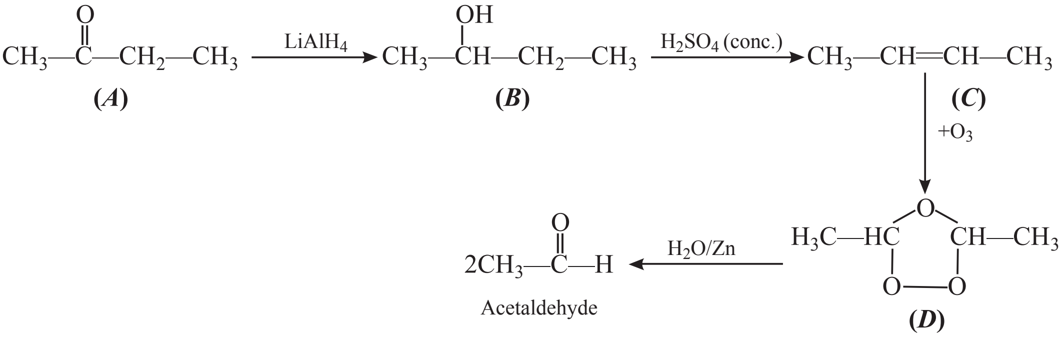
(*b*) Tollens' reagent. [*CBSE Sample Paper 2017*]

Ans. (*i*)

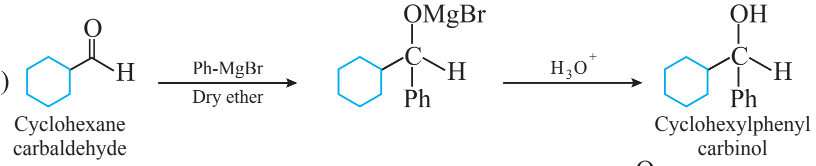


$$A = CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3,\quad B = CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-CH_3,\quad C = CH_3-CH=CH-CH_3$$

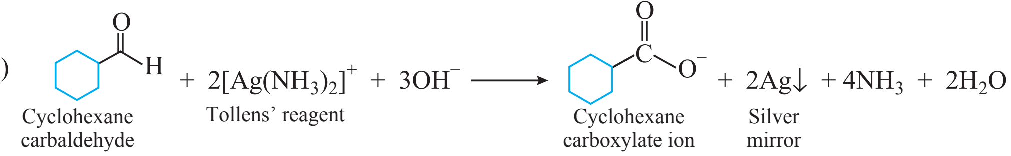
The reactions are as follows:



(*ii*) (*a*)



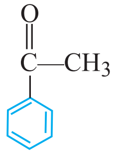
(*b*)



Q. 3. **Write the structures of *A, B, C, D* and *E* in the following reactions:** [*CBSE Delhi 2016*]

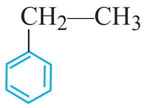
$$\begin{tikzcd}
C_6H_6 \arrow[r, "CH_3COCl", "Anhyd.\ AlCl_3"'] & A \arrow[r, "Zn\text{-}Hg/conc.\ HCl"] \arrow[d, "NaOI"] & B \arrow[r, "(i)\ KMnO_4\text{–}KOH,\ \Delta", "(ii)\ H_3O^+"'] & C \\
 & D + E & &
\end{tikzcd}$$

Ans. *A* =



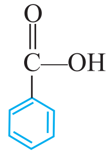
Acetophenone

; *B* =



Ethyl benzene

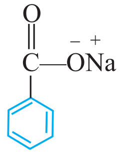
; *C* =



Benzoic acid

; *D* or *E* = CHI_3 ; *E* or *D* =

Iodoform



Sodium benzoate

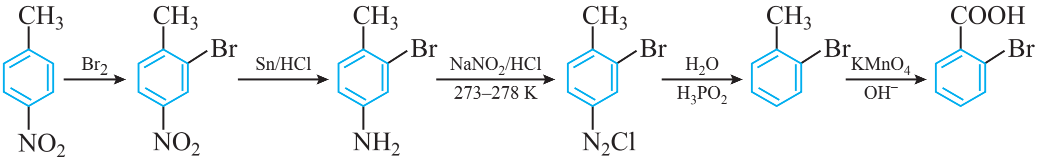
Q. 4. **(*i*) Carry out the following conversions:** **[*CBSE 2019 (56/4/1)*]**

(*a*) *p*-nitrotoluene to 2-bromobenzoic acid

(*b*) Propanoic acid to acetic acid

(*ii*) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds, B and C. Compound B gives positive Fehling test and also reacts with iodine and NaOH solution. Compound C does not give Fehling solution test but forms iodoform. Identify the compounds A, B and C.

Ans. (*i*) (*a*)



(*b*) $CH_3CH_2COOH \xrightarrow[\text{Heat}]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2$

$\xrightarrow[273\text{ K}]{HNO_3} CH_3CH_2OH \xrightarrow{KMnO_4/H^+ \text{ or } OH^-} CH_3COOH$

(*ii*) A : 2-Methylbut-2-ene/$CH_3CH{=}C(CH_3)_2$

B: Ethanal/Acetaldehyde /CH_3CHO

C: Propanone/Acetone /CH_3COCH_3

Q. 5. **(*i*) Write the structures of *A, B, C* and *D* in the following reactions:**

$$\begin{tikzcd}
C_6H_5COCl \arrow[r, "H_2/Pd - BaSO_4"] & A \arrow[r, "conc.\ NaOH"] \arrow[d, "CH_3MgBr/H_3O^+"] & B + C \\
& D &
\end{tikzcd}$$

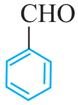
(*ii*) Distinguish between the following:

(*a*) C_6H_5—$COCH_3$ and C_6H_5—$COCH_2CH_3$

(*b*) Propanal and butan-2-one **[*CBSE (F) 2014*]**

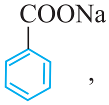
(*iii*) Write the structure of 2-hydroxybenzaldehyde. **[*CBSE Chennai 2015*]**

Ans. (*i*) A =



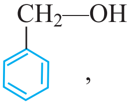
Benzaldehyde

, B or C =



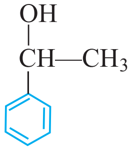
Sodium benzoate

, C or B =



Benzyl alcohol

, D =



1-Phenyl ethanol

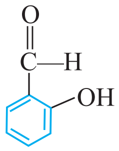
(*ii*) (*a*) $C_6H_5COCH_3$ being a methyl ketone gives iodoform test while $C_6H_5COCH_2CH_3$ does not.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \longrightarrow C_6H_5COONa + \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow} + 2NaOH$$

(*b*) Propanal being an aldehyde reduces Tollens' reagent to silver mirror but propanone being a ketone does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + \underset{\substack{\text{Silver}\\\text{mirror}}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{\text{Tollens' reagent}} \text{No silver mirror}$$

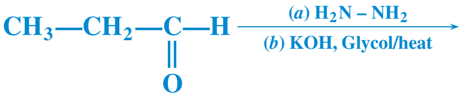
(*iii*) 

Q. 6. **(*i*) Carry out the following conversions:**

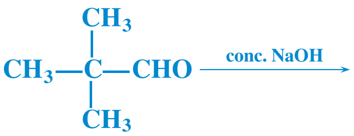
(*a*) Benzoic acid to aniline

(*b*) Bromomethane to ethanol

(*ii*) Write the structure of major product(s) in the following:

(*a*) 

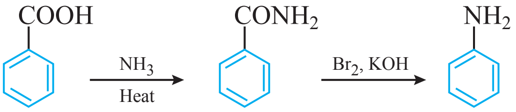
$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[(b)\ \text{KOH, Glycol/heat}]{(a)\ H_2N-NH_2}$$

(*b*) 

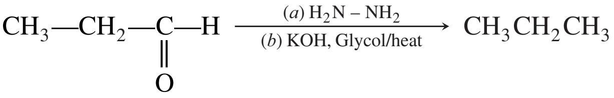
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO \xrightarrow{\text{conc. NaOH}}$$

(*c*) 

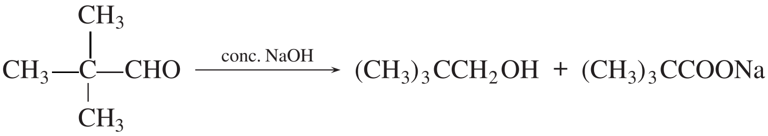
[*CBSE 2019 (56/4/1)*]

Ans. (*i*) (*a*) 

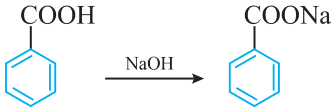
(*b*) $CH_3Br \xrightarrow{\text{KCN (alc.)}} CH_3CN \xrightarrow[H^+/OH^-]{H_2O} CH_3COOH \xrightarrow[H_3O^+]{\text{LiAlH}_4\text{/Ether or } B_2H_6} CH_3CH_2OH$

(*ii*) (*a*) 

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow[(b)\ \text{KOH, Glycol/heat}]{(a)\ H_2N-NH_2} CH_3CH_2CH_3$$

(*b*) 

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO \xrightarrow{\text{conc. NaOH}} (CH_3)_3CCH_2OH + (CH_3)_3CCOONa$$

(*c*) 

Q. 7. **(*i*) Give a simple chemical test to distinguish between benzaldehyde and ethanal.** [*CBSE (F) 2013*]

(*ii*) Bring out the following conversions:

(*a*) 4-Nitrotoluene to 2-bromobenzoic acid

(*b*) Ethylcyanide to 1-phenyl propanone

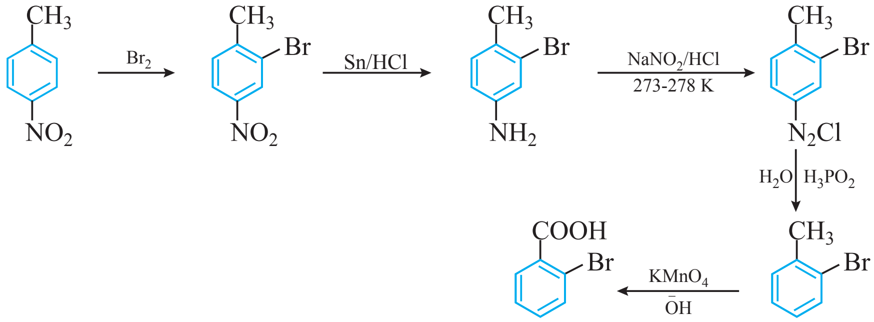
(*iii*) A and B are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

Ans. (*i*) **Benzaldehyde and Ethanal**

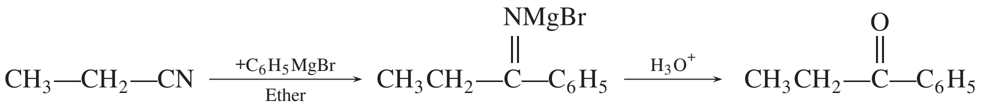
Ethanal reacts with NaOI (I_2/NaOH) to form yellow precipitate of iodoform while benzaldehyde does not give this test.

$$CH_3CHO + 3I_2 + 3NaOH \longrightarrow HCO\overset{-}{O}\overset{+}{Na} + \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3\downarrow} + 3NaI + 3H_2O$$

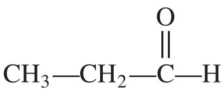
(*ii*) (***a***) **4-Nitrotoluene to 2-bromobenzoic acid**



(***b***) **Ethylcyanide to 1-phenyl propanone**

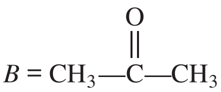


$$CH_3-CH_2-CN \xrightarrow[\text{Ether}]{+C_6H_5MgBr} CH_3CH_2-\overset{\overset{NMgBr}{\|}}{C}-C_6H_5 \xrightarrow{H_3O^+} CH_3CH_2-\overset{\overset{O}{\|}}{C}-C_6H_5$$

(*iii*) 

$A = CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

Propanal



$B = CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

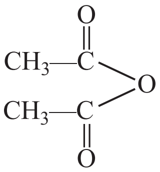
Propanone

Reaction involved:

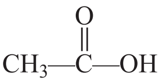
$$\underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 3I_2 + 4NaOH \xrightarrow{\Delta} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + CH_3-\overset{\overset{O}{\|}}{C}-O^{-}-Na^{+} + 3NaI + 3H_2O$$

Q. 8. **An organic compound 'A' on treatment with ethyl alcohol gives carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with $KMnO_4$ also gives 'B'. B on heating with $Ca(OH)_2$ gives 'E' with molecular formula C_3H_6O. 'E' does not give Tollens' test or reduce Fehling solution but forms 2, 4-dinitrophenyl hydrazone. Identify A, B, C, D, E.** **[*HOTS*]**

Ans. A =

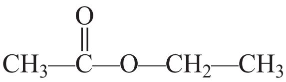


Acetic anhydride



$B = CH_3-\overset{\overset{O}{\|}}{C}-OH$

Acetic acid

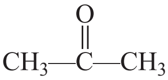


$C = CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

Ethyl acetate

$D = CH_3-CH_2-OH$

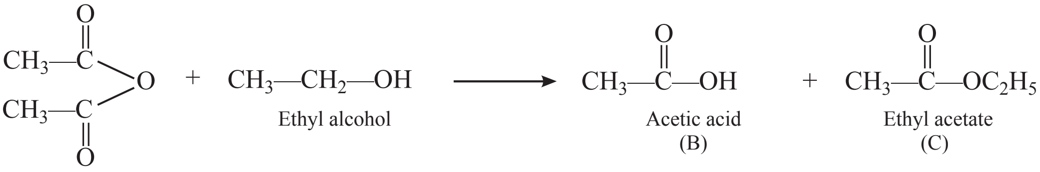
Ethyl alcohol

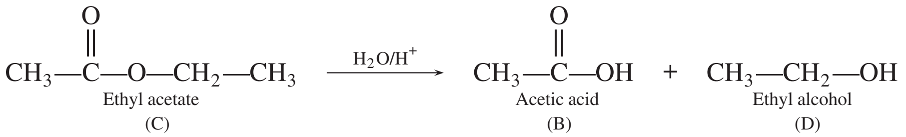


$E = CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

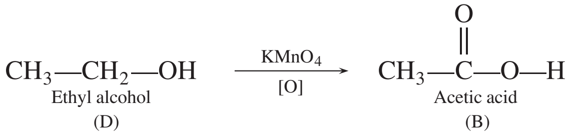
Acetone

Reactions are:

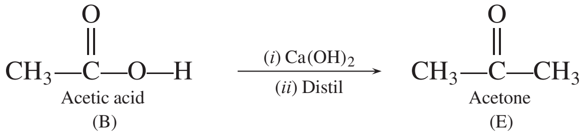




$$\underset{\substack{\text{Ethyl acetate}\\ \text{(C)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3} \xrightarrow{H_2O/H^+} \underset{\substack{\text{Acetic acid}\\ \text{(B)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\substack{\text{Ethyl alcohol}\\ \text{(D)}}}{CH_3-CH_2-OH}$$



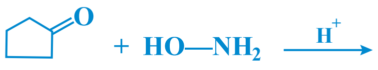
$$\underset{\substack{\text{Ethyl alcohol}\\ \text{(D)}}}{CH_3-CH_2-OH} \xrightarrow[\text{[O]}]{KMnO_4} \underset{\substack{\text{Acetic acid}\\ \text{(B)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H}$$



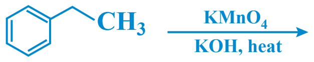
$$\underset{\substack{\text{Acetic acid}\\ \text{(B)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H} \xrightarrow[(ii)\ \text{Distil}]{(i)\ Ca(OH)_2} \underset{\substack{\text{Acetone}\\ \text{(E)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

Q. 9. Complete each synthesis by giving missing starting material, reagent or products:

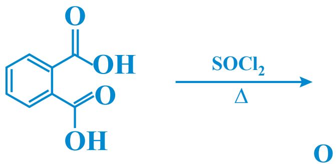
(*i*)



(*ii*)



(*iii*)

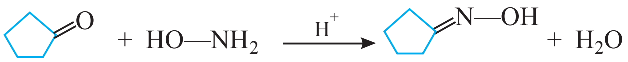


(*iv*)

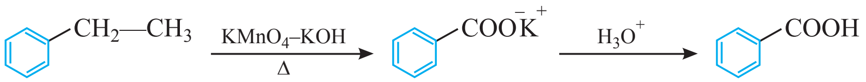
(*v*)

[*CBSE Sample Paper 2017*]

Ans. (*i*)

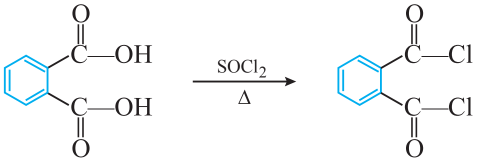


(*ii*)



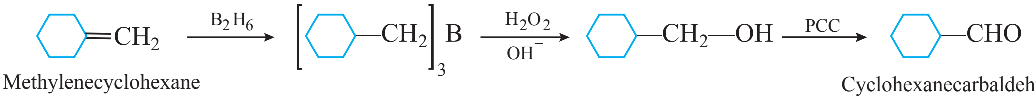
Ethylbenzene Benzoic acid

(*iii*)



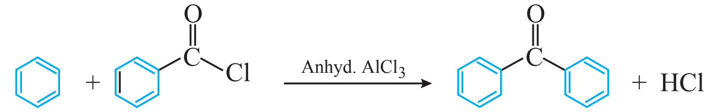
Phthalic acid Phthaloyl chloride

(*iv*)



Methylenecyclohexane Cyclohexanecarbaldehyde

(*v*)



Benzene Benzoyl chloride Benzophenone

Q. 10. **(*i*) Write the structures of *A*, *B*, *C* and *D* in the following reactions:**

$$\begin{tikzcd}
CH_3CN \arrow[r, "(i)\ SnCl_2—HCl", "(ii)\ H_2O"'] & A \arrow[r, "dil.\ NaOH"] \arrow[d, "HCN"] & B \arrow[r, "Heat"] & C \\
 & D & &
\end{tikzcd}$$

(*ii*) Distinguish between:

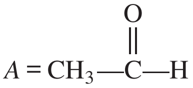
(*a*) $C_6H_5—CH{=}CH—COCH_3$ and $C_6H_5—CH{=}CH—COCH_2CH_3$

(*b*) CH_3CH_2COOH and HCOOH

(*iii*) Arrange the following in the increasing order of their boiling points:

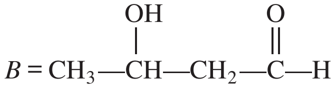
CH_3CH_2OH, CH_3COCH_3, CH_3COOH **[*CBSE North 2016*]**

Ans. (*i*)



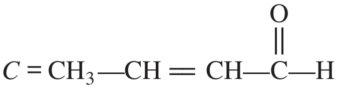
$A = CH_3—\overset{\overset{\large O}{\|}}{C}—H$

Ethanal



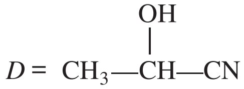
$B = CH_3—\overset{\overset{\large OH}{|}}{CH}—CH_2—\overset{\overset{\large O}{\|}}{C}—H$

3-Hydroxybutanal



$C = CH_3—CH = CH—\overset{\overset{\large O}{\|}}{C}—H$

But-2-enal



$D = CH_3—\overset{\overset{\large OH}{|}}{CH}—CN$

2-Hydroxy propanenitrile

(*ii*) (*a*) $C_6H_5CH{=}CH—COCH_3$ on warming with NaOI (I_2/NaOH) gives yellow precipitate of iodoform while $C_6H_5CH{=}CH—CO—CH_2—CH_3$ does not.

$$C_6H_5CH = CHCOCH_3 + 3NaOI \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3\downarrow} + C_6H_5CH = CH—CO\overset{-}{O}\overset{+}{Na} + 2NaOH$$

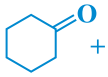
(*b*) Formic acid reduces Tollens' reagent to metallic silver while propionic acid does not.

$$\underset{\text{Formic acid}}{HCOOH} + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2 + 2H_2O + 4NH_3$$

(*iii*) $CH_3—CO—CH_3 < CH_3—CH_2—OH < CH_3—COOH$

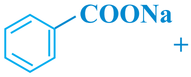
Q. 11. **(*i*) Write the product(s) in the following reactions:**

(*a*)



+ HCN $\longrightarrow$?

(*b*)



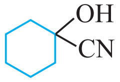
+ NaOH $\xrightarrow[\Delta]{CaO}$?

(*c*) $CH_3—CH{=}CH—CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL–H}$?

(*ii*) Give simple chemical tests to distinguish between the following pairs of compounds:

(*a*) Butanal and Butan-2-one **(*b*) Benzoic acid and Phenol** **[*CBSE (AI) 2017*]**

Ans. (*i*) (*a*)



Cyclohexane cyanohydrin

(*b*)

Benzene

(*c*) $\underset{\text{But-2-en-1-al}}{CH_3—CH = CH—CHO}$

(*ii*)(*a*) Butanal being an aldehyde reduces Tollens' reagent to give silver mirror but butan-2-one being a ketone does not.

$$\underset{\text{Butanal}}{CH_3—CH_2—CH_2—CHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow$$

$$\underset{\text{Butanoate ion}}{CH_3—CH_2—CH_2—COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(*b*) Benzoic acid decomposes $NaHCO_3$ to produce brisk effervescence due to evolution of CO_2 while phenol does not.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5CO\overset{-}{O}\overset{+}{Na}} + CO_2\uparrow + H_2O$$

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. **Toluene can be oxidised to benzoic acid by**
   (*a*) $KMnO_4$(alk.) (*b*) $K_2Cr_2O_7$
   (*c*) Both (*d*) None
2. **Carbonyl group undergoes**
   (*a*) Electrophilic addition reaction (*b*) Nucleophilic addition reactions
   (*c*) Both (*d*) None
3. **Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives**
   (*a*) Acetic acid (*b*) Acetaldehyde
   (*c*) Formaldehyde (*d*) Formic acid

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.* **(3 × 1 = 3)**

4. **Assertion (*A*)** : Acetic acid does not undergo haloform reaction.
   Reason (*R*) : Acetic acid has no alpha hydrogen.
5. **Assertion (*A*)** : 2, 2-Dimethylpropanal undergoes Cannizzaro reaction with conc. NaOH.
   Reason (*R*) : Cannizzaro reaction is a disproportionation reaction.
6. **Assertion (*A*)** : Nitration of benzoic acid gives *m*-nitrobenzoic acid.
   Reason (*R*) : Carboxyl group increases the electron-density at *meta*-position.

Answer the following questions:

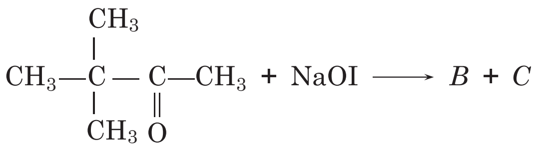
7. Write the IUPAC name of the following compound:

(1)

8. How will you distinguish between ethanol and ethanal? **(1)**
9. Complete the following reactions by identifying *A*, *B* and *C*.

   (*i*) $A + H_2(g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CH—CHO$

   (*ii*)



$$CH_3—\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}—\underset{\underset{\large O}{\|}}{C}—CH_3 + NaOI \longrightarrow B + C$$

(2)

10. Give reasons for the following:

(*i*) Benzaldehyde reduces Tollens' reagent but not the Fehling's or Benedict's solution.

(*ii*) $(CH_3)_2CH—CHO$ undergoes aldol condensation whereas $(CH_3)_3C—CHO$ does not.

[CBSE (F) 2017] **(2)**

11. Write the reagents required in the following reactions: ***[CBSE Allahabad 2015]***

(*i*) $CH_2{=}CH—CH_2OH \xrightarrow{?} CH_2{=}CH—CHO$

(*ii*) $CH_3—COOH \xrightarrow{?} CH_3—CONH_2$ **(2)**

12. An organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It does not reduce Tollens' or Fehling's reagent and does not decolourise bromine water also. On oxidation with chromic acid (H_2CrO_4), it gives a carboxylic acid (B) with molecular formula $C_7H_6O_2$. Deduce the structures of A and B. **(2)**

13. Write the products formed when $(CH_3)_3C—CHO$ reacts with the following:

(*i*) Zinc amalgam and dilute hydrochloric acid

(*ii*) Concentrated sodium hydroxide solution ***[CBSE 2020 (56/3/2)]***

(*iii*) Semicarbazide and a weak acid ***[CBSE 2019 (56/5/2)]*** **(3)**

14. Write the chemical equations for the following conversions (not more than 2 steps):

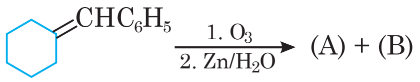
(*i*) Ethyl benzene to benzene

(*ii*) Acetaldehyde to butane-1, 3-diol

(*iii*) Acetone to propene **(3)**

15. An organic compound 'A' (C_3H_4) on hydration in presence of $H_2SO_4/HgSO_4$ gives compound 'B' (C_3H_6O). Compound 'B' gives white crystalline product (D) with sodium hydrogensulphite. It gives negative Tollens' test and positive iodoform's test. On drastic oxidation 'B' gives compound 'C' ($C_2H_4O_2$) along with formic acid. Identify compounds 'A', 'B' and 'C' and explain all the reactions. **(3)**

16. Identify the unknown organic compounds (A) to (E) in the following series of chemical reactions.

(*i*) 

(*ii*) $(A) + (B) \xrightarrow{\text{dil. NaOH}} (C) + H_2O$

(*iii*) $(C) \xrightarrow[\text{2. Zn/H}_2\text{O}]{\text{1. O}_3} (A) + (D)$

(*iv*) $(D) \xrightarrow[\Delta]{H_2/Ni} (E)$ **(5)**

Answers

1. (*c*) **2.** (*b*) **3.** (*a*) **4.** (*c*) **5.** (*b*) **6.** (*c*)

Amines

basic concepts

1. Introduction

Alkyl or aryl derivatives of ammonia are regarded as amines. These are obtained by replacing one or more hydrogen atoms by alkyl or aryl groups. Amines are classified as primary, secondary or tertiary depending upon whether one, two or three atoms of hydrogen have been replaced by alkyl or aryl groups.

$$NH_3 \xrightarrow[+CH_3]{-H} \underset{\substack{\text{Methylamine}\\ 1^\circ(\text{Primary})}}{CH_3NH_2} \xrightarrow[+CH_3]{-H} \underset{\substack{\text{Dimethylamine}\\ 2^\circ(\text{Secondary})}}{(CH_3)_2NH} \xrightarrow[+CH_3]{-H} \underset{\substack{\text{Trimethylamine}\\ 3^\circ(\text{Tertiary})}}{(CH_3)_3N}$$

Thus, characteristic functional groups for 1°, 2° or 3° amines are:

$$\underset{\text{Primary}}{—NH_2} \qquad \underset{\text{Secondary}}{—\overset{|}{N}H} \qquad \underset{\text{Tertiary}}{—\overset{|}{N}—}$$

Amines are said to be ‘simple’ when all the alkyl or aryl groups are the same, and ‘mixed’ when they are different.

There is another class of compounds wherein all the four hydrogen atoms of an ammonium salt have been replaced by alkyl or aryl groups. Such compounds are named as quaternary ammonium salts.

$$[NH_4]^+X^- \xrightarrow[+4R]{-4H} \underset{\text{Tetra alkylammonium halide}}{[NR_4]^+X^-}$$

2. Structure of Amines

Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore sp^3 hybridised and the geometry of amines is pyramidal. Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle C—N—E, (where E is C or H) is less than 109.5°; for instance, it is 108° in case of trimethylamine as shown in Fig. 13.1 alongside.

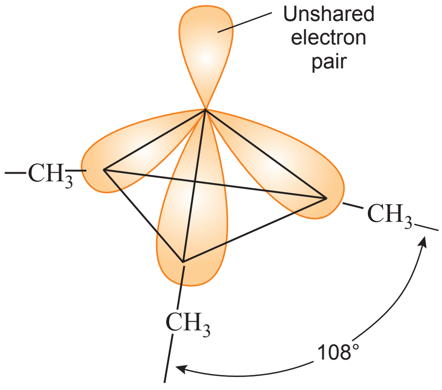
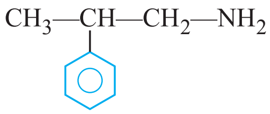


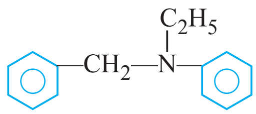
Fig. 13.1: Pyramidal Trimethylamine

3. Nomenclature

In the trivial system, amines are named as alkylamine but in the IUPAC system, these are named as alkanamine (replacing ‘e’ of alkane with amine).

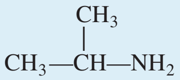
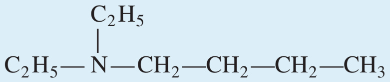
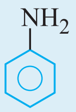
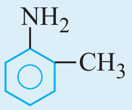
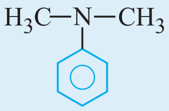


2-Phenyl propanamine (1°)



N-Benzyl-N-ethyl benzenamine

Table 13.1: Nomenclature of Some Amines

Common Name	Structural Formula	IUPAC Name
Ethyl amine	$CH_3—CH_2—NH_2$	Ethanamine
Isopropyl amine	 $CH_3—\overset{\overset{CH_3}{\vert}}{CH}—NH_2$	Propan-2-amine
Ethyl methyl amine	$CH_3—CH_2—NH—CH_3$	N-Methylethanamine
N, N-Diethylbutylamine	 $C_2H_5—\overset{\overset{C_2H_5}{\vert}}{N}—CH_2—CH_2—CH_2—CH_3$	N, N-Diethylbutan-1- amine
Allylamine	$CH_2{=}CH—CH_2—NH_2$	Prop-2-en-1-amine
Hexamethylenediamine	$H_2N—(CH_2)_6—NH_2$	Hexane-1, 6-diamine
Aniline		Benzenamine or Aniline
o-Toluidine		2-Methylaniline
N, N-Dimethylaniline		N, N-Dimethylbenzenamine

4. **Preparation of Amines:** Amines are prepared by the following methods:

(*a*) Reduction of nitro compounds:

$$R—NO_2 + 3H_2 \xrightarrow{Ni} \underset{1° \text{ amine}}{R—NH_2} + 2H_2O$$

$$\underset{\text{Nitroethane}}{CH_3—CH_2—NO_2} + 6[H] \xrightarrow[\text{Sn/HCl (conc.)}]{\text{Fe/HCl (conc.)}\ \text{or}} \underset{\text{Ethanamine}}{CH_3—CH_2—NH_2} + 2H_2O$$

(*b*) Ammonolysis of alkyl halides:

$$R—X + \underset{\text{(excess)}}{2NH_3} \longrightarrow \underset{\substack{1° \text{ amine} \\ \text{(Major product)}}}{R—NH_2} + NH_4X$$

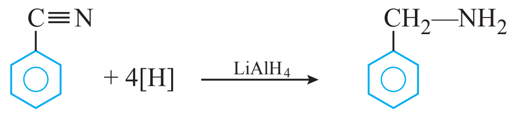
If alkyl halide is in excess, the amine formed further reacts with alkyl halide to form 2°, 3° amines and finally quaternary ammonium salts.

$$\underset{1° \text{ amine}}{R—NH_2} \xrightarrow{+R—X} \underset{2° \text{ amine}}{R_2NH} \xrightarrow{+R—X} \underset{3° \text{ amine}}{R_3N} \xrightarrow{+R—X} \underset{\substack{\text{Quaternary} \\ \text{ammonium salt}}}{R_4N^+X^-}$$

(*c*) Reduction of nitriles:

$$R—C \equiv N + 2H_2 \xrightarrow{Ni} \underset{1° \text{ amine}}{R—CH_2—NH_2}$$

$$R—C \equiv N + 4[H] \xrightarrow[\text{or } LiAlH_4]{Na(Hg)/C_2H_5OH} \underset{1° \text{ amine}}{R—CH_2—NH_2}$$



Benzyl amine

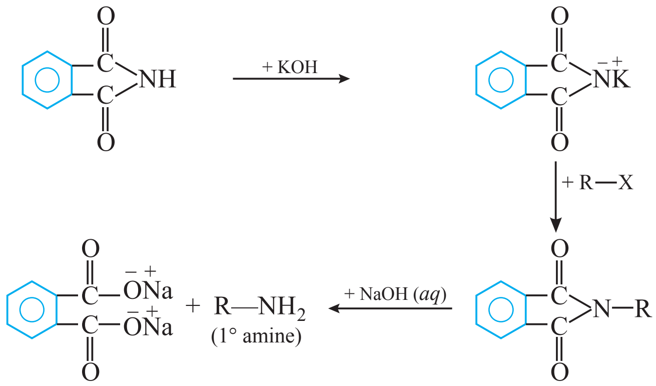
(*d*) Reduction of amides:

$$\underset{\text{Acid amide}}{R\text{—}CONH_2} + 4[H] \xrightarrow{LiAlH_4/\text{ether}} \underset{1^\circ\text{ amine}}{R\text{—}CH_2\text{—}NH_2} + H_2O$$

(*e*) Hoffmann's bromamide degradation reaction:

$$\underset{\text{Acid amide}}{R\text{—}CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{1^\circ\text{ amine}}{R\text{—}NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

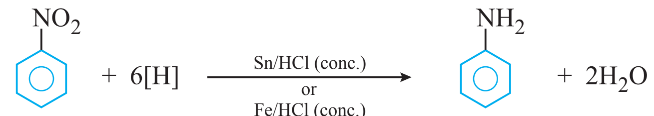
(*f*) Gabriel phthalimide synthesis:



Aromatic amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

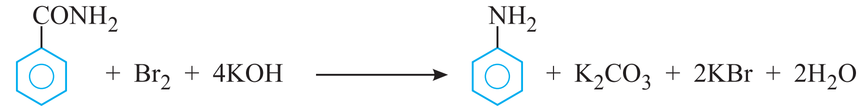
Preparation of Aniline:

(*i*) From nitrobenzene



Nitrobenzene Aniline

(*ii*) By Hoffmann bromamide degradation reaction



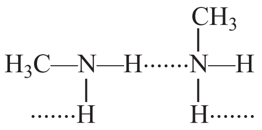
Benzamide Aniline

5. Physical Properties

(*i*) The lower members are combustible gases, members from C_3 to C_{11} are volatile liquids and from C_{12} onwards are solids. Lower aromatic amines are liquids while the higher ones are low melting solids.

(*ii*) Pure amines are almost colourless but develop colour on keeping in air for long time, especially, the aromatic amines. The colouration is due to oxidation of amines by air.

(*iii*) The boiling point increases with the increase in molecular weight. However, primary and secondary amines have higher boiling points than the tertiary amines of the same molecular weight. This is again due to the possibility of intermolecular hydrogen bonding between molecules of primary as well as secondary amines.



The hydrogen bonding between amine molecules is weaker than that between alcohols or carboxylic acids therefore amines have lower boiling points than the alcohols or carboxylic acids of comparable molecular masses.

(*iv*) The lower members are readily soluble in water, the solubility in water decreases and in organic solvents (alcohol and ether) increases with the increase in molecular weight.

Solubility of all the three classes of aliphatic amines in water is due to the formation of hydrogen bond between amine and water molecules. However, in higher amines, the alkyl group predominates over the amino group with the result that they have less tendency for forming hydrogen bond with water. This explains why the higher amines are insoluble in water.

Aromatic amines are insoluble in water. This is because of the larger hydrocarbon part. Thus, aniline is almost insoluble in water. However, all amines are quite soluble in organic solvents like benzene, ether, alcohol, etc.

6. **Basic Character of Amines:** Amines have a lone 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 K_b and pK_b values as explained below.

$$R—NH_2 + H_2O \rightleftharpoons R—\overset{+}{N}H_3 + \overset{-}{O}H$$

$$K_b = \frac{[R—\overset{+}{N}H_3][\overset{-}{O}H]}{[R—NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b stronger is the base.

(*a*) Amines versus alcohols, ethers and esters: Since nitrogen is less electronegative than oxygen, it is in a better position to accommodate the positive charge of the proton. Therefore, amines are more basic than alcohols, ethers, esters, etc.

(*b*) Alkylamines versus ammonia: In aliphatic amines, the electron-releasing alkyl groups stabilise their ammonium cations by dispersing the positive charge, and in parent amines make the nitrogen unshared electrons more available for sharing with a proton. Thus, the basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions.

Basicity Order: $(Et)_2NH > Et_3N > EtNH_2 > NH_3$; $(Me)_2NH > MeNH_2 > (Me)_3N > NH_3$

In gas phase, where the solvent effect is missing, the basic trend in nature is as expected, *i.e.*, tertiary amine > secondary amine > primary amine > ammonia.

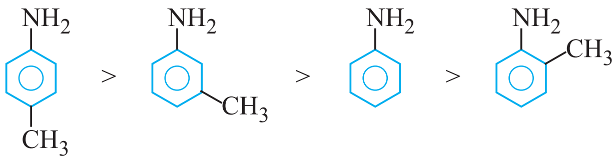
Anomalous basic strength of tert-alkylamines: In aqueous solution, the substituted ammonium cations are stabilised not only by electron-releasing effect of the alkyl groups but also by solvation with water molecules. It is a combination of electron-releasing, H-bonding and steric factors that determine the stability of the ammonium cations in solution and thereby resulting in the basic strength order of aliphatic amines as secondary > tertiary > primary amines.

(*c*) Aromatic amines versus ammonia and aliphatic amines: Aromatic amines are weaker bases than ammonia and aliphatic amines. Since resonance stabilises an aromatic amine more than it stabilises its ammonium cation, the proton acceptability and thereby basic strength of aromatic amines would be less. It may also be argued that due to resonance, unshared electrons on nitrogen in aromatic amines are less available for sharing with a proton—a feature opposite to that in alkyl amines.

(*d*) Effect of substituent on the basicity of aromatic amines:

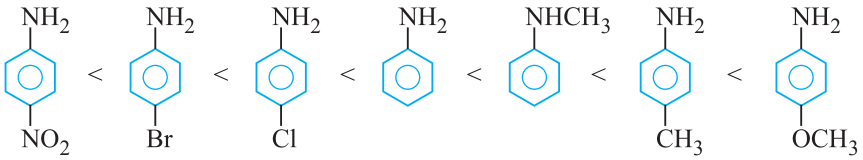
(*i*) Electron-donating groups such as —CH_3, —OCH_3, –NH_2, etc., increase the basicity while electron-withdrawing substituents such as —NO_2, —CN, halogens, etc., decrease the basicity of amines. The effect of these substituents is more at *p*- than at *m*-positions.

(*ii*) Among the isomeric toluidines, the basic strength with respect to aniline decreases as:



(*iii*) The order of basic strength of some amino compounds:

Ortho-substituted anilines are weaker bases than aniline irrespective of the nature of the substituent. This is called ortho-effect and it is probably due to a combination of steric and electronic factors.



7. Chemical Properties of Amines:

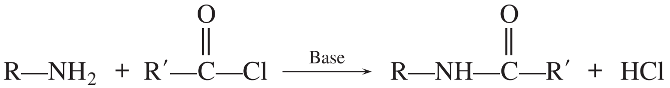
(*a*) Alkylation:

$$\underset{\text{Ethylamine}}{CH_3—CH_2—NH_2} \xrightarrow[-\,HBr]{+CH_3—CH_2—Br} (CH_3—CH_2)_2NH$$

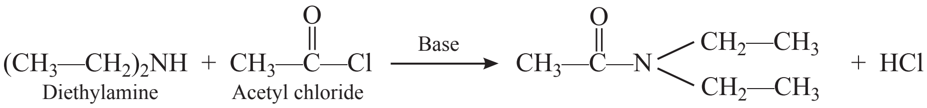
$$(CH_3—CH_2)_2NH \xrightarrow[-\,HBr]{+CH_3—CH_2—Br} \underset{\text{Triethylamine}}{(CH_3—CH_2)_3N}$$

$$\underset{\text{Triethylamine}}{(CH_3—CH_2)_3N} \xrightarrow{+CH_3—CH_2—Br} \underset{\text{Tetraethyl ammonium bromide}}{(CH_3—CH_2)_4NBr}$$

(*b*) Acylation:

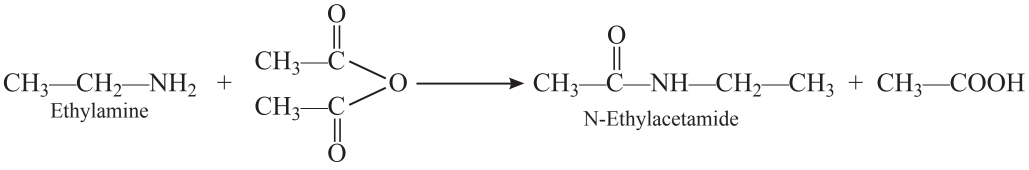


$$R—NH_2 + R'—\overset{\overset{\large O}{\|}}{C}—Cl \xrightarrow{\text{Base}} \underset{\text{N - substituted amide}}{R—NH—\overset{\overset{\large O}{\|}}{C}—R'} + HCl$$



Diethylamine Acetyl chloride

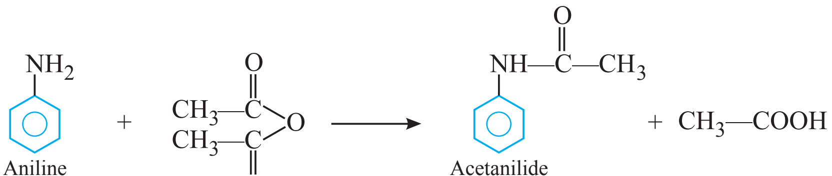
N, N-Diethylacetamide



Ethylamine

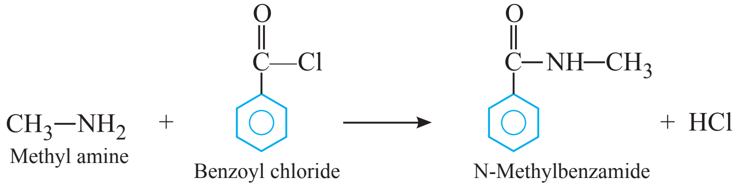
N-Ethylacetamide

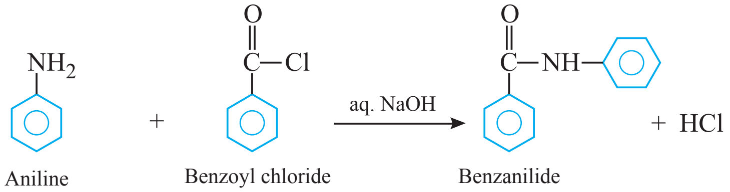
Acetic anhydride



Aniline

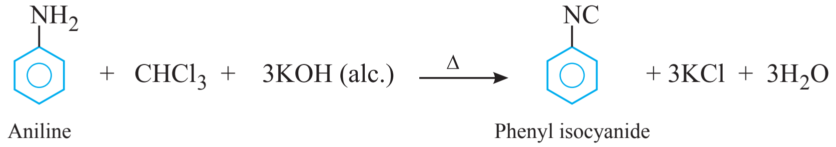
Acetanilide
or
N-Phenylethanamide





(*c*) Reaction with chloroform (Carbylamine reaction):

$$R—NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} \underset{\text{Alkyl carbylamine}}{R—NC} + 3KCl + 3H_2O$$



(*d*) Reaction with nitrous acid:

Reaction with nitrous acid helps in distinguishing between amines. Primary amines react with nitrous acid to form alcohols.

$$\underset{1°\ \text{amine}}{R—NH_2} + HONO \xrightarrow{NaNO_2/HCl} R—OH + N_2 + H_2O$$

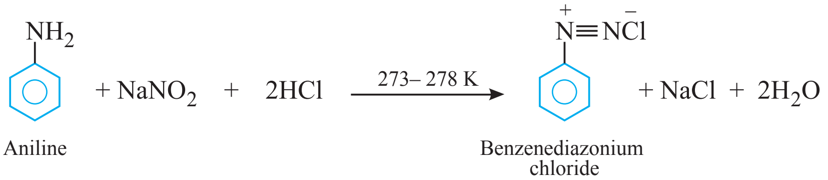
Secondary amines react with nitrous acid to form a yellow green oily layer of N-nitrosoamines. N-Nitrosoamines on warming with a crystal of phenol and a few drops of conc. H_2SO_4 form green solution which when treated with aqueous NaOH, turns deep blue and then red on dilution. This reaction is called Liebermann's nitroso reaction.

$$\underset{2°\ \text{Amine}}{R_2NH} + HNO_2 \longrightarrow \underset{\text{N-Nitrosoamine}}{R_2N—N=O} + H_2O$$

tert-Amines readily dissolve in nitrous acid forming crystalline trialkyl ammonium nitrite.

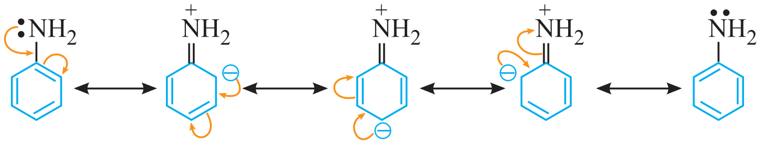
$$R_3N + HNO_2 \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{R_3\overset{+}{N}HNO_2^-}$$

(*e*) Diazotization:

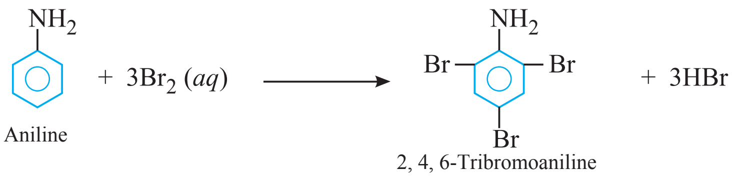


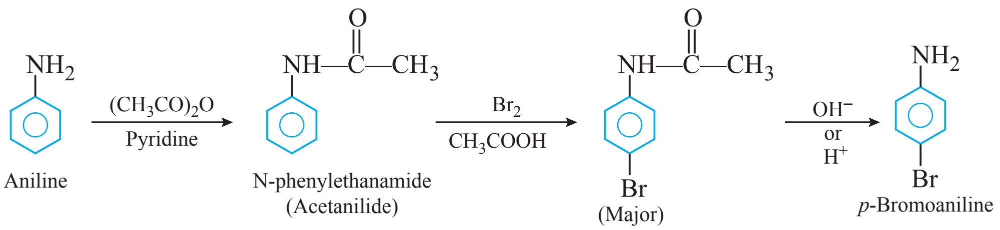
(*f*) Electrophilic substitution reactions:

Due to resonance, electron density increases at ortho and para positions as compared to meta positions. Therefore, $—NH_2$ group directs the incoming group to ortho and para positions.

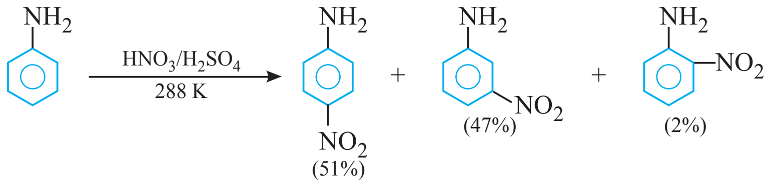


(*i*) Bromination:

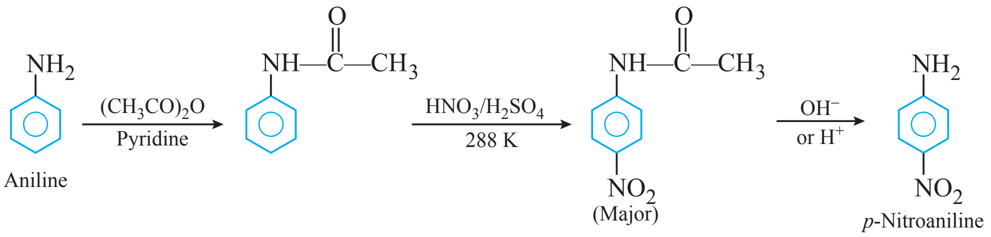




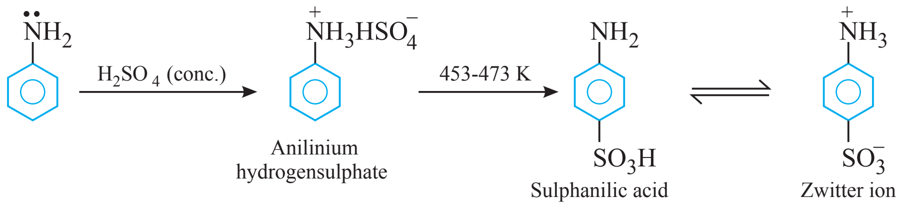
(*ii*) Nitration:



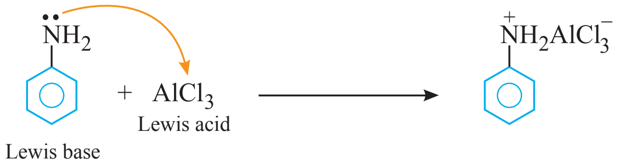
In strongly acidic medium, significant amount of meta isomer is obtained. This is due to the formation of anilinium ion which is meta directing. However, the *p*-nitro derivative can be obtained as the major product by protecting the —NH_2 group by acetylation reaction.



(*iii*) Sulphonation:



(*iv*) Friedel–Crafts reaction:



Due to salt formation, nitrogen of aniline acquires positive charge and thus acts as a strong deactivating group and hence does not allow Friedel–Crafts reaction to occur.

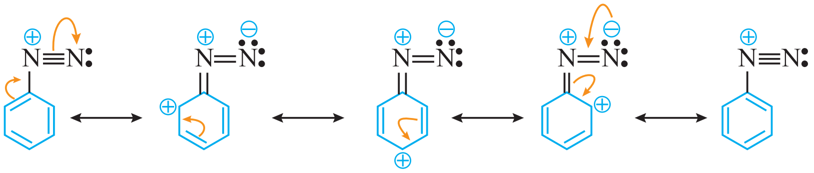
8. Diazonium Salts

(*a*) General formula: $R\overset{+}{N}_2X^-$

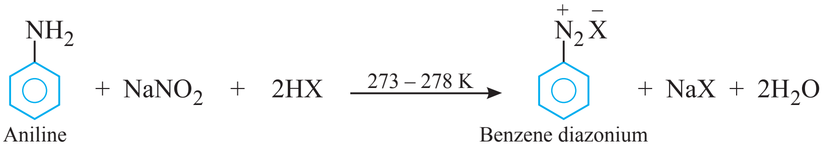
where R stands for an aryl group and X^- ion may be Cl^-, Br^-, HSO_4^-, BF_4^-, etc. The $\overset{+}{N}_2(—\overset{+}{N} \equiv N)$ is called the diazonium group.

(*b*) Stability of diazonium salts:

Arenediazonium salts are much more stable than alkyl diazonium salts. The stability of arene diazonium salt is due to the dispersal of the positive charge over the benzene ring as shown below.



(*c*) Preparation of diazonium salts



This process of conversion of a primary aromatic amine into its diazonium salt is called diazotization.

9. Chemical Properties of Diazonium Salts:

The reactions of diazonium salts can be divided into two categories, namely

(*a*) Reactions involving displacement of nitrogen.

(*b*) Reactions involving retention of diazo group.

(*a*) Reactions involving displacement of nitrogen:

(*i*) Replacement by halide or cyanide ion:

$$\left.\begin{array}{l} Ar\overset{+}{N}_2X^- \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2 \\ Ar\overset{+}{N}_2X^- \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2 \\ Ar\overset{+}{N}_2X^- \xrightarrow{CuCN/KCN} ArCN + N_2 \end{array}\right\} \text{Sandmeyer's reactions}$$

$$\left.\begin{array}{l} Ar\overset{+}{N}_2X^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuX \\ Ar\overset{+}{N}_2X^- \xrightarrow{Cu/HBr} ArBr + N_2 + CuX \end{array}\right\} \text{Gatterman's reaction}$$

(*ii*) Replacement by iodide ion:

$$\underset{\text{Benzene diazonium chloride}}{Ar\overset{+}{N}_2Cl^-} + KI \longrightarrow \underset{\text{Iodobenzene}}{ArI} + KCl + N_2$$

(*iii*) Replacement by fluoride ion:

$$Ar\overset{+}{N}_2Cl^- + HBF_4 \longrightarrow Ar\overset{+}{N}_2BF_4^- \xrightarrow{\Delta} Ar—F + BF_3 + N_2$$

(*iv*) Replacement by H:

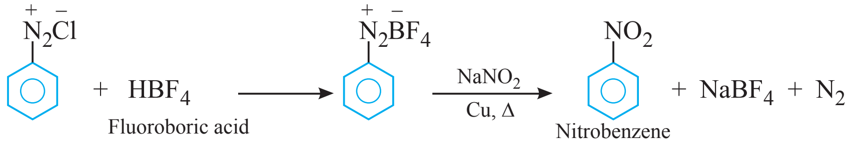
$$Ar\overset{+}{N}_2Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

$$Ar\overset{+}{N}_2Cl^- + CH_3—CH_2—OH \longrightarrow ArH + N_2 + CH_3—CHO + HCl$$

(*v*) Replacement by hydroxyl group:

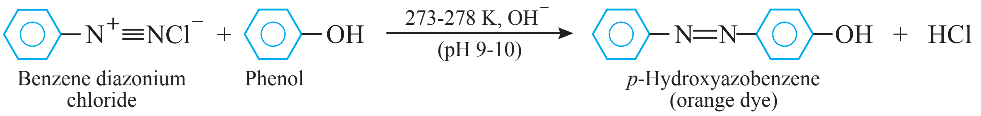
$$Ar\overset{+}{N}_2Cl^- + H_2O \xrightarrow{\Delta} \underset{\text{Phenol}}{ArOH} + N_2 + HCl$$

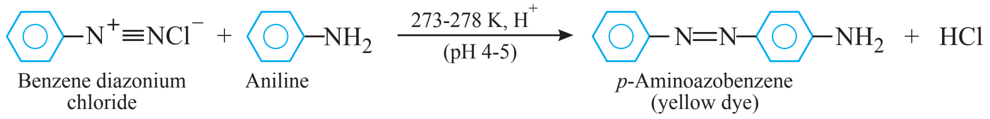
(*vi*) Replacement by —NO_2 group:

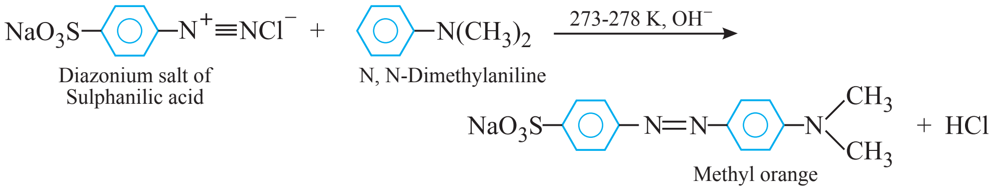


(*b*) **Reactions involving retention of diazo group:**

Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula, Ar—N=N—Ar is called coupling reaction. The mechanism is basically that of electrophilic substitution where the diazonium ion is electrophile. In this reaction, the nitrogen atoms of the diazo group are retained in the product. The coupling with phenols takes place in mildly alkaline medium while with amines, it occurs under faintly acidic conditions. For example,



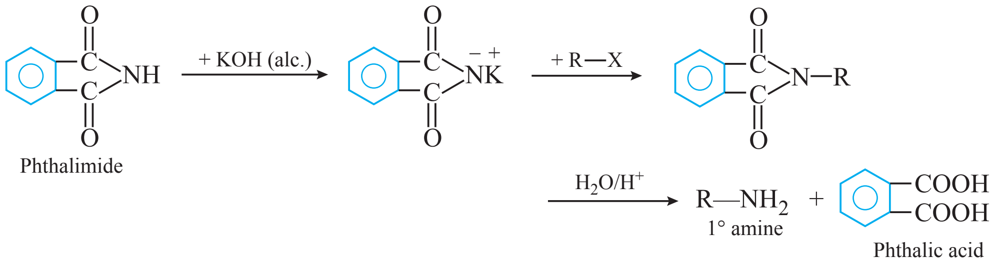




Coupling generally occurs at the *p*-position, w.r.t., the hydroxyl or the amino group, if free, otherwise it takes place at the *o*-position.

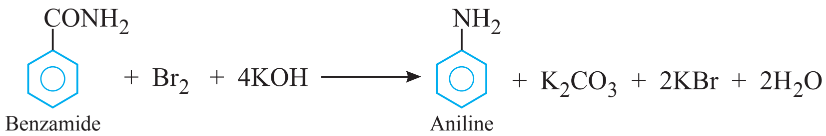
10. Some Important Name Reactions

(*a*) **Gabriel phthalimide synthesis:** This reaction is used for the preparation of aliphatic primary amines. In this reaction, phthalimide is first of all treated with ethanolic KOH to form potassium phthalimide. Potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide, which on hydrolysis with dilute hydrochloric acid gives a primary amine as the product.

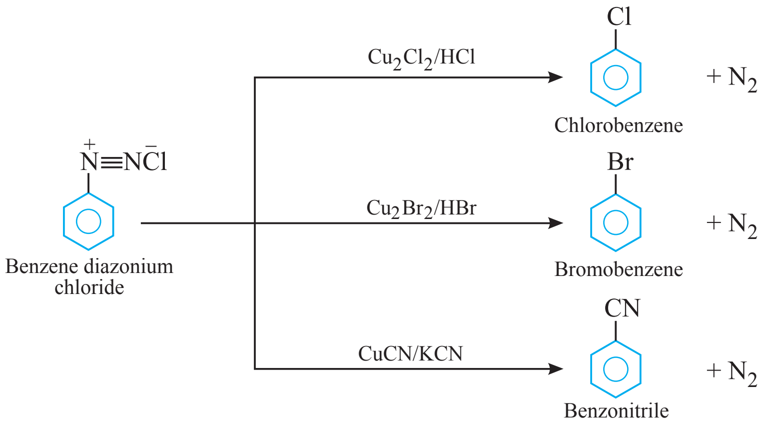


(*b*) **Hoffmann bromamide reaction:** When a primary acid amide is heated with an aqueous or ethanolic solution of NaOH or KOH and bromine (*i.e.*, NaOBr or KOBr), it gives a primary amine with one carbon atom less.

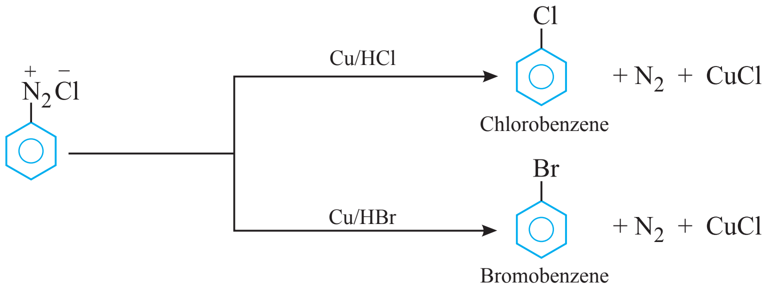
$$\underset{\text{Acid amide}}{R\text{—}CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{1^\circ\text{ amine}}{R\text{—}NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$



(*c*) **Sandmeyer's reaction:** The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene in the presence of Cu (I) ion. This reaction is called Sandmeyer's reaction.

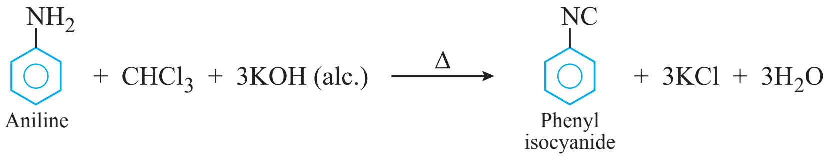


(*d*) **Gatterman's reaction:** Chlorine or bromine can be introduced in benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



(*e*) **Carbylamine reaction (Isocyanide test):** Aliphatic and aromatic primary amines when heated with chloroform and alcoholic solution of KOH give isocyanides (carbylamines) which have extremely unpleasant smell.

$$\underset{1^\circ\text{ amine}}{R\text{—}NH_2} + CHCl_3 + 3KOH\ (\text{alc.}) \xrightarrow{\Delta} \underset{\substack{\text{Alkyl}\\ \text{isocyanide}}}{R\text{—}NC} + 3KCl + 3H_2O$$



11. Uses of Amines:

(*i*) The quaternary ammonium salts of long chain aliphatic amines are used as detergents, *e.g.*, cetyltrimethyl ammonium chloride.

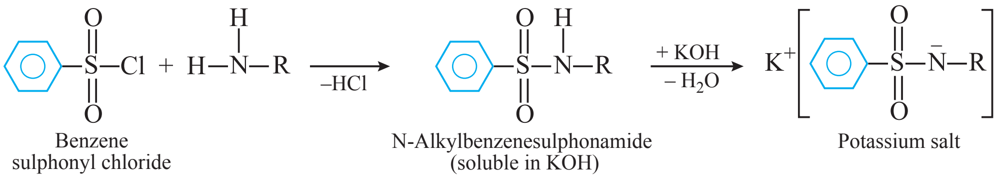
(*ii*) Low molecular mass aliphatic amines are used as reagents in organic synthesis and as intermediates in the manufacture of drugs.

(*iii*) Aniline is used in the manufacture of dyes, dye intermediates and sulpha drugs.

12. Test for Amines

(*a*) Hinsberg's test: In this test, the amine is first treated with Hinsberg's reagent (benzenesulphonyl chloride) and then shaken with aqueous KOH solution when the three amines behave in different ways.

(*i*) A 1° amine gives a clear solution which on acidification gives an insoluble N-alkyl benzene sulphonamide.



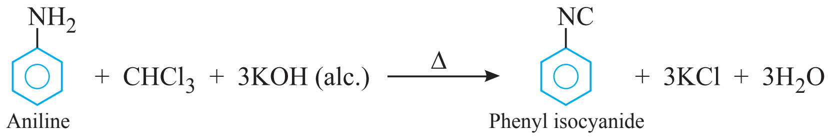
(*ii*) A 2° amine gives an insoluble N, N-dialkyl benzene sulphonamide which remains unaffected on addition of acid.

(*iii*) A 3° amine does not react at all.

$$\underset{\text{Benzene sulphonyl chloride}}{C_6H_5SO_2Cl} + \underset{3^\circ\text{ amine}}{R_3N} \xrightarrow{KOH} \text{No reaction}$$

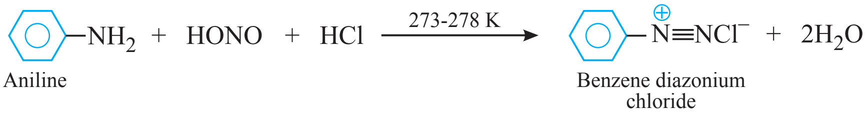
(*b*) Isocyanide test (Carbylamine test): Primary amines (aliphatic as well as aromatic) react with chloroform in the presence of alcoholic KOH to form foul smelling carbylamine.

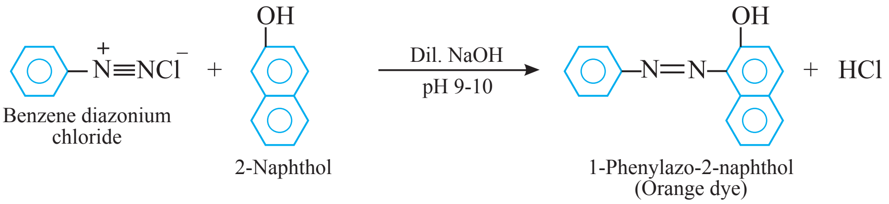
$$\underset{1^\circ\text{ amine}}{R\text{—}NH_2} + CHCl_3 + 3KOH\text{ (alc.)} \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R\text{—}NC} + 3KCl + 3H_2O$$



Secondary and tertiary amines (aliphatic as well as aromatic) do not give this test.

(*c*) Azo dye test: It involves the reaction of any aromatic primary amine with HNO_2 ($NaNO_2$ + dil. HCl) at 273–278 K followed by treatment with an alkaline solution of 2-naphthol, where a brilliant yellow, orange or red coloured dye is obtained.





Aliphatic primary amines under these conditions give a brisk evolution of N_2 gas with the formation of primary alcohols, *i.e.*, the solution remains clear.

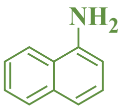
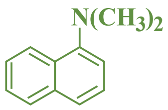
$$RNH_2 + HONO \xrightarrow{273\text{-}278K} \underset{\text{Alcohol}}{R\text{—}OH} + N_2\uparrow + H_2O$$

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + HONO \xrightarrow{273\text{-}278K} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2\uparrow + H_2O$$

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Classify the following amines as primary, secondary or tertiary:

(a)  **(b)**  **(c)** $(C_2H_5)_2CHNH_2$ **(d)** $(C_2H_5)_2NH$

Ans. (*a*) Primary (*b*) Tertiary (*c*) Primary (*d*) Secondary

Q. 2. **(*a*) Write structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.**

(*b*) Write IUPAC names of all the isomers.

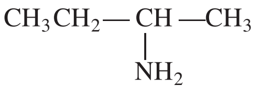
(*c*) What type of isomerism is exhibited by different pairs of amines?

Ans. (*a*) and (*b*)

Primary amines:

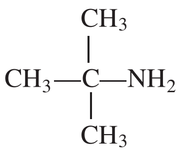
(*i*) $CH_3CH_2CH_2CH_2NH_2$

Butanamine

(*ii*) 

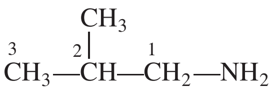
$CH_3CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$

Butan-2-amine

(*iii*) 

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-NH_2$

2-methylpropan-2-amine

(*iv*) 

$\overset{3}{C}H_3-\overset{\displaystyle CH_3}{\overset{|}{\overset{2}{C}H}}-\overset{1}{C}H_2-NH_2$

2-Methylpropanamine

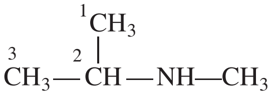
Secondary amines:

(*v*) $CH_3-CH_2-NH-CH_2CH_3$

N-Ethylethanamine

(*vi*) $CH_3CH_2CH_2-NH-CH_3$

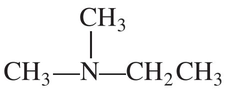
N-Methylpropanamine

(*vii*) 

$\overset{3}{C}H_3-\overset{\displaystyle {}^1CH_3}{\overset{|}{\overset{2}{C}H}}-NH-CH_3$

N-Methylpropan-2-amine

Tertiary amine:

(*viii*) 

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-CH_2CH_3$

N, N-Dimethylethanamine

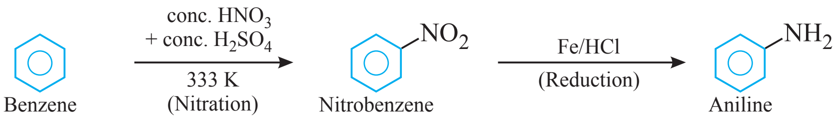
(*c*) Chain isomers: (*i*) & (*iv*), (*ii*) & (*iii*)

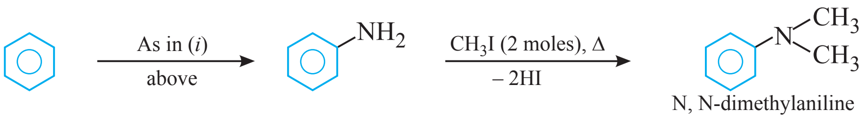
Position isomers: (*i*) & (*ii*), (*vi*) & (*vii*)

Metamers: (*v*) & (*vi*), (*v*) and (*vii*)

Functional isomers: All primary amines are functional isomers of secondary and tertiary amines and vice versa.

Q. 3. How will you convert: (*i*) Benzene into aniline, (*ii*) Benzene into N, N-dimethylaniline, (*iii*) $Cl(CH_2)_4$—Cl into hexan-1, 6-diamine?

Ans. (*i*) 

(*ii*) 

(*iii*) $\underset{\text{1,6-Dichlorobutane}}{Cl—(CH_2)_4—Cl} \xrightarrow{\text{Ethanolic NaCN}} N \equiv C—(CH_2)_4—C \equiv N$

$$\xrightarrow{H_2/Ni} \underset{\text{Hexane-1,6-diamine}}{H_2N—CH_2—(CH_2)_4—CH_2—NH_2}$$

or

$$\underset{\text{Hexane-1,6-diamine}}{H_2N—(CH_2)_6—NH_2}$$

Q. 4. Arrange the following in increasing order of their basic strength:

(*a*) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3 , $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$

(*b*) $C_2H_5NH_2$, $(C_2H_5)_2$ NH, $(C_2H_5)_3N$, $C_6H_5NH_2$

(*c*) CH_3NH_2 , $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

Ans. (*a*) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(*b*) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(*c*) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

Q. 5. Complete the following acid–base reactions and name the products:

(*i*) $CH_3CH_2CH_2NH_2 + HCl \longrightarrow$

(*ii*) $(C_2H_5)_3N + HCl \longrightarrow$

Ans. (*i*) $\underset{n\text{-Propylamine}}{CH_3CH_2CH_2\ddot{N}H_2} + H—Cl \longrightarrow \underset{n\text{-Propylammonium chloride}}{CH_3CH_2CH_2\overset{+}{N}H_3\,Cl^-}$

(*ii*) $\underset{\text{Triethylamine}}{(C_2H_5)_3\ddot{N}} + H—Cl \longrightarrow \underset{\text{Triethylammonium chloride}}{(C_2H_5)_3\overset{+}{N}HCl^-}$

Q. 6. Write the reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Ans. $\underset{\text{Amine}}{C_6H_5—\ddot{N}H_2} + CH_3—I \longrightarrow \underset{\text{N-Methylanilinium iodide}}{[C_6H_5\overset{+}{N}H_2CH_3]I^-}$

$$2[C_6H_5\overset{+}{N}H_2CH_3]\,I^- + Na_2CO_3 \longrightarrow \underset{\text{N-Methylaniline}}{2C_6H_5NHCH_3} + CO_2 + 2NaI$$

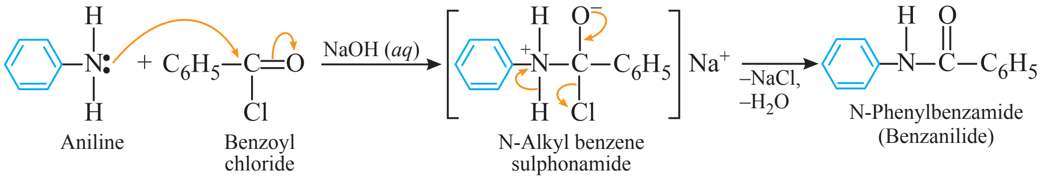
$$C_6H_5\ddot{N}HCH_3 \xrightarrow[Na_2CO_3]{+\,CH_3I} \underset{\text{N, N-Dimethylaniline}}{C_6H_5N(CH_3)_2}$$

$$C_6H_5\ddot{N}(CH_3)_2 + CH_3—I \longrightarrow \underset{\text{N, N, N-Trimethylanilinium iodide}}{C_6H_5\overset{+}{N}(CH_3)_3I^-}$$

$$2C_6H_5\overset{+}{N}(CH_3)_3\,I^- + Na_2CO_3 \longrightarrow \underset{\text{N, N, N-Trimethylanilinium carbonate}}{[C_6H_5\overset{+}{N}(CH_3)_3]_2CO_3^{2-}} + 2NaI$$

Q. 7. Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

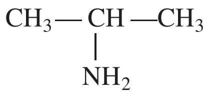
Ans.



Q. 8. Write structures of different isomers corresponding to the molecular formula, C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Ans. In all, four structural isomers are possible. These are as follows:

Primary amines: $\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2}$

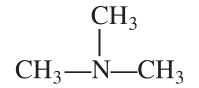


$$\underset{NH_2}{CH_3—\underset{|}{CH}—CH_3}$$

Propan-2-amine

Secondary amines: $CH_3—NH—C_2H_5$
N-Methylethanamine

Tertiary amines:



$CH_3—\overset{\overset{CH_3}{|}}{N}—CH_3$

N,N-dimethylmethanamine

Only primary amines react with HNO_2 to liberate N_2 gas

$$\underset{\text{Propan-1-amine}}{CH_3CH_2CH_2NH_2} + HNO_2 \longrightarrow \underset{\substack{\text{Propan-1-ol}\\\text{(Major product)}}}{CH_3CH_2CH_2OH} + H_2O + N_2$$

Propan-2-amine

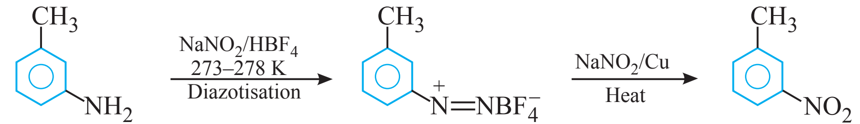
Propan-2-ol
(Major product)

Q. 9. Convert:

(*i*) 3-Methylaniline into 3-nitrotoluene

(*ii*) Aniline into 1, 3, 5-tribromobenzene.

Ans. (*i*)

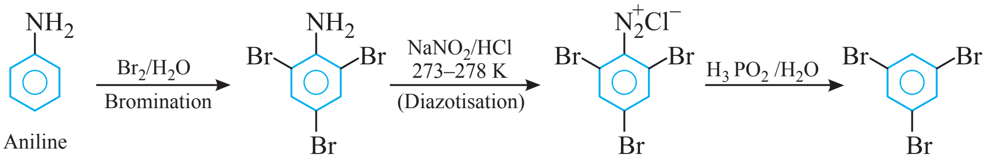


3-Methylaniline

3-Methylbenzene diazonium fluoroborate

3-Nitrotoluene

(*ii*)



Aniline

2, 4, 6-Tribromoaniline

1, 3, 5-Tribromobenzene

NCERT Textbook Exercises

Q. 1. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(*i*) $(CH_3)_2CHNH_2$ **(*ii*) $CH_3(CH_2)_2NH_2$**

(*iii*) $CH_3NHCH(CH_3)_2$ **(*iv*) $(CH_3)_3CNH_2$**

(*v*) $C_6H_5NHCH_3$ **(*vi*) $(CH_3CH_2)_2NCH_3$**

(*vii*) *m*-$BrC_6H_4NH_2$

Ans. (*i*) Propan-2-amine (primary) (*ii*) Propan-1-amine (primary)

(*iii*) N-Methylpropan-2 amine (secondary) (*iv*) 2-Methylpropan-2-amine (primary)

(*v*) N-Methylbenzenamine or N-Methylaniline (secondary)

(*vi*) N-Ethyl-N-methylethanamine (tertiary)

(*vii*) 3-Bromobenzenamine or 3-Bromoaniline (primary).

Q. 2. Give one chemical test to distinguish between the following pairs of compounds:

(*i*) Methylamine and dimethylamine **(*ii*) Secondary and tertiary amines**

(*iii*) Ethylamine and aniline **(*iv*) Aniline and benzylamine**

(*v*) Aniline and N-methylaniline

Ans. (*i*) Methylamine is 1° amine, therefore, it gives carbylamine test, *i.e.*, when heated with an alcoholic solution of KOH and $CHCl_3$ it gives an offensive smell of methyl carbylamine. In contrast, dimethylamine is a secondary amine and hence does not give this test.

$$\underset{\substack{\text{Methylamine}\\(1^\circ\text{ amine})}}{CH_3NH_2} + CHCl_3 + \underset{(\text{alc.})}{3KOH} \xrightarrow{\text{Heat}} \underset{\substack{\text{Methyl carbylamine}\\(\text{offensive smell})}}{CH_3NC} + 3KCl + 3H_2O$$

$$\underset{\substack{\text{Dimethylamine}\\(2^\circ\text{ amine})}}{(CH_3)_2NH} \xrightarrow[\text{Heat}]{CHCl_3/KOH(\text{alc.})} \text{No reaction.}$$

(*ii*) By Hinsberg's reagent (benzenesulphonyl chloride). The amine is treated with benzenesulphonyl chloride and shaken with alkali solution when the two amines behave in different ways:

(*a*) Secondary amines form dialkyl benzenesulphonamide which does not react with alkali and hence it remains insoluble.

(*b*) Tertiary amines do not react with benzenesulphonyl chloride at all.

$$C_6H_5SO_2Cl + \underset{\substack{\text{Secondary}\\\text{amine}}}{HNR_2} \longrightarrow \underset{\substack{\text{Dialkyl}\\\text{benzenesulphonamide}}}{C_6H_5SO_2NR_2} \xrightarrow{KOH} \text{No reaction}$$

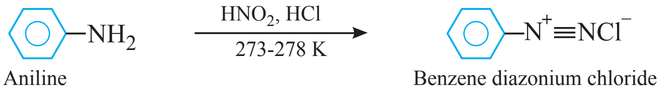
$$C_6H_5SO_2Cl + \underset{\substack{\text{Tertiary}\\\text{amine}}}{R_3N} \longrightarrow \text{No reaction}$$

(*iii*) Ethylamine is primary aliphatic amine while aniline is a primary aromatic amine. These may be distinguished by the azo dye test: Refer to Basic Concepts Point 12(*c*).

(*iv*) Benzylamine reacts with nitrous acid to form a diazonium salt which being unstable even at low temperature, decomposes with evolution of N_2 gas.

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow[HCl]{HNO_2} \underset{\text{Unstable}}{[C_6H_5CH—\overset{+}{N} \equiv NCl^-]} \xrightarrow[\text{Decomposes}]{H_2O} \underset{\text{Benzylalcohol}}{C_6H_5CH_2OH} + N_2\uparrow + HCl$$

Aniline reacts with HNO_2 to form benzene diazonium chloride which is stable at 273-278 K and hence does not decompose to evolve N_2 gas.



(*v*) Aniline being a primary amine gives carbylamine test, *i.e.*, when heated with an alcoholic solution of KOH and $CHCl_3$, it gives an offensive smell of phenyl isocyanide. In contrast, N-methylaniline, being secondary amine does not give this test.

$$\underset{\substack{\text{Aniline}\\(1^\circ\text{ amine})}}{C_6H_5NH_2} + CHCl_3 + \underset{(\text{alc.})}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{Phenyl isocyanide}\\(\text{offensive})}}{C_6H_5NC} + 3KCl + 3H_2O$$

$$\underset{\text{N-Methylaniline }(2^\circ\text{ amine})}{C_6H_5—NH—CH_3} \xrightarrow{CHCl_3/KOH(\text{alc.})} \text{No reaction.}$$

Q. 3. Account for the following:

(*i*) pK_b of aniline is more than that of methylamine.

(*ii*) Ethylamine is soluble in water, whereas aniline is not.

(*iii*) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(*iv*) Although amino group is *o*- and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

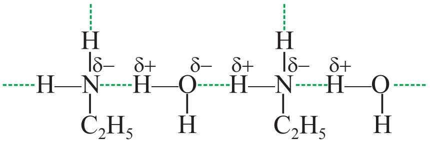
(*v*) Aniline does not undergo Friedel–Crafts reaction. **[*CBSE 2020 (56/5/1)*]**

(*vi*) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(*vii*) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Ans. (*i*) In aniline due to resonance, the lone pair of electrons on the N-atom are delocalised over the benzene ring. Due to this, electron density on the nitrogen decreases. On the other hand, in CH_3NH_2, +I-effect of CH_3 increases the electron density on the N-atom. Consequently aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

(*ii*) Ethylamine dissolves in water because it forms H-bonds with water molecules as shown below:



In aniline, due to the large hydrocarbon part the extent of H-bonding decreases considerably and hence aniline is insoluble in water.

(*iii*) Methylamine being more basic than water, accepts a proton from water, liberating OH^- ions.

$$CH_3\ddot{N}H_2 + H{-}OH \longrightarrow CH_3{-}\overset{+}{N}H_3 + OH^-$$

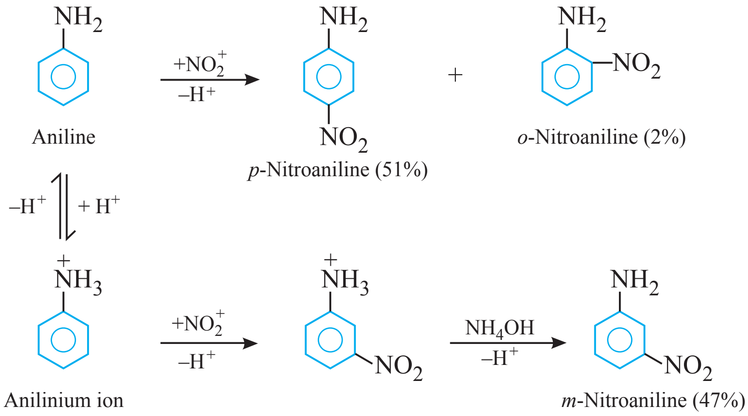
These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\substack{\text{Hydrated ferric oxide}\\ \text{(Brown ppt.)}}}{2Fe(OH)_3 \text{ or } Fe_2O_3.3H_2O}$$

(*iv*) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4. In presence of these acids, most of aniline gets protonated to form anilinium ion. Thus, in presence of acids, the reaction mixture consists of aniline and anilinium ion. The $—NH_2$ group in aniline is *o, p*-directing and activating while the $—\overset{+}{N}H_3$ group in anilinium ion is *m*-directing and deactivating.

Nitration of aniline mainly gives *p*-nitroaniline. On the other hand, the nitration of anilinium ion gives *m*-nitroaniline.



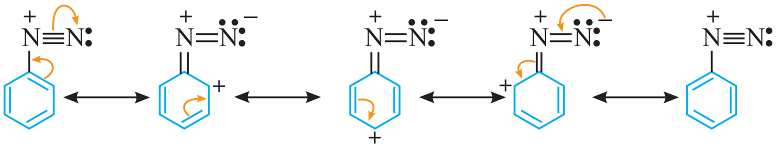
Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of the amino group.

(*v*) Aniline being a Lewis base, reacts with Lewis acid $AlCl_3$ to form a salt.

$$\underset{\text{Lewis base}}{C_6H_5NH_2} + \underset{\text{Lewis acid}}{AlCl_3} \longrightarrow C_6H_5\overset{+}{N}H_2AlCl_3^-$$

As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reaction. Consequently, aniline does not undergo Friedel–Crafts reaction.

(*vi*) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring as shown below:



(*vii*) Gabriel phthalimide reaction gives pure primary amines without any contamination of secondary and tertiary amines. Therefore, it is preferred for synthesising primary amines.

Q. 4. Arrange the following:

(*i*) In decreasing order of the pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(*ii*) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH and CH_3NH_2

(*iii*) In increasing order of basic strength:

(*a*) Aniline, *p*-nitroaniline and *p*-toluidine

(*b*) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(*iv*) In decreasing order of basic strength in gas phase:

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(*v*) In increasing order of boiling point:

C_2H_5OH, $(CH_3)_2$ NH, $C_2H_5NH_2$

(*vi*) In increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans. (*i*) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(*ii*) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

(*iii*) (*a*) *p*-nitroaniline < aniline < *p*-toluidine.

(*b*) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(*iv*) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(*v*) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(*vi*) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Q. 5. How will you convert

(*i*) Ethanoic acid to methanamine **(*ii*) Hexanenitrile to 1-aminopentane**

(*iii*) Methanol to ethanoic acid **(*iv*) Ethanamine to methanamine**

(*v*) Ethanoic acid to propanoic acid **(*vi*) Methanamine to ethanamine**

(*vii*) Nitromethane to dimethylamine **(*viii*) Propanoic acid to ethanoic acid?**

Ans. (*i*)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3(\text{excess})} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*ii*)

$$\underset{\text{Hexanenitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{Hydrolysis}]{H_3O^+} \underset{\text{Hexanoic acid}}{CH_3(CH_2)_4COOH} \xrightarrow{PCl_5} \underset{\text{Hexanoyl chloride}}{CH_3(CH_2)_4COCl}$$

$$\xrightarrow[\Delta]{NH_3(\text{excess})} CH_3(CH_2)_4CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Aminopentane}}{CH_3(CH_2)_4NH_2}$$

(*iii*)

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN(\text{alc.})} \underset{\text{Ethanenitrile}}{CH_3CN} \xrightarrow{H_3O^+} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

(*iv*)

$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow[\text{(oxidation)}]{CrO_3-H_2SO_4} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*v*)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[-\ KI]{+\ KCN} \underset{\text{Ethyl cyanide}}{CH_3CH_2CN}$$

$$\xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(*vi*)

$$\underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Methanol}}{CH_3OH} \xrightarrow{P/I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow[-\ KI]{KCN} \underset{\text{Ethanenitrile}}{CH_3CN} \xrightarrow[\text{Reduction}]{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

(*vii*)

$$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow{Sn/HCl} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{CHCl_3\ +\ KOH} \underset{\text{Methyl isocyanide}}{CH_3NC} \xrightarrow[\text{(Reduction)}]{Na/C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3NHCH_3}$$

(*viii*) $$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Propionamide}}{CH_3CH_2CONH_2}$$

$$\xrightarrow{Br_2/KOH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Q. 6. Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

Ans. Refer to Basic Concepts Point 12(*a*).

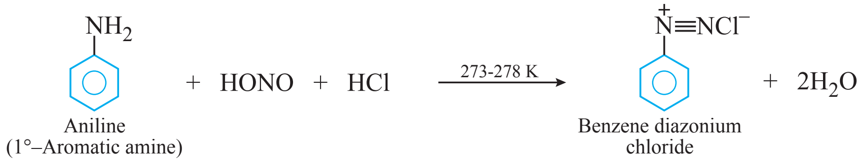
Q. 7. Write short notes on the following:

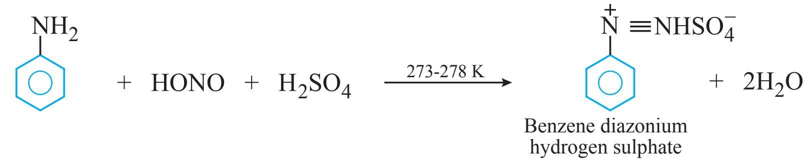
(*i*) Carbylamine reaction **(*ii*) Diazotisation**
(*iii*) Hofmann's bromamide reaction **(*iv*) Coupling reaction**
(*v*) Ammonolysis **(*vi*) Acetylation**
(*vii*) Gabriel phthalimide synthesis

Ans. (*i*) Refer to Basic Concepts Point 10(*e*).

(*ii*) **Diazotisation reaction:** When a cold solution of a primary aromatic amine in a dilute mineral acid (HCl or H_2SO_4) is treated with a cold solution of nitrous acid (generated *in situ* by the action of dil. HCl or dil. H_2SO_4 on $NaNO_2$) at 273-278 K, arene diazonium salt is formed. This reaction is called diazotization reaction. For example,

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

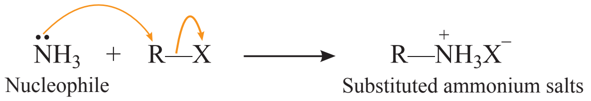




(*iii*) Refer to Basic Concepts Point 10(*b*).

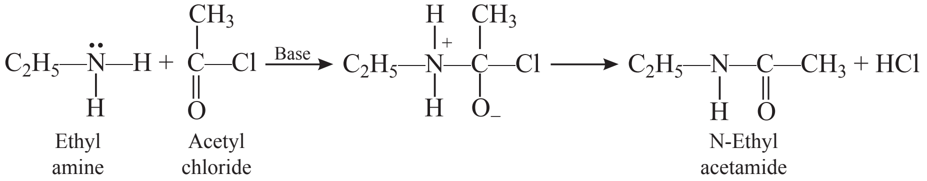
(*iv*) Refer to Basic Concepts Point 9(*b*).

(*v*) **Ammonolysis:** The process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.

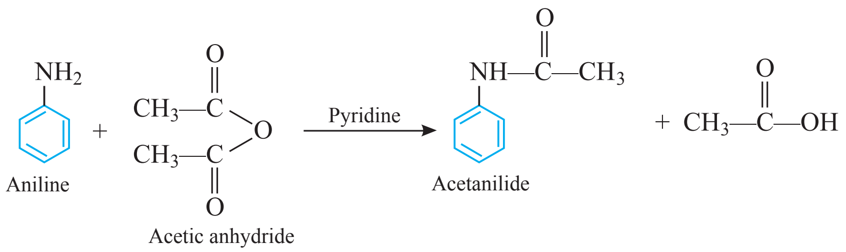


$$\underset{(1^\circ)}{R{-}NH_2} \xrightarrow{+R{-}X} \underset{(2^\circ)}{R_2NH} \xrightarrow{+RX} \underset{(3^\circ)}{R_3N} \xrightarrow{+RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

(*vi*) **Acetylation:** The process of introducing an acetyl group ($CH_3-\overset{\overset{O}{\|}}{C}-$) into a molecule is called acetylation.



$$\underset{\text{Ethyl amine}}{C_2H_5-\ddot{N}H-H} + \underset{\text{Acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow{\text{Base}} C_2H_5-\overset{+}{N}H_2-\underset{O^-}{\overset{CH_3}{C}}-Cl \longrightarrow \underset{\text{N-Ethyl acetamide}}{C_2H_5-NH-\overset{O}{\overset{\|}{C}}-CH_3} + HCl$$



(*vii*) Refer to Basic Concepts Point 10(*a*).

Q. 8. Accomplish the following conversions:

(*i*) Nitrobenzene to benzoic acid

(*ii*) Benzene to *m*-bromophenol

(*iii*) Benzoic acid to aniline

(*iv*) Aniline to 2, 4, 6-tribromofluorobenzene

(*v*) Benzyl chloride to 2-phenylethanamine

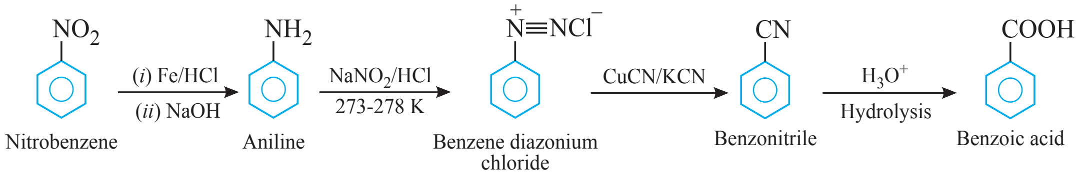
(*vi*) Chlorobenzene to *p*-chloroaniline

(*vii*) Aniline to *p*-bromoaniline

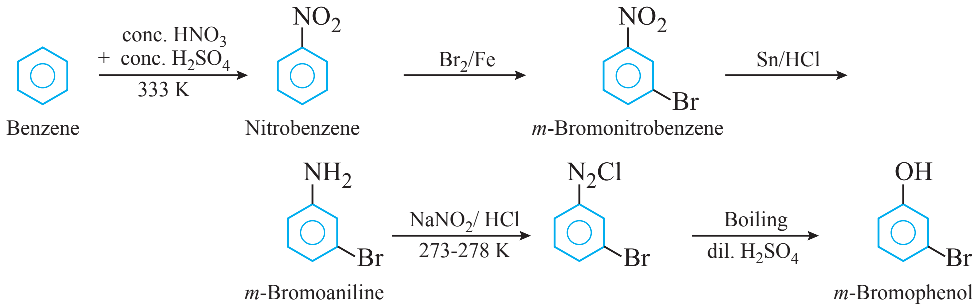
(*viii*) Benzamide to toluene

(*ix*) Aniline to benzyl alcohol

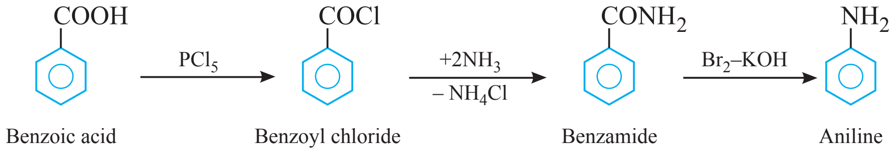
Ans. (*i*)



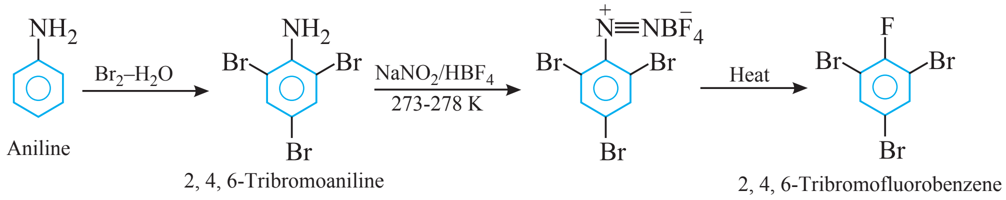
(*ii*)



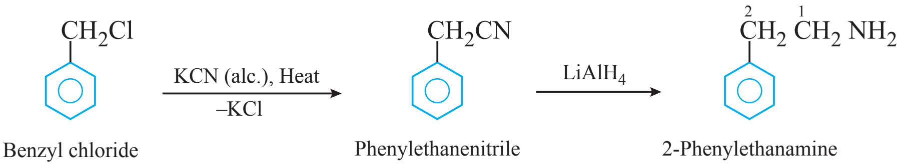
(*iii*)



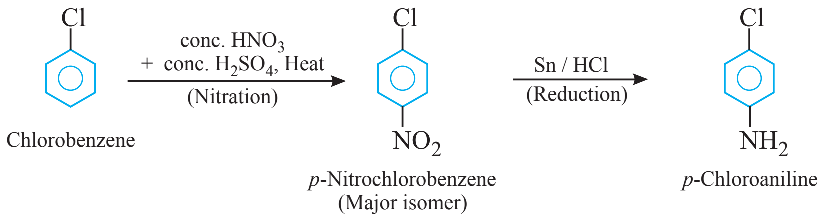
(*iv*)

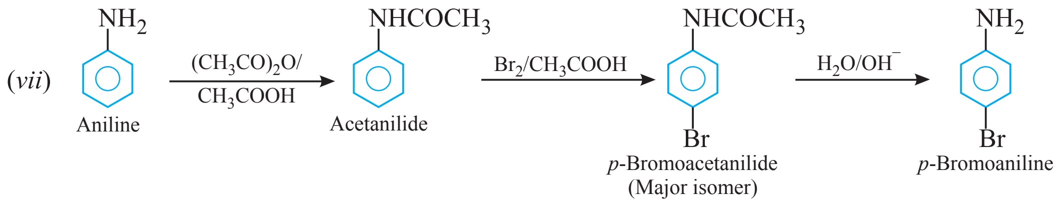


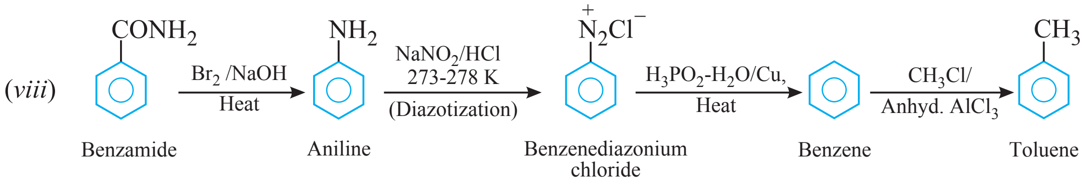
(*v*)

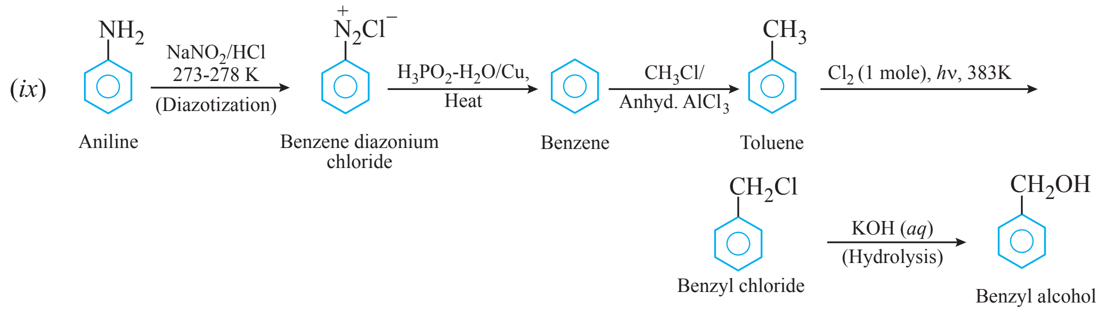


(*vi*)









Q. 9. Give the structures of *A, B* and *C* in the following reactions:

(*i*) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

(*ii*) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

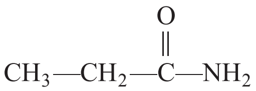
(*iii*) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(*iv*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(*v*) $CH_3COOH \xrightarrow[Heat]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(*vi*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

Ans. (*i*) $\underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow{NaCN} \underset{\text{Propanenitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{OH^-}$



$$\underset{\text{Propanamide (B)}}{CH_3—CH_2—\overset{\overset{O}{||}}{C}—NH_2} \xrightarrow{NaOH + Br_2} \underset{\text{Ethanamine (C)}}{CH_3—CH_2—NH_2}$$

(*ii*) $\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} \xrightarrow{CuCN} \underset{\text{Cyanobenzene (A)}}{C_6H_5CN} \xrightarrow[\text{Hydrolysis}]{H_2O/H^+} \underset{\text{Benzoic acid (B)}}{C_6H_5COOH} \xrightarrow{NH_3}$

$$C_6H_5COONH_4 \xrightarrow{Heat} \underset{\text{Benzamide (C)}}{C_6H_5CONH_2}$$

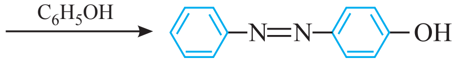
(*iii*) $\underset{\text{Bromoethane}}{CH_3CH_2Br} \xrightarrow{KCN} \underset{\text{Propane nitrile (A)}}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{Propan-1-amine (B)}}{CH_3CH_2CH_2NH_2}$

$$\xrightarrow[0°C]{HNO_2} [CH_3CH_2CH_2\overset{+}{N}{\equiv}NCl^-] \xrightarrow{H_2O} \underset{\text{Propanol (C)}}{CH_3CH_2CH_2OH}$$

(*iv*) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273K]{NaNO_2 + HCl} \underset{\text{Benzenediazonium chloride (B)}}{C_6H_5\overset{+}{N}{\equiv}NCl^-} \xrightarrow[Heat]{H_2O/H^+} \underset{\text{Phenol (C)}}{C_6H_5OH}$

(*v*) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{Heat}]{NH_3} \underset{\text{Ethanamide (A)}}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{\text{Methanamine (B)}}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} \underset{\text{Methanol (C)}}{CH_3OH}$

(*vi*) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273\text{ K}]{NaNO_2/HCl} \underset{\text{Benzenediazonium chloride (B)}}{C_6H_5—\overset{+}{N}\equiv NCl^-}$



p-Hydroxyazobenzene (C)

Q. 10. An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound '*C*' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds *A*, *B* and *C*.

Ans. (*i*) To find out the structures of compounds '*B*' and '*C*'.

(*a*) Since compound '*C*' with molecular formula C_6H_7N is formed from compound '*B*' on treatment with Br_2 + KOH compound 'B' must be an amide and '*C*' must be an amine, the only amine having the molecular formula C_6H_7N is $C_6H_5NH_2$ (aniline).

(*b*) Since '*C*' is aniline, the amide from which it is formed must be benzamide. Thus, compound '*B*' is benzamide.

The chemical equation showing the conversion of '*B*' to '*C*' is

$$\underset{\substack{\text{Benzamide }(B)\\(\text{M.F.} = C_7H_7NO)}}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} \underset{\substack{\text{Aniline }(C)\\(\text{M.F.} = C_6H_7N)}}{C_6H_5NH_2}$$

(*ii*) To find out the structure of compound '*A*'.

As compound '*B*' is formed from compound '*A*' with aqueous ammonia and heating, therefore, compound '*A*' must be benzoic acid.

$$\underset{\text{Benzoic acid }(A)}{C_6H_5COOH} \xrightarrow[(ii)\text{ Heat}]{(i)\text{ aq. }NH_3} \underset{\text{Benzamide }(B)}{C_6H_5CONH_2}$$

Q. 11. Complete the following reactions:

(*i*) $C_6H_5NH_2 + CHCl_3 + \text{alc.KOH} \longrightarrow$

(*ii*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(*iii*) $C_6H_5NH_2 + H_2SO_4(\text{conc.}) \longrightarrow$

(*iv*) $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

(*v*) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

(*vi*) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

(*vii*) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu,\ \Delta]{(i)\ HBF_4}$

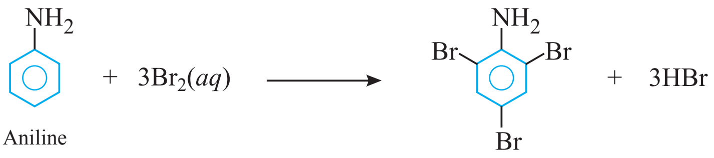
Ans. (*i*) $\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \xrightarrow[\text{(Carbylamine reaction)}]{\text{Heat}} \underset{\substack{\text{Phenyl isocyanide}\\\text{(Offensive smell)}}}{C_6H_5N \equiv C} + 3KCl + 3H_2O$

(*ii*) $\underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$

(*iii*) $\underset{\text{Aniline}}{C_6H_5NH_2} + H_2SO_4\text{ (conc.)} \longrightarrow \underset{\text{Anilinium hydrogen sulphate}}{C_6H_5\overset{+}{N}H_3HSO_4^-}$

(*iv*) $\underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5N_2Cl} + C_2H_5OH \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethanal}}{CH_3CHO} + N_2 + HCl$

(*v*)



Aniline

2, 4, 6-Tribromoaniline

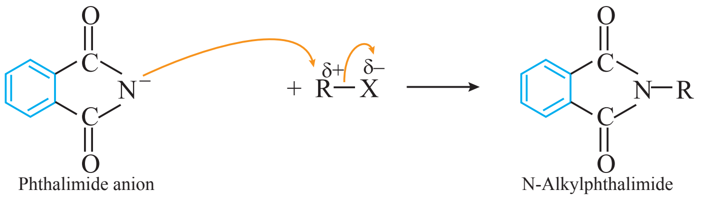
(*vi*) $\underset{\text{Aniline}}{C_6H_5NH_2} + (CH_3CO)_2O \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH$

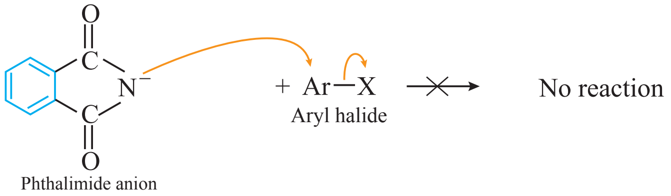
(*vii*) $$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} \xrightarrow{HBF_4} \underset{\text{Benzenediazonium tetrafluoroborate}}{C_6H_5\overset{+}{N}_2BF_4^-} \xrightarrow[\text{Heat}]{NaNO_2/Cu} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + BF_3 + NaF$$

Q. 12. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

[*CBSE 2020 (56/5/1)*]

Ans. The success of Gabriel phthalimide reaction depends upon the nucleophilic attack by the phthalimide anion on the organic halogen compound.

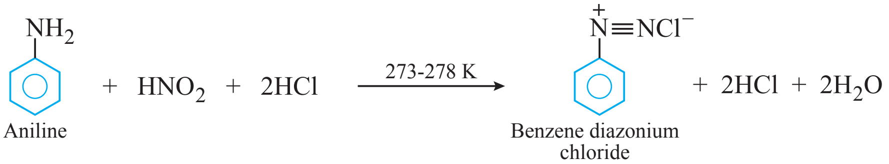




Aryl halides do not undergo nucleophilic substitution reactions easily because the carbon–halogen bond acquires partial double bond character due to resonance, therefore aromatic primary amines cannot be prepared by Gabriel phthalimide reaction.

Q. 13. Write the reactions of (*i*) aromatic and (*ii*) aliphatic primary amines with nitrous acid.

Ans. Aromatic primary amines react with HNO_2 at 273-278 K to form aromatic diazonium salts.



Aliphatic primary amines also react with HNO_2 at 273–278 K to form aliphatic diazonium salts. But these are unstable even at this low temperature and thus decompose readily to form a mixture of compounds consisting of alkyl chlorides, alkenes and alcohols, out of which alcohols generally predominate.

$$CH_3CH_2NH_2 + HNO_2 + HCl \xrightarrow{273-278\text{ K}} \underset{\substack{\text{Ethanediazonium chloride}\\ \text{(unstable)}}}{[CH_3CH_2—\overset{+}{N} \equiv N]Cl^-} \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + HCl$$

Q. 14. Give plausible explanation for each of the following:

(*i*) Why are amines less acidic than alcohols of comparable molecular masses?

(*ii*) Why do primary amines have higher boiling point than tertiary amines?

(*iii*) Why are aliphatic amines stronger bases than aromatic amines? **[*CBSE 2020 (56/5/1)*]**

Ans. (*i*) Loss of a proton from an amine gives amide ion while loss of a proton from alcohol gives an alkoxide ion as shown below:

$$\underset{\text{Amine}}{R—NH_2} \longrightarrow \underset{\text{Amide ion}}{R—NH^-} + H^+$$

$$\underset{\text{Alcohol}}{R—O—H} \longrightarrow \underset{\text{Alkoxide ion}}{R—O^-} + H^+$$

As O is more electronegative than N, RO^- can accommodate the negative charge more easily than the RNH^- can accommodate the negative charge.

RO^- is more stable than RNH^-. Therefore, amines are less acidic than alcohols.

(*ii*) In primary amines, two hydrogen atoms are present on N-atom and they undergo extensive intermolecular hydrogen bonding which results in association of molecules while in tertiary amines, no hydrogen atom is present on N-atom. Hence there is no hydrogen bonding in tertiary amines. As a result of this primary amines have higher boiling point than tertiary amines.

(*iii*) Aliphatic amines are stronger bases than aromatic amines because:

(*a*) due to resonance in aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalised over the benzene ring and thus is less easily available for protonation.

(*b*) the aryl amine ions have lower stability than the corresponding alkyl amines, *i.e.*, protonation of aromatic amines is not favoured.

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. The correct IUPAC name for $CH_2{=}CHCH_2NHCH_3$ is [*NCERT Exemplar*]

(*a*) Allylmethylamine (*b*) 2-amino-4-pentene

(*c*) 4-aminopent-1-ene (*d*) N-methylprop-2-en-1-amine

2. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is ___________. [*NCERT Exemplar*]

(*a*) Sodium amide, $NaNH_2$ (*b*) Sodium azide, NaN_3

(*c*) Potassium cyanide, KCN (*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

3. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is ___________. [*NCERT Exemplar*]

(*a*) excess H_2 (*b*) Br_2 in aqueous NaOH

(*c*) iodine in the presence of red phosphorus (*d*) $LiAlH_4$ in ether

4. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine? [*NCERT Exemplar*]

(*a*) H_2 (excess)/Pt (*b*) $LiAlH_4$ in ether (*c*) Fe and HCl (*d*) Sn and HCl

5. Amongst the given set of reactants, the most appropriate for preparing 2° amine is ___________. [*NCERT Exemplar*]

(*a*) 2° R—Br + NH_3

(*b*) 2° R—Br + NaCN followed by H_2/Pt

(*c*) 1° R—NH_2 + RCHO followed by H_2/Pt

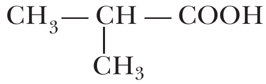
(*d*) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat

6. The best reagent for converting, 2-phenylpropanamide into 1-phenylethanamine is ___________. [*NCERT Exemplar*]

(*a*) excess H_2/Pt (*b*) NaOH/Br_2 (*c*) $NaBH_4$/methanol (*d*) $LiAlH_4$/ether

7. An organic compound 'A' on treatment with NH_3 gives 'B' which on heating gives 'C'. 'C' when treated with Br_2 in the presence of KOH produces ethylamine. Compound 'A' is

(*a*) CH_3—CH_2—CH_2—COOH (*b*) CH_3COOH

(*c*) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

(*d*) CH_3—CH_2—COOH

8. The source of nitrogen in Gabriel synthesis of amines is ___________. [*NCERT Exemplar*]

(*a*) Sodium azide, NaN_3 (*b*) Sodium nitrite, $NaNO_2$

(*c*) Potassium cyanide, KCN (*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

9. Which of the following statements about primary amines is 'false'?

(*a*) Alkylamines are stronger bases than arylamines.

(*b*) Alkylamines are stronger bases than ammonia.

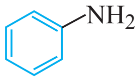
(*c*) Alkylamines react with nitrous acid to produce alcohols.

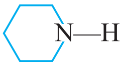
(*d*) Arylamines react with nitrous acid to produce phenols.

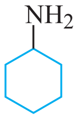
10. Amongst the following, the strongest base in aqueous medium is ____________. [*NCERT Exemplar*]

(*a*) CH_3NH_2 (*b*) $NCCH_2NH_2$ (*c*) $(CH_3)_2NH$ (*d*) $C_6H_5NHCH_3$

11. Which of the following is the weakest Brönsted base? [*NCERT Exemplar*]

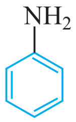
(*a*) 

(*b*) 

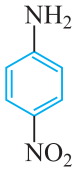
(*c*) 

(*d*) CH_3NH_2

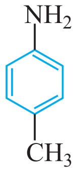
12. The correct increasing order of basic strength for the following compounds is ____________. [*NCERT Exemplar*]



(I)



(II)



(III)

(*a*) II < III < I (*b*) III < I < II (*c*) III < II < I (*d*) II < I < III

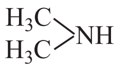
13. Which of the following has highest pK_b value?

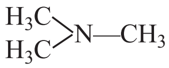
(*a*) $CH_3CH_2NH_2$ (*b*) NH_3

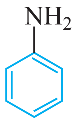
(*c*) CH_3NH_2 (*d*) $C_6H_5NH_2$

14. The most reactive amine towards dilute hydrochloric acid is ____________. [*NCERT Exemplar*]

(*a*) $CH_3—NH_2$

(*b*) 

(*c*) 

(*d*) 

15. The order of reactivity of halides with amines is

(*a*) RBr > RI > RCl (*b*) RI > RBr > RCl

(*c*) RCl > RBr > RI (*d*) RI > RCl > RBr

16. Benzylamine may be alkylated as shown in the following equation:

$$C_6H_5CH_2NH_2 + R—X \longrightarrow C_6H_5CH_2NHR$$

Which of the following alkylhalides is best suited for this reaction through S_N1 mechanism? [*NCERT Exemplar*]

(*a*) CH_3Br (*b*) C_6H_5Br (*c*) $C_6H_5CH_2Br$ (*d*) C_2H_5Br

17. Carbylamine reaction is used as a test for

(*a*) primary amines (*b*) aromatic amines

(*c*) primary and secondary amines (*d*) secondary and tertiary amines

18. Which of the following compounds will dissolve in an alkali solution after it undergoes reaction with Hinsberg's reagent?

(*a*) $(CH_3)_3N$ (*b*) CH_3NH_2 (*c*) $(C_2H_5)_2NH$ (*d*) $C_6H_5NHC_6H_5$

19. Methylamine reacts with HNO_2 to form ____________. [*NCERT Exemplar*]

(*a*) $CH_3—O—N=O$ (*b*) $CH_3—O—CH_3$ (*c*) CH_3OH (*d*) CH_3CHO

20. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is ____________. [*NCERT Exemplar*]

(*a*) NO_2 (*b*) NO^+ (*c*) NO_2^+ (*d*) NO_2^-

21. Which of the following will be most stable diazonium salt $R\overset{+}{N_2}\overset{-}{X}$?

(*a*) $CH_3CH_2\overset{+}{N_2}\overset{-}{X}$ (*b*) $C_6H_5\overset{+}{N_2}\overset{-}{X}$ (*c*) $CH_3\overset{+}{N_2}\overset{-}{X}$ (*d*) $C_6H_5CH_2\overset{+}{N_2}\overset{-}{X}$

22. Reduction of nitrobenzene by which of the following reagent gives aniline? [*NCERT Exemplar*]

(*a*) Sn/HCl (*b*) Fe/HCl (*c*) H_2-Pd (*d*) Sn/NH_4OH

23. Which of the following cannot be prepared by Sandmeyer's reaction? [*NCERT Exemplar*]

(*a*) Chlorobenzene (*b*) Bromobenzene (*c*) Iodobenzene (*d*) Fluorobenzene

Answers

1. (*d*) **2.** (*c*) **3.** (*d*) **4.** (*b*) **5.** (*c*) **6.** (*b*) **7.** (*d*) **8.** (*d*) **9.** (*d*) **10.** (*c*)
11. (*a*) **12.** (*d*) **13.** (*d*) **14.** (*b*) **15.** (*b*) **16.** (*c*) **17.** (*a*) **18.** (*b*) **19.** (*c*) **20.** (*c*)
21. (*b*) **22.** (*a*,*b*,*c*) **23.** (*c*, *d*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- **(*a*)** ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***
- **(*b*)** ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***
- **(*c*)** ***Assertion (A) is correct, but Reason (R) is incorrect statement.***
- **(*d*)** ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. Assertion (*A*) : Hoffmann's bromamide reaction is given by primary amines.
Reason (*R*) : Primary amines are more basic than secondary amines.

2. Assertion (*A*) : In order to convert R–Cl to pure R–NH_2, Gabriel-phthalimide synthesis can be used.
Reason (*R*) : With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1°, 2° or 3° amines.

3. Assertion (*A*) : Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.
Reason (*R*) : Aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

4. Assertion (*A*) : Butan-1-ol is more soluble in water than butan-1-amine.
Reason (*R*) : Alcohols are less polar than amines.

5. Assertion (*A*) : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason (*R*) : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

6. Assertion (*A*) : Acetanilide is less basic than aniline.
Reason (*R*) : Acetylation of aniline results in decrease of electron density on nitrogen.

7. Assertion (A) : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.
Reason (*R*) : Acyl group sterically hinders the approach of further acyl groups.

8. Assertion (*A*) : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents
Reason (*R*) : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

9. Assertion (*A*) : Reduction of *m*-dinitrobenzene with ammonium sulphide gives *m*-nitroaniline.
Reason (*R*) : *m*-nitroaniline formed gets precipitated and hence further reduction is prevented.

10. Assertion (*A*) : N-Ethylbenzene sulphonamide is soluble in alkali.
Reason (*R*) : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

11. Assertion (*A*) : N, N-Diethylbenzene sulphonamide is insoluble in alkali.
Reason (*R*) : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Answers

1. (*a*) **2.** (*c*) **3.** (*a*) **4.** (*c*) **5.** (*d*) **6.** (*d*) **7.** (*c*) **8.** (*d*) **9.** (*c*) **10.** (*d*)
11. (*b*)

Passage-based/Case-based Questions

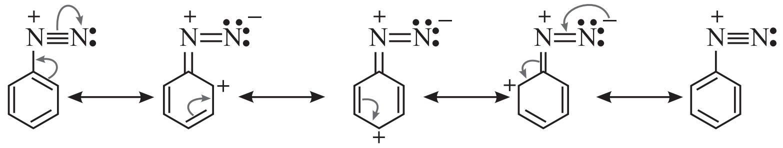
Read the given passages and answer the questions that follow.

PASSAGE–1

The conversion of primary amines into diazonium salts is known as diazotization. Arene diazonium salts are generally colourless crystalline solids highly soluble in water. These salts are more stable than aliphatic diazonium salts and undergo a number of substitution reactions due to excellent leaving ability of diazo group as N_2. Arene diazonium salts also couple with phenols and amines to form coloured azo dyes. Such type of reactions are known as coupling reactions.

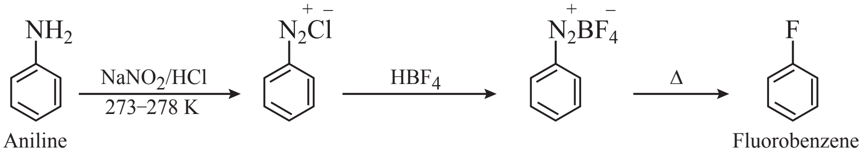
1. Why are arene diazonium salts more stable than aliphatic diazonium salts?

Ans. Arene diazonium salts are more stable than aliphatic diazonium salts due to dispersal of positive charge on the benzene ring as shown below.



2. How will you convert: Aniline to fluorobenzene?

Ans.



3. Why are benzenediazonium salts soluble in water?

Ans. Being ionic, they are soluble in water.

4. What is diazotisation?

Ans. The reaction of converting aromatic primary amines into diazonium salts by treatment with a solution of nitrous acid at 273 K–278 K is called diazotisation.

5. What product is formed when aniline is first diazotised and then reacted with phenol in the alkaline medium?

Ans. *p*-hydroxyazobenzene.

PASSAGE–2

Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Larger the value of K_b or smaller the value of pK_b stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as —CH_3, —OCH_3, —NH_2, etc., increase the basicity while electron-withdrawing substituents such as —NO_2, —CN, halogens. etc. decrease the basicity of amines. The effect of these substituents is more at *p*- than at *m*-positions.

1. Arrange the following in increasing order of their basic strength:

$C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$

Ans. $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

2. Arrange the following compounds in increasing order of their acidic strength:

Methylamine, dimethylamine, aniline, N-methylaniline

Ans. dimethylamine < methylamine < N-methylaniline < aniline.

3. Rearrange the following in increasing order of their basic strength:

***p*-toluidine, N, N-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline**

Ans. *p*-nitroaniline < aniline < *p*-toluidine < N, N-dimethyl-*p*-toluidine.

4. Which is more acidic, aniline or ammonia?

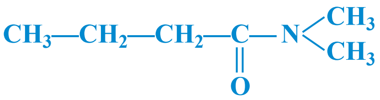
Ans. Due to delocalization of the lone pair of electrons of the N-atom of aniline over the benzene ring, aniline is more acidic than ammonia.

5. $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. Give reason.

Ans. The basicity of amine in aqueous solution depends upon the stability of the substituted ammonium cation. Here the combination of three factors, +ve I effect of CH_3 groups, hydrogen bonding and steric hindrance favour greater stability for ammonium cation of dimethyl amine than ammonium cation of trimethyl amine. Hence dimethylamine is stronger base than trimethyl amine.

Very Short Answer Questions [1 mark]

Q. 1. Write the IUPAC name of the given compound:

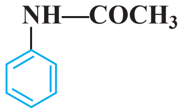


$$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-N\begin{matrix}CH_3\\CH_3\end{matrix}$$

[CBSE (F) 2016]

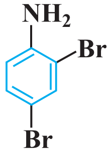
Ans. N, N – Dimethylbutanamide

Q. 2. Write the IUPAC name of the given compound: *[CBSE East 2016]*



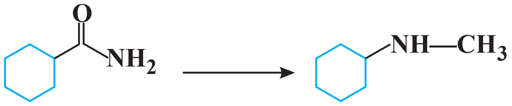
Ans. N- Phenylethanamide

Q. 3. Write the IUPAC name of the given compound: *[CBSE South 2016]*

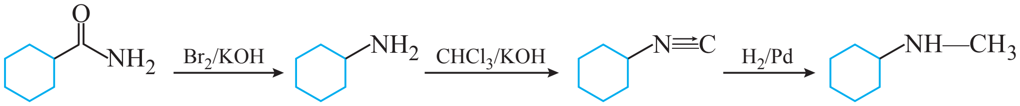


Ans. 2,4-Dibromobenzenamine or 2,4-Dibromoaniline

Q. 4. Suggest a route by which the following conversion can be accomplished. *[NCERT Exemplar]* *[HOTS]*



Ans.



Q. 5. Why do amines behave as nucleophiles?

Ans. Due to the presence of a lone pair of electrons on nitrogen atom, amines behave as nucleophiles.

Q. 6. What is the role of pyridine in the acylation reaction of amines? *[NCERT Exemplar]*

Ans. Pyridine and other bases are used to remove the side product, *i.e.*, HCl from the reaction mixture.

Q. 7. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene? *[NCERT Exemplar]*

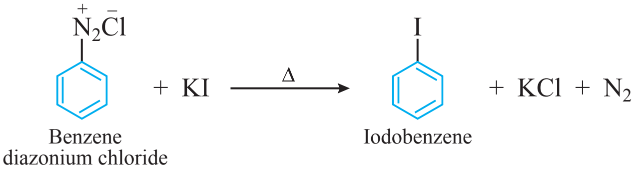
Ans. HNO_3 acts as a base in the nitrating mixture and provides the electrophile NO_2^+.

Q. 8. The conversion of primary aromatic amines into diazonium salts is known as __________ . *[CBSE (AI) 2014]*

Ans. Diazotisation.

Q. 9. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt. *[CBSE Delhi 2008]*

Ans.



Benzene diazonium chloride

Iodobenzene

Q. 10. Why is benzene diazonium chloride not stored and is used immediately after its preparation? *[NCERT Exemplar]*

Ans. Benzene diazonium chloride is very unstable.

Q. 11. What are the reactions involved in the reductive removal of nitro group from an aromatic compound? *[HOTS]*

Ans.

$$\underset{\text{Nitrobenzene}}{C_6H_5—NO_2} \xrightarrow[\text{Reduction}]{\text{Sn/HCl}} \underset{\text{Aniline}}{C_6H_5—NH_2} \xrightarrow[\text{(Diazotisation)}]{\text{NaNO}_2\text{/HCl} \atop 273-278} \underset{\text{Benzenediazonium chloride}}{C_6H_5—\overset{+}{N}\equiv NCl^-} \xrightarrow[\text{(Reduction)}]{\text{Aq. }H_3PO_2} \underset{\text{Benzene}}{C_6H_6}$$

Short Answer Questions–I [2 marks]

Q. 1. Identify *A* and *B* in each of the following processes: *[CBSE (AI) 2010]*

(*i*) $CH_3CH_2Cl \xrightarrow{\text{NaCN}} A \xrightarrow[\text{Ni/H}_2]{\text{Reduction}} B$

(*ii*) $C_6H_5NH_2 \xrightarrow{\text{NaNO}_2\text{/HCl}} A \xrightarrow[\text{OH}^-]{C_6H_5NH_2} B$

Ans. (*i*) $CH_3CH_2Cl \xrightarrow{\text{NaCN}} \underset{\substack{\text{Ethyl cyanide} \\ (A)}}{CH_3CH_2CN} \xrightarrow[\text{Ni/H}_2]{\text{Reduction}} \underset{\substack{n\text{-Propyl amine} \\ (B)}}{CH_3CH_2CH_2NH_2}$

(*ii*)

Benzene diazonium chloride (A)

p–aminoazobenzene (B)

Q. 2. Arrange the following: *[CBSE Guwahati 2015]*

(*i*) In increasing order of their basic strength

$C_6H_5—NH_2$, $CH_3—CH_2—NH_2$, $CH_3—NH—CH_3$

(*ii*) In increasing order of solubility in water

$CH_3—NH_2$, $(CH_3)_3N$, $CH_3—NH—CH_3$

Ans. (*i*) $C_6H_5NH_2 < CH_3—CH_2—NH_2 < CH_3NHCH_3$

(*ii*) $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2$

Q. 3. Account for the following:

(*i*) Aniline gets coloured on standing in air for a long time.

(*ii*) $MeNH_2$ is stronger base than MeOH. *[NCERT Exemplar]*

Ans. (*i*) Due to electron-donating effect (+R-effect) of $—NH_2$ group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products.

(*ii*) Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, $MeNH_2$ is more basic than MeOH.

Q. 4. Account for the following: **[*CBSE (AI) 2014*] [*HOTS*]**

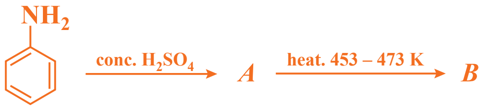
(*i*) pK_b of aniline is more than that of methylamine.

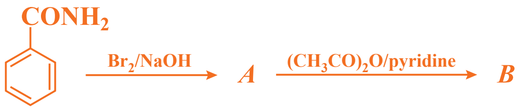
(*ii*) Although trimethylamine and *n*-propylamine have the same molecular weight, but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

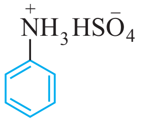
Ans. (*i*) Refer to Ans. 3(*i*) NCERT Textbook Exercises.

(*ii*) *n*-Propylamine has two H-atoms on the N-atom and hence undergoes intermolecular H-bonding, thereby raising its boiling point. Trimethylamine, $(CH_3)_3N$, being a tertiary amine does not have any H-atom on the N-atom. As a result, it does not undergo H-bonding and hence its boiling point is low.

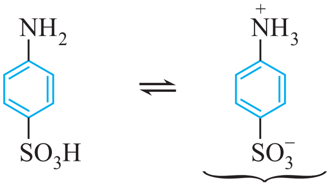
Q. 5. Write structures of compounds A and B in each of the following reactions: **[*CBSE 2019 (56/3/2)*]**

(*i*) 

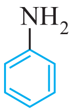
(*ii*) 

Ans. (*i*) *A* = 

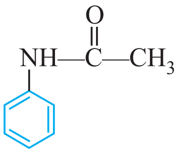
Anilinium hydrogensulphate

; *B* = 

Zwitter ion
Sulphanilic acid

(*ii*) *A* = 

Aniline

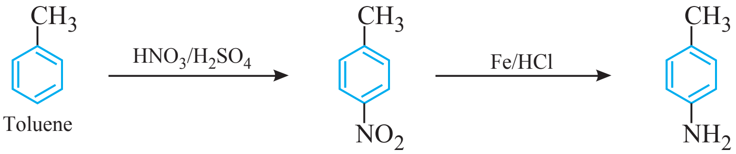
; *B* = 

Acetanilide

Q. 6. How will you carry out the following conversions?

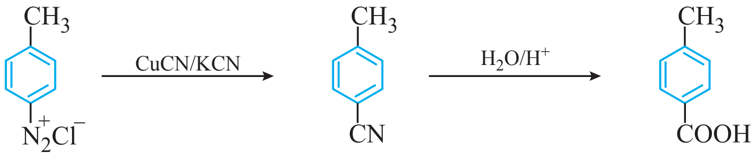
(*i*) toluene ⟶ *p*-toluidine

(*ii*) *p*-toluidine diazonium chloride ⟶ *p*-toluic acid **[*NCERT Exemplar*]**

Ans. (*i*) 

Toluene

p-Toluidine

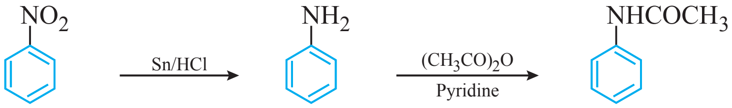
(*ii*) 

p-Toluic acid

Q. 7. Write the following conversions:

(*i*) nitrobenzene ⟶ acetanilide

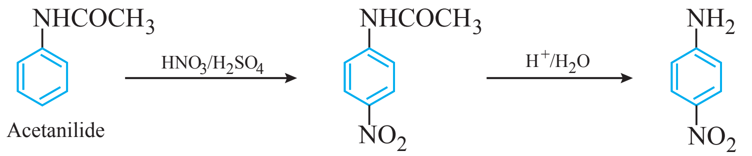
(*ii*) acetanilide ⟶ *p*-nitroaniline **[*NCERT Exemplar*]**

Ans. (*i*) 

Nitrobenzene

Acetanilide

(*ii*)



Acetanilide

p-nitroaniline

Short Answer Questions–II [3 marks]

Q. 1. (*i*) Arrange the following compounds in increasing order of dipole moment.

$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH [*NCERT Exemplar*]

(*ii*) Give possible explanation for each of the following:

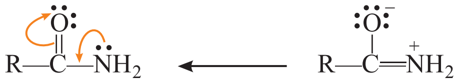
(*a*) The presence of a base is needed in the ammonolysis of alkyl halides.

(*b*) Amides are more acidic than amines.

Ans. (*i*) $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$

(*ii*) (*a*) To remove HX formed so that the reaction shifts in the forward direction.

(*b*)



$$R—\overset{\overset{\large\ddot{O}:}{||}}{C}—\ddot{N}H_2 \longleftarrow R—\overset{\overset{:\ddot{O}:^-}{|}}{C}=\overset{+}{N}H_2$$

Due to +R effect, availability of lone pair of electron on N of —NH_2 group decreases. As a result, acid amide is much weaker base than amines. Because of the positive charge on N, as a result of resonance, N can easily lose a proton and behaves, as a weak acid.

Q. 2. Write the structures of *A*, *B* and *C* in the following:

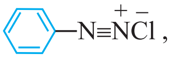
(*i*) $C_6H_5—CONH_2 \xrightarrow{Br_2/aq.\ KOH} A \xrightarrow[0-5°C]{NaNO_2 + HCl} B \xrightarrow{KI} C$

(*ii*) $CH_3—Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3 + alc. KOH} C$ [*CBSE Delhi 2016*]

Ans. (*i*) *A* =

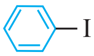
Aniline

B =



Benzene diazonium chloride

C =



Iodobenzene

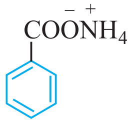
(*ii*) *A* = CH_3CN, Methyl cyanide; *B* = $CH_3—CH_2—NH_2$, Ethyl amine; *C* = $CH_3—CH_2—N \rightrightarrows C$ Ethyl isocyanide

Q. 3. Complete the following reactions:

(*i*) $C_6H_5—COOH \xrightarrow{NH_3} A \xrightarrow{Heat} B \xrightarrow{Br_2/KOH} C$

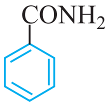
(*ii*) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273-278 K]{NaNO_2 + HCl} B \xrightarrow{CuCN} C$ [*CBSE East 2016*]

Ans. (*i*) *A* =



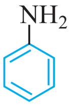
Ammonium benzoate

, *B* =



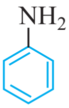
Benzamide

, *C* =



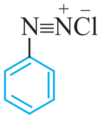
Aniline

(*ii*) *A* =



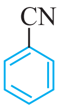
Aniline

, *B* =



Benzene diazonium chloride

, *C* =



Benzonitrile

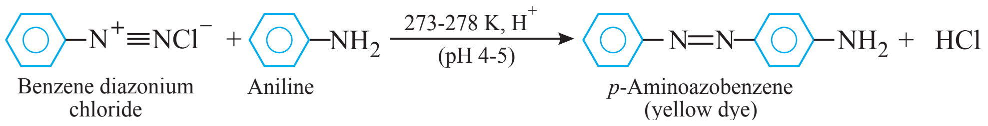
Q. 4. Complete the following chemical equations: **[*CBSE Delhi 2010*]**

(*i*) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$

(*ii*) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$

(*iii*) $RNH_2 + CHCl_3 + KOH \longrightarrow$

Ans. (*i*)



(*ii*) $$\underset{\text{Benzene diazonium chloride}}{C_6H_5\overset{+}{N_2}Cl^-} + \underset{\text{Ethanol}}{CH_3-CH_2-OH} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + CH_3-CHO + HCl$$

(*iii*) $$\underset{1^\circ \text{ amine}}{R-NH_2} + CHCl_3 + 3KOH\,(\text{alc.}) \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R-NC} + 3KCl + 3H_2O$$

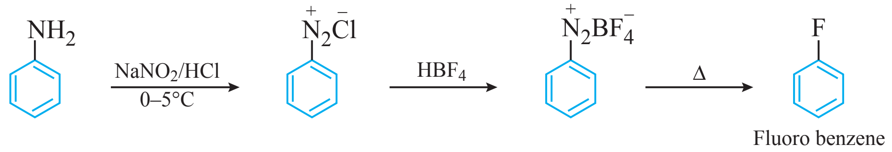
Q. 5. How are the following conversions carried out:

(*i*) Aniline to fluorobenzene

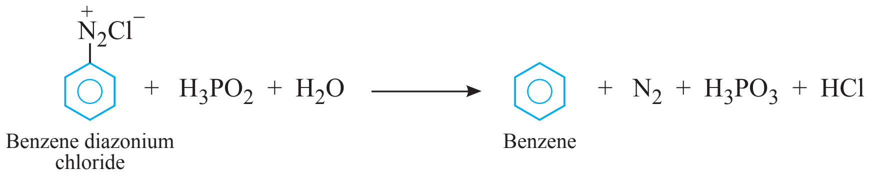
(*ii*) Benzene diazonium chloride to benzene

(*iii*) Methyl chloride to ethylamine **[*CBSE (F) 2013*]**

Ans. (*i*) Aniline to fluorobenzene



(*ii*) Benzene diazonium chloride to benzene



(*iii*) Methyl chloride to ethylamine

$$\underset{\text{Methyl chloride}}{CH_3-Cl} \xrightarrow{\text{alc, KCN}} CH_3-CN \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

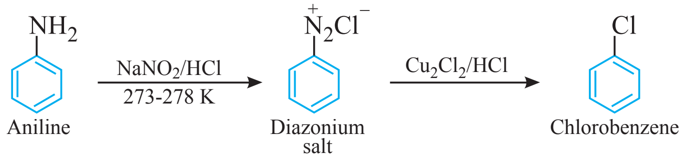
Q. 6. How will you convert the following:

(*i*) Aniline to chlorobenzene

(*ii*) Ethanoic acid to methanamine

(*iii*) Benzene diazonium chloride to phenol **[*CBSE (F) 2013*]**

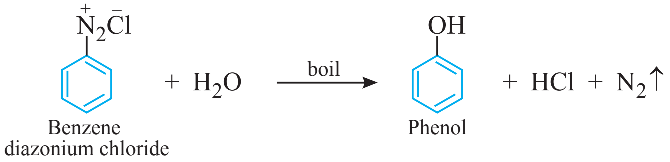
Ans. (*i*) Aniline to chlorobenzene



(*ii*) Ethanoic acid to methanamine

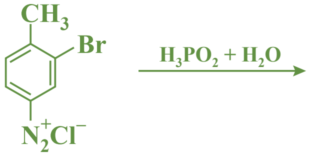
$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*iii*) Benzene diazonium chloride to phenol

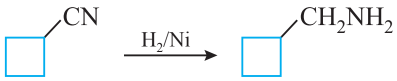


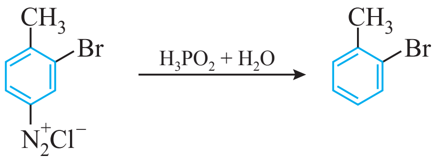
Q. 7. Complete the following reactions: **[*CBSE 2019 (56/2/1)*]**

(*i*)


(*ii*)


(*iii*)


Ans. (*i*)


(*ii*)


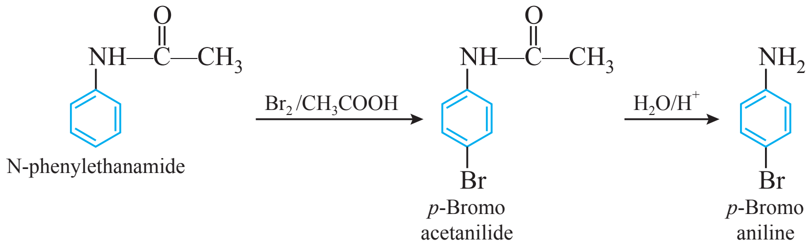
(*iii*)

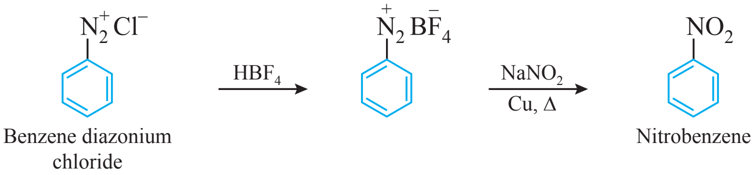

Q. 8. How do you convert the following:

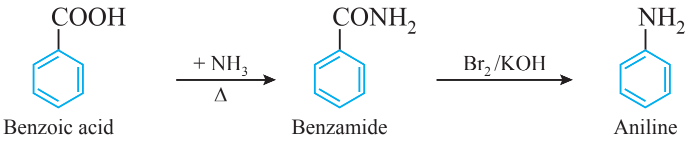
(*i*) N-phenylethanamide to *p*-bromoaniline

(*ii*) Benzene diazonium chloride to nitrobenzene

(*iii*) Benzoic acid to aniline **[*CBSE 2019 (56/2/1)*]**

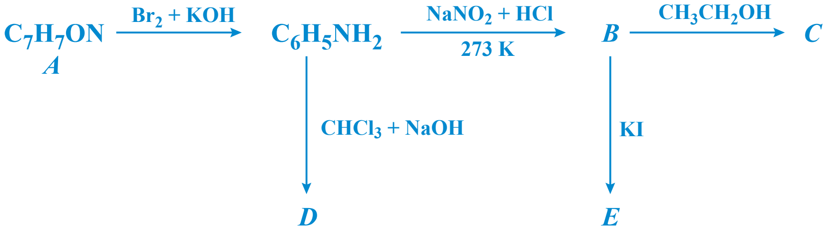
Ans. (*i*)


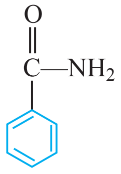
(*ii*)


(*iii*)


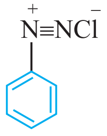
Long Answer Questions [5 marks]

Q. 1. An aromatic compound '*A*' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of *A, B, C, D* and *E* in the following reactions: [*CBSE Delhi 2015*] [*HOTS*]



Ans. *A* = 

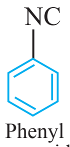
Benzamide

; *B* = 

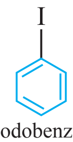
Benzene diazonium chloride

; *C* = 

Benzene

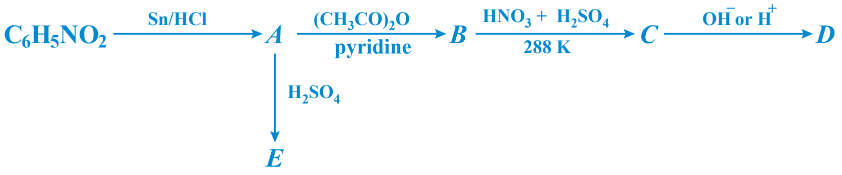
; *D* = 

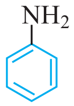
Phenyl isocyanide

; *E* = 

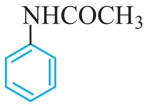
Iodobenzene

Q. 2. Write the structures of *A, B, C, D* and *E* in the following reactions: **[*CBSE (F) 2017*]**

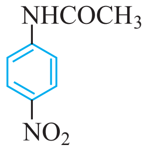


Ans. *A* = 

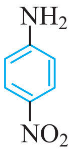
Aniline

, *B* = 

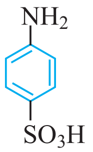
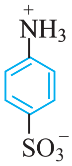
Acetanilide

, *C* = 

p-Nitroacetanilide

D = 

p-Nitroaniline

, *E* =  $\rightleftharpoons$ 

Sulphanilic acid

Q. 3. (*i*) Write the structures of main products when aniline reacts with the following reagents:

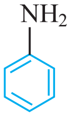
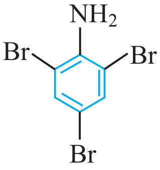
(*a*) Br_2 water (*b*) HCl (*c*) $(CH_3CO)_2O$/pyridine

(*ii*) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

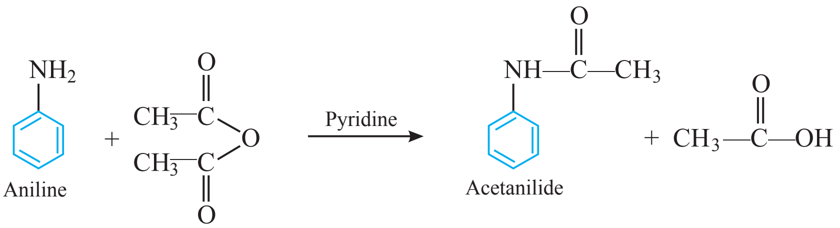
(*iii*) Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$ **[*CBSE Delhi 2015*]**

Ans. (*i*) (*a*)  + $3Br_2$ (water) $\longrightarrow$  + 3HBr

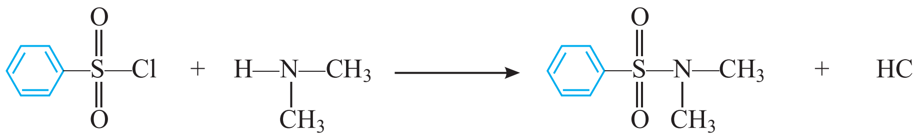
2,4,6-Tribromoaniline

(b) 
Aniline   Anilinium chloride

(c) 
Aniline   Acetic anhydride   Acetanilide

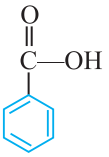
(ii) $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

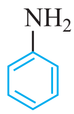
(iii) Dimethyl amine and trimethyl amine can be distinguished by using Hinsberg's reagent, *i.e.*, $C_6H_5SO_2Cl$. When treated with Hinsberg's reagent dimethylamine being a 2° amine gives N, N-dimethyl benzene sulphonamide which is insoluble in aqueous KOH solution while trimethyl amine being a 3° amine does not react with Hinsberg's reagent.

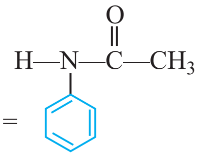

Benzene sulphonyl chloride   N,N-Dimethyl benzene sulphonamide (insoluble in KOH)

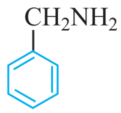
Q. 4. An aromatic compound '*A*' of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of *A, B, C, D* and *E* in the following reactions: **[*CBSE Allahabad 2015*]**

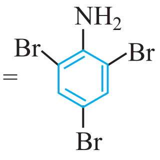
$$\begin{tikzcd} \underset{A}{(C_7H_6O_2)} \arrow[r, "NH_3/\text{heat}"] & C_6H_5CONH_2 \arrow[r, "Br_2 + NaOH"] \arrow[d, "LiAlH_4/\text{ether}"] & B \arrow[r, "(CH_3CO)_2O"] \arrow[d, "Br_2(aq)"] & C \\ & D & E & \end{tikzcd}$$

Ans. *A* = 
Benzoic acid

; *B* = 
Aniline

; *C* = 
N-Phenyl ethanamide

D = 
Benzylamine

; *E* = 
2,4,6-Tribromo aniline

Q. 5. **(*i*) How will you bring about the following conversions?**

- **(*a*) Ethanamine into methanamine**
- **(*b*) Aniline into 1,3,5-tribromobenzene**
- **(*c*) Aniline into 4-bromoaniline**

(*ii*) Account for the following: ***[CBSE 2019 (56/5/2)]***

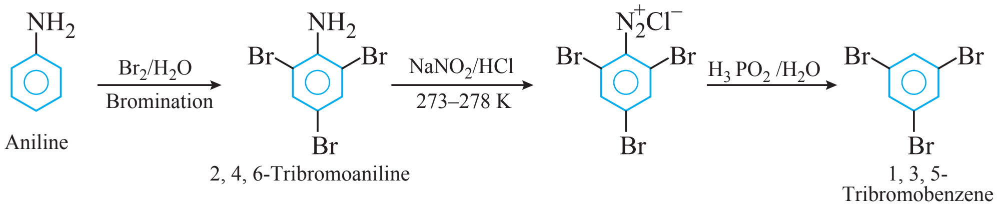
- **(*a*) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.**
- **(*b*) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.**

Ans. (*i*) (*a*)

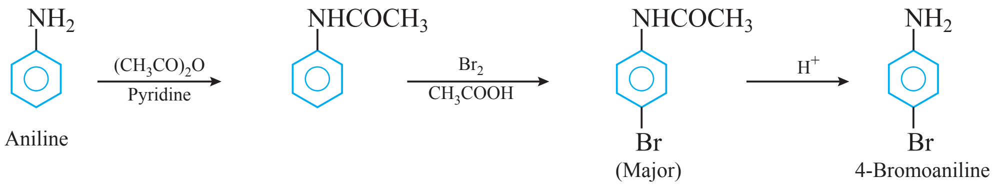
$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow[{[O]}]{CrO_3/H_2SO_4} CH_3COOH$$

$$CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2 \xrightarrow{+Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*b*)



(*c*)



(*ii*) (*a*) Refer to Ans. 3(*iii*) of NCERT Textbook Exercises.

(*b*) Refer to Ans. 3(*vi*) of NCERT Textbook Exercises.

Q. 6. **A hydrocarbon 'A', (C_4H_8) on reaction with HCl gives a compound 'B', (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C', ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. Identify the compounds 'A' to 'D'. Explain the reactions involved.** ***[HOTS]***

Ans. $(A) \xrightarrow{\text{Ozonolysis}} 2CH_3CHO$

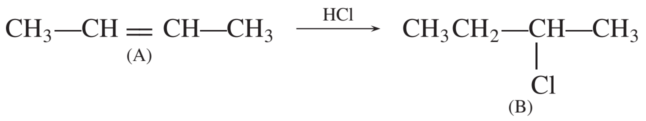
$\underset{(A)}{C_4H_8} \xrightarrow{HCl} \underset{(B)}{C_4H_9Cl}$ Addition of HCl has occurred on 'A'. This implies 'A' is an alkene.

$\underset{(B)}{C_4H_9Cl} \xrightarrow{NH_3} \underset{(C)}{C_4H_{11}N}$ Cl in compound 'B' is substituted by NH_2 to give 'C'.

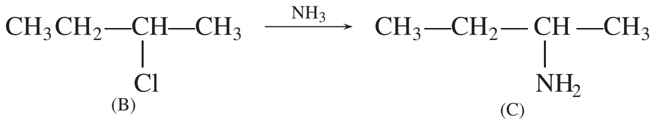
$(C) \xrightarrow[H_2O]{NaNO_2/HCl} (D)$ 'C' gives a diazonium salt with $NaNO_2$/HCl that liberates N_2 to give optically active alcohol. This means that 'C' is a primary amine. Number of carbon atoms in amine is same as compound 'A'.

Since products of ozonolysis of compound 'A' are $CH_3—CH{=}O$ and $O{=}CH—CH_3$. Therefore, the compound 'A' is $CH_3—CH{=}CH—CH_3$.

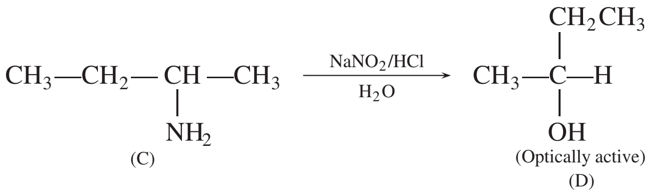
On the basis of structure of 'A', the reactions can be explained as follows:



$$\underset{(A)}{CH_3—CH = CH—CH_3} \xrightarrow{HCl} \underset{(B)}{CH_3CH_2—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_3}$$

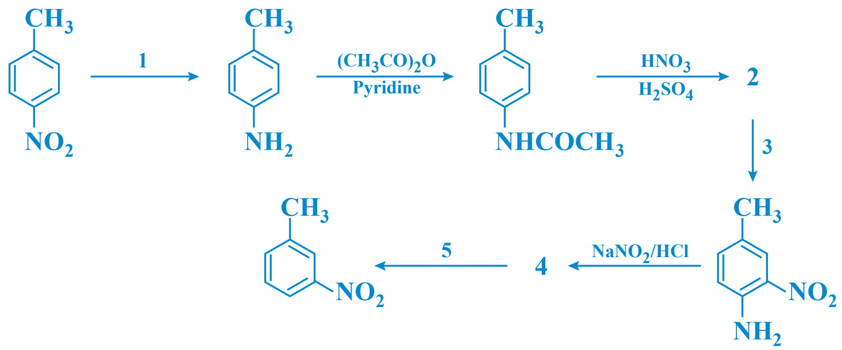


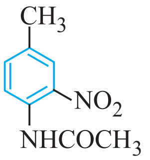
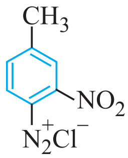
$$\underset{(B)}{CH_3CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3} \xrightarrow{NH_3} \underset{(C)}{CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3}$$



$$\underset{(C)}{CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3} \xrightarrow[H_2O]{NaNO_2/HCl} \underset{\substack{\text{(Optically active)}\\(D)}}{CH_3-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-H}$$

Q. 7. Predict the reagents or the products in the following reaction sequence: **[*HOTS*]**

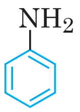
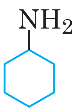
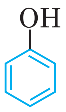
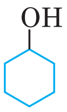


Ans. 1. Sn–HCl (conc.) 2.  3. H_2O/H^+ 4.  5. H_3PO_2/H_2O

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. **Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is**
   - (*a*) Hoffmann Bromamide reaction
   - (*b*) Gabriel phthalimide synthesis
   - (*c*) Sandmeyer reaction
   - (*d*) Reaction with NH_3
2. **Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride?**
   - (*a*) Aniline
   - (*b*) Phenol
   - (*c*) Anisole
   - (*d*) Nitrobenzene
3. **Which of the following compounds is the weakest Brönsted base?**
   - (*a*) 
   - (*b*) 
   - (*c*) 
   - (*d*) 

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

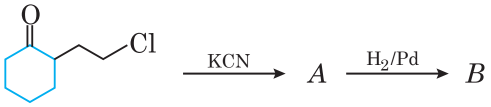
- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.* **(3 × 1 = 3)**

4. **Assertion (*A*) :** Nitromethane can give aldol condensation.
   Reason (*R*) : α-Hydrogen of nitromethane is acidic.
5. **Assertion (*A*) :** All compounds containing an odd number of nitrogen atoms have odd masses and those containing even number of N atoms have even masses.
   Reason (*R*) : Nitrogen rule can be applied to both aliphatic and aromatic compounds.
6. **Assertion (*A*) :** Tertiary amines have lower boiling points than those of primary and secondary amines of comparable molecular masses.
   Reason (*R*) : Tertiary amines are unable to form intermolecular hydrogen bonds.

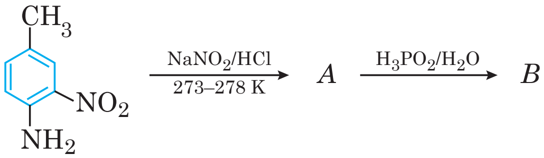
Answer the following questions:

7. Give an example of a zwitter ion. **(1)**
8. Convert Aniline into *p*-nitroaniline. **(1)**
9. How are the following conversions carried out?
   (*i*) Ethanamine to N-ethylethanamide
   (*ii*) Chloroethane to propan-1-amine **[*CBSE (F) 2009*] (2)**
10. Predict, giving reasons, the order of basicity of the following compounds in
   (*i*) gaseous phase and
   (*ii*) in aqueous solutions $(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3. **(2)**
11. Explain the observed K_b order:
   $Et_2NH > Et_3N > EtNH_2$ in aqueous solution **(2)**
12. Identify A and B in the following reaction.

(*i*)



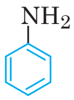
(*ii*)



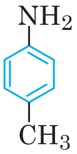
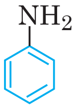
(2)

13. In the following pairs which one is more basic and why?

(*i*) CH_3NH_2 or



(*ii*) CH_3NH_2 or NH_3

(*iii*)  or  **(3)**

14. Give reasons:

(*i*) Acetylation of aniline reduces its activation effect.

(*ii*) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(*iii*) Although $—NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline. ***[CBSE Delhi 2017]*** **(3)**

15. (*i*) Illustrate the following reactions:

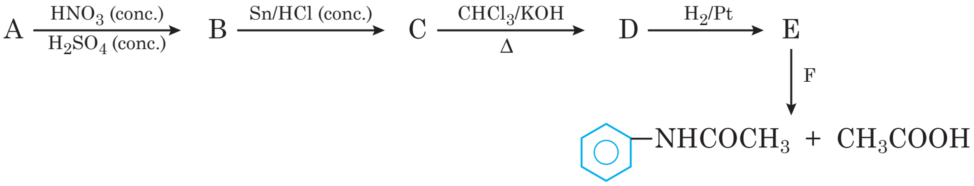
(*a*) Sandmeyer's reaction

(*b*) Gattermann's reaction.

(*ii*) Write a chemical test to distinguish between aniline and methylamine.

[CBSE Sample Paper 2017] **(3)**

16. Write structures of reagents/organic compounds (A to F) in the following sequence of reactions:



(5)

Answers

1. (*b*) **2.** (*d*) **3.** (*c*) **4.** (*a*) **5.** (*b*) **6.** (*a*)

Chapter–14

Biomolecules

basic concepts

1. **Biomolecules:** Macromolecules which are naturally occurring in biological systems are called biomolecules. Examples: polysaccharides (starch, cellulose, etc.), proteins, enzymes, vitamins, hormones, etc.
2. **Carbohydrates:** These are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis, *e.g.*, glucose, sucrose, cellulose, starch, etc.
3. **Classification of carbohydrates:**
   - (*a*) **Monosaccharides:** The simple carbohydrates that cannot be broken further into smaller units on hydrolysis, *e.g.*, glucose and fructose, ribose, etc.
   - (*b*) **Oligosaccharides:** These are the carbohydrates which on hydrolysis give two to ten units of monosaccharides, *e.g.*, sucrose, maltose, raffinose, stachyose, etc.
   - (*c*) **Polysaccharides:** These are the carbohydrates which produce a large number of monosaccharide units on hydrolysis, *e.g.*, starch, cellulose, etc.

   Importance of carbohydrates:

   (*i*) Carbohydrates act as biofuel to provide energy for functioning of living systems.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2832\text{ kJ}$$

   (*ii*) Carbohydrates are used as storage molecules as starch in plants and glycogen in animals.

   (*iii*) D-Ribose and 2-Deoxy-D-ribose are present in RNA and DNA, respectively.

   (*iv*) Cellulose acts as structural material of cell walls of bacteria and plants.

   (*v*) Carbohydrates provide raw material for many important industries like textiles, paper, lacquers and breweries.

4. (*i*) **Reducing sugars:** Those carbohydrates which contain free aldehydic or ketonic group and reduce Fehling's solution and Tollens' reagent are called reducing sugars, *e.g.*, all monosaccharides, maltose and lactose.

   (*ii*) **Non-reducing sugars:** Those sugars which do not have free aldehydic or ketonic group and do not reduce Fehling's solution or Tollens' reagent are called non-reducing sugars, *e.g.*, sucrose.

5. **Preparation of Glucose**

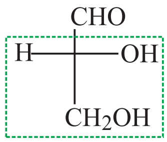
   (*a*) **From sucrose:**

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

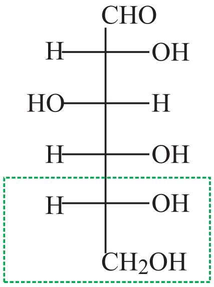
(*b*) **From starch:** Commercially, glucose is obtained by hydrolysis of starch by boiling it with dil. H_2SO_4 at 393 K under pressure.

$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{393K; 2-3 atm}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

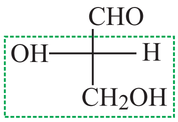
6. (*a*) **Structure of Glucose:** Glucose is a six carbon straight chain aldose which has one aldehydic group (—CHO), one primary hydroxyl group (—CH_2OH) and four secondary hydroxyl groups (—CHOH). If the —OH group attached to C-5 is on the right side, the glucose is assigned D–configuration; if the —OH group attached to C-5 is on the left side, it is assigned L–configuration. The (+) and (–) signs represent the optical rotation as dextro and laevo, respectively and have no relationship with D and L configuration.



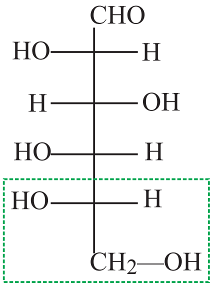
D-(+)-Glyceraldehyde



D-(+)-Glucose

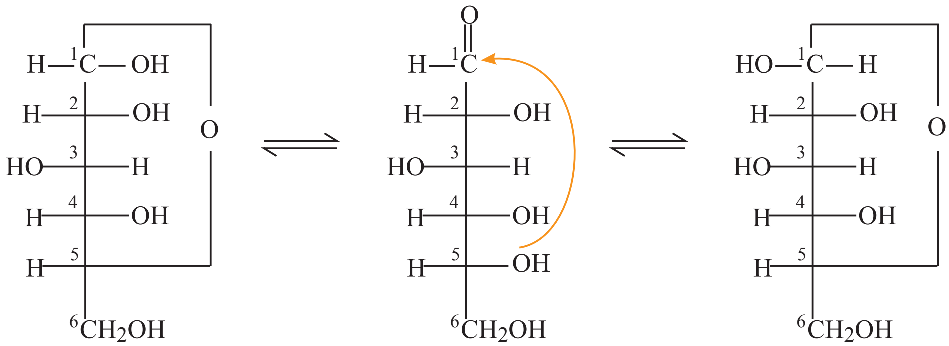


L-(–)-Glyceraldehyde



L-(–)-Glucose

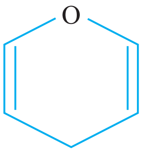
(*b*) **Cyclic structure of glucose:** The glucose has been shown to possess cyclic structure represented as follows:



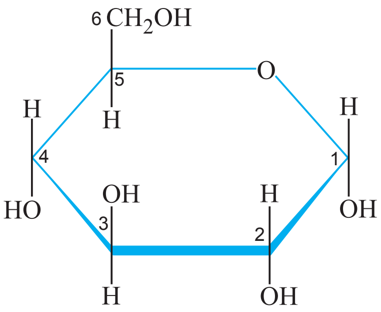
α-D-(+)-Glucose

β-D-(+)-Glucose

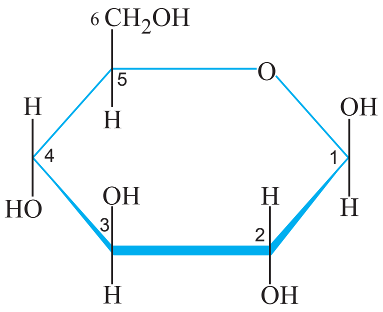
Haworth Structures



Pyran

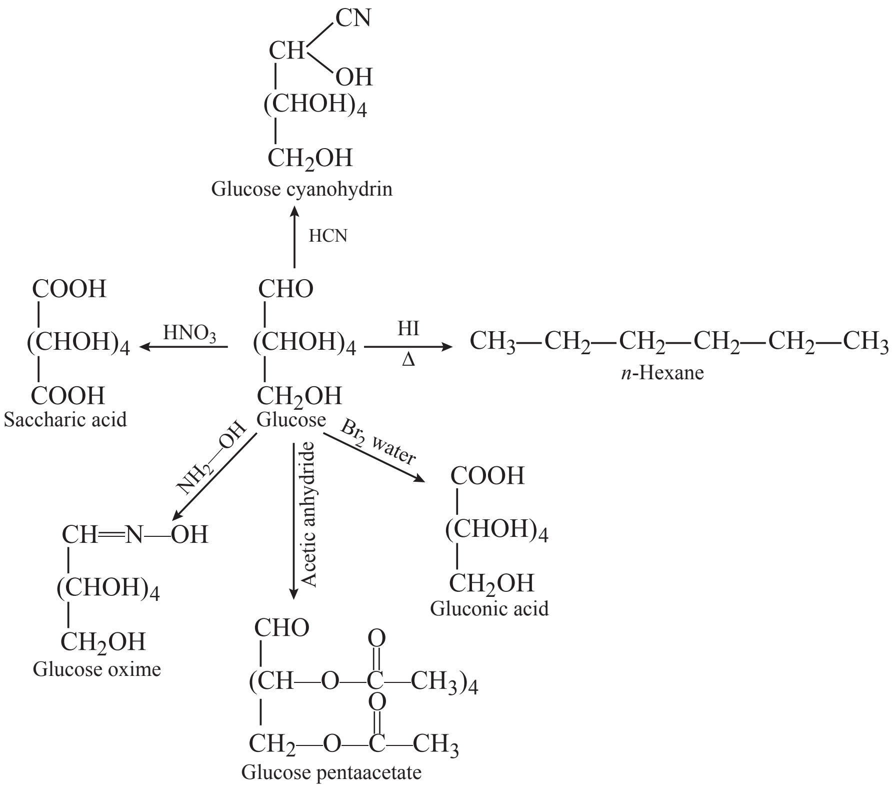


α-D-(+)-Glucopyranose

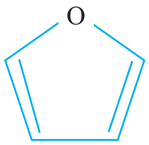


β-D-(+)-Glucopyranose

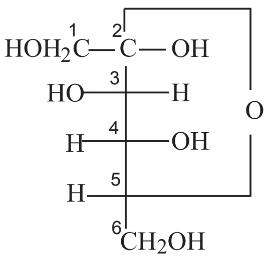
7. Reactions of Glucose



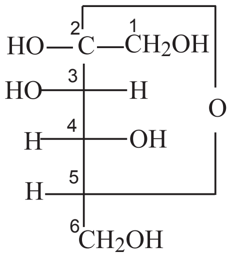
8. Structure of Fructose: Fructose is a ketohexose and has the molecular formula $C_6H_{12}O_6$. It belongs to D-series and is a laevorotatory compound.



Furan

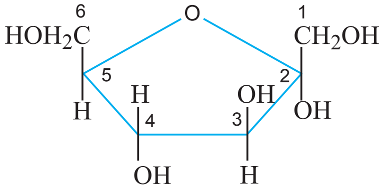


α-D-(–)-Fructofuranose

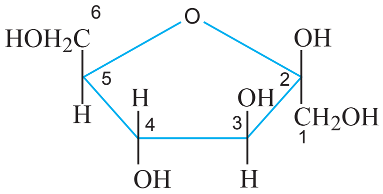


β-D-(–)-Fructofuranose

The cyclic structures of two anomers of fructose are represented by Haworth structures as given below.



α-D-(–)-Fructofuranose



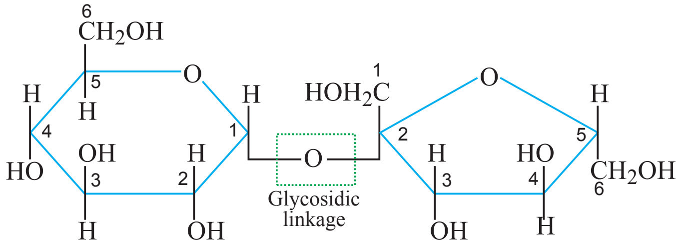
β-D-(–)-Fructofuranose

9. Disaccharides: The sugar which on hydrolysis gives two units of monosaccharides is called disaccharide. Disaccharides are crystalline solids and are soluble in water. Sucrose, maltose and lactose are disaccharides.

Hydrolysis of sucrose is called inversion of cane sugar. Sucrose is a disaccharide because on hydrolysis, it produces two monosaccharides namely D-(+)-glucose and D-(–)-fructose.

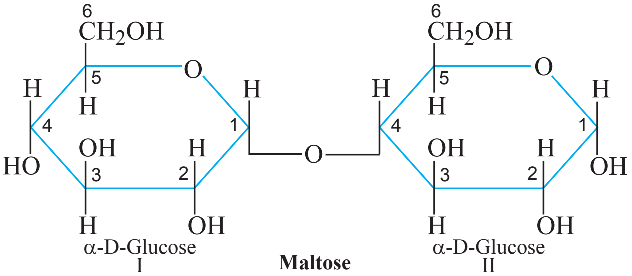
$$\underset{\substack{\text{Sucrose}\\ \text{(disaccharide)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{D-(+)-Glucose}\\ \text{(monosaccharide)}}}{C_6H_{12}O_6} + \underset{\substack{\text{D-(–)-Fructose}\\ \text{(monosaccharide)}}}{C_6H_{12}O_6}$$

(*a*) **Ring structure of a sucrose molecule:** A sucrose molecule is composed of α-glucose and β-fructose units.



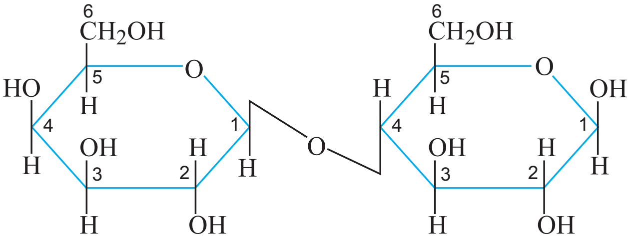
Sucrose

(*b*) **Ring structure of a maltose molecule:** A maltose molecule is composed of two α-D-glucose units in which C-1 of one glucose (I) is linked to C-4 of another glucose unit (II).



Maltose

(*c*) **Ring structure of a lactose molecule:** A lactose molecule is composed of β-D-galactose and β-D-glucose units.

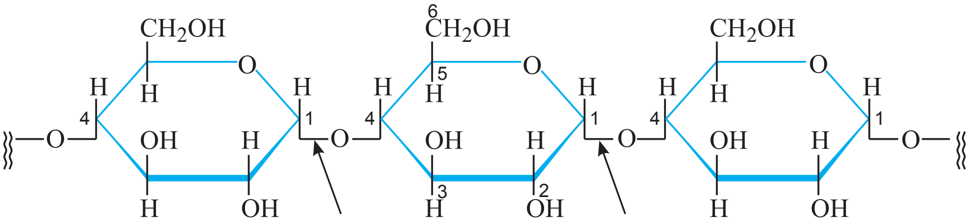


Lactose

10. Polysaccharides: Polysaccharides are the carbohydrates which yield a large number of monosaccharide molecules upon hydrolysis. Starch, cellulose and glycogen are examples of polysaccharides.

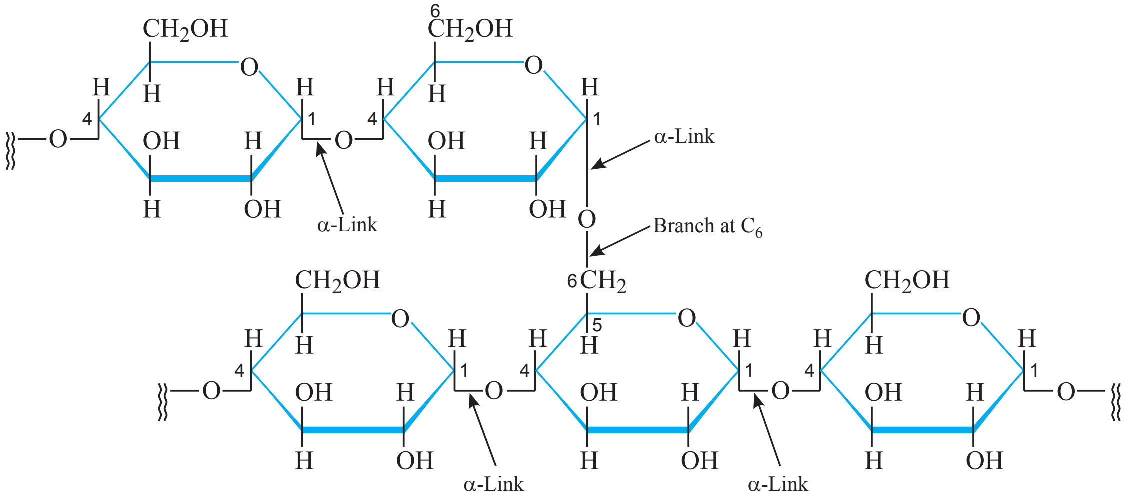
(*a*) **Starch:** The fundamental unit of starch is α-D-glucose.

Structure of starch: Starch is a polymer of α-glucose and consists of two components—amylose and amylopectin. Amylose is a long unbranched chain with 200–1000 α-D-(+)-glucose units held by C1–C4 glycosidic linkage.



Amylose

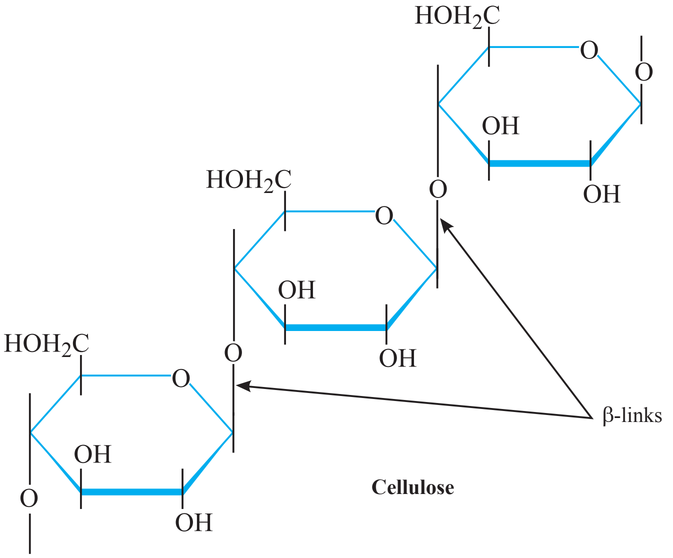
Amylopectin is a branched chain polymer of α-D-glucose units in which the chain is formed by C1–C4 glycosidic linkage, whereas branching occurs by C1–C6 glycosidic linkage.



Amylopectin

(b) **Cellulose:** Cellulose is a polysaccharide. The fundamental structural unit of cellulose is β-D-glucose.

Structure of cellulose: Cellulose is a linear polymer of β-D-glucose which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.



Cellulose

11. Amino acids: Those compounds, whose molecule contains both the carboxylic acid group and the amino group are called amino acids. There are twenty amino acids which form protein. The amino acids which are synthesised in body are known as non-essential amino acids, *e.g.*, glycine, alanine. Those amino acids which cannot be synthesised in body and must be obtained through diet are known as essential amino acids, *e.g.*, valine, lysine.

Amino acids have also been classified as neutral, acidic and basic amino acids. Amino acids like glycine, valine, etc. which contain one —NH_2 and one —COOH group are called neutral amino acids. Those amino acids such as aspartic acid, glutamic acid, etc. which contain one —NH_2 group and two —COOH groups are called acidic amino acids and amino acids such as lysine, histidine, etc., which contain two —NH_2 groups and one —COOH group are called basic amino acids.

12. Proteins are complex nitrogenous organic molecules which are essential for growth and maintenance of body. Chemically, proteins are the polymers of α-amino acids which are linked by peptide bonds $(\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—NH—})$.

(*a*) **Types of proteins based on molecular shape:**

(*i*) **Fibrous proteins:** They have thread-like molecules which tend to lie side by side to form fibres, *e.g.*, keratin, collagen, myosin, fibroin, etc. In such proteins, the molecules are held together by hydrogen and disulphide bonds. They are insoluble in water. They are the chief structural materials of animal tissues.

(*ii*) **Globular proteins:** They have molecules which are folded into compact units that often form spheroidal shapes. The area of contact between molecules are small and inter-molecular forces are comparatively weak, *e.g.*, insulin, thyroglobulin, albumin, haemoglobin and fibrinogen. In clotting of blood, fibrinogen gets converted into fibrous protein, fibrin.

(*b*) **Structure of Proteins:** There are four levels at which the structure of proteins are studied. These are primary, secondary, tertiary and quarternary levels.

(*i*) **Primary structure of proteins:** The sequence in which various amino acids are arranged in a protein is called its primary structure. Any change in the sequence of amino acids creates different protein which alters biological functions.

(*ii*) **Secondary structure of proteins:** It refers to shape in which a long polypeptide chain exists. A protein may assume α-helix structure or β-pleated sheet structure. The α-helix structure results due to regular coiling of polypeptide chain which is stabilised by intramolecular hydrogen bonding. Keratin in hair, nails, wool and myosin in nucleus have α-helix structure. In β-pleated sheet structure, all peptide chains are stretched to nearly maximum extension and then arranged side by side and held together by intermolecular hydrogen bonding. Silk has β-pleated sheet structure.

(*iii*) **Tertiary structure of proteins:** The tertiary structure of proteins represents overall folding of the polypeptide chain, *i.e.*, further folding of the secondary structure. It gives rise to two major molecular shapes, *viz.*, fibrous and globular. The main forces which stabilise 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals forces and electrostatic force of attraction.

(*iv*) **Quaternary structure:** 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.

(*c*) **Denaturation of Proteins:** When a protein in its native form is subjected to a change, such as change in temperature or change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact, *e.g.*, coagulation of egg while on boiling, curdling of milk, etc.

13. (*a*) **Enzymes:** Enzymes are essential biological catalysts which are required to catalyse biological reactions, *e.g.*, maltose, lactose, invertase, etc. Almost all the enzymes are globular proteins.

(*b*) **Oxidoreductase enzymes:** Enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate.

(*c*) **Phenylketonuria:** Disease caused by deficiency of the enzyme phenylalanine hydroxylase.

(*d*) **Albinism:** Disease caused due to deficiency of an enzyme tyrosinase.

(*e*) **Streptokinase:** Enzyme which dissolves the blood clot formed in coronary artery which leads to heart trouble.

14. Nucleic Acids: Nucleic acids are long chain polymers of nucleotides. They play an important role in transmission of hereditary characteristics and biosynthesis of proteins.

Types of nucleic acids: There are two types of nucleic acids. These are DNA and RNA.

(*a*) **Constituents of nucleic acids:**

(*i*) Pentose sugar (*ii*) Phosphoric acid (*iii*) Nitrogenous bases.

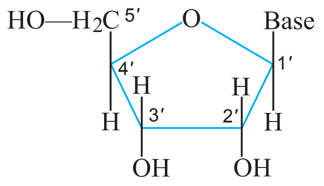
In DNA, β-D-2-deoxyribose sugar is present while in RNA β-D-ribose sugar is present.

Nitrogen containing bases: There are two types of nitrogen containing bases found in nucleic acids. These are pyrimidines and purines.

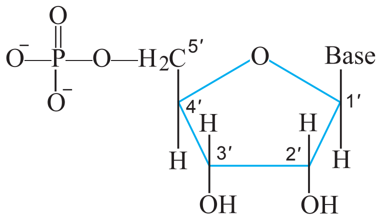
Pyrimidines: There are three bases derived from pyrimidines. These are cytosine (C), thymine (T) and uracil (U). In DNA, T is present but in RNA, U is present.

Purines: There are two bases derived from purine. These are adenine (A) and guanine (G).

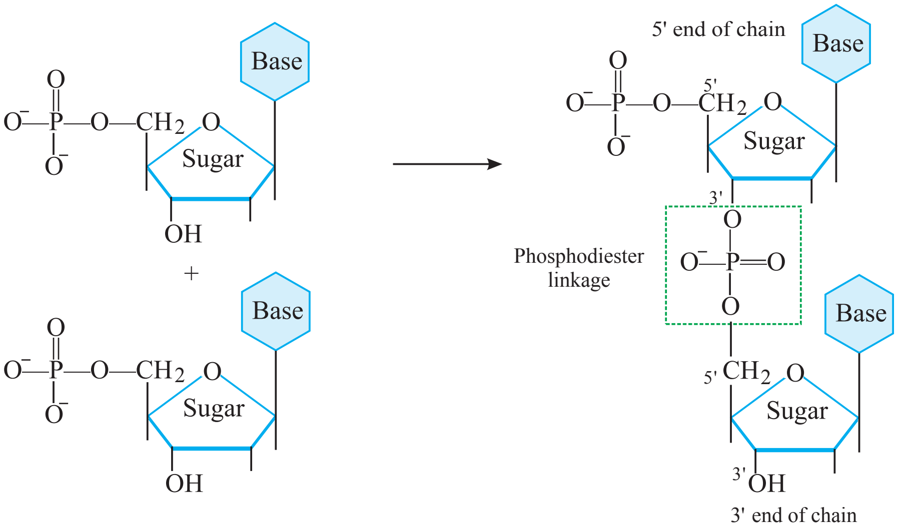
Nucleoside: A unit formed by the attachment of a base to 1′-position of sugar is known as nucleoside.



Nucleotide: When nucleoside is linked to phosphoric acid at 5′-position of sugar moiety, the unit obtained is called nucleotide.



Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.



Formation of dinucleotide

(*b*) **Deoxyribonucleic acid (DNA):** It contains a pentose sugar deoxyribose, and adenine, guanine, thymine and cytosine bases. A phosphate group is present at C-5 of the sugar unit. The repeating units, deoxyribonucleotides, are linked by phosphate group. Thus, they are the biopolymers of deoxyribonucleotides and have double helix structure of polynucleotides. The two strands of DNA are said to be complementary to each other. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine. They are responsible for genetic characteristics and for sending information and instruction in the cell for the synthesis of specific protein.

(*c*) **Ribonucleic acid (RNA):** It contains ribose sugar, bases from pyrimidine bases—uracil and cytosine, and two bases from purine base—adenine and guanine. A phosphate group is present at C-5 of the sugar unit. The repeating units, ribonucleotides, are linked by phosphate group. They are the polymers of ribonucleotide and have a single helix structure. RNA is associated with the process of learning and memory storage, and helps in biosynthesis of protein.

15. Functions of Nucleic Acids: Two main functions of nucleic acids are:

(*a*) **Replication or heredity transfer:** The double helix of DNA is the storehouse of the genetic information of the organism which is contained in the sequence of bases A, T, C, G on the strands of DNA. The process by which a DNA molecule produces two identical molecules of itself in the nucleus of the cell is called replication.

(*b*) **Protein synthesis:** This is brought about in two steps:

(*i*) **Transcription:** Copying of sequence of bases from the DNA strand onto the RNA molecule is called transcription. During transcription, the double helix of the DNA partially unwinds and one of the two DNA strands serves as a template for the synthesis of RNA strand called messenger RNA (*m*RNA) which is complementary to a segment of the DNA chain.

(*ii*) **Translation:** This is the process in which *m*RNA directs protein synthesis in the cytoplasm of cell with involvement of transfer RNA (*t*RNA) and ribosomal particles (*r*RNA protein complexes).

16. (*a*) **Codon:** The sequence of nucleotides in *m*RNA molecules are read in a serial order in sets of three (triplet) at a time. Each triplet is called a codon. It specifies one amino acid. The *m*RNA codon recognises the amino acids through *t*RNAs which carry specific amino acids.

(*b*) **Gene:** The sequence of bases or nucleotides in the DNA molecule which regulates the synthesis of a specific protein is called a gene. Every protein in the cell has a corresponding gene. The relationship between a nucleotide triplet (codon) and the amino acid is called genetic code.

(*c*) **Mutation:** The chemical change in the sequence of bases in the DNA molecule can lead to synthesis of protein with an altered amino acid sequence is called mutation. This is brought about spontaneously by exposure to UV-rays, X-rays and chemicals.

17. **Vitamins:** Vitamins are generally regarded as 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.

Vitamins are classified into two groups depending upon their solubility in fat or water:

(*i*) **Fat-soluble vitamins:** Vitamins A, D, E and K are soluble in fat and oils but insoluble in water. They are stored in liver and adipose tissues.

(*ii*) **Water-soluble vitamins:** Vitamins belonging to group B and vitamin C are soluble in water. They must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Table 14.1: Some Important Vitamins, their Sources and their Deficiency Diseases

S. No.	Name of Vitamins	Sources	Deficiency Diseases
1.	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye), night blindness
2.	Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri-beri (loss of appetite, retarded growth)
3.	Vitamin B_2 (Riboflavin)	Milk, egg white, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4.	Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5.	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6.	Vitamin C (Ascorbic acid)	Citrus fruits, *amla* and green leafy vegetables.	Scurvy (bleeding gums)
7.	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8.	Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness
9.	Vitamin K	Green leafy vegetables	Increased blood clotting time

18. **Hormones:** Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are released directly in the blood stream. From here these are transported to the site of their action.

Functions of hormones:

(*i*) They help to maintain the balance of biological activities in the body. For example, insulin keeps the blood glucose level within the range, epinephrine and norepinephrine mediate response to external stimuli, growth hormones and sex hormones play role in growth and development.

(*ii*) The hormones released by gonads are responsible for development of secondary sexual characters.

(*iii*) Adrenal cortex release glucocorticoids and mineralocorticoids. The glucocorticoids control the carbohydrate metabolism, modulate inflammatory reactions and are involved in reactions to stress. The mineralocorticoids control the level of excretion of water and salt by the kidney.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Glucose or sucrose are soluble in water but cyclohexane or benzene (simple six-membered ring compounds) are insoluble in water. Explain.

Ans. Glucose contains five —OH groups and sucrose (molecular mass = 342) contains eight —OH groups. These —OH groups form hydrogen bonds with water. Because of this extensive intermolecular hydrogen-bonding, glucose and sucrose are soluble in water.

On the other hand, benzene (molecular mass = 78) and cyclohexane (molecular mass = 84) are simple molecules having low molecular masses. Even then they are insoluble in water as these compounds do not contain —OH groups and hence do not form hydrogen bonds with water.

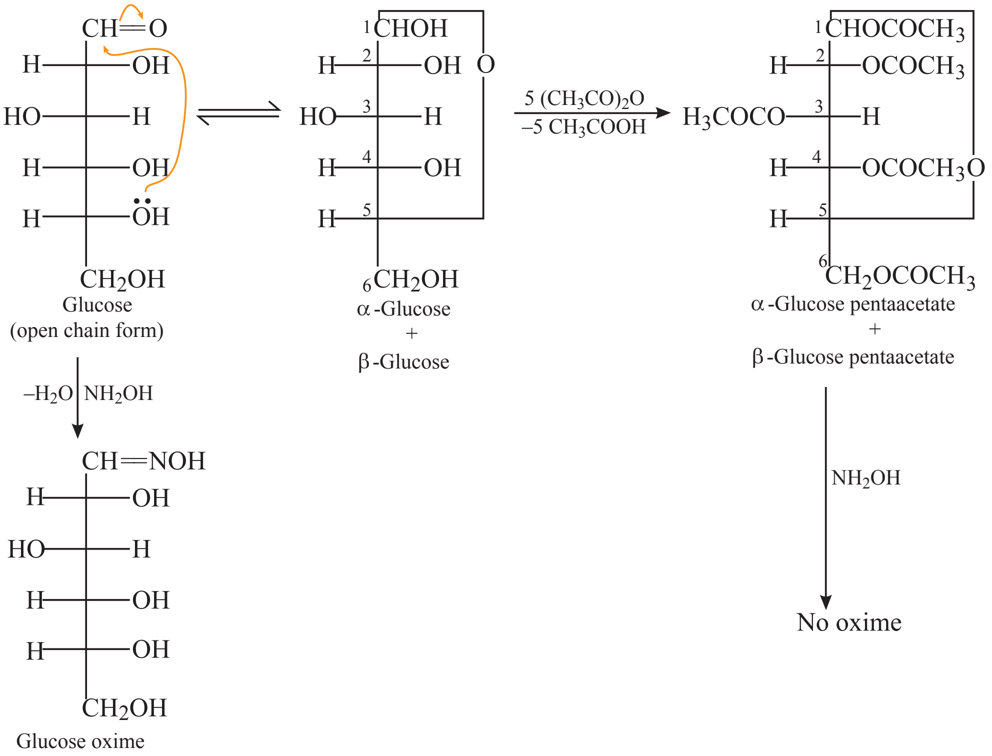
Q. 2. What are the expected products of hydrolysis of lactose? ***[CBSE 2019 (56/2/3)]***

Ans. On hydrolysis, lactose gives two molecules of monosaccharides, *i.e.*, one molecule of D-(+)-glucose and one molecule of D-(+)-galactose.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Lactase}]{H_3O^+} \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(+)-Galactose}}{C_6H_{12}O_6}$$

Q. 3. How do you explain the absence of aldehyde group in the pentaacetate of D-glucose? ***[CBSE 2020 (56/3/3)]***

Ans. The cyclic hemiacetal form of glucose contains an —OH group at C-1 which gets hydrolysed in the aqueous solution to produce the open chain aldehydic form which then reacts with NH_2OH to form the corresponding oxime. Therefore, glucose contains an aldehydic group. On the other hand, when glucose is reacted with acetic anhydride, the —OH group at C-1, along with the four other —OH groups at C-2, C-3, C-4 and C-6 form a pentaacetate. As the pentaacetate of glucose does not contain a free —OH group at C-1, it cannot get hydrolysed in aqueous solution to produce the open chain aldehydic form and thus glucose pentaacetate does not react with NH_2OH to form glucose oxime.



Q. 4. The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

Ans. The amino acids exist as zwitter ions, $H_3\overset{+}{N}—CHR—COO^-$. Because of this dipolar salt-like character, they have strong dipole–dipole attractions. So, their melting points are higher than halo acids which do not have salt-like character. Moreover, due to this salt-like character, they interact strongly with H_2O. Thus, solubility in water of amino acids is higher than that of the corresponding halo acids which do not have salt-like character.

Q. 5. Where does the water present in the egg go after boiling the egg?

Ans. On boiling the egg, the proteins undergo denaturation and the water present in the egg gets absorbed or adsorbed in the denaturated proteins probably through H-bonding.

Q. 6. Why cannot vitamin C be stored in our body?

Ans. Vitamin C is soluble in water, hence, it is readily excreted in urine and thus cannot be stored in the body.

Q. 7. What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?

Ans. Besides thymine, the two products are 2-deoxy-D-ribose and phosphoric acid.

Q. 8. When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structure of RNA? ***[HOTS]***

Ans. A DNA molecule has two strands in which the four complementary bases pair each other, *viz*., cytosine (C) always pairs with guanine (G) while thymine (T) always pairs with adenine (A). Therefore, when a DNA molecule is hydrolysed, the molar amounts of cytosine is always equal to that of guanine and that of adenine is always equal to that of thymine. RNA also contains four bases, the first three are same as in DNA but the fourth one is uracil (U).

As in RNA, there is no relationship between the quantities of four bases (C, G, A and U) obtained, therefore, the base-pairing principle, *viz*., A pairs with U and C pairs with G is not followed. So, unlike DNA, RNA has a single strand.

NCERT Textbook Exercises

Q. 1. What are monosaccharides?

Ans. Monosaccharides are carbohydrates which cannot be further hydrolysed to simpler molecules. The general formula is $(CH_2O)_n$ where $n = 3 - 7$.

Q. 2. What are reducing sugars?

Ans. Carbohydrates which reduce Fehling's solution to red precipitate of Cu_2O or Tollens' reagent to metallic Ag are called reducing sugars. All monosaccharides (both aldoses and ketoses) and disaccharides except sucrose are reducing sugars.

Q. 3. Write two main functions of carbohydrates in plants.

Ans. ***(i)*** **Structural material for cell walls:** The polysaccharide, cellulose acts as the chief structural material of the cell walls.

(ii) **Reserve food material:** The polysaccharide, starch is the major reserve food material in the plants.

Q. 4. Classify the following into monosaccharides and disaccharides: Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.

Ans. **Monosaccharides:** Ribose, 2-deoxyribose, galactose and fructose.

Disaccharides: Maltose and lactose.

Q. 5. What do you understand by the term glycosidic linkage?

Ans. The linkage between two monosaccharide units in a oligosaccharide or a polysaccharide through oxygen atom is called glycosidic linkage.

Q. 6. What is glycogen? How is it different from starch? ***[CBSE (F) 2012]***

Ans. Glycogen is a polymer of α–D–glucose. The carbohydrates are stored in animal body as glycogen. Starch is also a polymer of α–D–glucose and consist of two components amylose and amylopectin. Amylose is linear chain polymer of α–D–glucose. Both glycogen and amylopectin are branched chain polymers of α–D–glucose but glycogen is more highly branched than amylopectin. Starch is the main storage polysaccharide of plants.

Q. 7. What are the hydrolysis products of (*i*) sucrose (*ii*) lactose? *[CBSE (AI) 2010, 2013, 2014]*

Ans. Both sucrose and lactose are disaccharides. Sucrose on hydrolysis gives one molecule each of glucose and fructose. Lactose on hydrolysis gives one molecule each of glucose and galactose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Invertase}]{H_3O^+} \underset{\text{D-(+) -Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Lactase}]{H_3O^+} \underset{\text{D-(+) -Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(+) -Galactose}}{C_6H_{12}O_6}$$

Q. 8. What is the basic structural difference between starch and cellulose? *[CBSE 2019 (56/2/2)]*

OR

Starch and cellulose both contain glucose units as monomer, yet they are structurally different. Explain. *[CBSE 2020 (56/1/2)]*

Ans. Starch consists of amylose and amylopectin.

Amylose is a long unbranched chain with α-D(+)-glucose units that are held together with C1–C4 glycosidic linkage. Amylopectin is a highly branched chain polymer of α-D-glucose units in which glycosidic linkage is present between C1–C4 atoms and branching occurs through C1–C6 glycosidic linkage. For figures refer to Basic Concept Point 10(*a*).

Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose units and C4 of next glucose units. For figure refer to Basic Concepts Point 10(*b*).

Q. 9. What happens when D-glucose is treated with the following reagents? *[CBSE 2019 (56/5/2)]*

(*i*) HI (*ii*) Bromine water (*iii*) HNO_3

Ans. Refer to Basic Concepts Point 7.

Q. 10. Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.

Ans. The following reactions cannot be explained by its open chain structure proposed by Baeyer:

(*i*) Despite having an aldehydic group, glucose does not give Schiff's test and it does not react with sodium bisulphite and ammonia.

(*ii*) The pentaacetate of glucose does not react with hydroxylamine indicating absence of —CHO group.

(*iii*) When D-glucose is treated with methyl alcohol in presence of dry hydrogen chloride gas, it gives two isomeric mono methyl derivatives known as α-D-glucoside and methyl β-D-glucoside. These glucosides does not reduce Fehling's solution and also do not react with hydrogen cyanide or hydroxylamine indicating the absence of free —CHO group.

Q. 11. What are essential and non-essential amino acids? Give two examples of each type. *[CBSE Delhi 2010]*

Ans. α-Amino acids which are required for health and growth of human beings but are not synthesised by the human body are known as essential amino acids. Examples: valine, leucine, phenylalanine, etc. On the other hand, α-amino acids which are needed for health and growth of human beings and are synthesised by the human body are called non-essential amino acids. Examples: glycine, alanine, aspartic acid, etc.

Q. 12. Define the following terms as related to proteins:

(*i*) Peptide linkage (*ii*) Primary structure (*iii*) Denaturation *[CBSE (AI) 2014; 2019 (56/5/2)]*

Ans. (*i*) A **peptide linkage** is an amide ($—\overset{\overset{\displaystyle O}{\|}}{C}—NH—$) linkage formed between —COOH group of one α-amino acid and —NH_2 group of other α-amino acid by loss of a water molecule.

(*ii*) The specific sequence in which various α-amino acids present in a protein are linked to one another is called its **primary structure**. Any change in its primary structure creates a new protein.

(*iii*) When a protein in its native form is subjected to a change, such as change in temperature or change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation of protein**. During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact, *e.g.*, coagulation of egg while on boiling, curdling of milk, etc.

Q. 13. What are common types of secondary structure of proteins?

Ans. The conformation which the polypeptide chains assume as a result of hydrogen bonding is known as the secondary structure of the proteins. The two types of secondary structures are α-helix and β-pleated sheet structure.

Q. 14. What type of bonding helps in stabilising the α-helix structure of proteins?

Ans. The α-helix structure of proteins is stabilised by intramolecular H-bonding between C—O of one amino acid residue and the N—H of the fourth amino acid residue in the chain.

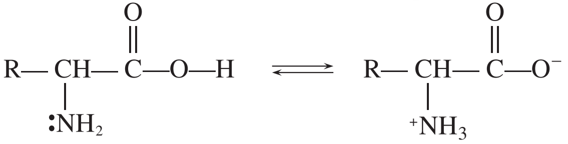
Q. 15. Differentiate between globular and fibrous proteins. *[CBSE 2019 (56/5/2), 2020 (56/5/1)]*

Ans. Refer to Basic Concepts Point 12(*a*).

Q. 16. How do you explain the amphoteric behaviour of amino acids?

Ans. Amino acids contain 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 with both acids and bases.



$$R-\underset{\substack{|\\ :NH_2}}{CH}-\overset{\substack{O\\ \|}}{C}-O-H \rightleftharpoons R-\underset{\substack{|\\ {}^{+}NH_3}}{CH}-\overset{\substack{O\\ \|}}{C}-O^-$$

Q. 17. What are enzymes?

Ans. Enzymes are biological catalysts. Each biological system requires a different enzyme. So, as compared to conventional catalysts, enzymes are specific and efficient in their action. They are required in only small quantity and work at optimum temperature (310 K) and pH (7.4) under 1 atmospheric pressure. Chemically, they are globular proteins. However, some enzymes are also associated with some non-protein components called the co-factors for their activity. Cofactors are of two types:

(*i*) **Inorganic ions** such as Zn^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Co^{2+}, etc.

(*ii*) **Organic molecules:** These are of two types:

(*a*) **Coenzymes:** These are usually derived from vitamins such as thymine, riboflavin, niacin, etc. They are loosely held to the protein and can be easily separated by dialysis.

(*b*) **Prosthetic group:** They are also derived from vitamins such as biotin but are tightly held to the protein molecule by covalent bonds. They can be separated only by careful hydrolysis.

Q. 18. What is the effect of denaturation on the structure of proteins?

Ans. During denaturation, 2° and 3° structures of proteins are destroyed but 1° structure remains intact. Due to denaturation, the globular proteins (soluble in H_2O) are converted into fibrous proteins (insoluble in H_2O) and their biological activity is lost. For example, boiled egg which contains coagulated proteins cannot be hatched.

Q. 19. How are vitamins classified? Name the vitamin responsible for the coagulation of blood.

Ans. Vitamins are classified into two groups depending upon their solubility in water or fat.

(*i*) **Water-soluble vitamins:** These include vitamin B-complex (B_1, B_2, B_5, *i.e.*, nicotinic acid, B_6, B_{12}, pantothenic acid, biotin, *i.e.*, vitamin H and folic acid) and vitamin C.

(*ii*) **Fat-soluble vitamins:** These include vitamin A, D, E and K. These are stored in liver and adipose tissues (fat storing tissues).

Vitamin K is responsible for coagulation of blood.

Q. 20. Why are vitamin A and vitamin C essential to us? Give their important sources.

Ans. Vitamin A is essential for us because its deficiency can cause xerophthalmia (hardening of cornea of eye) and night blindness.

Sources: Carrots, fish liver oil, butter and milk.

Vitamin C: Vitamin C is essential for us because its deficiency causes scurvy (bleeding gums) and pyorrhea (loosening and bleeding of teeth).

Sources: *Amla*, citrus fruits and green leafy vegetables.

Q. 21. What are nucleic acids? Mention their two important functions.

Ans. Nucleic acids are biomolecules which are found in the nuclei of all living cells in the form of nucleoproteins or chromosomes (proteins containing nucleic acids as the prosthetic group).

These are of two types: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The two main functions of nucleic acids are:

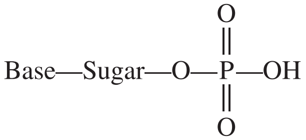
(*i*) DNA is responsible for transmission of hereditary effects from one generation to another. This is because of the unique property of replication during cell division and the transfer of two identical DNA strands to the daughter cells.

(*ii*) DNA and RNA are responsible for synthesis of all proteins essential for the growth and maintenance of our body. Actually, the proteins are synthesised by various RNA molecules (*r*RNA, *m*RNA and *t*RNA) in the cell but the message for the synthesis of a particular protein is present in DNA.

Q. 22. What is the difference between a nucleoside and a nucleotide? ***[CBSE Delhi 2010; (F) 2013]***

Ans. A nucleoside is formed when 1-position of pyrimidine (cytosine, thymine or uracil) or 9-position of purine (guanine or adenine) base is connected to C-1 of sugar (ribose or deoxyribose) by a β-linkage. Hence, in general, nucleosides may be represented as: Sugar–Base.

A nucleotide contains all the three basic compounds of nucleic acids, *i.e.*, a phosphoric acid group, a pentose sugar and a nitrogenous base. These are obtained by esterification of C'_5 — OH group of the pentose sugar by phosphoric acid. Thus, in general, a nucleotide is represented as:

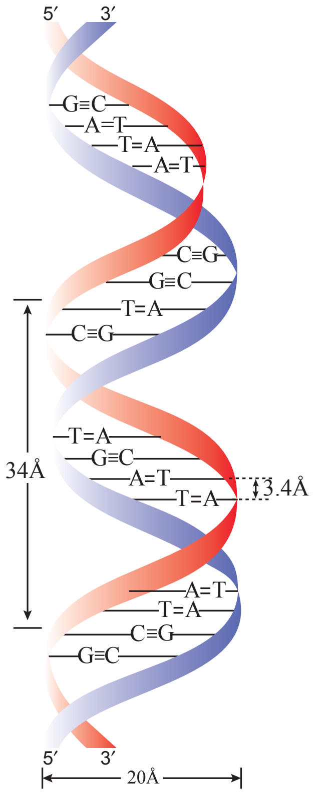


$$\text{Base—Sugar—O—}\overset{\overset{\displaystyle \text{O}}{\|}}{\underset{\underset{\displaystyle \text{O}}{\|}}{\text{P}}}\text{—OH}$$

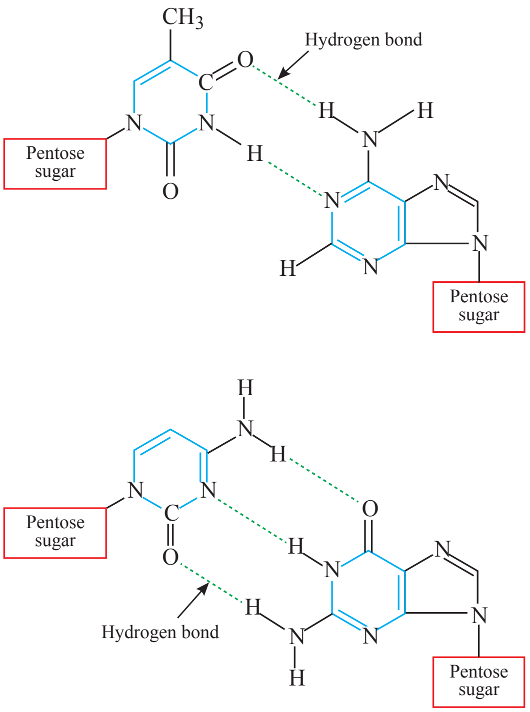
For figures refer to Basic Concepts Point 14(*a*).

Q. 23. The two strands in DNA are not identical but are complementary. Explain. ***[CBSE 2020 (56/1/2)]***

Ans. The two strands in DNA molecule are held together through hydrogen bonds between purine base of one strand and pyrimidine base of the other and vice versa. Because of different sizes and geometries of the base, the only possible pairing in DNA are G (guanine) and C (cytosine) through three H-bonds (*i.e.*, C≡G) and between A (adenine) and T (thymine) through two H-bonds (*i.e.*, A = T). Due to this base-pairing principle, the sequence of bases in one strand automatically fixes the sequence of bases in the other strand. Thus, the two strands are not identical but are complementary.



(a) The double strand helix structure for DNA



(b) Base pair in DNA

Q. 24. Write the important structural and functional differences between DNA and RNA.

Ans.

	Structural differences	
	DNA	**RNA**
(*i*)	The sugar present in DNA is 2-deoxy-D-(–)-ribose.	The sugar present in RNA is D-(–)-ribose.
(*ii*)	DNA contains cytosine and thymine as pyrimidine bases.	RNA contains cytosine and uracil as pyrimidine bases.
(*iii*)	DNA has a double stranded α-helix structure.	RNA has a single stranded α-helix structure.
(*iv*)	DNA molecules are very large; their molecular mass may vary from $6 \times 10^6 - 16 \times 10^6$ u.	RNA molecules are much smaller with molecular mass ranging from 20,000 to 40,000 u.
	Functional differences	
(*i*)	DNA has unique property of replication.	RNA usually does not replicate.
(*ii*)	DNA controls the transmission of hereditary effects.	RNA controls the synthesis of proteins.

Q. 25. What are the different types of RNA found in the cell? *[CBSE Delhi 2013]*

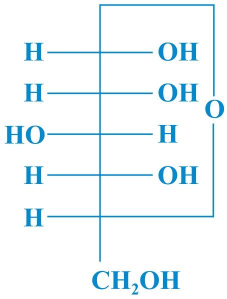
Ans. There are three types of RNAs:

(*i*) Ribosomal RNA (*r*RNA) (*ii*) Messenger RNA (*m*RNA) (*iii*) Transfer RNA (*t*RNA)

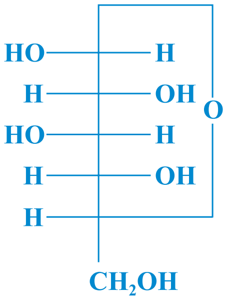
Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

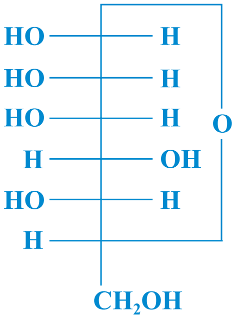
1. **Three cyclic structures of monosaccharides are given below which of these are anomers.** *[NCERT Exemplar]*



(I)



(II)

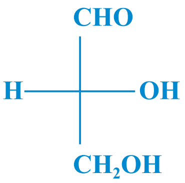


(III)

(*a*) I and II (*b*) II and III

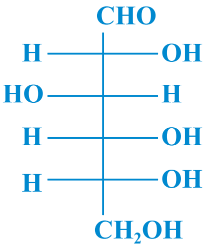
(*c*) I and III (*d*) III is anomer of I and II

2. **Optical rotations of some compounds along with their structures are given below which of them have D configuration.** *[NCERT Exemplar]*



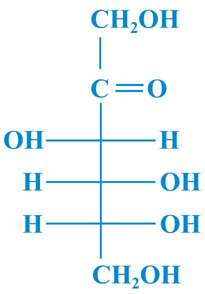
(+) rotation

(I)



(+) rotation

(II)



(–) rotation

(III)

(*a*) I, II, III (*b*) II, III (*c*) I, II (*d*) III

3. Which of the following statements is not true about glucose? *[NCERT Exemplar]*

(*a*) It is an aldohexose.
(*b*) On heating with HI it forms n-hexane.
(*c*) It is present in furanose form.
(*d*) It does not give 2,4-DNP test.

4. Which of the following reactions of glucose can be explained only by its cyclic structure? *[NCERT Exemplar]*

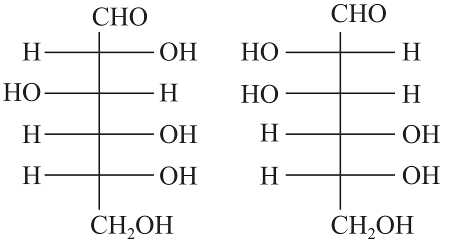
(*a*) Glucose forms pentaacetate.
(*b*) Glucose reacts with hydroxylamine to form an oxime.
(*c*) Pentaacetate of glucose does not react with hydroxylamine.
(*d*) Glucose is oxidised by nitric acid to gluconic acid.

5. Which of the following reaction confirms the presence of carbonyl group ($> C=O$) in glucose?

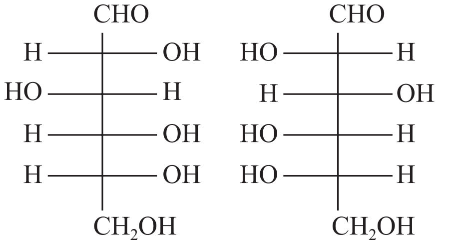
(*a*) Reaction with HI
(*b*) Reaction with hydroxylamine
(*c*) Reaction with HCN
(*d*) Both (*b*) and (*c*)

6. Which of the following pairs represents anomers? *[NCERT Exemplar]*

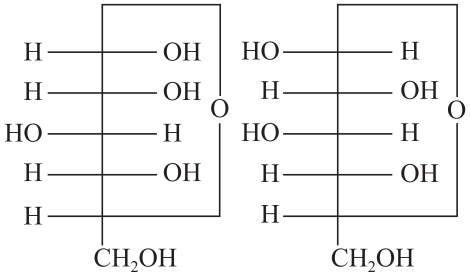
(*a*)



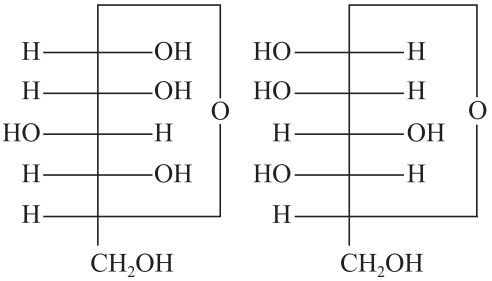
(*b*)



(*c*)



(*d*)



7. Fructose reduces Tollens' reagent due to

(*a*) Primary alcoholic group
(*b*) Asymmetric carbons
(*c*) Secondary alcoholic groups
(*d*) Enolisation of fructose followed by conversion to aldehyde by base

8. Carbohydrates are classified on the basis of their behaviour on hydrolysis and also as reducing or non-reducing sugar. Sucrose is a __________. *[NCERT Exemplar]*

(*a*) monosaccharide
(*b*) disaccharide
(*c*) reducing sugar
(*d*) non-reducing sugar

9. Amylopectin is insoluble in water and constitutes about

(*a*) 15–20% of starch (*b*) 20–40% of starch (*c*) 50–70% of starch (*d*) 80–85% of starch

10. Cellulose is not digestible by human beings due to absence of cellulose hydrolysing enzyme called

(*a*) cellulase (*b*) invertase (*c*) zymase (*d*) urease

11. Glycogen is a branched chain polymer of α-D-glucose units in which chain is formed by C1—C4 glycosidic linkage whereas branching occurs by the formation of C1—C6 glycosidic linkage. Structure of glycogen is similar to __________. *[NCERT Exemplar]*

(*a*) Amylose (*b*) Amylopectin (*c*) Cellulose (*d*) Glucose

12. Which of the following polymer is stored in the liver of animals? *[NCERT Exemplar]*

(*a*) Amylose (*b*) Cellulose (*c*) Amylopectin (*d*) Glycogen

13. Which of the following naturally occurring $\alpha-$ aminoacids is optically inactive?

(*a*) Glycine (*b*) Alanine (*c*) Leucine (*d*) Valine

14. Each polypeptide in a protein has aminoacids linked with each other in a specific sequence. This sequence of amino acids is said to be __________. *[NCERT Exemplar]*

(*a*) primary structure of proteins. (*b*) secondary structure of proteins.
(*c*) tertiary structure of proteins. (*d*) quaternary structure of proteins.

15. Proteins can be classified into two types on the basis of their molecular shape *i.e.*, fibrous proteins and globular proteins. Examples of globular proteins are : *[NCERT Exemplar]*

(*a*) Insulin (*b*) Keratin (*c*) Albumin (*d*) Myosin

16. Proteins are found to have two different types of secondary structures viz. α-helix and β-pleated sheet structure. α-helix structure of protein is stabilised by : *[NCERT Exemplar]*

(*a*) Peptide bonds (*b*) van der Waals forces (*c*) Hydrogen bonds (*d*) Dipole-dipole interactions

17. Which of the following B group vitamins can be stored in our body? *[NCERT Exemplar]*

(*a*) Vitamin B_1 (*b*) Vitamin B_2 (*c*) Vitamin B_6 (*d*) Vitamin B_{12}

18. Which of the following acids is a vitamin? *[NCERT Exemplar]*

(*a*) Aspartic acid (*b*) Ascorbic acid (*c*) Adipic acid (*d*) Saccharic acid

19. Nucleic acids are the polymers of __________. *[NCERT Exemplar]*

(*a*) nucleosides (*b*) nucleotides (*c*) bases (*d*) sugars

20. Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present? *[NCERT Exemplar]*

(*a*) 5′ and 3′ (*b*) 1′ and 5′ (*c*) 5′ and 5′ (*d*) 3′ and 3′

21. DNA and RNA contain four bases each. Which of the following bases is not present in RNA? *[NCERT Exemplar]*

(*a*) Adenine (*b*) Uracil (*c*) Thymine (*d*) Cytosine

22. The presence or absence of hydroxyl group on which carbon atom of sugar differentiate RNA and DNA

(*a*) 2nd (*b*) 4th (*c*) 3rd (*d*) 1st

23. Which one is the complementary base of cytosine in one strand to that in other strand of DNA? *[CBSE 2020 (56/4/3)]*

(*a*) Adenine (*b*) Guanine (*c*) Thymine (*d*) Uracil

Answers

1. (*a*) **2.** (*a*) **3.** (*c*) **4.** (*c*) **5.** (*d*) **6.** (*c*) **7.** (*d*) **8.** (*b, d*) **9.** (*d*) **10.** (*a*)
11. (*b*) **12.** (*d*) **13.** (*a*) **14.** (*a*) **15.** (*a*, *c*) **16.** (*c*) **17.** (*d*) **18.** (*b*) **19.** (*b*) **20.** (*a*)
21. (*c*) **22.** (*a*) **23.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(b) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(c) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(d) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. Assertion (*A*) : Deoxyribose, $C_5H_{10}O_4$ is a carbohydrate.
Reason (*R*) : Carbohydrates are hydrates of carbon so compounds which follow $C_x(H_2O)_y$ formula are carbohydrates.

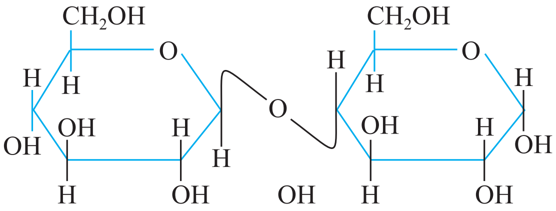
2. Assertion (*A*) : D (+) – Glucose is dextrorotatory in nature.
Reason (*R*) : ‘D’ represents its dextrorotatory nature.

3. Assertion (*A*) **:** Reducing sugars undergo mutarotation.
Reason (*R*) **:** During mutarotation, one pure anomer is converted into an equilibrium mixture of two anomers.

4. Assertion (*A*) **:** Sucrose is a non-reducing sugar.
Reason (*R*) **:** In sucrose, the aldehydic group of glucose and ketonic group of fructose are not free.

5. Assertion (*A*) **:** A solution of sucrose in water is dextrorotary but on hydrolysis in presence of little hydrochloric acid, it becomes laevoratory.
Reason (*R*) **:** Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

6. Assertion (*A*) **:** β-glycosidic linkage is present in maltose,



Reason (*R*) **:** Maltose is composed of two glucose units in which C1 of one glucose unit is linked to C4 of another glucose unit.

7. Assertion (*A*) **:** All naturally occurring α-aminoacids except glycine are optically active.
Reason (*R*) **:** Most naturally occurring amino acids have L-configuration.

8. Assertion (*A*) **:** Glycine must be taken through diet.
Reason (*R*) **:** It is a non-essential amino acid.

9. Assertion (*A*) **:** Proteins are made up of α-amino acids.
Reason (*R*) **:** During denaturation, secondary and tertiary structures of proteins are destroyed.

10. Assertion (*A*) **:** In presence of enzyme, substrate molecule can be attacked by the reagent effectively.
Reason (*R*) **:** Active sites of enzymes hold the substrate molecule in a suitable position.

11. Assertion (*A*) **:** Vitamin D can be stored in our body.
Reason (*R*) **:** Vitamin D is fat soluble vitamin.

Answers

1. (*c*) **2.** (*c*) **3.** (*a*) **4.** (*a*) **5.** (*c*) **6.** (*d*) **7.** (*b*) **8.** (*d*) **9.** (*b*) **10.** (*a*)
11. (*a*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The most abundant biomolecules of the living system are proteins. They are polymers of α-amino acids connected to each other by peptide linkage. Amino acids contain amino (—NH_2) and carboxyl (—COOH) group. Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. They behave like salts rather than simple amines or carboxylic acids. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion.

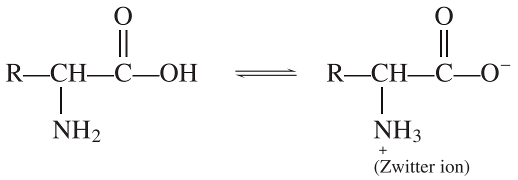
The amino acids, which can be synthesised in the body, are known as non-essential amino acids. On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids.

1. **The K_a and K_b values of α-amino acid are very low. Why?**

Ans. In α-amino acids the acidic group is $—\overset{+}{N}H_3$, instead of —COOH group as in carboxylic acids and basic group is $—COO^-$ instead of $—NH_2$ group as in amines. That is why they have low values of K_a and K_b.

2. **Draw the structure of zwitter ion.**

Ans.



$$R—\underset{NH_2}{\underset{|}{CH}}—\overset{\overset{O}{\|}}{C}—OH \rightleftharpoons R—\underset{\underset{+}{NH_3}}{\underset{|}{CH}}—\overset{\overset{O}{\|}}{C}—O^-$$

(Zwitter ion)

3. **Name the alpha amino acid which is optically inactive.**

Ans. Glycine

4. **4. Name two essential amino acids.**

Ans. Valine, Leucine

5. **Give any two properties of amino acids.**

Ans. (*i*) Amino acids are water soluble.

(*ii*) They have high melting point.

PASSAGE–2

Carbohydrates, proteins, nucleic acids, etc. form the basis of life and are responsible for the growth and maintenance of living systems. Therefore, they are referred to as biomolecules. Carbohydrates are widely distributed in nature. Carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Glucose, fructose, sucrose, starch, cellulose, etc. are some naturally occurring carbohydrates. They act as the major source of energy for animals and human beings.

Monosaccharides are the simple carbohydrates that cannot be broken further into smaller units on hydrolysis, *e.g.*, glucose and fructose, ribose, etc. Oligosaccharides are the carbohydrates which on hydrolysis give two to ten units of monosaccharides, *e.g.*, sucrose, maltose, raffinose, stachyose, etc. Polysaccharides are the carbohydrates which produce a large number of monosaccharide units on hydrolysis, *e.g.*, starch, cellulose, etc.

1. **Which carbohydrate provides instant energy to the body?**

Ans. Glucose

2. **Which disaccharide is found only in animals and not in plants?**

Ans. Lactose

3. **Which carbohydrate is the main constituent of plant cell wall?**

Ans. Cellulose

4. **Write the name of two monosaccharides obtained on hydrolysis of lactose sugar.**

Ans. D-(+)-Glucose and D-(+)-Galactose

5. **Which one of the following is a polysaccharide?**

Starch, Maltose, Fructose, Glucose

Ans. Starch

Very Short Answer Questions [1 mark]

Q. 1. Why are carbohydrates generally optically active?

Ans. Carbohydrates have chiral or asymmetric carbon atom.

Q. 2. What happens when glucose is treated with bromine water? *[CBSE (F) 2010]*

Ans. When glucose is treated with bromine water it forms gluconic acid.

$$HOCH_2—(CHOH)_4—CHO \xrightarrow{Br_2/H_2O} \underset{\text{Gluconic acid}}{HOCH_2—(CHOH)_4—COOH}$$

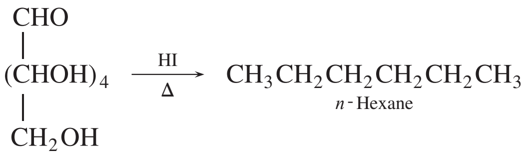
Q. 3. What happens when glucose reacts with nitric acid? *[CBSE (F) 2010]*

Ans. Glucose gets oxidised to succinic acid

$$HOCH_2—(CHOH)_4—CHO \xrightarrow{HNO_3} \underset{\text{Succinic acid}}{HOOC—(CHOH)_4—COOH}$$

Q. 4. Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain. *[CBSE (AI) 2012]*

Ans. On prolonged heating with HI, glucose gives *n*-hexane.



$$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow[\Delta]{HI} \underset{n\text{-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

Q. 5. Which component of starch is a branched polymer of α-glucose and insoluble in water? *[CBSE Delhi 2014]*

Ans. Amylopectin

Q. 6. Which of the two components of starch is water soluble? *[CBSE Delhi 2014]*

Ans. Amylose is water soluble whereas amylopectin is water insoluble component.

Q. 7. Name two α-amino acids which form a dipeptide which is 100 times more sweet than cane sugar. *[NCERT Exemplar]*

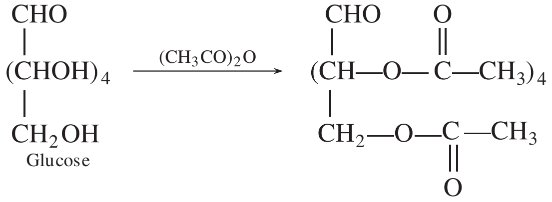
Ans. Aspartic acid and phenylalanine.

Q. 8. What type of bonding helps in stabilising the α-helix structure of proteins? *[CBSE Delhi 2013]*

Ans. The α-helix structure of proteins is stabilised by intramolecular H-bonding between C═O of one amino acid residue and the N—H of the fourth amino acid residue in the chain.

Q. 9. How do you explain the presence of five —OH groups in glucose molecule? *[NCERT Exemplar] [HOTS]*

Ans. Glucose gives pentaacetate derivative on acetylation with acetic anhydride. This confirms the presence of five —OH groups.



$$\underset{\text{Glucose}}{\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}} \xrightarrow{(CH_3CO)_2O} \begin{array}{l}CHO \quad\quad O\\ | \quad\quad\quad\quad \|\\ (CH—O—C—CH_3)_4\\ |\\ CH_2—O—\underset{\underset{O}{\|}}{C}—CH_3\end{array}$$

Glucose pentaacetate

Q. 10. What are biocatalysts? Give an example. *[CBSE (F) 2014]*

Ans. Enzymes are termed as biocatalysts as they catalyse numerous reactions that occur in the bodies of animals and plants to maintain life process *e.g.*, invertase, pepsin, urease.

Q. 11. What are three types of RNA molecules which perform different functions? *[CBSE Delhi 2013]*

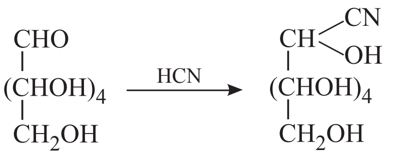
Ans. There are three types of RNAs:

(*i*) Ribosomal RNA (*r*RNA)
(*ii*) Messenger RNA (*m*RNA)
(*iii*) Transfer RNA (*t*RNA)

Short Answer Questions–I [2 marks]

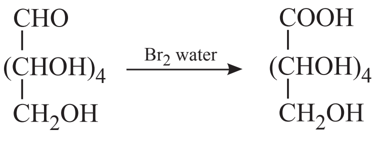
Q. 1. Write the reactions involved when D-glucose is treated with the following reagents:
(*i*) HCN **(*ii*) Br_2 water** *[CBSE (F) 2013]*

Ans. (*i*) HCN (*ii*) Br_2 water



$$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{HCN} \begin{array}{l}CH\begin{smallmatrix}CN\\OH\end{smallmatrix}\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$$

D-Glucose Glucose cyanohydrin



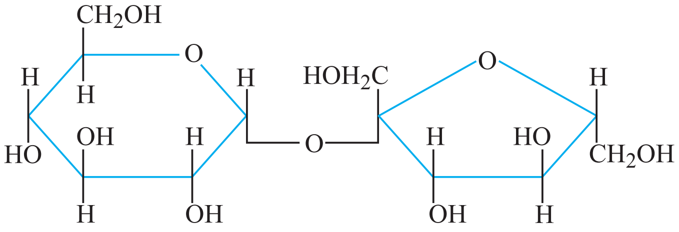
$$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow{Br_2\text{ water}} \begin{array}{l}COOH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$$

D-Glucose Gluconic acid

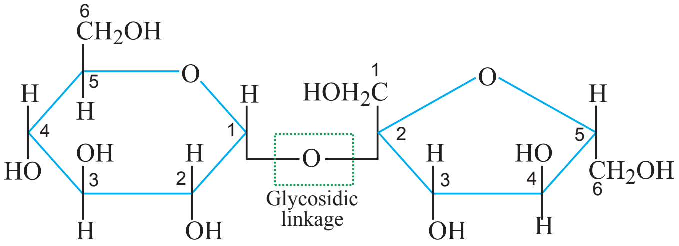
Q. 2. How do you explain the presence of an aldehydic group in a glucose molecule? ***[NCERT Exemplar]***

Ans. Glucose reacts with hydroxylamine to form a monoxime and adds one molecule of hydrogen cyanide to give cyanohydrin so it contains a carbonyl group which can be an aldehyde or a ketone. On mild oxidation with bromine water, glucose gives gluconic acid which is a six carbon carboxylic acid. This indicates that carbonyl group present in glucose is an aldehydic group.

Q. 3. Label the glucose and fructose units in the following disaccharide and identify anomeric carbon atoms in these units. Is the sugar reducing in nature? Explain. ***[NCERT Exemplar] [HOTS]***



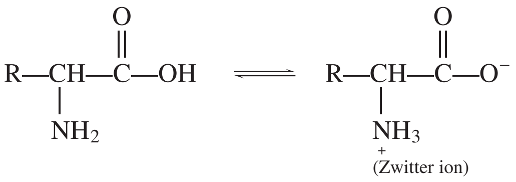
Ans. C-l of glucose unit and C-2 of fructose unit are anomeric carbon atoms in the given disaccharide. The disaccharide is non-reducing sugar because —OH groups attached to anomeric carbon atoms are involved in the formation of glycosidic bond.



α-D-Glucose **Sucrose** β-D-Fructose

Q. 4. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain. ***[NCERT Exemplar]***

Ans. In aqueous solution, the carboxyl group loses a proton and amino group accepts a proton to form a zwitter ion.



$$\underset{NH_2}{\underset{|}{R—CH}}—\overset{\overset{O}{\|}}{C}—OH \rightleftharpoons \underset{\overset{+}{N}H_3\text{ (Zwitter ion)}}{\underset{|}{R—CH}}—\overset{\overset{O}{\|}}{C}—O^-$$

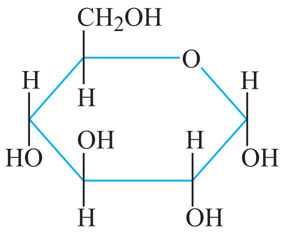
Q. 5. Explain what is meant by the following:

(*i*) peptide linkage

(*ii*) pyranose structure of glucose. ***[CBSE (AI) 2011; (F) 2011]***

Ans. (*i*) Refer to NCERT Textbook Exercises, Q. 12(*i*).

(*ii*) The six-membered cyclic structure of glucose is called pyranose structure (α- or β-), in analogy with heterocylic compound pyran.



α-D-(+)-Glucopyranose

Q. 6. Describe what you understand by primary structure and secondary structure of proteins.

[CBSE Delhi 2011; (F) 2011]

Ans. **Primary structure:** The specific sequence in which the various α-amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.

Secondary structure: The conformation which the polypeptide chain assumes as a result of hydrogen bonding is known as secondary structure. The two types of secondary structures are α-helix and β-pleated sheet structures.

In α-helix structure, the polypeptide chain forms all the possible hydrogen bonds by twisting into a right-handed screw (helix) with the —NH group of each amino acid residue hydrogen bonded to the $>C=O$ groups of an adjacent turn of the helix. In β-pleated structure, all peptide chains are stretched out to nearly maximum extension and then laid side by side and are held together by hydrogen bonds.

Q. 7. **(*i*) What type of linkage is present in nucleic acids?**

(*ii*) Give one example each for fibrous protein and globular protein. *[CBSE Central 2016]*

Ans. (*i*) Phosphodiester linkage.

(*ii*) **Fibrous protein:** Myosin, keratin, collagen, etc.

Globular protein: Insulin, haemoglobin, etc.

Q. 8. Name the bases present in RNA. Which one of these is not present in DNA?

[CBSE Delhi 2011, 2020 (56/3/3)]

Ans. The bases present in RNA are adenine (A), guanine (G), cytosine (C) and uracil (U). Uracil is not present in DNA.

Q. 9. If one strand of a DNA has the sequence —ATGCTTCA—, what is the sequence of the bases in the complementary strand?

Ans. As we know that in DNA molecule, adenine (A) always pairs with thymine (T) and cytosine (C) always pairs with guanine (G). Thus,

Sequence of bases in one strand:	A T G C T T C A
Sequence of bases in the complementary strand:	T A C G A A G T

Short Answer Questions–II [3 marks]

Q. 1. Define the following terms: *[CBSE (AI) 2014]* *[CBSE 2020 (56/3/2)]*

(*i*) Glycosidic linkage

(*ii*) Invert sugar **(*iii*) Oligosaccharides**

Ans. (*i*) The linkage between two monosaccharides through oxygen atom in an oligosaccharide or a polysaccharide is known as glycosidic linkage.

(*ii*) Sucrose is dextrorotatory (+ 66.5°) but after hydrolysis it gives an equimolar mixture of D-(+)-glucose and D-(–)-fructose, which is laevorotatory. This change of specific rotation from dextrorotation to laevorotation is called inversion of sugar and the mixture obtained is called invert sugar.

(*iii*) Carbohydrates which on hydrolysis give two to ten molecules of monosaccharides are called oligosaccharides *e.g.*, sucrose.

Q. 2. **(*i*) Which of the following biomolecules is insoluble in water? Justify.**

Insulin, Haemoglobin, Keratin.

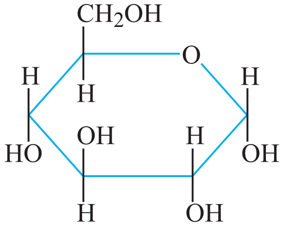
(*ii*) Draw the Haworth structure for α-D-Glucopyranose.

(*iii*) Write chemical reaction to show that glucose contains aldehyde as carbonyl group.

[CBSE Sample Paper 2015]

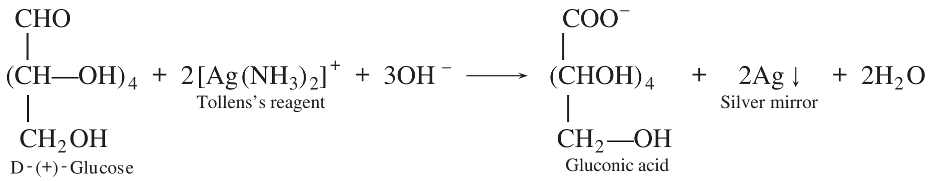
Ans. (*i*) Keratin being a fibrous protein insoluble in water.

(*ii*)



α-D-(+)-Glucopyranose

(*iii*) Glucose reduces Tollens' reagent to metallic silver.



$$\underset{\text{D-(+)-Glucose}}{\begin{array}{c}\text{CHO}\\ |\\ (\text{CH—OH})_4\\ |\\ \text{CH}_2\text{OH}\end{array}} + \underset{\text{Tollens's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow \underset{\text{Gluconic acid}}{\begin{array}{c}\text{COO}^-\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{—OH}\end{array}} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O$$

Q. 3. (*i*) Give one structural difference between amylose and amylopectin

(*ii*) Name the protein and its shape present in oxygen carrier in human body.

(*iii*) Name two fat storing tissues in human body. ***[CBSE Sample Paper 2014]***

Ans. (*i*) Amylose is a long unbranched chain polymer of α-D(+) glucose.

Amylopectin is a branched chain polymer of α-D glucose.

(*ii*) Globular protein and its shape is spherical.

(*iii*) Liver and adipose tissue.

Q. 4. (*i*) A non-reducing disaccharide 'A' on hydrolysis with dilute acid gives an equimolar mixture of D-(+)-glucose and D-(–)-fructose.

$$\underset{[\alpha]_D = +66.5^\circ}{\mathbf{A}} + \mathbf{H_2O} \xrightarrow{\mathbf{HCl}} \underset{52.5^\circ}{\mathbf{C_6H_{12}O_6}} + \underset{-92.4^\circ}{\mathbf{C_6H_{12}O_6}}$$

Identify A. What is the mixture of D-(+)-glucose and D-(–)-fructose known as? Name the linkage that holds the two units in the disaccharide.

(*ii*) α-amino acids have relatively higher melting points than the corresponding halo acids. Explain. ***[CBSE Sample Paper 2016] [HOTS]***

Ans. (*i*)
- A = $C_{12}H_{22}O_{11}$ (sucrose).
- Invert sugar.
- Glycosidic linkage.

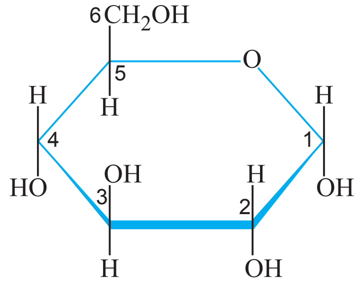
(*ii*) α-Amino acids act as zwitter ions, ($H_3\overset{+}{N}$—CHR—COO^-) or dipolar ions. Due to this dipolar salt-like structure, they have strong dipole-dipole interactions. Therefore, their melting points are higher than the corresponding halo acids which do not exist as zwitter ions.

Q. 5. (*i*) Draw the pyranose structure of glucose.

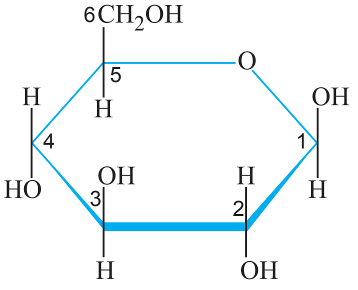
(*ii*) What type of linkage is present in proteins?

(*iii*) Give one example each for water-soluble vitamins and fat-soluble vitamins. ***[CBSE (F) 2016]***

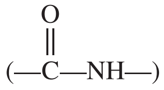
Ans. (*i*)



α-D-(+) Glucopyranose



β-D-(+) Glucopyranose

(*ii*) Peptide linkage 

$$(\text{—}\overset{\overset{\large O}{\|}}{C}\text{—NH—})$$

(*iii*) Vitamin C and B group vitamins are water soluble vitamins.

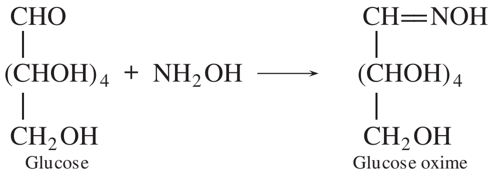
Vitamins A, D, E and K are fat soluble vitamins.

Q. 6. (*i*) Write the product obtained when D-glucose reacts with H_2N—OH.

(*ii*) Amino acids show amphoteric behaviour. Why?

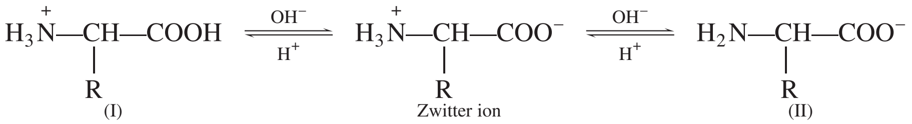
(*iii*) Why cannot vitamin C be stored in our body? ***[CBSE Patna 2015]***

Ans. (*i*)



$$\underset{\text{Glucose}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} + NH_2OH \longrightarrow \underset{\text{Glucose oxime}}{\begin{array}{c}CH{=}NOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}}$$

(*ii*) In aqueous solution, amino acids exist as a zwitter ion. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.



$$\underset{\text{(I)}}{H_3\overset{+}{N}-\underset{\underset{R}{|}}{CH}-COOH} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Zwitter ion}}{H_3\overset{+}{N}-\underset{\underset{R}{|}}{CH}-COO^-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{(II)}}{H_2N-\underset{\underset{R}{|}}{CH}-COO^-}$$

In acidic medium COO^- ion of the zwitter ion accepts a proton to form the cation (I) while in basic medium $\overset{+}{N}H_3$ loses a proton to form the cation (II).

(*iii*) As vitamin C is water soluble, therefore, it is readily excreted in urine and hence cannot be stored in the body.

Long Answer Question [5 marks]

Q. 1. (*i*) (*a*) What is the difference between native protein and denatured protein?

(*b*) Which one of the following is a disaccharide?

Glucose, Lactose, Amylose, Fructose

(*c*) Write the name of the vitamin responsible for the coagulation of blood. **[*CBSE 2019 (56/4/3)*]**

(*ii*) Define the following terms:

(*a*) Native protein **[*CBSE 2020 (56/3/2)*]**

(*b*) Nucleotide **[*CBSE 2019 (56/2/2)*]**

Ans. (*i*) (*a*) Protein found in a biological system with unique three-dimensional structure and biological activity is called native protein.

When a protein in its native form is subjected to change such as change in temperature, change in pH, its 2° and 3° structures are destroyed and it loses its biological activity. The protein thus formed is called denatured protein.

(*b*) Lactose

(*c*) Vitamin K.

(*ii*) (*a*) Protein found in biological system with unique three dimensional structure and biological activity is called native protein.

(*b*) A unit formed by the combination of nitrogenous base , pentose sugar and phosphate.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. (3 × 1 = 3)

1. Which of the following is laevorotatory?

(*a*) Glucose (*b*) Sucrose (*c*) Fructose (*d*) None of these

2. Amino acids are best represented as:

(*a*) dipolar ions (*b*) isoelectric ions (*c*) amphoteric ions (*d*) zwitter ions

3. Which one of the following is a peptide hormone?

(*a*) Testosterone (*b*) Glucagon (*c*) Adrenaline (*d*) Thyroxine

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- *(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*
- *(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*
- *(c) Assertion (A) is correct, but Reason (R) is incorrect statement.*
- *(d) Assertion (A) is incorrect, but Reason (R) is correct statement.* **(3 × 1 = 3)**

4. **Assertion (A) :** The pyrimidine base uracil is present in RNA.
Reason (R) : RNA controls the synthesis of proteins.

5. **Assertion (A) :** Enzymes are globular proteins.
Reason (R) : Enzymes are regenerated during reactions.

6. **Assertion (A) :** Maltose is a reducing sugar, one molecule of which gives two molecules of D-glucose on hydrolysis.
Reason (R) : Maltose has a 1, 4 β-glycosidic linkage.

Answer the following questions:

7. What are anomers? Give one example. **(1)**

8. What type of protein is present in keratin. **[CBSE 2020 (56/4/3)] (1)**

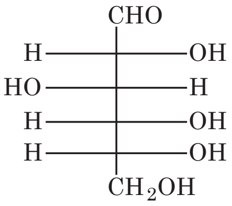
9. Which forces are responsible for the stability of α-helix? Why is it named as 3.6_{13} helix? **(2)**

10. Write the reactions showing the presence of following in the open structure of glucose:
(*i*) five —OH groups (*ii*) a carbonyl group **[CBSE 2020 (56/4/3)] (2)**

11. Define enzymes. How do enzymes differ from ordinary chemical catalysts? **(2)**

12. What is essentially the difference between α-form of glucose and β-form of glucose? **[CBSE Delhi 2011] (2)**

13. The Fischer projection of D-Glucose is given alongside.
(*i*) Give the Fischer projection of L-Glucose.
(*ii*) What happens when L-Glucose is treated with Tollens' reagent? **(2)**



14. Define the following terms:
(*i*) Polysaccharides (*ii*) Amino acids (*iii*) Enzymes **[CBSE (F) 2014] (3)**

15. (*i*) Name the three major classes of carbohydrates and give an example of each of these classes.
(*ii*) What type of linkage is responsible for the primary structure of proteins?
(*iii*) Name the location where protein synthesis occurs in our body. **(3)**

16. (*i*) Write about the following on protein synthesis:
(*a*) Name the location where protein synthesis occurs.
(*b*) How do 64 codons code for only 20 amino acids?
(*c*) Which of the two bases of the codon are more important for coding? **(3)**
(*ii*) What deficiency diseases are caused due to lack of vitamins A, B_1, B_6 and K in human diet?

17. (*i*) Comment on the specificity of enzyme action. What is the most important reason for their specificity?
(*ii*) (*a*) What are the products of hydrolysis of maltose?
(*b*) Name the vitamin whose deficiency causes pernicious anaemia. **[CBSE 2019 (56/2/2)] (3)**

Answers

1. (*c*) **2.** (*d*) **3.** (*b*) **4.** (*c*) **5.** (*a*) **6.** (*c*)

Chapter–15

Polymers

basic concepts

1. **Polymers:** Polymers are the high molecular mass macromolecules, formed by the combination of large number of simple molecules called monomers. The process by which monomers are converted into polymers is called polymerisation.

$$\underset{\substack{\text{Ethene}\\\text{(Monomer)}}}{nCH_2 = CH_2} \xrightarrow[\text{traces of } O_2]{350-570\text{ K, }1000-2000\text{ atm}} \underset{\substack{\text{Polythene}\\\text{(Polymer)}}}{-\!\!(CH_2-CH_2)\!\!-_n}$$

2. **Classification of Polymers**

   (*a*) Classification based on sources:

   (*i*) Natural polymers: Polymers found in nature, mostly in plants and animals are called natural polymers, *e.g.*, proteins, natural rubber, etc.

   (*ii*) Semisynthetic polymers: Polymers which are obtained by making some modifications in natural polymers by artificial means, *e.g.*, nitrocellulose, cellulose acetate, etc.

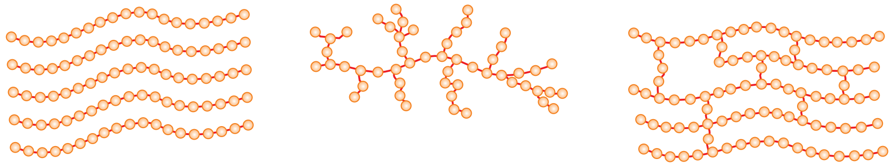
   (*iii*) Synthetic polymers: These are man-made polymers prepared in the laboratory, *e.g.*, polythene, teflon, nylon, etc.

   (*b*) Classification based on structure of polymers:

   (*i*) Linear polymers: These polymers consist of long and straight chains, *e.g.*, high density polythene, polyvinyl chloride, nylon, etc.

   (*ii*) Branched chain polymers: These polymers contain linear chains having some branches, *e.g.*, low density polythene, glycogen, etc.

   (*iii*) Cross-linked or Network Polymers: In this type of polymers, the initially formed linear polymer chains are joined together to form three dimensional network structure. Due to presence of cross links these polymers are also called cross-linked polymers, *e.g.*, bakelite, melamine, etc.



(a) Linear chain (b) Branched chain (c) Cross-linked

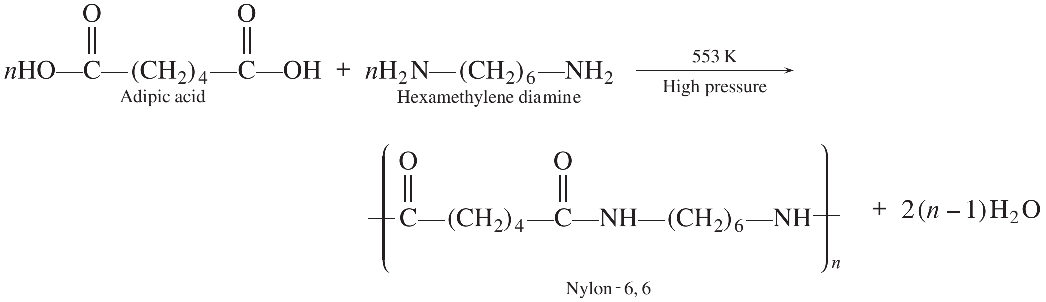
Fig. 15.1: Structure of polymer

(*c*) Classification based on mode of polymerisation:

(*i*) **Addition polymers:** The addition polymers are formed by the repeated addition of same or different monomer molecules. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives. Polythene is an example of addition polymer.

$$\underset{\text{Ethene}}{nCH_2=CH_2} \xrightarrow[\text{Ziegler - Natta catalyst}]{\text{333 - 343 K, 6 - 7 atm}} \underset{\text{High density polythene}}{-\!\!\left(CH_2-CH_2\right)\!\!-_n}$$

(*ii*) **Condensation polymers:** The condensation polymers are formed by the repeated condensation reaction between different bifunctional or trifunctional monomer units usually with elimination of small molecules such as water, alcohol, hydrogen chloride, etc. Nylon-6, nylon-6, 6 and terylene are some examples.



$$\underset{\text{Adipic acid}}{nHO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Hexamethylene diamine}}{nH_2N-(CH_2)_6-NH_2} \xrightarrow[\text{High pressure}]{\text{553 K}}$$

$$\underset{\text{Nylon - 6, 6}}{\left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH-\right]_n} + 2(n-1)H_2O$$

(*d*) Classification based on molecular forces:

(*i*) **Elastomers:** These are the polymers having the weakest intermolecular forces of attraction between the polymer chains. The weak forces permit the polymer to be stretched. A few 'cross links' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. Elastomers thus possess an elastic character, *e.g.*, buna-S, buna-N, neoprene, etc.

(*ii*) **Fibres:** These are the polymers which have the strongest intermolecular forces such as hydrogen bonds or dipole–dipole interactions. These polymers can be used for making fibre as their molecules are long and thread-like. Nylon-6, 6 and terylene are some common fibres.

(*iii*) **Thermoplastics:** These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. These are linear or slightly branched chain polymers capable of repeatedly softening on heating and hardening on cooling, *e.g.*, polythene, polyproplene, polystyrene, polyvinyl chloride, etc.

(*iv*) **Thermosetting polymers:** These polymers are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linking in moulds and again become infusible. These polymers cannot be reshaped, *e.g.*, bakelite, urea–formaldehyde resins, etc.

Table 15.1: Differences between Thermoplastic and Thermosetting Polymers

S.No.	Thermoplastic Polymers	Thermosetting Polymers
(*i*)	These polymers soften on heating and harden on cooling.	On heating they undergo excessive cross linking and become hard.
(*ii*)	These polymers can be remoulded, recast and reshaped.	These polymers cannot be remoulded or reshaped.
(*iii*)	These are less brittle and soluble in some organic solvents.	These are more brittle and insoluble in organic solvents.
(*iv*)	These are formed by addition polymerisation.	These are formed by condensation polymerisation.
(*v*)	These polymers have usually linear structures.	These polymers have three dimensional cross-linked structures.
(*vi*)	Examples: Polyethylene, PVC, teflon, nylon, etc.	Examples: Bakelite, urea–formaldehyde resin, terylene, etc.

3. Types of polymerisation reactions

There are two broad types of polymerisation reactions:

(*a*) Addition polymerisation. (*b*) Condensation polymerisation.

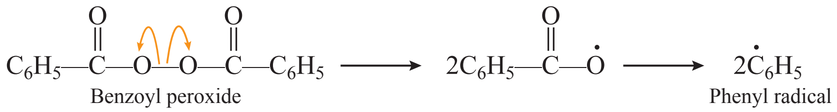
(*a*) Addition polymerisation: This type of polymerisation involves successive addition of monomer units to the growing chain carrying a reactive intermediate such as a free radical or anion.

Depending upon the nature of the reactive species involved addition polymerisation occurs by the following three mechanisms:

(*i*) Free radical polymerisation, (*ii*) Cationic polymerisation, (*iii*) Anionic polymerisation

Free radical polymerisation: A variety of alkenes or dienes and their derivatives are polymerised in the presence of a free radical generating initiator like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. For example, the polymerisation of ethene to polythene consists of heating or exposing to light, a mixture of ethene with a small amount of benzoyl peroxide initiator. The sequence of steps may be depicted as follows:

Chain initiation steps: Benzoyl peroxide undergo homolytic fission to form free radicals.



$$\underset{\text{Benzoyl peroxide}}{C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5} \longrightarrow 2C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}\dot{O} \longrightarrow \underset{\text{Phenyl radical}}{2\dot{C}_6H_5}$$

$$\dot{C}_6H_5 + CH_2{=}CH_2 \longrightarrow C_6H_5{-}CH_2{-}\dot{C}H_2$$

Chain propagating step:

$$C_6H_5{-}CH_2{-}\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5{+}CH_2{-}CH_2{+}_n CH_2{-}\dot{C}H_2$$

Chain termination step: The chain reaction stops when two free radical chains combine.

$$2C_6H_5{+}CH_2{-}CH_2{+}_n CH_2{-}\dot{C}H_2 \longrightarrow$$

$$\underset{\text{Polythene}}{C_6H_5{+}CH_2{-}CH_2{+}_n CH_2{-}CH_2{-}CH_2{+}CH_2{-}CH_2{+}_n C_6H_5}$$

(*b*) Condensation polymerisation: It occurs through a series of independent reactions (or steps). Each step involves the condensation between two bifunctional monomer units with elimination of simple molecule such as water, alcohol, etc., and leads to the formation of the polymer. Since the polymer is formed in a stepwise manner, the process is called step growth polymerisation, *e.g.,* Nylon-6,6, dacron, bakelite, etc.

Table 15.2: Differences between Addition and Condensation Polymerisation

S.No.	Addition Polymerisation	Condensation Polymerisation
(*i*)	They are formed by adding monomers to a growing polymer chain without loss of any molecules.	Monomers combine together with the loss of small molecules like H_2O, NH_3, CO_2, CH_3OH, etc.
(*ii*)	It involves chain reaction.	It does not involve chain reaction.
(*iii*)	They are formed from unsaturated compounds.	Monomers have di or polyfunctional groups.
(*iv*)	**Examples:** Polythene, polypropene, PVC, teflon, etc.	**Examples:** Nylon-6,6, nylon-6, terylene, glyptal, bakelite, etc.

4. Preparation of Some Important Addition Polymers

(*a*) Polythene

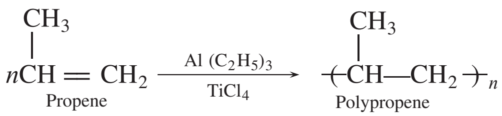
(*i*) Low density polythene (LDP): It is used in the insulation of electricity carrying wires, and manufacture of squeeze bottles, toys and flexible pipes.

$$\underset{\text{Ethene}}{nCH_2{=}CH_2} \xrightarrow[\text{traces of } O_2]{350\text{-}570\text{ K, }1000\text{-}2000\text{ atm}} \underset{\text{LDP}}{{+}CH_2{-}CH_2{+}_n}$$

(*ii*) High density polythene (HDP): It is used for manufacturing buckets, dustbins, pipes, bottles, etc.

$$\underset{\text{Ethene}}{nCH_2=CH_2} \xrightarrow[TiCl_4\ +\ (C_2H_5)_3Al]{333-343\ K,\ 6-7\ atm} \underset{\text{HDP}}{-\!\!(CH_2-CH_2)\!\!-_n}$$

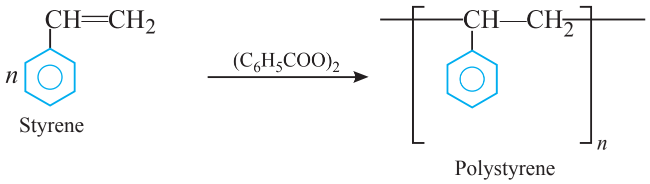
(*b*) Polypropene:



$$\underset{\text{Propene}}{n\overset{\overset{\large CH_3}{|}}{C}H=CH_2} \xrightarrow[TiCl_4]{Al\,(C_2H_5)_3} \underset{\text{Polypropene}}{-\!\!(\overset{\overset{\large CH_3}{|}}{C}H-CH_2)\!\!-_n}$$

Uses: Manufacture of toys, ropes, pipes, carpet fibres, etc.

(*c*) Polystyrene:



Uses: As insulator, wrapping material, manufacture of toys, radio and television cabinets.

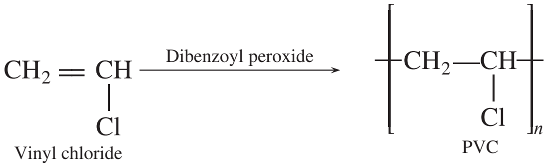
(*d*) Polyhaloolefins: These polymers are derived from halogen substituted olefins.

(*i*) Tetrafluoroethene (Teflon):

$$\underset{\text{Tetrafluoroethene}}{nCF_2=CF_2} \xrightarrow[\text{High pressure}]{(NH_4)_2S_2O_8} \underset{\text{Teflon}}{-\!\!(CF_2-CF_2)\!\!-_n}$$

Uses: Making oil seals and gaskets, coating utensils to make them non-sticky.

(*ii*) Polyvinyl chloride (PVC):

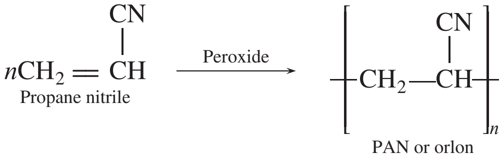


$$\underset{\text{Vinyl chloride}}{CH_2=\underset{\underset{\large Cl}{|}}{C}H} \xrightarrow{\text{Dibenzoyl peroxide}} \underset{\text{PVC}}{\left[-CH_2-\underset{\underset{\large Cl}{|}}{C}H-\right]_n}$$

Uses: Manufacture of rain coats, water pipes, electrical insulation, hand bags, vinyl flooring.

(*e*) Polyacrylates: These polymers are obtained from the ester of acrylic acid ($CH_2=CH-COOH$).

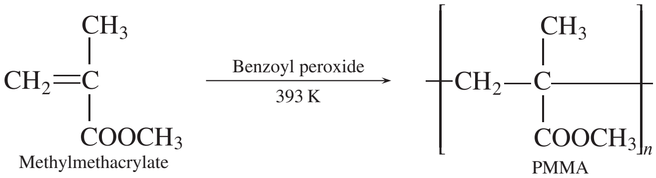
(*i*) Polyacrylonitrile (PAN) or orlon or acrylane:



$$\underset{\text{Propane nitrile}}{nCH_2=\overset{\overset{\large CN}{|}}{C}H} \xrightarrow{\text{Peroxide}} \underset{\text{PAN or orlon}}{\left[-CH_2-\overset{\overset{\large CN}{|}}{C}H-\right]_n}$$

Uses: As a substitute for wool in the manufacture of commercial fibres such as orlon which is used for making clothes, carpets and blankets.

(*ii*) Polymethylmethacrylate (PMMA):



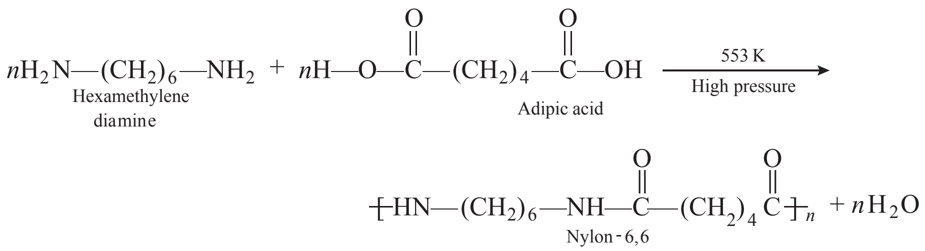
$$\underset{\text{Methylmethacrylate}}{CH_2=\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large COOCH_3}{|}}{C}}} \xrightarrow[393\ K]{\text{Benzoyl peroxide}} \underset{\text{PMMA}}{\left[-CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large COOCH_3}{|}}{C}}-\right]_n}$$

Uses: Manufacture of transparent objects such as aircraft windows, plastic jewellery, lenses, domes and sky lights.

5. Some Important Condensation Polymers

(*a*) Polyamides: Polymers possessing amide linkages (—CONH—) are called polyamides.

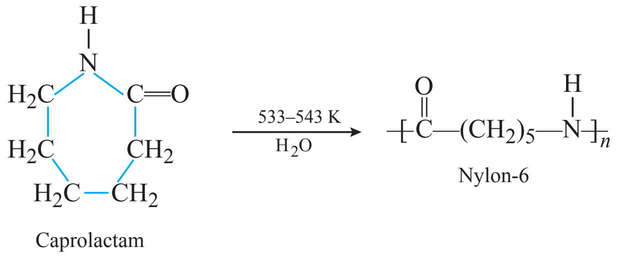
(*i*) Nylon-6, 6:



$$nH_2N-(CH_2)_6-NH_2 + nH-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{High pressure}]{553\text{ K}} \left[HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n + nH_2O$$

Uses: In making sheets, bristles for brushes and in textile industry.

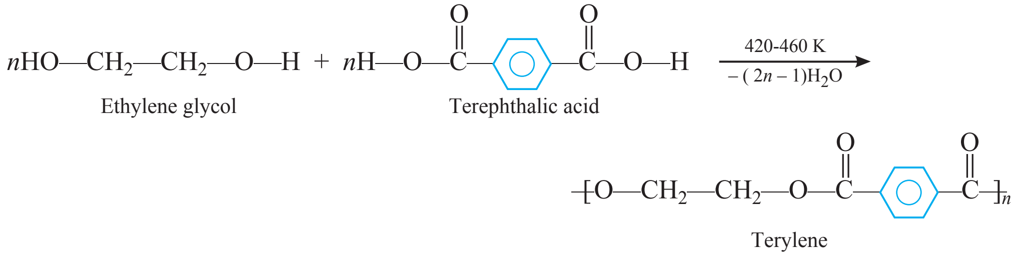
(*ii*) Nylon-6:



Uses: Manufacture of tyre cords, fabrics and ropes.

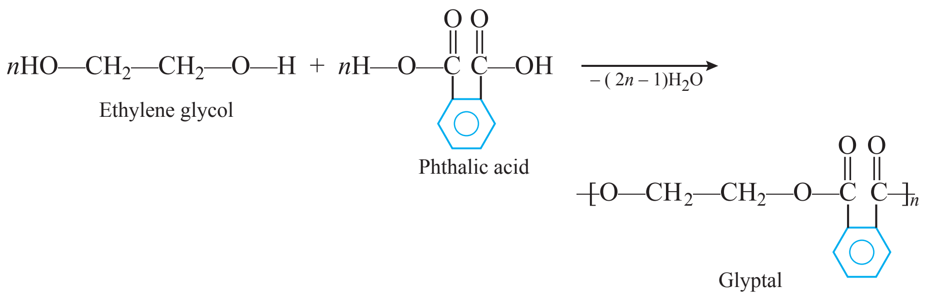
(*b*) Polyesters: Polymers possessing ester linkages ($-\overset{O}{\overset{\|}{C}}-O-$) are called polyesters and are prepared by the condensation polymerisation of dicarboxylic acids with diols.

(*i*) Dacron or terylene:



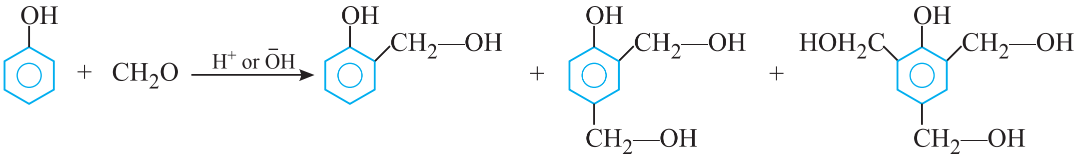
Uses: Manufacture of wash and wear fabrics, tyre cords, sails and seat belts.

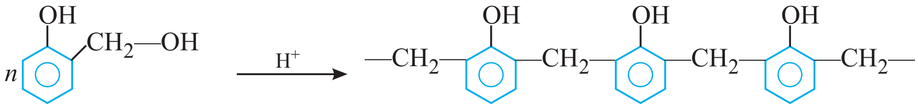
(*ii*) Glyptal:



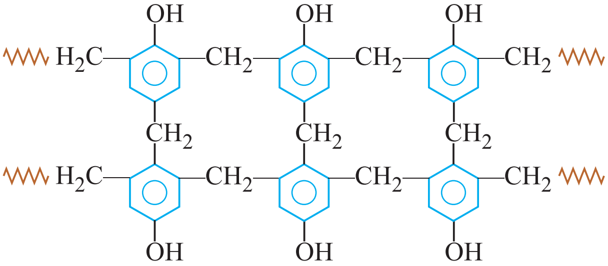
Uses: Manufacture of paints, lacquer and building materials.

(*c*) **Phenol–formaldehyde polymer (Bakelite and related polymers):** These are obtained by condensation reaction of phenol with formaldehyde in the presence of either an acid or base catalyst. The initial product could be a linear product, novolac.





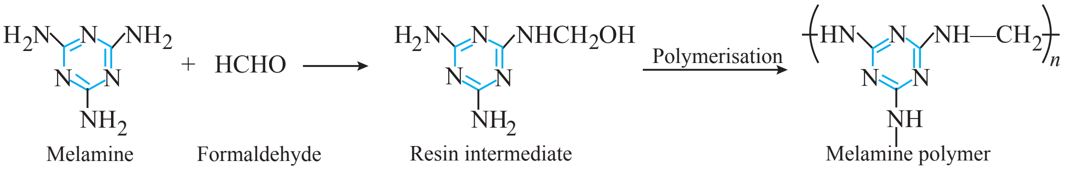
Novolac on heating with formaldehyde undergoes cross linking to form bakelite.



Uses: Novolac is used in paints.

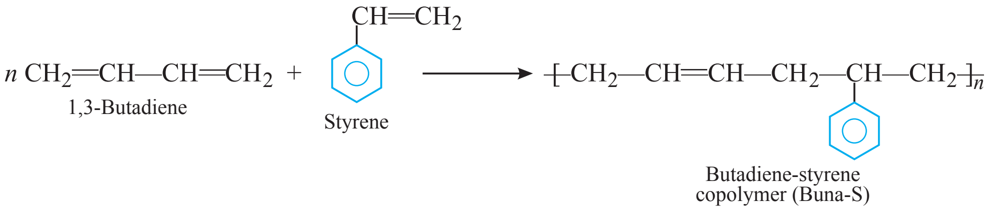
Bakelite is used for making combs, phonograph records, electrical switches and handles of various utensils.

(*d*) **Melamine–formaldehyde polymer:** Melamine–formaldehyde polymer is formed by condensation polymerisation of melamine and formaldehyde.



Uses: It is used in the manufacture of unbreakable crockery.

6. **Copolymerisation:** When two or more different monomers are allowed to polymerise together, the product formed is called a copolymer and the process is called copolymerisation. Copolymers have properties different from homopolymers.

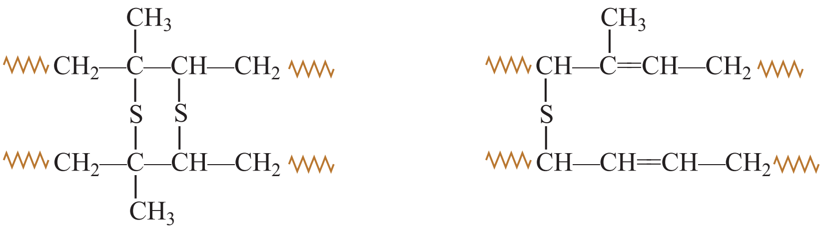


Uses: Buna-S is used for the manufacture of autotyres, floor tiles, footwear components, cable insulation, etc.

7. Rubber

(*a*) Natural rubber: Natural rubber may be considered as a linear polymer of isoprene (α-methyl-1, 3-butadiene) and is also called as *cis*-1, 4-polyisoprene. The *cis*-polyisoprene consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

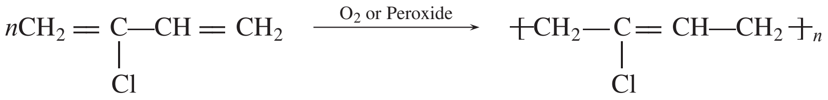
(*b*) Vulcanisation: Vulcanisation is the heating of natural rubber with sulphur and an appropriate additive to improve its physical properties. On vulcanisation, sulphur forms cross-links at the reactive sites of the double bond and thus rubber gets stiffened.



Vulcanised rubber molecules

(*c*) Synthetic rubber: Synthetic rubbers are either homopolymers of 1, 3-butadiene derivatives or copolymers of 1, 3-butadiene or its derivative with another unsaturated monomer.

Neoprene:



$$n\,CH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2 \xrightarrow{O_2\text{ or Peroxide}} \left[CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2\right]_n$$

Chloroprene   Neoprene

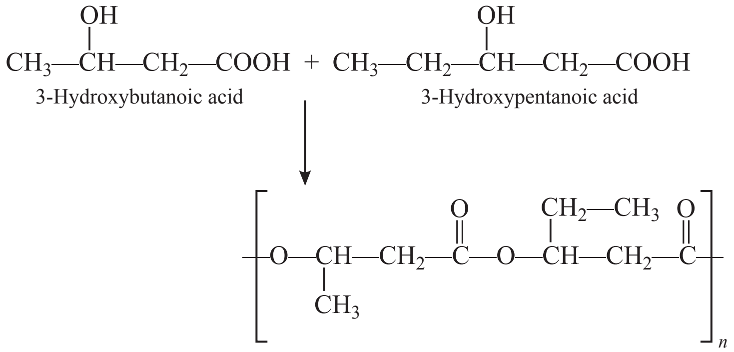
Uses: In the manufacture of conveyor belts, gaskets and hoses.

8. Biodegradable Polymers

Polymers that can be broken into small segments by enzyme-catalysed reactions are called biodegradable polymers. The required enzymes are produced by microorganisms. Since carbon–carbon bonds of chain growth polymers are inert to enzyme catalysed reactions, these polymers are non-biodegradable. To overcome this, certain bonds in the chain are to be inserted so that it can be made biodegradable. One such method to make a polymer biodegradable is to insert hydrolysable ester group into the polymer.

Aliphatic polyester, are biodegradable polymers and many of them are important commercial biomaterial. Some important examples are given below.

(*i*) Poly-β-hydroxybutyrate-co-b-hydroxy valerate (PHBV): This is a copolymer of 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid.

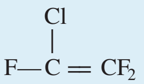
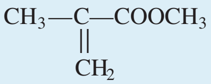


PHBV

Uses: It is used in speciality packaging, orthopaedic devices and in controlled release of drugs.

(*ii*) Nylon-2-Nylon-6: It is an alternating polyamide copolymer of glycine (H_2NCH_2-COOH) and amino caproic acid ($H_2N-(CH_2)_5\,COOH$) and is biodegradable.

9. Addition Polymers at a Glance

S.No.	Polymer	Monomer	Uses
1.	Polythene	Ethene ($CH_2{=}CH_2$)	Electrical insulator, packing materials, film, bottles, etc.
2.	Polypropene	Propene ($CH_3{-}CH{=}CH_2$)	Storage battery tanks
3.	Polystyrene	Styrene ($C_6H_5{-}CH{=}CH_2$)	In combs, plastic handles, toys
4.	Polyvinyl chloride (PVC)	$CH_2{=}CHCl$ Vinyl chloride	Pipes, raincoats, vinyl floorings
5.	Polytetrafluoro ethane (PTFE) or Teflon	$CF_2{=}CF_2$ Tetrafluoroethene	Non-stick kitchenwares, electrical insulator
6.	Polymono chlorotrifluoro ethene	 $F-\overset{\overset{Cl}{\vert}}{C}=CF_2$ Monochlorotrifluoro ethene	Non-stick kitchenwares
7.	Buna-S	1, 3-Butadiene and styrene	Automobile, tyres
8.	Buna-N	1,3-Butadiene and acrylonitrile	Used for storing oil and solvents
9.	Neoprene	2-Chloro-1, 3-butadiene (Chloroprene)	Insulation conveyor belt
10.	Polymethyl methacrylate (PMMA) (Perspex, Lucite or Acrylite)	 $CH_3-\underset{\underset{CH_2}{\Vert}}{C}-COOCH_3$	Substitute of glass and decorative material
11.	Polyethyl acrylate	$CH_2{=}CH{-}COOC_2H_5$ Ethyl prop-2-enoate	Lacquers, films, hose piping
12.	Polyacrylonitrile or orlon	$CH_2{=}CH{-}C{\equiv}N$ Vinyl cyanide	For making clothes, carpets and blankets

10. Natural Polymers at a Glance

S.No.	Polymer	Monomer	Class	Uses
1.	Cellulose	β-Glucose	Biopolymer	Occurs in cotton, cell wall
2.	Starch	α-Glucose	Biopolymer	Food material storage in plants
3.	Proteins	Amino acids	Biopolymer	Essential for growth
4.	Nucleic acid	Nucleotides	Biopolymer	Essential for life perpetuation
5.	Rayon (Artificial Silk)	β-Glucose	Processed cellulose	Fabrics, surgical dressings
6.	Natural rubber	*cis*-Isoprene (*Cis*-2-methyl-1, 3-butadiene)	Natural polymer, elastomer	Used for tyres after vulcanisation
7.	Gutta percha	*trans*-Isoprene	Natural polymer, elastomer	Rubber-like material

11. Condensation Polymers at a Glance

S.No	Polymer	Monomer	Uses
1.	Terylene (Dacron)	Terephthalic acid and ethylene glycol	Ropes, safety belts, tyre cord
2.	Glyptal (Alkyl Resin)	Phthalic acid and ethylene glycol	Binding material, paints and in preparation of mixed plastics
3.	Nylon-6 (Perlon)	Caprolactam (cyclic amide)	Fibre, plastic, tyre cords and ropes
4.	Nylon-6, 6	Adipic acid and hexamethylene diamine	Sheets, bristles for brushes and in textile industry
5.	Bakelite	Phenol and formaldehyde	Electric switches and switch boards
6.	Melamine-formaldehyde resin	Melamine and formaldehyde	Crockery
7.	Urea–formaldehyde resin	Urea and formaldehyde	Crockery and laminated sheets

NCERT Textbook Questions

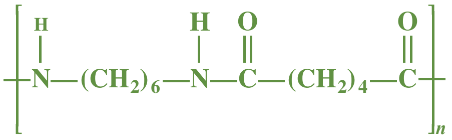
NCERT Intext Questions

Q. 1. What are polymers?

Ans. Refer to Basic Concepts Point 1.

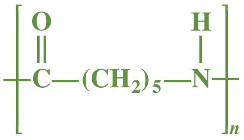
Q. 2. Write the names of monomers of the following polymers: **[*HOTS*]**

(*i*)



$$\left[\!-\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_6-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}-\!\right]_n$$

(*ii*)



$$\left[\!-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_5-\overset{\displaystyle H}{\overset{|}{N}}-\!\right]_n$$

(*iii*) $\lbrack\!-CF_2-CF_2-\!\rbrack_n$

Ans. (*i*) Hexamethylenediamine [$H_2N-(CH_2)_6-NH_2$] and adipic acid [$HOOC-(CH_2)_4-COOH$]

(*ii*) Caprolactam

(*iii*) Tetrafluoroethene, ($F_2C{=}CF_2$)

Q. 3. Classify the following as addition and condensation polymers:

Terylene, Bakelite, Polyvinyl chloride, Polythene.

Ans. **Addition polymers:** Polyvinyl chloride, polythene.

Condensation polymers: Terylene, bakelite.

Q. 4. Explain the difference between Buna-N and Buna-S.

Ans. Both are copolymers. Buna-N is a copolymer of 1, 3-butadiene and acrylonitrile while Buna-S is a copolymer of 1,3-butadiene and styrene.

Q. 5. Arrange the following polymers in increasing order of their intermolecular forces. **[*CBSE (F) 2013*]**

Nylon 6,6, Buna-S, Polythene.

Ans. In order of increasing intermolecular forces:

Buna-S < Polythene < Nylon 6, 6.

NCERT Textbook Exercises

Q. 1. Explain the term polymer and monomer.

Ans. **Polymers:** Refer to Basic Concepts Point 1.

Monomers: Simple and reactive molecules from which the polymers are prepared either by addition or condensation are called monomers. For example, vinyl chloride, ethene, formaldehyde, acrylonitrile, phenol, etc.

Q. 2. What are natural and synthetic polymers? Give two examples of each type.

Ans. Refer to Basic Concepts Point 2.

Q. 3. Distinguish between the terms homopolymer and copolymer and give an example of each.

Ans. **Homopolymer:** Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers. For example, polythene, PAN, teflon, nylon-6, etc.

Copolymer: Polymers whose repeating structural units are derived from two or more types of monomer molecules are called copolymers. For example, Buna-S, Buna-N, nylon-6,6, polyester, bakelite, etc.

Q. 4. How do you explain the functionality of a monomer?

Ans. Functionality of a monomer is the number of binding sites in a molecule. For example, the functionality of ethene, propene, styrene, acrylonitrile is one and that of 1, 3-butadiene, adipic acid, terephthalic acid, hexamethylenediamine is two.

Q. 5. Define the term polymerisation.

Ans. Polymerisation is a process of formation of a high molecular mass polymer from one or more monomers by linking together a large number of repeating structural units through covalent bonds.

Q. 6. Is $\text{-}\!\!\left(\text{NH—CHR—CO}\right)\!\!\text{-}_n$, a homopolymer or copolymer?

Ans. It is a homopolymer because the repeating structural unit has only one type of monomer, *i.e.*, NH_2—CHR—COOH.

Q. 7. Why do elastomers possess elastic properties?

Ans. In elastomers, the polymer chains are held together by the weak intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released.

Q. 8. How can you differentiate between addition and condensation polymerisation? **[*CBSE (AI) 2009*]**

Ans. Refer to Table 15.2.

Q. 9. Explain the term copolymerisation and give two examples.

Ans. When a mixture containing more than one monomeric species is allowed to polymerise, the product obtained is called copolymer and the process is called copolymerisation. For example, Buna–S, a copolymer of 1,3-butadiene and styrene and Buna–N, a copolymer of 1, 3-butadiene and acrylonitrile.

Q. 10. Write the free radical mechanism for the polymerisation of ethene. **[*CBSE Delhi 2016*]**

Ans. Refer to Basic Concepts Point 3(*a*).

Q. 11. Define thermoplastics and thermosetting polymers with two examples of each. **[*CBSE (AI) 2013*]**

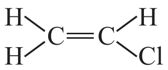
Ans. **Thermoplastic polymers:** These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

Thermosetting polymers: These polymers are cross-linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldehyde resins, etc.

Q. 12. Write the monomers used for getting the following polymers:

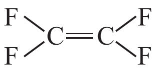
(*i*) Polyvinyl chloride (*ii*) Teflon (*iii*) Bakelite.

Ans. (*i*)



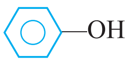
Vinyl chloride

(*ii*)



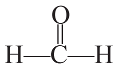
Tetrafluoroethene

(*iii*)



Phenol

and



$H-\overset{\overset{\large O}{\|}}{C}-H$

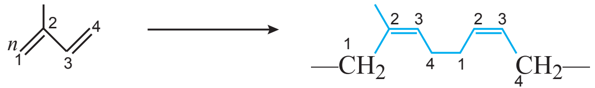
Formaldehyde

Q. 13. Write the name and structure of one of the common initiators used in free radical addition polymerisation.

Ans. Benzoyl peroxide

Q. 14. How does the presence of double bonds in rubber molecules influence their structure and reactivity?

Ans. Natural rubber is *cis*-polyisoprene and is obtained by 1, 4-polymerisation of isoprene units. In rubber molecule, double bonds are located between C_2 and C_3 of each isoprene unit. These *cis*-double bonds do not allow the polymer chains to come closer for effective interactions and hence intermolecular forces are quite weak. Thus, natural rubber, has a randomly coiled structure and hence shows elasticity.



Isoprene

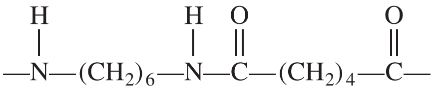
cis-Polyisoprene
(Natural rubber)

Q. 15. Discuss the main purpose of vulcanisation of rubber.

Ans. Natural rubber becomes soft at high temperatures (> 335 K) and brittle at low temperatures (< 283 K) and shows high water absorption capacity. It is soluble in non-polar solvents and is non-resistant to attack by oxidising agents. To improve upon these physical properties, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K and 415 K. On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.

Q. 16. What are the monomeric repeating units of Nylon-6 and Nylon-6, 6? **[*HOTS*]**

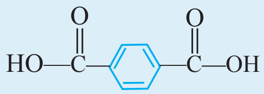
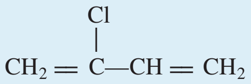
Ans. The monomeric repeating unit of Nylon-6 is $-\overset{\overset{\large O}{\|}}{C}-(CH_2)_5-\overset{\overset{\large H}{|}}{N}-$ which is derived from caprolactam. The monomeric repeating unit of Nylon-6, 6 is derived from two monomers, hexamethylenediamine and adipic acid and has the following structure:



$$-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-$$

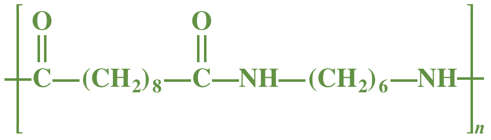
Q. 17. Write the names and structures of the monomers of the following polymers:
(*i*) Buna-S (*ii*) Buna-N (*iii*) Dacron (*iv*) Neoprene

Ans.

S.No.	Polymers	Monomer Names	Monomer Structures
(*i*)	Buna-S	1, 3-Butadiene, Styrene	$CH_2=CH-CH=CH_2$ $C_6H_5CH=CH_2$
(*ii*)	Buna-N	1, 3-Butadiene, Acrylonitrile	$CH_2=CH-CH=CH_2$ $CH_2=CH-CN$
(*iii*)	Dacron	Ethylene glycol Terephthalic acid	$HOCH_2-CH_2OH$ 
(*iv*)	Neoprene	Chloroprene	 $CH_2=\overset{\overset{Cl}{\vert}}{C}-CH=CH_2$

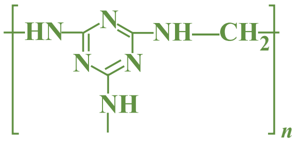
Q. 18. Identify the monomer in the following polymer structures: **[*HOTS*]**

(i)



$$\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH-\right]_n$$

(ii)

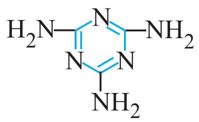


Ans. Monomers are:

(*i*) $HOOC-(CH_2)_8-COOH$ and $H_2N-(CH_2)_6-NH_2$

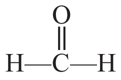
Decanedioic acid or Sebacic acid — Hexamethylenediamine

(*ii*)



1, 3, 5-Triazine-2, 4, 6-triamine

and

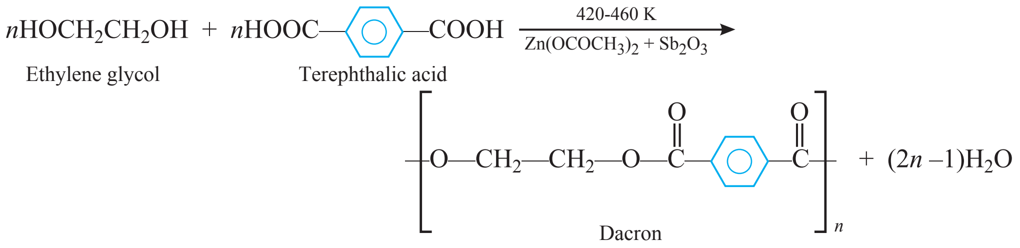


$$H-\overset{\overset{O}{\|}}{C}-H$$

Formaldehyde

Q. 19. How is dacron obtained from ethylene glycol and terephthalic acid?

Ans. Dacron is obtained by condensation polymerisation of ethylene glycol and terephthalic acid with the elimination of water molecules. The reaction is carried out at 420–460 K in the presence of a catalyst consisting of a mixture of zinc acetate and antimony trioxide.



Q. 20. **What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester.**

Ans. Polymers which disintegrate by themselves over a period of time either by bacterial degradation or by enzymatic hydrolysis or by oxidation in environment are called biodegradable polymers. PHBV, nylon-2-nylon-6 are biodegradable aliphatic polyesters.

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. Which of the following is not an example of natural polymer?

(*a*) Wool (*b*) Silk (*c*) Leather (*d*) Nylon

2. Which of the following polymers of glucose is stored by animals? *[NCERT Exemplar]*

(*a*) Cellulose (*b*) Amylose (*c*) Amylopectin (*d*) Glycogen

3. Which of the following is not a semisynthetic polymer? *[NCERT Exemplar]*

(*a*) *cis*-polyisoprene (*b*) Cellulose nitrate (*c*) Cellulose acetate (*d*) Vulcanised rubber

4. Chemically rayon is

(*a*) Cellulose nitrate (*b*) Cellulose sulphate (*c*) Cellulose acetate (*d*) Cellulose phosphate

5. Which of the following statements is not true about low density polythene? *[NCERT Exemplar]*

(*a*) Tough (*b*) Hard

(*c*) Poor conductor of electricity (*d*) Highly branched structure

6. Which of the following describes a chain terminating step in addition polymerisation?

(*a*) Reaction of two radicals(*b*)Formation of phenyl radical

(*c*) Addition of radical to ethane (*d*) Formation of bigger radicals.

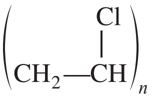
7. The commercial name of polyacrylonitrile is ________________. *[NCERT Exemplar]*

(*a*) Dacron (*b*) Orlon (acrilan) (*c*) PVC (*d*) Bakelite

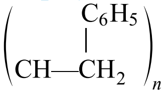
8. Orlon is a polymer of:

(*a*) Styrene (*b*) Tetrafluoroethylene (*c*) Vinyl chloride (*d*) Acrylonitrile

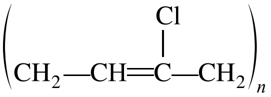
9. Which of the following structures represent Neoprene polymer?

(*a*) 

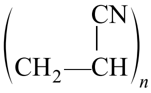
$\left(CH_2-\overset{Cl}{\overset{|}{C}H}\right)_n$

(*b*) 

$\left(\overset{C_6H_5}{\overset{|}{C}H}-CH_2\right)_n$

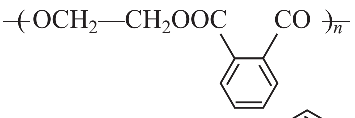
(*c*) 

$\left(CH_2-CH=\overset{Cl}{\overset{|}{C}}-CH_2\right)_n$

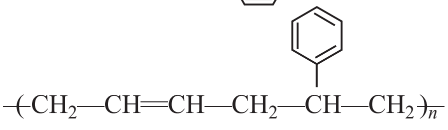
(*d*) 

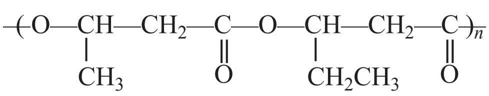
$\left(CH_2-\overset{CN}{\overset{|}{C}H}\right)_n$

10. In which of the following polymers ethylene glycol is one of the monomer units? *[NCERT Exemplar]*

(*a*) 

(*b*) $+\!\!(CH_2-CH_2)\!\!+_n$

(*c*) 

(*d*) 

$+\!\!(O-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}})\!\!+_n$

11. Nylon is an example of

(*a*) Polyamide (*b*) Polyester (*c*) Polyethene (*d*) Polysaccharide

12. Nylon-6 is made from

(*a*) 1, 3-Butadiene (*b*) chloroprene (*c*) adipic acid (*d*) caprolactam

13. Soft drinks and baby feeding bottles are generally made up of:

(*a*) Polyester (*b*) Polyurethane (*c*) Polyurea (*d*) Polystyrene

14. Which of the following statement is not correct?

(*a*) Terylene is polyester polymer
(*b*) Caprolactum is the monomer of nylon-6
(*c*) Phenol formaldehyde resin is known as bakelite
(*d*) The monomer of natural rubber is butadiene

15. Which of the following polymers, need atleast one diene monomer for their preparation? [*NCERT Exemplar*]

(*a*) Dacron (*b*) Buna-S (*c*) Neoprene (*d*) Novolac

16. Which of the following is a thermosetting plastic?

(*a*) PVC (*b*) PVA (*c*) Bakelite (*d*) Perspex

17. Which of the following are characteristics of thermosetting polymers? [*NCERT Exemplar*]

(*a*) Heavily branched cross linked polymers.
(*b*) Linear slightly branched long chain molecules.
(*c*) Become infusible on moulding so cannot be reused.
(*d*) Soften on heating and harden on cooling, can be reused.

18. Novolac on heating with formaldehyde forms

(*a*) Melamine (*b*) Buna-N (*c*) Buna-S (*d*) Bakelite

19. Natural rubber is a polymer of:

(*a*) Styrene (*b*) Styrene and 1, 3 butadiene
(*c*) Tetrafluoroethylene (*d*) 2-methyl 1, 3-butadiene

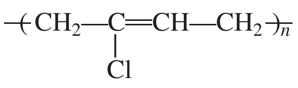
20. Heating of rubber with sulphur is known as:

(*a*) galvanisation (*b*) bessemerisation (*c*) vulcanisation (*d*) sulphonation

21. Biodegradable polymer which can be produced from glycine and aminocaproic acid is

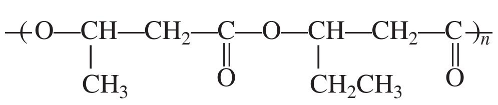
(*a*) PHBV (*b*) buna-N (*c*) nylon2-nylon6 (*d*) nylon6, 6

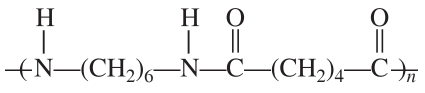
22. Which of the following polymer is biodegradable? [*NCERT Exemplar*]

(*a*)

$\left(CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2 \right)_n$

(*b*)

$\left(CH_2-CH=CH-CH_2-CH_2-\overset{CN}{\overset{|}{C}H} \right)_n$

(*c*)

$\left(O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}} \right)_n$

(*d*)

$\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right)_n$

23. Polymer used in bullet proof glass is:

(*a*) PMMA (*b*) Laxan (*c*) Nomex (*d*) Kevlar

Answers

1. (*d*) **2.** (*d*) **3.** (*a*) **4.** (*c*) **5.** (*d*) **6.** (*a*) **7.** (*b*) **8.** (*d*) **9.** (*c*) **10.** (*a*)
11. (*a*) **12.** (*d*) **13.** (*d*) **14.** (*d*) **15.** (*b, c*) **16.** (*c*) **17.** (*a, c*) **18.** (*d*) **19.** (*d*) **20.** (*c*)
21. (*c*) **22.** (*c*) **23.** (*b*)

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- ***(a)*** ***Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).***
- ***(b)*** ***Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).***
- ***(c)*** ***Assertion (A) is correct, but Reason (R) is incorrect statement.***
- ***(d)*** ***Assertion (A) is incorrect, but Reason (R) is correct statement.***

1. Assertion (*A*) **:** Rayon is a semi synthetic polymer and is taken as a better choice than cotton fabric.
Reason (*R*) **:** Mechanical and aesthetic properties of celluose can be improved by acetylation.

2. Assertion (*A*) **:** Olefinic monomers undergo addition polymerisation.
Reason (*R*) **:** Polymerisation of vinylchloride is initiated by peroxides/persulphates.

3. Assertion (*A*) **:** Low density polythene is used in the insulation of electricity carrying wires.
Reason (*R*) **:** Low density polythene is chemically inert and tough.

4. Assertion (*A*) **:** Zeigler-Natta catalyst is a mixture of triethylaluminium and titanium tetrachloride.
Reason (*R*) **:** Zeigler-Natta catalyst is used to make low density polythene.

5. Assertion (*A*) **:** Polyamides are best used as fibres because of high tensile strength.
Reason (*R*) **:** Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence provide high tensile strength to polymers.

6. Assertion (*A*) **:** Network polymers are thermosetting.
Reason (*R*) **:** Network polymers have high molecular mass.

7. Assertion (*A*) **:** Ordinary rubber is an elastomer.
Reason (*R*) **:** The intermolecular forces of attraction between the polymer chains are weak van der Waals' forces.

8. Assertion (*A*) **:** Polytetrafluoroethene is used in making non-stick cookwares.
Reason (*R*) **:** Fluorine has highest electronegativity.

9. Assertion (*A*) **:** PTFE has high thermal stability and chemical inertness.
Reason (*R*) **:** It is a themoplastic.

10. Assertion (*A*) **:** Phenol-Formaldehyde polymer is a thermosetting polymer.
Reason (*R*) **:** It can be melted time and again without any change.

11. Assertion (*A*) **:** 5% of sulphur is added to natural rubber for manufacturing tyre tubes.
Reason (*R*) **:** It acts as a cross linking agent and thus makes the rubber stiffer.

12. Assertion (*A*) **:** For making rubber synthetically, isoprene molecules are polymerised.
Reason (*R*) **:** Neoprene (a polymer of chloroprene) is a synthetic rubber.

13. Assertion (*A*) **:** Most of the synthetic polymers are not biodegradable.
Reason (*R*) **:** Polymerisation process induced toxic character in organic molecules.

Answers

1. (*b*) **2.** (*b*) **3.** (*b*) **4.** (*c*) **5.** (*a*) **6.** (*b*) **7.** (*a*) **8.** (*b*) **9.** (*b*) **10.** (*c*)
11. (*a*) **12.** (*d*) **13.** (*c*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

There are two broad types of polymerization reactions, *i.e.*, the addition or chain growth polymerization and condensation or step growth polymerization. In the addition polymerization, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds, *e.g.*, alkenes, alkadienes and their derivatives. This mode of polymerization leads to an increase in chain length and chain growth can take place through the formation of either free radicals or ionic species while condensation polymerization generally involves a repetitive condensation reaction between two bi-functional or trifunctional monomeric units. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, hydrogen chloride, etc. and lead to the formation of high molecular mass condensation polymers. In these 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 functionalized species and is independent of each other, this process is also called step growth polymerization.

1. **What do you understand by addition polymers?**

Ans. Polymers which are formed by repeated addition of monomer molecules containing double and triple bonds are called addition polymers. Examples are polythene, PVC, PAN, PMMA, etc.

2. **Write the monomer units of bakelite.**

Ans. Phenol and formaldehyde.

3. **Why are rubbers called elastomers?** [*NCERT Exemplar*]

Ans. Rubbers are stretched on application of force and regain original state after the force is removed. Therefore, these are called elastomers.

4. **Mention which of the following are addition polymers:**
(i) Terylene (ii) Nylon-6, 6 (iii) Neoprene (iv) Teflon.

Ans. Neoprene and teflon are addition polymers.

5. **Give one example of chain growth polymer.**

Ans. PVC (Poly vinyl chloride).

PASSAGE–2

A polymer is a large molecule of very high molecular mass formed by the repeated combination of a very large number of one or more types of small molecules called monomers. On the basis of the nature of repeating structural unit there are two types of polymers: homopolymers and copolymers. In homopolymers, the repeating structural units are derived from only one type of monomer units while in copolymers the structural units are derived from two or more types of monomer units. The naturally occurring polymeric species such as polysaccharides, proteins and nucleic acids, which are essential for life process are called biopolymers.

1. **Give one example of copolymer.**

Ans. Buna-N

2. **Identify the type of polymer.** [*NCERT Exemplar*]

—A—A—A—A—A—A—

Ans. Homopolymer

3. **Give an example of a copolymer formed by condensation polymerization ?**

Ans. Terylene

4. **Can a copolymer be formed in both addition and condensation polymerization? Explain.**

Ans. Yes, copolymers can be formed both in addition and condensation polymerization. For example, Buna-S is an addition copolymer of styrene and 1,3-butadiene.

5. Identify the type of polymer *[NCERT Exemplar]*

—A—B—B—A—A—A—B—A—

Ans. Copolymer.

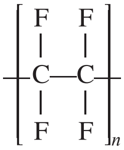
Very Short Answer Questions [1 mark]

Q. 1. Which of the following is a natural polymer?

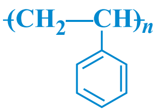
Buna-S, Proteins, PVC *[CBSE (AI) 2014]*

Ans. Proteins.

Q. 2. Give the structure and name of the polymer which is used for making non-stick utensils.

Ans. 

$\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}- \right]_n$, Teflon

Q. 3. Is  **a homopolymer or a copolymer?** *[CBSE (AI) 2013]*

Ans. Homopolymer.

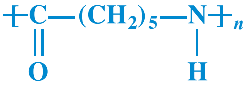
Q. 4. Give one example of a condensation polymer. *[CBSE (AI) 2013]*

Ans. Nylon-6,6 or Dacron

Q. 5. Based on molecular forces what type of polymer is neoprene? *[CBSE (AI) 2014]*

Ans. Elastomer

Q. 6. Write the names of monomers of the following polymer:



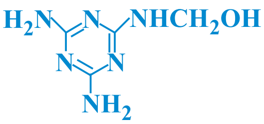
$\left[\underset{O}{\underset{\|}{C}}-(CH_2)_5-\underset{H}{\underset{|}{N}} \right]_n$ [CBSE (F) 2013]

Ans. Caprolactam.

Q. 7. Name a synthetic polymer which is an amide.

Ans. Nylon-6, 6.

Q. 8. How is the following resin intermediate prepared and which polymer is formed by this monomer unit?



(Resin intermediate) *[NCERT Exemplar] [HOTS]*

Ans. Melamine and formaldehyde are starting materials for this intermediate. Its polymerisation gives melamine polymer.

Q. 9. What is the commercial name of PMMA? What is its use?

Ans. The commercial name of PMMA (polymethylmethacrylate) is perspex. It is used as a substitute of glass. It is used for making lenses, transparent domes, aircraft windows and sky lights.

Short Answer Questions–I [2 marks]

Q. 1. Name the sub-groups into which polymers are classified on the basis of magnitude of intermolecular forces. *[CBSE Delhi 2011]*

Ans. On the basis of magnitude of intermolecular forces polymers are classified into following four sub-groups:

(*i*) Elastomers

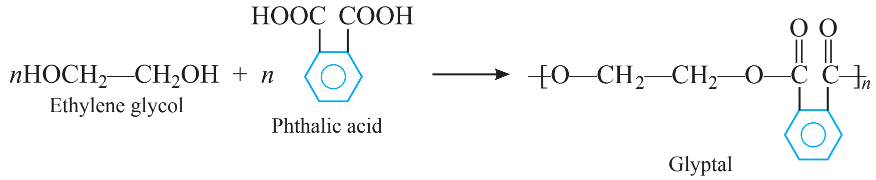
(*ii*) Fibres

(*iii*) Thermoplastic polymers

(*iv*) Thermosetting polymers

Q. 2. Write equations for the synthesis of the given polymers (*i*) Glyptal (*ii*) Teflon.

Ans. (*i*)



(*ii*) $$\underset{\text{Tetrafluoroethene}}{nCF_2=CF_2} \xrightarrow[\text{High pressure}]{\text{Catalyst}} \underset{\text{Teflon}}{(CF_2-CF_2)_n}$$

Q. 3. Write the name of monomers used for getting the following polymers: **[*CBSE (AI) 2014*]**

(*i*) Teflon **(*ii*) Buna-N**

Ans. (*i*) Tetrafluoroethene (*ii*) 1, 3–butadiene and acrylonitrile

Q. 4. Write the name of monomers used for getting the following polymers: **[*CBSE (AI) 2014*]**

(*i*) Bakelite **(*ii*) Neoprene**

Ans. (*i*) Phenol and formaldehyde (*ii*) Chloroprene

Q. 5. Differentiate the following pair of polymers based on the property mentioned against each.

(*i*) Novolac and bakelite (structure)

(*ii*) Buna-S and terylene (intermolecular forces of attraction)

Ans. (*i*) Novolac is a straight chain linear polymer but bakelite is cross linked.

(*ii*) Buna-S is an elastomer having weak van der Waal's intermolecular forces whereas terylene is a fibre having strong intermolecular hydrogen bonding.

Short Answer Questions–II [3 marks]

Q. 1. What are addition polymers? How are the two types of addition polymers different from each other? Give one example of each type. **[*CBSE (F) 2011*]**

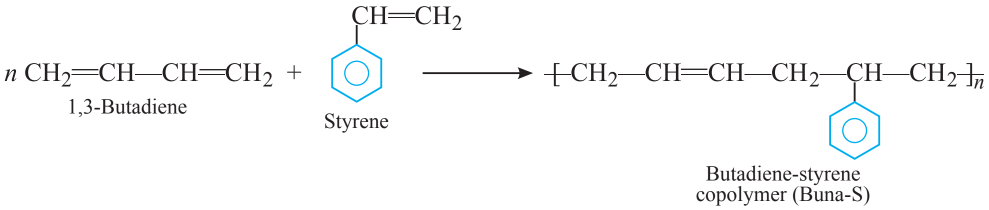
Ans. Polymers which are formed by the repeated addition of monomers molecules possessing double or triple bonds are called the addition polymers.

The two types of addition polymers are:

(***i***) **Homopolymers:** The addition polymers formed by the polymerisation of a single monomeric species are called homopolymers, *e.g.*, polythene.

$$\underset{\text{Ethene}}{nCH_2=CH_2} \xrightarrow[\text{traces of } O_2]{350\text{-}570\text{ K, }1000\text{-}2000\text{ atm}} \underset{\text{Polythene}}{(CH_2-CH_2)_n}$$

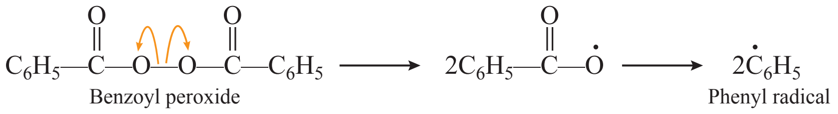
(***ii***) **Copolymers:** The polymers made by addition polymerisation from two different monomers are known as copolymers, *e.g.*, Buna-S.



Q. 2. Write the mechanism of free radical polymerisation of ethene. **[*CBSE Delhi 2016*]**

Ans. The sequence of steps governing the free radical polymerisation of ethene to form polythene are follows:

Chain initiation step: Benzoyl peroxide undergoes homolytic fission to form free radicals.



$$\underset{\text{Benzoyl peroxide}}{C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5} \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow \underset{\text{Phenyl radical}}{2\dot{C}_6H_5}$$

$$\dot{C}_6H_5 + \underset{\text{Ethene}}{CH_2=CH_2} \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

Chain propagating step:

$$C_6H_5{-}CH_2{-}\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$$

$$\big\downarrow$$

$$C_6H_5 \left(CH_2{-}CH_2 \right)_n CH_2{-}\dot{C}H_2$$

Chain termination step: The chain reaction stops when two free radical chains combine.

$$2C_6H_5 \left(CH_2{-}CH_2 \right)_n CH_2{-}\dot{C}H_2 \longrightarrow$$

$$\underset{\text{Polythene}}{C_6H_5 \left(CH_2{-}CH_2 \right)_n CH_2{-}CH_2{-}CH_2{-}CH_2 \left(CH_2{-}CH_2 \right)_n C_6H_5}$$

Q. 3. Explain the following processes with a suitable example in each case:

(*i*) Chain growth polymerisation

(*ii*) Step growth polymerisation.

Ans. (*i*) **Chain growth polymerisation:** This type of polymerisation involves the initial formation of a free radical or an ion (from small amount of initiator such as organic peroxide) to which monomers get added up by a chain reaction. Here, the polymers are exact multiples of organic monomeric molecules and have only carbon atoms in their main chain. Various steps involved in chain growth polymerisation of ethene are:

(*a*) $\text{Initiator} \xrightarrow[\text{split up}]{\text{Heat, light, etc.}} \underset{\text{Free radical}}{\dot{A}}$

(*b*) $\dot{A} + \underset{\text{Monomer}}{CH_2{=}CH_2} \longrightarrow \underset{\text{(Intermediate species)}}{A{-}CH_2{-}\dot{C}H_2}$

(*c*) $A{-}CH_2{-}\dot{C}H_2 + \underset{\text{Monomer}}{CH_2{=}CH_2} \longrightarrow \underset{\text{(Bigger intermediate species)}}{A{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2}$

Examples: polyethylene, teflon, etc.

(*ii*) **Step growth polymerisation:** This type of polymerisation involves a series of condensation reactions between simple monomers containing polar groups, with or without the elimination of small molecules like water, HCl, NH_3, etc. In addition to carbon atoms, these polymers contain other atoms also in their main chain. Steps may be illustrated as follows:

(*a*) $\underset{\text{Monomer}}{A} + \underset{\text{Monomer}}{B} \xrightarrow{\text{Condensation}} A{-}B$

(*b*) $A{-}B + A \xrightarrow{\text{Condensation}} A{-}B{-}A$

(*c*) $A{-}B + A{-}B \xrightarrow{\text{Condensation}} A{-}B{-}A{-}B \ldots\ldots$

Examples: Terylene, nylon, etc.

The step wise growth can also occur in another manner:

(*a*) $A + B \xrightarrow{\text{Condensation}} A{-}B$

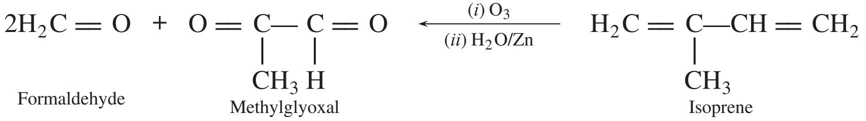
(*b*) $A{-}B + A{-}B \xrightarrow{\text{Condensation}} \underset{\text{Polymer}}{A{-}B{-}A{-}B \cdots\cdots (A{-}B)_n}$

Q. 4. A monomer of a polymer upon ozonolysis gives one mole of methylglyoxal and two moles of formaldehyde.

(*i*) Identify the monomer of the polymer.

(*ii*) Give its free radical mode of addition polymerisation. **[*HOTS*]**

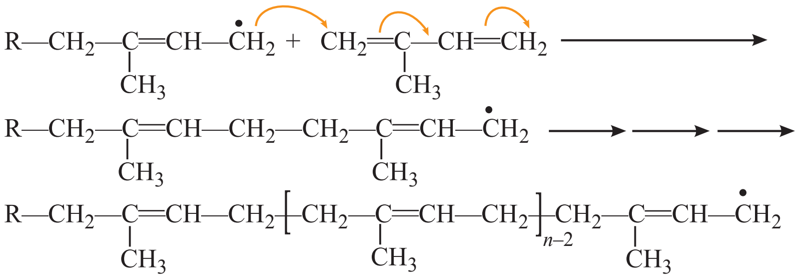
Ans. (*i*) As the monomer on ozonolysis gives one mole of methylglyoxal and two moles of formaldehyde, therefore, the monomer is isoprene.



$$\underset{\text{Formaldehyde}}{2H_2C{=}O} + \underset{\text{Methylglyoxal}}{O{=}\underset{CH_3}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}O} \xleftarrow[(ii)\ H_2O/Zn]{(i)\ O_3} \underset{\text{Isoprene}}{H_2C{=}\underset{CH_3}{\underset{|}{C}}-CH{=}CH_2}$$

(*ii*) The free radical mechanism of polymerisation of isoprene may be given as follows:

- **Chain initiation:** Initiator $\longrightarrow \underset{\text{Free radical}}{\dot{R}}$
- **Chain propagation:**

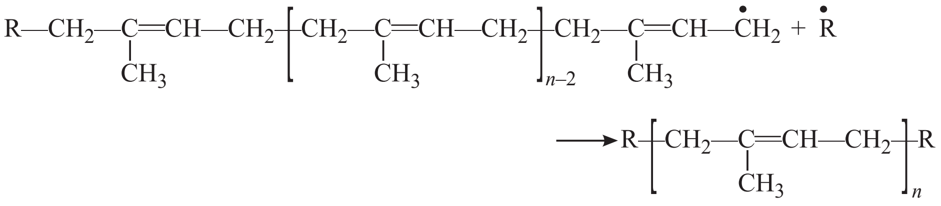


$$R-CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-\dot{C}H_2 + CH_2{=}\underset{CH_3}{\underset{|}{C}}-CH{=}CH_2 \longrightarrow$$

$$R-CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-CH_2-CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-\dot{C}H_2 \longrightarrow \longrightarrow \longrightarrow$$

$$R-CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-CH_2\left[CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-CH_2\right]_{n-2}CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-\dot{C}H_2$$

- **Chain termination:** One of the mode of chain termination is



$$R-CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-CH_2\left[CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-CH_2\right]_{n-2}CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-\dot{C}H_2 + \dot{R}$$

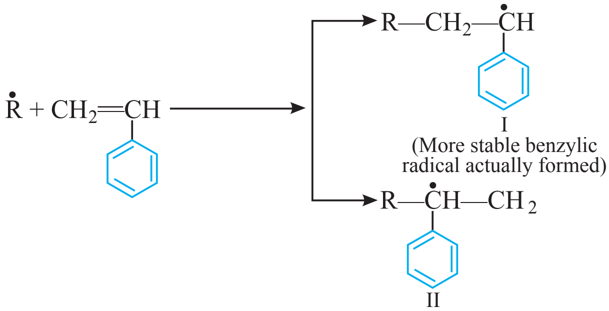
$$\longrightarrow R\left[CH_2-\underset{CH_3}{\underset{|}{C}}{=}CH-CH_2\right]_n R$$

Natural rubber

Q. 5. Explain why free radical polymerisation of styrene gives a product in which phenyl groups are on alternate carbon atoms rather than on adjacent carbon atoms. **[*HOTS*]**

Ans. During free radical polymerisation, the addition of free radical to monomer molecules occurs in accordance with Markovnikov's rule so as to give more stable benzylic free radical.

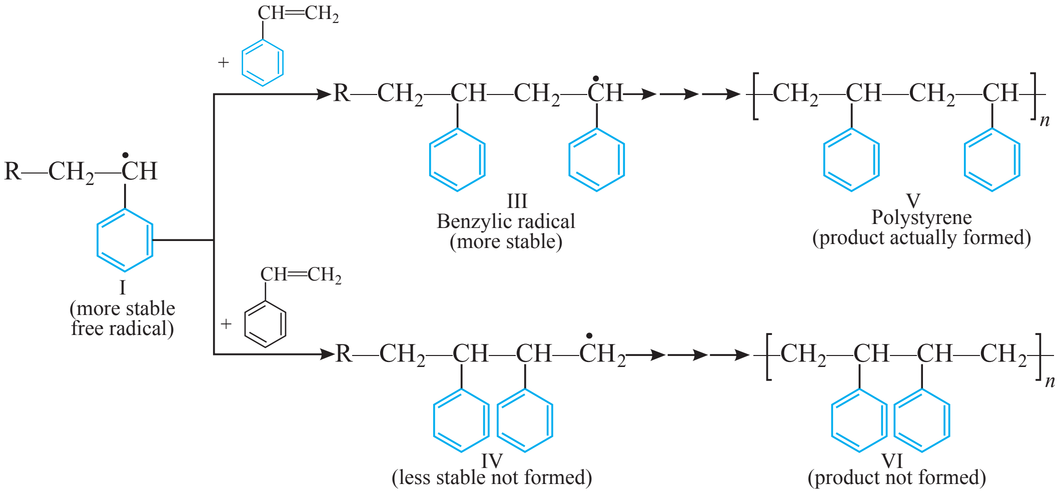
For example,



(More stable benzylic radical actually formed)

(Less stable radical, not formed)

This process goes on till polystrene (V) in which the phenyl groups are on alternate carbon atoms is obtained rather than the product (VI) in which the phenyl groups are on adjacent carbon atoms.



Q. 6. **(*i*) What is the role of *t*-butyl peroxide in the polymerisation of ethene?**

(*ii*) Identify the monomers in the following polymer:

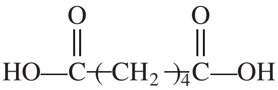
$\left[NH—(CH_2)_6—NH—CO—(CH_2)_4—CO \right]_n$

(*iii*) Arrange the following polymers in the increasing order of their intermolecular forces:

Polystyrene, Terylene, Buna-S ***[CBSE Delhi 2016]***

Ans. (*i*) It acts as a free radical generating initiator in the chain initiation step of polymerisation of ethene.

(*ii*) $H_2N\text{—}(CH_2)_6\text{—}NH_2$ Hexamethylene diamine



$HO—\overset{O}{\overset{\|}{C}}—(CH_2)_4—\overset{O}{\overset{\|}{C}}—OH$ Adipic acid

(*iii*) Buna-S < Polystyrene < Terylene

Q. 7. **(*i*) Write one example each of** ***[CBSE 2019 (56/2/3)]***

(*a*) Cross-linked polymer **(*b*) Natural polymer**

(ii) Arrange the following in the increasing order of their intermolecular forces.

Terylene, Buna-N, Polystyrene

(iii) Define biodegradable polymers with an example.

Ans. (*i*) (*a*) Bakelite, melamine, etc.

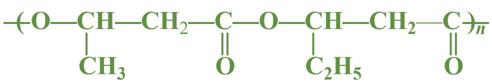
(*b*) Proteins, cellulose, starch, rubber (natural), etc.

(*ii*) Buna-N < Polystyrene < Terylene

(*iii*) Refer to Basic Concepts Point 8.

Q. 8. **(*i*) Is $\left[CH_2—CH(C_6H_5) \right]_n$ a homopolymer or copolymer? Give reason.** ***[CBSE 2019 (56/2/1)]***

(ii) Write the monomers of the following polymer:

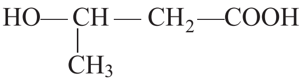


$\left(O—\underset{CH_3}{\underset{|}{CH}}—CH_2—\underset{O}{\underset{\|}{C}}—O—\underset{C_2H_5}{\underset{|}{CH}}—CH_2—\underset{O}{\underset{\|}{C}} \right)_n$

(*iii*) Write the role of benzoyl peroxide in polymerisation of ethene.

Ans. (*i*) It is a homopolymer because the repeating structural unit has only one type of monomer unit, *i.e.*, $CH_2 = CH — C_6H_5$

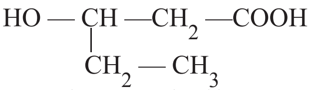
(*ii*)



$HO—\underset{CH_3}{\underset{|}{CH}}—CH_2—COOH$

3 - Hydroxybutanoic acid

,



$HO — \underset{CH_2 — CH_3}{\underset{|}{CH}} —CH_2 —COOH$

3-Hydroxy pentanoic acid

(*iii*) Benzoyl peroxide acts as a free radical generating initiator in polymerisation of ethene.

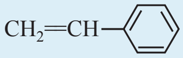
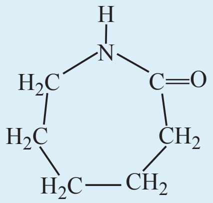
Q. 9. Which of the following polymers soften on heating and harden on cooling? What are the polymers with this property collectively called? What are the structural similarities between such polymers? Bakelite, urea–formaldehyde resin, polythene, polyvinyls, polystyrene. [*NCERT Exemplar*] [*HOTS*]

Ans. Polythene, polyvinyls and polystyrene soften on heating and harden on cooling. Such polymers are called thermoplastic polymers. These polymers are linear or slightly branched long chain molecules. These possess intermolecular forces whose strength lies between strength of intermolecular forces of elastomers and fibres.

Q. 10. Write the structure and name of the monomers of the following polymers:

(*i*) Buna-S **(*ii*) Nylon-6** **(*iii*) Teflon.** [*CBSE 2020 (56/1/2)*]

Ans.

S.No.	Polymers	Monomer Names	Monomer Structures
(*i*)	Buna-S	1, 3–Butadiene	$CH_2{=}CH{-}CH{=}CH_2$
		Styrene	
(*ii*)	Nylon-6	Caprolactam	
(*iii*)	Teflon	Tetrafluoroethene	$CF_2{=}CF_2$

Q. 11. Write names of monomer/s of the following polymers and classify them as addition or condensation polymers.

(*i*) Teflon **(*ii*) Bakelite** **(*iii*) Natural Rubber**

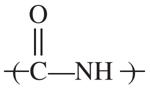
Ans.

	Polymers	Type	Monomer
(*i*)	Teflon	Addition	Tetrafluoroethene
(*ii*)	Bakelite	Condensation	Phenol and formaldehyde
(*iii*)	Natural rubber	Addition	*cis*-isoprene

Q. 12. Briefly describe the following terms giving one example of each:

(*i*) Polyolefins **(*ii*) Polyamides** **(*iii*) Polyesters**

Ans. **(*i*) Polyolefins:** These are polymers derived from unsaturated hydrocarbons, for example, polypropene.

(*ii*) Polyamides: The polymers having large number of amide linkage  $\left(\overset{\overset{\Large O}{\|}}{C}{-}NH \right)$ in the chain are called polyamides, for example, nylon-6, 6 and nylon-6.

(*iii*) Polyesters: These are the polycondensation products of dicarboxylic acids and diols. Dacron or terylene is the best known example of polyesters.

Q. 13. (*i*) Arrange the following polymers in increasing order of their intermolecular forces:

Polyvinylchloride, Neoprene, Terylene

(*ii*) Write one example each of

(*a*) Natural polymer

(*b*) Thermosetting polymer

(iii) What is the significance of numbers 6,6 in the polymer nylon-6, 6? [*CBSE 2019 (56/3/2)*]

Ans. (*i*) Neoprene < Polyvinylchloride < Terylene.

(*ii*) (*a*) Cellulose, starch, proteins, rubber (natural)

(*b*) Bakelite, urea-formaldehyde resins, etc.

(*iii*) In nylon-6, 6; two sixes stands for the two types of monomer molecules each containing six carbon atoms, *i.e.*, adipic acid ($HOOC—(CH_2)_4—COOH$) and hexamethylene diamine $[H_2N\text{—}(CH_2\text{—})_6NH_2]$.

Q. 14. Answer the following with reason: ***[CBSE 2019 (56/5/3)]***

(*i*) Is $(NH—CHR—CO)_n$, a homopolymer or copolymer?

(*ii*) Is PVC a condensation or addition polymer?

(*iii*) Is bakelite a thermoplastic or a thermosetting plastic?

Ans. (*i*) Refer to NCERT Textbook Exercises, Q. 6.

(*ii*) Addition polymer as it is formed by addition reaction of monomer vinyl chloride ($CH_2{=}CH—Cl$).

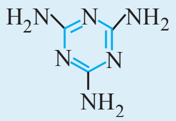
(*iii*) Bakelite is a thermosetting plastic as on heating it undergoes extensive crosslinking in moulds and again becomes infusible.

Q. 15. Write the structures of the monomers used for getting the following polymers:

(*i*) Polyvinyl chloride (PVC) **(*ii*) Melamine-formaldehyde polymer**

(*iii*) Buna-N ***[CBSE (AI) 2017; 2020 (56/3/2)]***

Ans.

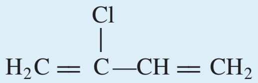
S.No.	Polymer	Monomer Name	Monomer Structure
(*i*)	PVC	Vinyl chloride	$CH_2{=}CH—Cl$
(*ii*)	Melamine-formaldehyde polymer	Melamine	
		Formaldehyde	HCHO
(*iii*)	Buna-N	1,3-Butadiene	$CH_2{=}CH—CH{=}CH_2$
		Acrylonitrile	$CH_2{=}CH—CN$

Q. 16. Write the names and structures of the monomers of the following polymers:

(*i*) Nylon–6, 6 **(*ii*) PHBV** **(*iii*) Neoprene**

[CBSE Delhi 2015; 2020 (56/1/2)]

Ans.

	Polymers	Monomer Structures	Monomer Names
(*i*)	Nylon-6, 6	$H_2N(CH_2)_6NH_2$ $HOOC—(CH_2)_4COOH$	Hexamethylene diamine Adipic acid
(*ii*)	PHBV	$CH_3CH(OH)CH_2COOH$ $CH_3CH_2CH(OH)CH_2COOH$	3-hydroxybutanoic acid 3-hydroxypentanoic acid
(*iii*)	Neoprene	 $H_2C{=}\overset{\displaystyle Cl}{\overset{\vert}{C}}—CH{=}CH_2$	Chloroprene

Q. 17. Mention two important uses for each of the following polymers: ***[CBSE (F) 2011]***

(*i*) Bakelite **(*ii*) Nylon 6,6** **(*iii*) PVC**

Ans. (*i*) It is used for making combs, fountain pen barrels, phonograph records.

It is used widely in making electrical goods such as switches, plugs, handles of various utensils.

(*ii*) It is used in making bristles for brushes, ropes.

It is used for making carpets and fabrics in textile industry.

(*iii*) It is used in the manufacture of raincoats, handbags, water pipes, vinyl flooring.

It is used for insulating electric wires.

Q. 18. What is vulcanisation? Why is it done? Why is diphenyl amine added to rubber?

Ans. Vulcanisation is a process of heating natural rubber with sulphur. This is done so as to make it more elastic, hard, more abrasion resistant by sulphur cross-linking. Diphenyl amine is added to rubber so as to prevent its oxidation.

Long Answer Question [5 marks]

Q. 1. **(*i*) Answer the following:**

(*a*) To have practical applications, why are cross links required in rubber? *[NCERT Exemplar]*

(*b*) Which factor imparts crystalline nature to a polymer like nylon? *[NCERT Exemplar]*

(*c*) Which type of biomolecules have some structural similarity with synthetic polyamides? What is this similarity? *[NCERT Exemplar]*

(*ii*) How does the presence of benzoquinone inhibit the free radical polymerisation of a vinyl derivative?

Ans. (*i*) (*a*) Cross links bind the planar polymer sheets thus increasing its elastomeric properties.

(*b*) Strong intermolecular forces like hydrogen bonding, lead to close packing of chains that imparts crystalline character.

(*c*) Proteins have structural similarity with synthetic polyamides. Polyamides and proteins both contain amide linkage.

(*ii*) Benzoquinone traps the radical intermediate to form a non-reactive radical, which is highly stabilised by resonance. Due to the lack of reactivity of this intermediate, further progress of the chain reaction is interrupted and the reaction stops.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. Terylene is:

(*a*) Polyamide (*b*) Polyethylene

(*c*) Polyvinyl chloride (*d*) Polyester

2. Zieglar Natta catalyst is used in the preparation of

(*a*) PVC (*b*) high density polythene

(*c*) low density polythene (*d*) dacron

3. Which of the following is a natural polymer?

(*a*) Protein (*b*) Polythene

(*c*) Buna-S (*d*) Bakelite

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. Assertion (*A*) : The elastomers can be stretched.
Reason (*R*) : The intermolecular forces in these polymers are very strong.

5. Assertion (*A*) : For natural polymers, the polydispersity index (PDI) is unity.
Reason (*R*) : Natural polymers are biodegradable.

6. **Assertion (*A*) :** Cationic addition polymerisation is facilitated in monomers containing electron-releasing groups.

Reason (*R*) : The electron-releasing groups stabilise the intermediate cation.

Answer the following questions:

7. Write the reaction involved in the formation of Buna-S. **(1)**

8. To have practical applications, why are cross links required in rubber? **(1)**

9. (*i*) Write one example each of
(*a*) Thermoplastic polymer
(*b*) Elastomers
(*ii*) Which factor provides crystalline nature to a polymer like Nylon? **(2)**

10. Give the chemical equation used for the synthesis of:
(*i*) Dacron
(*ii*) Buna-S **(2)**

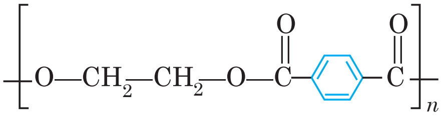
11. Differentiate between the following:
(*i*) Natural rubber and synthetic rubber
(*ii*) Nylon-6 and Nylon-6, 6. **(2)**

12. What are LDPE and HDPE? How are they prepared? **(2)**

13. Write:
(*i*) Reaction involved in the preparation of biodegradable polyester.
(*ii*) One use of Nylon-6, 6. **(2)**

14. (*i*) How does vulcanisation change the properties of natural rubber?
(*ii*) Name a synthetic polymer which is an ester. **(3)**

15. (*i*) What is the role of sulphur in the vulcanisation of rubber?
(*ii*) Identify the monomers in the following polymer: **[*CBSE (F) 2013*]**



(*iii*) Arrange the following polymers in the increasing order of their intermolecular forces:
Terylene, Polythene, Neoprene **[*CBSE Central 2016*]** **(3)**

16. Write the information asked in the following polymers:
(*i*) Bakelite–Materials used for preparation
(*ii*) Synthetic rubber–Monomer unit
(*iii*) Nylon-6, 6 –Materials required for preparation **(3)**

17. (*i*) Give an example of synthetic rubber and mention its main advantage.
(*ii*) Write the structure of the monomer 'dacron'.
(*iii*) Arrange the following polymers in the increasing order of their tensile strength:
Nylon-6, Buna-S, Polythene **(3)**

Answers

1. (*d*) **2.** (*b*) **3.** (*a*) **4.** (*c*) **5.** (*b*) **6.** (*a*)

Chapter–16

Chemistry in Everyday Life

basic concepts

1. (*a*) **Drugs:** Drugs are the chemical substances of low molecular masses (~100–500 u) which interact with macromolecular targets and produce a biological response.
   (*b*) **Medicines:** Drugs which produce a therapeutic and useful biological response.
   (*c*) **Chemotherapy:** The use of chemicals for treatment of diseases.

2. **Classification of Drugs**
   (*a*) **On the basis of pharmacological effect:** This classification is based on pharmacological effect of the drugs. It is useful for the doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem. For example, analgesics have pain killing effect, antiseptics kill or arrest the growth of microorganisms.
   (*b*) **On the basis of drug action:** It is based on the action of a drug on a particular biochemical process. For example, all antihistamines inhibit the action of histamines which causes inflammation in the body.
   (*c*) **On the basis of chemical structure:** It is based on the chemical structure of the drug. Drugs classified in this way share common structural features and often have similar pharmacological activity. For example, sulphonamides have common structural features as seen in Fig. 16.1.
   (*d*) **On the basis of molecular targets:** Drugs usually interact with biological macromolecules such as carbohydrates, proteins, lipids and nucleic acids called target molecules. This classification is based upon the type of the molecular target with which the drug interact. This is the most useful classification for medicinal chemists.

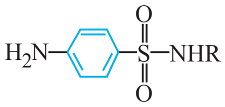
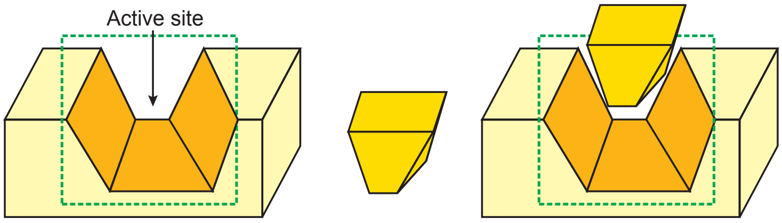


Fig. 16.1: Structural features of sulphonamides

3. **Enzymes:** Proteins which perform the role of biological catalysts in the body are called enzymes.
   (*a*) **Catalytic action of enzymes:** In their catalytic activity, enzymes perform two major functions:
      (*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. Substrates bind to the active site of the enzymes through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole–dipole interaction.
      (*ii*) The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction.



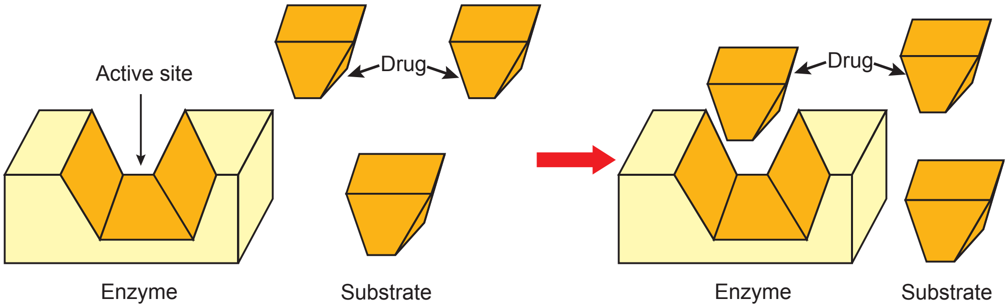
(a) (b) (c)

Fig. 16.2: (a) Active site of an enzyme, (b) Substrate, (c) Enzyme holding the substrate

(*b*) **Drug–enzyme interaction:** Drugs can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called enzyme inhibitors.

Drugs inhibit the attachment of substrates on active site of enzymes in two different ways:

(*i*) Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.



Drug and substrate competing for active site of enzyme

Drug blocks the active site of enzyme

Fig. 16.3: Drug and substrate competing for active site

(*ii*) Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is 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 synthesises the new enzyme.

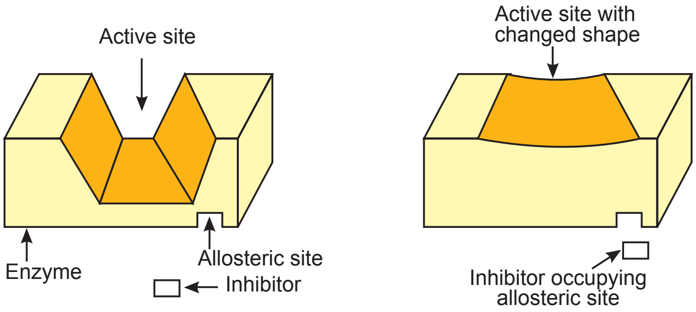


Fig. 16.4: Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site

- **Receptors:** Proteins that are crucial to body's communication process are called receptors. Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.

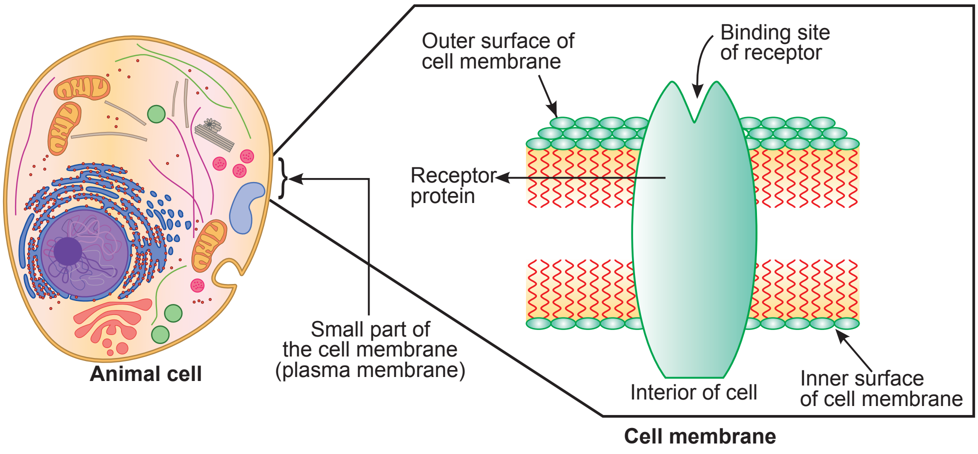


Fig. 16.5: Receptor protein embedded in the cell membrane with its active site opening on the outside region of the cell.

In the body, message between two neurons and that between neurons to muscles is communicated through certain chemicals. These chemicals, known as chemical messengers are received at the binding sites of receptor proteins. To accommodate a messenger, shape of the receptor site changes. This brings about the transfer of message into the cell. Thus, chemical messenger gives message to the cell without entering the cell.

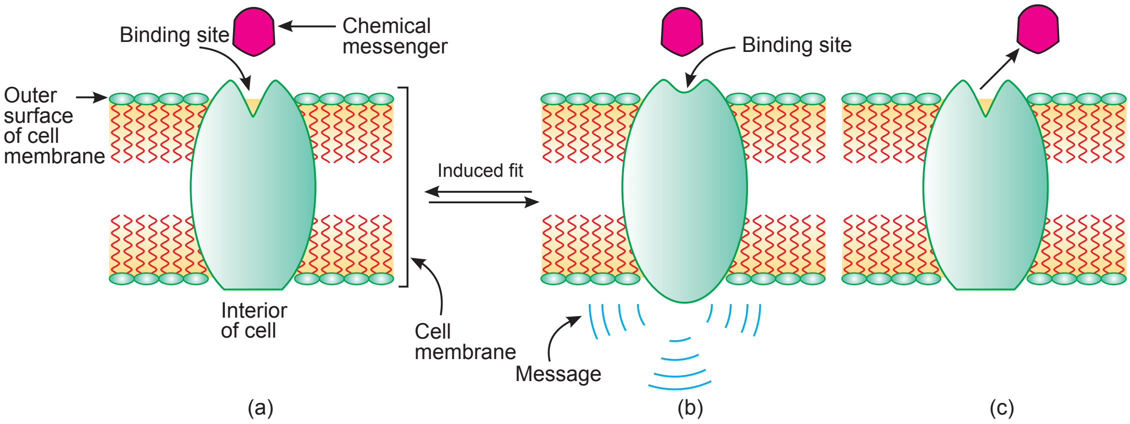


Fig. 16.6: (a) Receptor receiving chemical messenger
(b) Shape of the receptor changed after attachment of messenger
(c) Receptor regains structure after removal of chemical messenger

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

4. **Antihistamines:** Antihistamines are the drugs which interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effects. Brompheniramine, terfenadine, pheniramine maleate (avil), cetrizine and chlorpheniramine are some examples of antihistamines.
5. **Antacids:** These are the chemical substances which remove the excess acid in the stomach and raise the pH to appropriate level, *e.g.*, sodium hydrogencarbonate, a mixture of aluminium and magnesium hydroxide, ranitidine, etc.
6. **Neurologically Active Drugs:** Analgesics and tranquilizers are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

   (*a*) **Analgesic:** Drugs which reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system are called analgesics. These are classified as follows:

   (*i*) **Non-narcotic analgesics:** These drugs are non-addictive. Aspirin and paracetamol are important examples of non-narcotic analgesics. These drugs are effective in relieving skeletal pain such as that due to arthritis. These drugs have many other effects such as reducing fever and preventing platelet coagulation.

   (*ii*) **Narcotic analgesics:** These are the drugs which when administered in small doses relieve pain and produce sleep. Alkaloids like morphine, codeine and heroin belong to the class of narcotic analgesics. These are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.

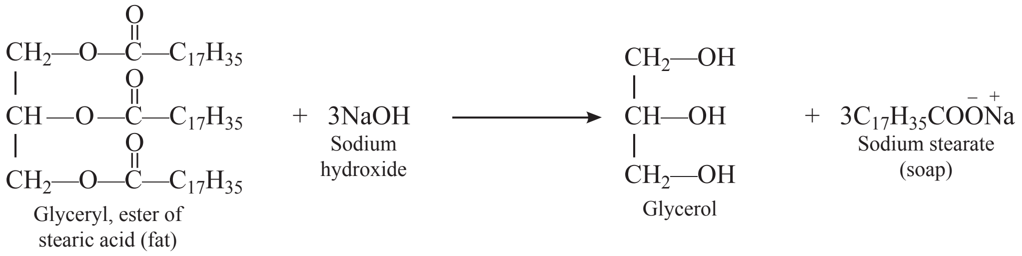
   (*b*) **Tranquilizers:** Tranquilizers are a class of chemical compounds used for the treatment of stress, fatigue, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being.

   Examples:

   - Tranquilizers like, chlordiazepoxide and meprobamate are used for relieving tension.
   - Iproniazid and phenelzine are used as antidepressant.
   - Barbiturates, *viz.*, veronal, amytal, nembutal, luminal and seconal are hypnotic, *i.e.*, sleep producing agents.
   - Equanil is used in controlling depression and hypertension.

7. **Antimicrobial:** An antimicrobial tends to destroy or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal drugs) or other parasites (antiparasitic drugs), selectively. Antiseptics, disinfectants and antibiotics are antimicrobial drugs.
   - (*a*) **Antiseptics:** These are the chemical substances which prevent the growth of microorganisms or kill them but are not harmful to the living human tissues. Antiseptics are applied to wounds, cuts, ulcers and diseased skin surfaces. 0.2% solution of phenol, dettol (a mixture of chloroxylenol and terpineol), bithionol, tincture of iodine (2–3% solution of iodine in alcohol–water), hydrogen peroxide and boric acid solution are some of the common antiseptics.
   - (*b*) **Disinfectants:** These are the chemical substances which kill microorganisms or stop their growth but are harmful to living tissues. These are used to kill the microorganisms present in floors, drains, toilets, etc. 1% of phenol, chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and SO_2 in very low concentration act as disinfectants.
   - (*c*) **Antibiotics:** These are the chemical substances produced wholly or partly by chemical synthesis, which in low concentrations inhibit the growth or destroy microorganisms by intervening in their metabolic processes. Antibiotics are of two types:
     - (*i*) Bactericidal antibiotics, which have cidal (killing) effect on microbes. *e.g.*, Penicillin, aminoglycosides, ofloxacin, etc.
     - (*ii*) Bacteriostatic antibiotics, which have static (inhibitory) effect on microbes. *e.g.*, erythromycin, tetracycline, chloramphenicol, etc.

   Spectrum: The full range of microorganism attacked by an antibiotic is called its spectrum. Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are called **broad spectrum antibiotics**. Those effective mainly against Gram-positive or Gram-negative bacteria are **narrow spectrum antibiotics**. Ampicillin, tetracycline, amoxycillin, chloramphenicol and ofloxacin are broad spectrum antibiotics. Penicillin G is a narrow spectrum antibiotic.
8. **Antifertility Drugs:** These are the chemical substances which are used to prevent unwanted pregnancies in women. For example, norethindrone, ethynylestradiol (novestrol) and mifepristone.
9. **Artificial Sweetening Agents:** These are the chemical compounds which are non-nutritive in nature and are used as substitutes for sugar in foods and beverages especially soft drinks. Some common artificial sweeteners are
   - **Saccharin (Ortho-sulphobenzimide):** It is useful as a sugar substitute for diabetic persons and those who need to control their calorie intake.
   - **Aspartame:** It is methyl ester of dipeptide formed from aspartic acid and phenylalanine. Aspartame is used only in cold foods and soft drinks as it is unstable at cooking temperature.
   - **Alitame:** It is a high potency sweetener. The control of sweetness of food is difficult while using alitame.
   - **Sucralose:** It is trichloroderivative of sucrose. It is stable at cooking temperature.
10. **Food Preservatives:** These are the chemical substances which are added to the food materials to prevent their spoilage due to microbial growth. The most commonly used preservative include table salt, vegetable oil, sugar, potassium metabisulphite and sodium benzoate.
11. **Antioxidants in Food:** Antioxidants are important and necessary food additives that help in food preservation by retarding the action of oxygen on food. These are more reactive towards oxygen than the food material they are protecting. For example, butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA). BHA is added to butter to increase its shelf-life.
12. **Soaps:** Soaps are sodium or potassium salts of long chain fatty acids. Soaps containing sodium salts are formed by heating fat (*i.e.*, glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as **saponification**.



In this reaction, esters of fatty acids are hydrolysed and the soap is obtained in the colloidal form. It is precipitated from the solution by adding sodium chloride. The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation. Soap is a good cleansing agent and is biodegradable. Soaps have two disadvantages:

- Soaps cannot be used in hard water as calcium and magnesium ions present in hard water form insoluble calcium and magnesium soaps, respectively.

$$\underset{\substack{\text{Soluble sodium}\\ \text{stearate (Soap)}}}{2C_{17}H_{35}CO\overset{-}{O}\overset{+}{Na}} + CaCl_2 \longrightarrow 2NaCl + \underset{\substack{\text{Insoluble}\\ \text{calcium stearate}}}{(C_{17}H_{35}COO)_2Ca}$$

  The insoluble soaps separate as scum in the water and hence a part of soap is wasted. In fact, this scum creates hindrance to washing because the precipitates of these soaps adhere onto fibres of the cloth as gummy mass.

- Soap cannot be used in acidic solutions as acid present in the solution precipitate the insoluble free fatty acids which adhere onto the fabrics and thus decreases the ability of soaps to remove oil from fabrics.

13. **Synthetic Detergents:** These are the cleansing agents which have all properties of soaps, but actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water. Synthetic detergents are of three types, namely anionic, cationic and non-ionic.

    (*i*) **Anionic detergents:** These are so named because large part of their molecules are anions and it is the anionic part of the molecule which is involved in the cleansing action. These are sodium salt of sulphonated long chain alcohols or hydrocarbons. For example, sodium lauryl sulphate, sodium dodecylbenzene sulphonate, etc. Anionic detergents are used in household work and in toothpastes.

    (*ii*) **Cationic detergents:** These are so called because large part of their molecules are cations and it is the cationic part of the molecule which is involved in the cleansing action. Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cetyltrimethyl ammonium bromide is a cationic detergent and used in hair conditioners. Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use.

    (*iii*) **Non-ionic detergents:** Non-ionic detergents do not contain any ion. These are esters of high molecular mass alcohols. One such detergent is formed when stearic acid reacts with polyethyleneglycol. Liquid dishwashing detergents are non-ionic type.

- The problem in the use of detergents is that if their hydrocarbon chain is highly branched then bacteria cannot degrade them easily. Slow degradation of detergents leads to their accumulation and this causes water pollution. Unbranched chain can be biodegraded more easily and hence pollution is prevented.

NCERT Textbook Questions

NCERT Intext Questions

Q. 1. Sleeping pills are recommended by doctors to the patients suffering from sleeplessness but it is not advisable to take its doses without consultation with the doctor. Why?

Ans. Most of the drugs taken in doses higher than recommended may cause harmful effects and act as poison. Therefore, a doctor should always be consulted before taking the medicine.

Q. 2. With reference to which classification has the statement, ‘ranitidine is an antacid’ been given?

Ans. This statement refers to the classification of drugs according to pharmacological effect because any drug which will be used to counteract the effect of excess acid in the stomach will be called an antacid.

Q. 3 Why do we require artificial sweetening agents?

Ans. (*i*) To control intake of calories.

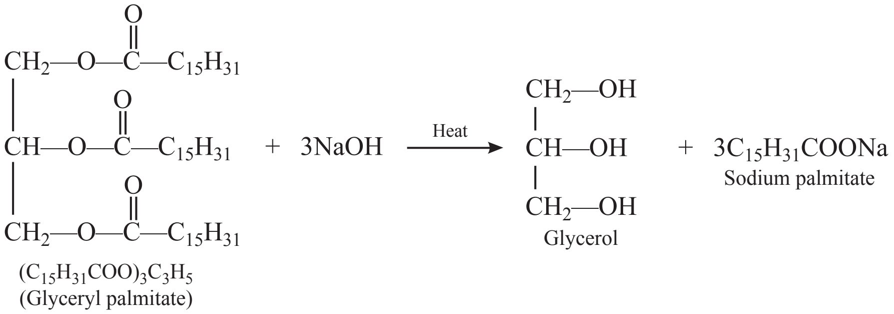
(*ii*) As a substitute of sugar for diabetics.

Q. 4. Write the chemical equation for preparing sodium soap from glyceryl oleate and glyceryl palmitate. Structural formulae of these compounds are given below:

(*i*) $(C_{15}H_{31}COO)_3C_3H_5$ —Glyceryl palmitate

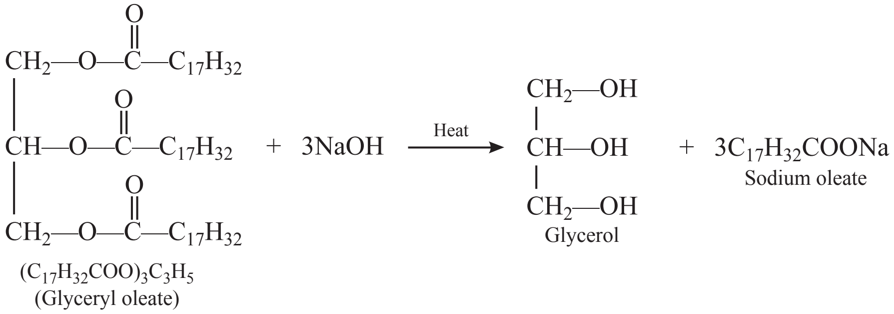
(*ii*) $(C_{17}H_{32}COO)_3C_3H_5$ —Glyceryl oleate

Ans. (*i*)



$$(C_{15}H_{31}COO)_3C_3H_5 + 3NaOH \xrightarrow{Heat} C_3H_5(OH)_3 + 3C_{15}H_{31}COONa$$

(*ii*)

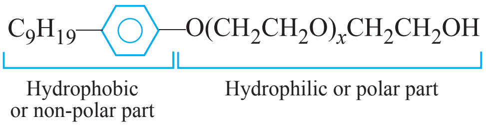


$$(C_{17}H_{32}COO)_3C_3H_5 + 3NaOH \xrightarrow{Heat} C_3H_5(OH)_3 + 3C_{17}H_{32}COONa$$

Q. 5. Following type of non-ionic detergents are present in liquid detergents, emulsifying agents and wetting agents. Label the hydrophilic and hydrophobic parts in the molecule. Identify the functional group(s) present in the molecule. **[*HOTS*]**

(x = 5 to 10)

Ans.



Functional groups present in the molecule are:

(*i*) ether (*ii*) alcohol.

NCERT Textbook Exercises

Q. 1. Why do we need to classify drugs in different ways?

Ans. Various methods of classification of drugs and the usefulness of such classification are as follows:

- Classification on the basis of pharmacological effect is useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem.
- Classification on the basis of drug action on a particular biochemical process is useful for choosing the correct lead compound for designing the synthesis of a desired drug.
- Classification on the basis of molecular targets is useful for medicinal chemists so that they can design a drug which is most effective for a particular receptor site.
- Classification on the basis of chemical structure helps us to design the synthesis of a number of structurally similar compounds having different substituents and then choosing the drug having the least toxicity.

Q. 2. Explain the term, target molecules or drug targets as used in medicinal chemistry.

Ans. Drugs interact with macromolecules such as proteins, carbohydrates, lipids and nucleic acids. Hence, these are called **drug targets**. These drug targets perform various functions in the body. For example, Proteins perform several roles in the body. Proteins which act as biological catalysts are called enzymes, those which are crucial in communication system are called receptors. Carrier proteins carry polar molecules across the cell membrane. Nucleic acids have coded genetic information in the cell, and carbohydrates and lipids form the structural part of cell membranes.

Q. 3. Name the macromolecules which are chosen as drug targets.

[CBSE Delhi 2014; CBSE Sample Paper 2016]

Ans. Macromolecules such as nucleic acids, proteins, carbohydrates and lipids are called drug targets.

Q. 4. Why should not medicines be taken without consulting the doctors?

Ans. Side effects are caused when a drug binds to more than one receptor site. So, a doctor must be consulted to choose the right drug which has the maximum affinity for a particular receptor site to have the desired effect. The dose of the drug is also crucial because some drugs like opiates in higher doses act as poisons and may cause death.

Q. 5. Define the term chemotherapy.

Ans. The branch of chemistry which deals with the treatment of diseases using chemicals is called chemotherapy.

Q. 6. Which forces are involved in holding the drugs to the active site of enzymes?

Ans. Ionic bonding, hydrogen bonding, dipole–dipole interactions or van der Waals interactions.

Q. 7. While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other?

Ans. Drugs designed to cure some ailment in one organ in the body do not affect the other because they work on different receptors. For example, secretion of histamine causes allergy. Also, it causes acidity due to release of hydrochloric acid in the stomach. As antiallergic and antacid drugs work on different receptors so, antihistamines remove allergy while antacids remove acidity.

Q. 8. Low level of noradrenaline is the cause of depression. What type of drugs are needed to cure this problem? Name two drugs.

Ans. In event of low level of neurotransmitter, noradrenaline, antidepressant drugs are required. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. If the enzyme is inhibited, noradrenaline is slowly metabolised and thus activates its receptor for longer periods of time thereby reducing depression. Two important drugs are iproniazid and phenelzine.

Q. 9. What is meant by the term 'broad spectrum antibiotics'? Explain. *[CBSE (F) 2009]*

Ans. Broad spectrum antibiotics are effective against several different types of harmful bacteria. Examples are tetracycline, ofloxacin, chloramphenicol, etc. Chloramphenicol can be used in case of typhoid, acute fever, dysentry, urinary infections, meningitis and pneumonia.

Q. 10. How do antiseptics differ from disinfectants? Give one example of each. *[CBSE Delhi 2009; (AI) 2012]*

Ans. Differences between antiseptics and disinfectants:

Antiseptics

- Antiseptics are chemical substances which prevent the growth of microorganisms and may even kill them but are not harmful to living tissues.
- Antiseptics are generally applied to living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
- Dettol, furacine, soframicine are antiseptics.

Disinfectants

- Disinfectants are chemical substances which kill microorganisms or stop their growth but are harmful to human tissues.
- Disinfectants are applied to inanimate objects such as floor, drainage system, instrument, etc.

Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and SO_2 in very low concentration are disinfectants.

Q. 11. Why are cimetidine and ranitidine better antacids than sodium hydrogen carbonate or magnesium or aluminium hydroxide? *[HOTS]*

Ans. $NaHCO_3$ or $Mg(OH)_2$ or $Al(OH)_3$, if taken in excess, makes the stomach alkaline and thus triggers the release of even more HCl which may cause ulcers in the stomach. On the other hand, cimetidine and ranitidine prevent the interaction of histamine with the receptor cells in the stomach wall and thus release lesser amount of HCl, hence are better antacids.

Q. 12. Name a substance which can be used as an antiseptic as well as disinfectant.
[CBSE Delhi 2008, CBSE Sample Paper 2016; CBSE 2020 (56/5/1)]

Ans. 0.2% solution of phenol acts as an antiseptic while 1% of the solution acts as a disinfectant.

Q. 13. What are the main constituents of dettol?

Ans. Chloroxylenol and α-terpineol in a suitable solvent.

Q. 14. What is tincture of iodine? What is its use?

Ans. A 2-3 per cent solution of iodine in alcohol-water mixture is known as tincture of iodine. It is used as an antiseptic.

Q. 15. What are food preservatives?

Ans. Chemical substances which are used to protect food against bacteria, yeasts and moulds are called preservatives. For example, sodium metabisulphite, sodium benzoate, etc.

Q. 16. Why is use of aspartame limited to cold foods and drinks? *[CBSE (F) 2012, 2014]*

Ans. Use of aspartame is limited to cold foods because it is unstable at cooking temperature.

Q. 17. What are artificial sweetening agents? Give two examples.

Ans. Artificial sweeteners are chemical substances which are sweet in taste but do not add any calories to our body. For example, saccharin, aspartame, sucralose, etc.

Q. 18. Name the sweetening agent used in the preparation of sweets for a diabetic patient.
[CBSE Delhi 2014]

Ans. Saccharin.

Q. 19. What problem arises in using alitame as artificial sweetener?

Ans. Alitame is a high potency artificial sweetener. Therefore, the control of sweetness of food is difficult while using it.

Q. 20. How are synthetic detergents better than soaps?

Ans. Detergents can be used both in soft and hard water as they produce foam even in hard water. The reason being that sulphonic acids and their calcium and magnesium salts are soluble in hard water but the fatty acids and their calcium and magnesium salts are insoluble.

Q. 21. Explain the following terms with suitable examples:
- **(*i*) Cationic detergents**
- **(*ii*) Anionic detergents**
- **(*iii*) Non-ionic detergents**

Ans. Refer to Basic Concepts Point 13.

Q. 22. What are biodegradable and non-biodegradable detergents? Give one example of each.
[CBSE (F) 2012]

Ans. Detergents having straight hydrocarbon chains are easily degraded by microorganisms and hence are called biodegradable detergents, whereas detergents containing branched hydrocarbon chains are not easily degraded by the microorganisms and hence are called non-biodegradable detergents. As a result, non-biodegradable detergents accumulate in rivers and waterways thereby causing severe water pollution.

Examples of biodegradable detergents are: sodium lauryl sulphate, sodium 4-(1-dodecyl) benzenesulphonate and sodium 4-(2-dodecyl) benzenesulphonate. An example of non-biodegradable detergent is sodium 4-(1, 3, 5, 7-tetramethyloctyl) benzenesulphonate.

Q. 23. Why do soaps not work in hard water?

Ans. Hard water contains calcium and magnesium salts. In hard water, soap gets precipitated as calcium and magnesium soap which being insoluble stick to the clothes as gummy mass. Therefore soaps do not work in hard water.

Q. 24. Can you use soaps and synthetic detergents to check the hardness of water?

Ans. Hard water contains calcium and magnesium ions. Soaps get precipitated as insoluble calcium and magnesium soaps in hard water but detergents do not. Synthetic detergents produce foam both in soft and hard water. Thus, soaps but not synthetic detergents can be used to check the hardness of water.

Q. 25. Explain the cleansing action of soaps. *[CBSE (AI) 2012]*

Ans. The cleansing action of soap is due to the fact that soap molecules, such as sodium stearate form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the oil droplet like the bristles (Fig. 16.7). Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

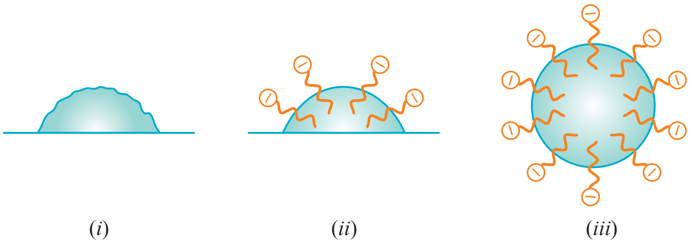


Fig. 16.7 (i) Oil or grease on cloth (ii) Stearate ions arranging around the oil droplet and (iii) Oil droplet surrounded by stearate ions (micelle formed).

Q. 26. If water contains dissolved calcium hydrogen carbonate, out of soaps and synthetic detergents, which one will you use for cleaning clothes?

Ans. Calcium bicarbonate makes water hard. Therefore, soap cannot be used as it gets precipitated in hard water. In contrast, a synthetic detergent does not precipitate in hard water because its calcium salt is also soluble in water. Hence, synthetic detergents can be used for cleaning clothes in hard water.

Q. 27. Label the hydrophilic and hydrophobic parts in the following compounds:

(*i*) $CH_3(CH_2)_{10}CH_2OS\overset{-}{O}_3\overset{+}{Na}$

(*ii*) $CH_3(CH_2)_{15}—\overset{+}{N}(CH_3)_3Br^-$

(*iii*) $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$

Ans. (*i*) $\underset{\text{Hydrophobic part}}{CH_3(CH_2)_{10}CH_2} — \underset{\text{Hydrophilic part}}{OS\overset{-}{O}_3\overset{+}{Na}}$

(*ii*) $\underset{\text{Hydrophobic part}}{CH_3(CH_2)_{15}} — \underset{\text{Hydrophilic part}}{\overset{+}{N}(CH_3)_3\,Br^-}$

(*iii*) $\underset{\text{Hydrophobic part}}{CH_3(CH_2)_{16}} — \underbrace{COO(CH_2CH_2O)_nCH_2CH_2OH}_{\text{Hydrophilic part}}$

Multiple Choice Questions [1 mark]

Choose and write the correct option(s) in the following questions.

1. **The most useful classification of drugs for medicinal chemists is ____________.** *[NCERT Exemplar]*
(*a*) on the basis of chemical structure.
(*b*) on the basis of drug action.
(*c*) on the basis of molecular targets.
(*d*) on the basis of pharmacological effect.

2. **Which of the following is not a target molecule for drug function in body?** *[NCERT Exemplar]*
(*a*) Carbohydrates
(*b*) Lipids
(*c*) Vitamins
(*d*) Proteins

3. **Which of the following statements is not true about enzyme inhibitors?** *[NCERT Exemplar]*
(*a*) Inhibit the catalytic activity of the enzyme.
(*b*) Prevent the binding of substrate.
(*c*) Generally a strong covalent bond is formed between an inhibitor and an enzyme.
(*d*) Inhibitors can be competitive or non-competitive.

4. Which of the following statements are incorrect about receptor proteins? *[NCERT Exemplar]*

(*a*) Majority of receptor proteins are embedded in the cell membranes.

(*b*) The active site of receptor proteins opens on the inside region of the cell.

(*c*) Chemical messengers are received at the binding sites of receptor proteins.

(*d*) Shape of receptor doesn't change during attachment of messenger.

5. Drugs which are useful when blocking of message is required are known as

(*a*) antagonists (*b*) agonists (*c*) antacids (*d*) antihistamines

6. Which of the following statements is correct about narcotic analgesics?

(*a*) They prevent platelet coagulation. (*b*) They prevent fever.

(*c*) They relieve pain and produce sleep. (*d*) They prevent heartattack.

7. The compound that causes general antidepressant action on the central nervous system belongs to the class of ______________ . *[NCERT Exemplar]*

(*a*) analgesics (*b*) tranquilizers (*c*) narcotic analgesics (*d*) antihistamines

8. Which of the following statements is correct? *[NCERT Exemplar]*

(*a*) Some tranquilisers function by inhibiting the enzymes which catalyse the degradation of noradrenaline.

(*b*) Tranquilisers are narcotic drugs.

(*c*) Tranquilisers are chemical compounds that do not affect the message transfer from nerve to receptor.

(*d*) Tranquilisers are chemical compounds that can relieve pain and fever.

9. Which statement about aspirin is not true? *[NCERT Exemplar]*

(*a*) Aspirin belongs to narcotic analgesics. (*b*) It is effective in relieving pain.

(*c*) It has antiblood clotting action. (*d*) It is a neurologically active drug.

10. Salvarsan is arsenic containing drug which was first used for the treatment of __________ *[NCERT Exemplar]*

(*a*) syphilis (*b*) typhoid (*c*) meningitis (*d*) dysentry

11. Which among of the following is not an antibiotic?

(*a*) Penicillin (*b*) Oxytocin (*c*) Tetracycline (*d*) Erythromycin

12. A narrow spectrum antibiotic is active against ______________ . *[NCERT Exemplar]*

(*a*) gram positive or gram negative bacteria. (*b*) gram negative bacteria only.

(*c*) single organism or one disease. (*d*) both gram positive and gram negative bacteria.

13. Compound which is added to soap to impart antiseptic properties is ______________ . *[NCERT Exemplar]*

(*a*) sodium laurylsulphate (*b*) sodium dodecylbenzenesulphonate

(*c*) rosin (*d*) bithional

14. Which of the following types of soap contain a gum called rosin?

(*a*) Toilet soaps (*b*) Medicated soaps (*c*) Transparent soaps (*d*) Shaving soaps

15. Which of the following statements is not correct? *[NCERT Exemplar]*

(*a*) Some antiseptics can be added to soaps.

(*b*) Dilute solutions of some disinfectants can be used as antiseptic.

(*c*) Disinfectants are antimicrobial drugs.

(*d*) Antiseptic medicines can be ingested.

16. Which is the correct statement about birth control pills? *[NCERT Exemplar]*

(*a*) Contain estrogen only.

(*b*) Contain progesterone only.

(*c*) Contain a mixture of estrogen and progesterone derivatives.

(*d*) Progesterone enhances ovulation.

17. Which of the following is used as a "morning after pill"?

(*a*) Norethindrone (*b*) Bithional

(*c*) Mifepristone (*d*) Ethynylestradiol

18. Which of the following will not enhance nutritional value of food?

(*a*) Minerals (*b*) Artificial sweeteners (*c*) Vitamins (*d*) Amino acids

19. Alitame is more stable than aspartame still it is not widely used because

(*a*) it is unstable at cooking temperature
(*b*) it is a high potency sweetener
(*c*) it excretes from the body in urine as such
(*d*) all of these

20. Which of the following are not used as food preservatives? [*NCERT Exemplar*]

(*a*) Table salt
(*b*) Sodium hydrogencarbonate
(*c*) Cane sugar
(*d*) Benzoic acid

21. Which of the following enhances leathering property of soap? [*NCERT Exemplar*]

(*a*) Sodium carbonate
(*b*) Sodium rosinate
(*c*) Sodium stearate
(*d*) Trisodium phosphate

22. Glycerol is added to soap. It functions _______________ . [*NCERT Exemplar*]

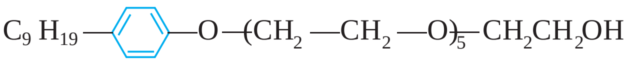
(*a*) as a filler
(*b*) to increase leathering
(*c*) to prevent rapid drying
(*d*) to make soap granules.

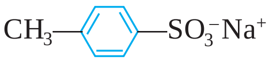
23. Polyethyleneglycols are used in the preparation of which type of detergents? [*NCERT Exemplar*]

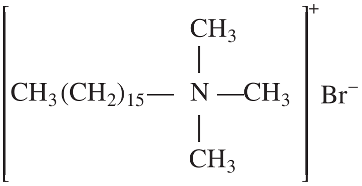
(*a*) Cationic detergents
(*b*) Anionic detergents
(*c*) Non-ionic detergents
(*d*) Soaps

24. Which of the following is an example of liquid dishwashing detergent? [*NCERT Exemplar*]

(*a*) $CH_3(CH_2)_{10}—CH_2OSO_3^-Na^+$

(*b*) 

(*c*) 

(*d*) 

$$\left[CH_3(CH_2)_{15}—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}—CH_3\right]^+ Br^-$$

Answers

1. (*c*)	**2.** (*c*)	**3.** (*c*)	**4.** (*b, d*)	**5.** (*a*)	**6.** (*c*)	**7.** (*b*)	**8.** (*a*)	**9.** (*a*)	**10.** (*a*)
11. (*b*)	**12.** (*a*)	**13.** (*d*)	**14.** (*d*)	**15.** (*d*)	**16.** (*c*)	**17.** (*c*)	**18.** (*b*)	**19.** (*b*)	**20.** (*b*)
21. (*b*)	**22.** (*c*)	**23.** (*c*)	**24.** (*b*)						

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(b) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(c) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(d) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. Assertion (*A*) : Enzymes have active sites that hold substrate molecule for a chemical reaction.
Reason (*R*) : Drugs compete with natural substrate by attaching covalently to the active site, of enzyme.

2. **Assertion (*A*) :** Competitive inhibitors compete with natural substrate for their attachment on the active sites of enzymes.
Reason (*R*) : In competitive inhibition, inhibitor binds to the allosteric site of the enzyme.

3. **Assertion (*A*) :** Non-competitive inhibitor inhibits the catalyic activity of enzyme by binding with its active site.
Reason (*R*) : Non-competitive inhibitor changes the shape of the active site in such a way that substrate can't recognise it.

4. **Assertion (*A*) :** Receptors are crucial to body's communication process.
Reason (*R*) : Receptors are proteins.

5. **Assertion (*A*) :** Chemical messenger gives message to the cell without entering the cell.
Reason (*R*) : Chemical messenger is received at the binding site of receptor proteins.

6. **Assertion (*A*) :** Chemical messengers are chemicals that enable communication of message between two neurons or between neurons and muscles.
Reason (*R*) : Chemicals enter the cell through receptor.

7. **Assertion (*A*) :** Metal hydroxides are better antacids than metal hydrogencarbonates.
Reason (*R*) : Metal hydroxides being insoluble do not increase the pH of the stomach above neutrality.

8. **Assertion (*A*) :** Terfenadine, an antihistamine does not affect the secretion of acid in stomach.
Reason (*R*) : Antiallergic and antacid drugs work on different receptors.

9. **Assertion (*A*) :** Sulpha drug contain sulphonamide group.
Reason (*R*) : Salvarsan is a sulpha drug.

10. **Assertion (*A*) :** Penicillin (G) is an antibiotic.
Reason (*R*) : Penicillin (G) is effective against gram positive as well as gram negative bacteria.

11. **Assertion (*A*) :** Sodium chloride is added to precipitate soap after saponification.
Reason (*R*) : Hydrolysis of esters of long chain fatty acids by alkali produces soaps in colloidal form.

12. **Assertion (*A*) :** Transparent soaps are made by dissolving soaps in ethanol.
Reason (*R*) : Ethanol makes things invisible.

Answers

1. (*c*) **2.** (*c*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*c*) **7.** (*a*) **8.** (*a*) **9.** (*c*) **10.** (*c*)
11. (*a*) **12.** (*c*)

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

An antimicrobial tends to destroy or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal drugs) or other parasites (antiparasitic drugs), selectively. Antiseptics, disinfectants and antibiotics are antimicrobial drugs. Antiseptics and disinfectants are the chemicals which either kill or prevent the growth of microorganisms. Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. Examples are furacine, soframycin, etc. These are not ingested like antibiotics. Bithionol (the compound is also called bithional) is added to soaps to impart antiseptic properties. Iodine is a powerful antiseptic. It is applied on to wounds. Iodoform is also used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes. Disinfectants are applied to inanimate objects such as floors, drainage system, instruments, etc. some substances can act as an antiseptic as well as disinfectant by varying the concentration. Antibiotics are the chemical substances produced wholly or partly by chemical synthesis, which in low concentrations inhibit the growth or destroy microorganisms by intervening in their metabolic process.

1. Give an example of a substance that can act as a disinfectant as well as antiseptic depending upon its concentration. (Specify concentration)

Ans. The 0.2% solution of phenol acts as an antiseptic whereas the 1% solution of phenol acts as disinfectant.

2. Name the chemicals responsible for the antiseptic properties of dettol.

Ans. Chloroxylenol and terpineol

3. What is meant by 'narrow spectrum antibiotics'?

Ans. Antibiotics which are mainly effective against Gram-positive or Gram-negative bacteria are known as narrow spectrum antibiotics, *e.g.*, penicillin G.

4. Give the name of one broad spectrum antibiotic.

Ans. Tetracycline

5. Which one of the following drugs is an antibiotic:

Morphine, Equanil, Chloramphenicol, Aspirin [*CBSE (F) 2014*]

Ans. Chloramphenicol

PASSAGE–2

Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap. These can be used both in soft and hard water as they give foam even in hard water. Some of the detergents give foam even in ice cold water. Synthetic detergents are mainly classified into three categories: 1. Anionic detergents, 2. Cationic detergents and 3. Non-ionic detergents. Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. Alkyl hydrogen sulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralized with alkali to form anionic detergents. Similarly, alkyl benzene sulphonates are obtained by neutralizing alkyl benzene sulphonic acids with alkali. Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. Cationic part possess a long hydrocarbon chain and a positive charge on nitrogen atom. Hence, these are called cationic detergents. Non-ionic detergents do not contain any ions in their constitution.

1. Give an example of an alkylbenzenesulphonate detergent.

Ans. Sodium 4-(2-dodecyl) benzenesulphonate

2. What is the chemical composition of cationic detergents?

Ans. Mostly acetates or chlorides of quaternary amines.

3. The cleansing action of synthetic detergents is not affected by hard water. Mention the reason for the same.

Ans. The anions of synthetic detergents do not precipitate in the presence of Ca^{2+} and Mg^{2+} ions.

4. Why are detergents preferred over soaps?

Ans. Unlike soaps, detergents can be used even in hard water because like sodium salts, calcium and magnesium salts of sulphonic acids are soluble in water.

5. Give one example of non-biodegradable detergents.

Ans. An example of non-biodegradable detergent is sodium 4-(1, 3, 5, 7-tetramethyloctyl) benezenesulphonate.

Very Short Answer Questions [1 mark]

Q. 1. Which site of an enzyme is called allosteric site? [*NCERT Exemplar*]

Ans. Sites different from active site of enzyme where a molecule can bind and affect the active site is called allosteric site. Some drugs may also bind at this site.

Q. 2. Where are receptors located? [*NCERT Exemplar*]

Ans. Receptors are embedded in cell membrane.

Q. 3. Name two types of chemical messengers.

Ans. Neurotransmitters and hormones.

Q. 4. What is the nature of an antacid?

Ans. Substances which reduce the release of excess HCl by preventing the interaction of histamine with the receptors present in the stomach wall are called antacids. The most commonly used antacids are cimetidine and ranitidine.

Q. 5. Name an antacid which prevents the formation of acid in the stomach.

Ans. Cimetidine or ranitidine.

Q. 6. What is the harmful effect of hyperacidity? [*NCERT Exemplar*]

Ans. It can cause ulcer in stomach.

Q. 7. Between sodium hydrogencarbonate and magnesium hydroxide which is a better antacid and why? [*NCERT Exemplar*] [*HOTS*]

Ans. Magnesium hydroxide is a better antacid because being insoluble it does not allow the pH to increase above neutral. Hydrogencarbonate being soluble, its excess can make the stomach alkaline and trigger the production of even more acid.

Q. 8. Define antihistamines with an example. [*CBSE (F) 2014*]

Ans. The drugs which interfere with the natural action of histamine by competing with histamine for binding of receptor where histamine exerts its effect are called antihistamine *e.g.*, brompheniramine, terfenadine, cetirizine etc.

Q. 9. How do the drugs like brompheniramine and terfenadine (seldane) act as antihistamines? [*HOTS*]

Ans. They interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

Q. 10. Aspirin is pain relieving antipyretic drug but can be used to prevent heart attack. Explain. [*NCERT Exemplar*] [*HOTS*]

Ans. Aspirin prevents platelet coagulation and thus has antiblood clotting action. Therefore, it can prevent blood clotting in heart.

Q. 11. Name two narcotics which are used as analgesics.

Ans. Morphine and codeine are used as analgesics.

Q. 12. Mention the pharmacological effect of most sulphonamides.

Ans. Sulphonamides are antibacterial.

Q. 13. Name an artificial sweetener which is derivative of sucrose. [*NCERT Exemplar*]

Ans. Sucralose.

Q. 14. What is aspartame and what is its use?

Ans. It is the methyl ester of the dipeptide derived from phenylalanine and aspartic acid. It is used as an artificial sweetener.

Q. 15. Name two α-amino acids which form a dipeptide which is 100 times more sweet than cane sugar. [*NCERT Exemplar*]

Ans. Aspartic acid and phenylalanine.

Q. 16. How are transparent soaps manufactured? [*NCERT Exemplar*]

Ans. Dissolving soap in ethanol followed by evaporating the excess solvent.

Q. 17. Why is glycerol added to shaving soaps?

Ans. Glycerol is added to shaving soaps to prevent rapid drying.

Short Answer Questions–I [2 marks]

Q. 1. Which site of an enzyme is called allosteric site? Explain its role in enzyme inhibition.

Ans. Site different from active site of an enzyme where a drug molecule can bind is called allosteric site. Binding of drug at the allosteric site changes the shape of the active site in such a way that natural substrate cannot recognise it. Because of this, the chemical change is inhibited.

Q. 2. What is the scientific explanation for the feeling of depression? [*NCERT Exemplar*]

Ans. A person suffers from depression when he has low levels of noradrenaline. Noradrenaline is a neurotransmitter that plays a role in mood changes. Low levels of noradrenaline lower the signal sending activity and make the person suffer from depression.

Q. 3. Give one important use each of the following in Pharmacy.

(*i*) Equanil **(*ii*) Morphine.**

Ans. (*i*) Equanil is a tranquilizer. It is used for removing depression and hypertension.

(*ii*) Morphine is an alkaloid. It is used as an analgesic.

Q. 4. List two major classes of antibiotics with examples of each class.

Ans. Two major classes of antibiotics are: Bactericidal and Bacteriostatic. Examples are:

(*i*) Bactericidal	**(*ii*) Bacteriostatic**
(*a*) Penicillin	(*a*) Erythromycin
(*b*) Aminoglycosides	(*b*) Tetracycline
(*c*) Ofloxacin	(*c*) Chloramphenicol

The full range of microorganisms attacked by an antibiotic is called its spectrum. Based on spectrum, antibiotics can be divided in two classes: (*a*) Broad spectrum antibiotics *e.g.*, chloramphenicol (*b*) Narrow spectrum antibiotics *e.g.*, penicillin G.

Q. 5. Answer the following questions:

(*i*) How do tranquilizers and analgesics work?

(*ii*) How does the branching of hydrocarbon chain of synthetic detergents affect their biodegradability? **[*NCERT Exemplar*]**

Ans. (*i*) Tranquilizers and analgesics work by altering the message transfer mechanism from nerve to receptor.

(*ii*) Less branching leads to easy biodegradability.

Short Answer Questions–II [3 marks]

Q. 1. (*i*) Which one of the following is a disinfectant?

0.2% solution of phenol or 1% solution of phenol

(*ii*) What is the difference between agonists and antagonists?

(*iii*) Write one example each of

(*a*) Artificial sweetener **(*b*) Antacids** **[*CBSE 2019 (56/3/2)*]**

Ans. (*i*) 1% solution of phenol.

(*ii*) Agonists are the drugs that mimic the natural messenger by switching on the receptor whereas antagonists are the drugs which bind to the receptor site and inhibit its natural function.

(*iii*) (*a*) Saccharin, sucralose, etc.

(*b*) Sodium hydrogen carbonate, a mixture of aluminium and magnesium hydroxide, ranitidine.

Q. 2. What are the following substances? Give one example of each one of them:

(*i*) Tranquilizers **(*ii*) Food preservatives**

(*iii*) Synthetic detergents **[*CBSE Delhi 2012, 2020 (56/5/3)*]**

Ans. (*i*) Tranquilizers are a class of chemical compounds used for the treatment of stress, fatigue, and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being, *e.g.*, iproniazid, chlordiazepoxide, equanil, luminal, etc.

(*ii*) Food preservatives are the chemical substances which are added to food materials to prevent their spoilage due to microbial growth and to retain their nutritive value for long periods. Preservatives prevent the rancidity of food and inhibit growth or kill the microorganisms. The most common preservatives used are sugar, vegetable oil, sodium benzoate, salts of ascorbic acid and propanoic acid.

(*iii*) Synthetic detergents are cleansing agents, which have all the properties of soaps but actually do not contain any soap. These can be used in both soft water and hard water as they produce foam even in hard water. These are mainly classified into three categories:

- Anionic detergents, *e.g.*, sodium dodecylbenzene sulphonate
- Cationic detergents, *e.g.*, cetyltrimethyl ammonium bromide
- Non-ionic detergents, *e.g.*, polyethylene glycol stearate

Q. 3. Differentiate between the following:

(*i*) Antiseptics and Disinfectants

(*ii*) Antacids and Antihistamines

(*iii*) Soaps and Detergents *[CBSE 2019 (56/5/2), 2020 (56/5/1)]*

Ans. (*i*) Refer to NCERT Textbook Questions, Q. 10.

(*ii*) Antacids are chemical substances which neutralize stomach acidity while antihistamines are drugs which treat allergies.

(*iii*) Soaps do not work in hard water while detergents work in hard water.

Q. 4. Define the following terms with a suitable example of each:

(*i*) Antiseptics

(*ii*) Bactericidal antibiotics

(*iii*) Cationic detergents *[CBSE 2019 (56/3/2), 2020 (56/3/3), 2020 (56/5/3)]*

Ans. (*i*) Antiseptics are the chemical substances which prevent the growth of microorganisms or may even kill them but are not harmful to living human tissues, *e.g.*, dettol, soframycin, boric acid, hydrogen peroxide, etc.

(*ii*) Bactericidal antibiotics are those antibiotics which have cidal (killing) effect on microbes, *e.g.*, penicillin, ofloxacin, etc.

(*iii*) Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions *e.g.*, cetyltrimethyl ammonium bromide.

Q. 5. (*i*) Pick out the odd one from the following on the basis of their medicinal properties:

Equanil, Seconal, Bithional, Luminal

(*ii*) What type of detergents are used in dishwashing liquids?

(*iii*) Why is the use of aspartame limited to cold foods? *[CBSE 2019 (56/2/1)]*

Ans. (*i*) Bithional is an antiseptic while the remaining three are tranquilizers.

(*ii*) Non-ionic detergents.

(*iii*) The use of aspartame is limited to cold foods because it is unstable at cooking temperature.

Q. 6. (*i*) What are antidepressant drugs? Give an example.

(*ii*) Name the sweetening agent used in preparation of sweets for a diabetic patient.

(*iii*) Why are detergents non-biodegradable? *[CBSE 2019 (56/4/3)]*

Ans. (*i*) Antidepressant drugs are the tranquilizers which inhibit the enzymes that catalyse the degradation of noradrenaline, an important neurotransmitter, *e.g.*, iproniazid, phenelzine.

(*ii*) Saccharin.

(*iii*) If the hydrocarbon chain of detergent is highly branched then the side chain stop bacteria from attacking and breaking the chain. This makes it non-biodegradable.

Long Answer Question [5 marks]

Q. 1. (*i*) (*a*) Why is bithional added to soap? *[CBSE Paper 2018]*

(*b*) What is tincture of iodine? Write its one use.

(*c*) Among the following, which one acts as a food preservative?

Aspartame, Aspirin, Sodium Benzoate, Paracetamol

(*ii*) Give reasons for the following:

(*a*) Sulpha drugs work like antibiotics but they are not antibiotics.

(*b*) Soaps are biodegradable whereas detergents are non-biodegradable.

Ans. (*i*) (*a*) Bithional acts as an antiseptic agent and reduces the odour produced by bacterial decomposition of organic matter on the skin.

(*b*) Refer to NCERT Textbook Exercises, Q. 14.

(*c*) Sodium benzoate

(*ii*) (*a*) This is because sulpha drugs are purely synthetic while antibiotics may be either wholly or partially obtained from microorganisms.

(*b*) Soap molecules have straight hydrocarbon chains which are easily degraded by bacteria present in the sewage water. On the other hand, detergent molecules have branched hydrocarbon chains which are either not attacked or slowly attacked by bacteria present in sewage water.

Self-Assessment Test

Time allowed: 1 hour **Max. marks: 30**

Choose and write the correct answer for each of the following. **(3 × 1 = 3)**

1. Chloroquine is an effective drug for

(*a*) pain (*b*) fever

(*c*) malaria (*d*) pneumonia

2. Aspirin acts as

(*a*) analgesic (*b*) antipyretic

(*c*) antimalarial (*d*) both antipyretic and analgesic

3. The medicines which lowers the body temperature are known as

(*a*) analgesic (*b*) antipyretic

(*c*) antibiotic (*d*) pheromones

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. **(3 × 1 = 3)**

4. Assertion (*A*) : Receptor proteins show selectivity for one chemical messenger over the other.

Reason (*R*) : Chemical messenger binds to the receptor site and inhibits its natural function.

5. Assertion (*A*) : All chemicals added to food items are called food preservatives.

Reason (*R*) : All these chemicals increase the shelf life of stored food.

6. Assertion (*A*) : Preservative are added to food items.

Reason (*R*) : Preservatives inhibit the growth of microorganisms.

Answer the following questions:

7. What is an antipyretic. Give an example. **(1)**

8. What is the mode of action of antimicrobial drugs? **(1)**

9. Why are certain drugs called enzyme inhibitors? **(2)**

10. What are the functions performed by histamine in the body? **(2)**

11. What is the advantage of using antihistamines over antacids in the treatment of acidity? **(2)**

12. How do antidepressant drugs counteract feeling of depression? **(2)**

13. If soap has high alkali content it irritates skin. How can the amount of excess alkali be determined? What can be the source of excess alkali? **(2)**

14. Answer the following questions:

(*i*) Which class of drugs is used in sleeping pills?

(*ii*) What is the commonality between the antibiotic arsphenamine and azodye?

(*iii*) Pickles have a long shelf-life and do not get spoiled for months. Why? **(3)**

15. Answer the following questions:

(*i*) Name the antibiotic used specifically for treatment of typhoid fever.

(*ii*) What is the medicinal use of Narcotic drugs? **[*NCERT Exemplar*]**

(*iii*) Which category of the synthetic detergents is used in toothpaste? **(3)**

16. Explain the following terms giving one example of each type:

(*i*) Antiseptics

(*ii*) Antibiotics

(*iii*) Anionic detergents **[*CBSE 2019 (56/2/1)*] (3)**

17. Answer the following questions:

(*i*) Pick out the odd one from among the following on the basis of their medicinal properties mentioning the reason: Luminal, Seconal, Phenacetin, Equanil.

(*ii*) What are pathogens?

(*iii*) Name any two macromolecules chosen as drug targets. **(3)**

Answers

1. (*c*) **2.** (*d*) **3.** (*b*) **4.** (*c*) **5.** (*d*) **6.** (*a*)

Part-B

Competency-based Questions
[Case-based Questions from CBSE Question Bank]

Competency-based Questions

[Case-based Questions from CBSE Question Bank]

Case-based/Passage-based Questions

I. ***Read the given passage and answer the questions that follow.***

In spite of the predictions of stable noble gas compounds since at least 1902, unsuccessful attempts at their synthesis gave rise to the widely held opinion that noble gases are not only noble but also inert. It was not until 1962 that this dogma was shattered when Bartlett in Canada published the first stable noble gas compound $XePtF_6$. This discovery triggered a worldwide frenzy in this area, and within a short time span many new xenon, radon, and krypton compounds were prepared and characterized. The recent discoveries show the ability of xenon to act as a ligand. The discovery by Seppelt's group that more than one xenon atom can attach itself to a metal center which in the case of gold leads to surprisingly stable Au-Xe bonds. The bonding in $[AuXe_4]^{2+}$ involves 4 Xe ligands attached by relatively strong bonds to a single Au(II) center in a square planar arrangement with a Xe-Au bond length of about 274 pm. This discovery provides not only the first example of multiple xenon ligands but also represents the first strong metal-xenon bond.

(**Source:** *Christe, K.O. (2001). A renaissance in noble gas chemistry. Angewandte Chemie International Edition, 40(8), 1419-1421.*)

1. In the complex ion $[AuXe_4]^{2+}$, Xe acts as:

(*a*) central atom (*b*) ligand (*c*) chelating agent (*d*) electrophile

2. Hybridisation shown by Au in $[AuXe_4]^{2+}$ is:

(*a*) sp^3 (*b*) sp^3d (*c*) sp^3d^2 (*d*) sp^2

3. Compounds of noble gases except ___________ are known.

(*a*) Krypton (*b*) Radon (*c*) Helium (*d*) Xenon

4. Xe is a ___________ ligand.

(*a*) ambidentate (*b*) bidentate (*c*) unidentate (*d*) hexadentate

Answers

1. (*b*) **2.** (*b*) **3.** (*c*) **4.** (*c*)

II. ***Read the given passage and answer the questions that follow.***

Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapour pressure and the added solute particles affect the formation of pure solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapour pressure lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity.

(Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J. (2017). Freezing point depression of different Sucrose solutions and coconut water.)

1. When a non volatile solid is added to pure water it will:

(*a*) boil above 100°C and freeze above 0°C
(*b*) boil below 100°C and freeze above 0°C
(*c*) boil above 100°C and freeze below 0°C
(*d*) boil below 100°C and freeze below 0°C

2. Colligative properties are:

(*a*) dependent only on the concentration of the solute and independent of the solvent's and solute's identity.
(*b*) dependent only on the identity of the solute and the concentration of the solute and independent of the solvent's identity.
(*c*) dependent on the identity of the solvent and solute and thus on the concentration of the solute.
(*d*) dependent only on the identity of the solvent and the concentration of the solute and independent of the solute's identity.

3. Assume three samples of juices A, B and C have glucose as the only sugar present in them. The concentration of sample A, B and C are 0.1 M, 0.5 M and 0.2 M respectively. Freezing point will be highest for the fruit juice:

(*a*) A
(*b*) B
(*c*) C
(*d*) All have same freezing point

4. Identify which of the following is a colligative property:

(*a*) freezing point (*b*) boiling point (*c*) osmotic pressure (*d*) all of the above

Answers

1. (*c*) **2.** (*d*) **3.** (*a*) **4.** (*c*)

III. ***Read the given passage and answer the questions that follow.***

The rate of a reaction, which may also be called its velocity or speed, can be defined with relation to the concentration of any of the reacting substances, or to that of any product of the reaction. If the species chosen is a reactant which has a concentration c at time t the rate is $-dc/dt$, while the rate with reference to a product having a concentration x at time t is $-dx/dt$. Any concentration units may be used for expressing the rate; thus, if moles per liter are employed for concentration and seconds for the time, the units for the rate are moles litre^{-1} sec^{-1}. For gas reactions pressure units are sometimes used in place of concentrations, so that legitimate units for the rate would be (mm. Hg) sec^{-1} and atm. sec^{-1}. The order of a reaction concerns the dependence of the rate upon the concentrations of reacting substances; thus, if the rate is found experimentally to be proportional to the α^{th} power of the concentration of one of the reactants A, to the β^{th} power of the concentration of a second reactant B, and so forth, *via*.,

$$\text{rate} = kC_A^{\alpha}C_B^{\beta} \qquad ...(i)$$

the over-all order of the reaction is simply

$$n = \alpha + \beta + ... \qquad ...(ii)$$

Such a reaction is said to be of the α^{th} order with respect to the substance A, the β^{th} order with respect to B and so on ...

(Laidler, K. J., & Glasstone, S. (1948). Rate, order and molecularity in chemical kinetics. Journal of Chemical Education, 25(7), 383.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

1. Assertion : Rate of reaction is a measure of change in concentration of reactant with respect to time.
Reason : Rate of reaction is a measure of change in concentration of product with respect to time.

2. Assertion : For a reaction:

$$P + 2Q \longrightarrow \text{Products},$$

Rate = $k\,[P]^{1/2}[Q]^1$ so the order of reaction is 1.5.

Reason : Order of reaction is the sum of stoichiometric coefficients of the reactants.

3. Assertion : The unit of k is independent of order of reaction.

Reason : The unit of k is moles $L^{-1}\ s^{-1}$.

4. Assertion : Reactions can occur at different speeds.

Reason : Rate of reaction is also called speed of reaction.

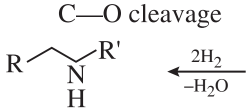
Answers

1. (*b*) **2.** (*c*) **3.** (*d*) **4.** (*b*)

IV. ***Read the given passage and answer the questions that follow.***

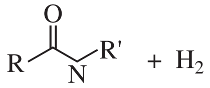
Reduction of carboxylic acids and their derivatives plays an important role in organic synthesis, in both laboratory and industrial processes. Traditionally, the reduction is performed using stochiometric amounts of hydride reagents, generating stochiometric amounts of waste. A much more attractive, atom-economical approach is a catalytic reaction using H_2; however, hydrogenation of carboxylic acid derivatives under mild conditions is a very challenging task, with amides presenting the highest challenge among all classes of carbonyl compounds. Very few examples of the important hydrogenation of amides to amines, in which the C—O bond is cleaved with the liberation of water (Scheme 1), were reported. C—O cleavage of amides can also be affected with silanes as reducing agents.

Scheme 1. General Scheme



We have now prepared the new, dearomatized, bipyridine-based pincer complex 3, catalyst 3 (Here referred as Cat. 3). Remarkably, it efficiently catalyzes the selective hydrogenation of amides to form amines and alcohols (eq 1). The reaction proceeds under mild pressure and neutral conditions, with no additives being required. Since the reaction proceeds well under anhydrous conditions, hydrolytic cleavage of the amide is not involved in this process.

Scheme 2.



(Balaraman, E., Gnanaprakasam, B., Shimon, L. J., & Milstein, D. (2010). Direct hydrogenation of amides to alcohols and amines under mild conditions. Journal of the American Chemical Society, 132(47), 16756-16758.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(*a*) ***Assertion and reason both are correct statements and reason is correct explanation for assertion.***

(*b*) ***Assertion and reason both are correct statements but reason is not correct explanation for assertion.***

(*c*) ***Assertion is correct statement but reason is wrong statement.***

(*d*) ***Assertion is wrong statement but reason is correct statement.***

1. Assertion : The use of catalyst 3 is an efficient method of preparation of primary amines.

Reason : Use of catalyst 3 is a step down reaction.

2. Assertion : Use of hydride catalyst or hydrogen brings about cleavage of C—O bond in amides.

Reason : Hydride catalyst or hydrogen cause to reduction of amides.

3. Assertion : N-methyl ethanamide on reaction with catalyst 3 will yield ethanol and methanamine.
Reason : Use of Catalyst 3 brings about cleavage of C—N bond of amides

4. Assertion : Aniline can be prepared from suitable amide using catalyst.
Reason : The use of catalyst 3 is limited to aliphatic amides only.

Answers

1. (*b*) **2.** (*b*) **3.** (*a*) **4.** (*c*)

V. ***Read the given passage and answer the questions that follow.***

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, nucleophilic reagent and solvent.

Influences of halogen: No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is, the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is $I^- < Br^- < Cl^- < F^-$ and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$. Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is $RI > RBr > RCl > RF$. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on S_N1 mechanism. If the leaving group is not easy to leave, the reaction is based on S_N2 mechanism.

Influences of solvent polarity: In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane in 25°C water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both S_N1 and S_N2 reactions, but with different results. Generally speaking, weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1 reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favourable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example, ethanol containing water).

(*Ding, Y. (2013). A Brief Discussion on Nucleophilic Substitution Reaction on Saturated Carbon Atom. In Applied Mechanics and Materials (Vol. 312, pp. 433-437). Trans Tech Publications Ltd.*)

1. S_N1 mechanism is favoured in which of the following solvents:
(*a*) benzene (*b*) carbon tetrachloride (*c*) acetic acid (*d*) carbon disulphide

2. Nucleophilic substitution will be fastest in case of:
(*a*) 1-Chloro-2,2-dimethyl propane (*b*) 1-Iodo-2,2-dimethyl propane
(*c*) 1-Bromo-2,2-dimethyl propane (*d*) 1-Fluoro-2,2-dimethyl propane

3. S_N1 reaction will be fastest in which of the following solvents?
(*a*) Acetone (dielectric constant 21) (*b*) Ethanol (dielectric constant 24)
(*c*) Methanol (dielectric constant 32) (*d*) Chloroform (dielectric constant 5)

4. Polar solvents make the reaction faster as they:
(*a*) destabilize transition state and decrease the activation energy
(*b*) destabilize transition state and increase the activation energy
(*c*) stabilize transition state and increase the activation energy
(*d*) stabilize transition state and decrease the activation energy

5. S_N1 **reaction will be fastest in case of:**

(*a*) 1-Chloro-2-methyl propane (*b*) 1-Iodo-2-methyl propane

(*c*) 1-Chlorobutane (*d*) 1-Iodobutane

Answers

1. (*c*) **2.** (*b*) **3.** (*c*) **4.** (*d*) **5.** (*b*)

VI. ***Read the given passage and answer the questions that follow.***

Within the 3*d* series, manganese exhibits oxidation states in aqueous solution from +2 to +7, ranging from Mn^{2+} (a*q*) to MnO_4^- (*aq*). Likewise, iron forms both Fe^{2+}(*aq*) and Fe^{3+}(*aq*) as well as the FeO_4^{2-} ion. Cr and Mn form oxyions CrO_4^{2-}, MnO_4^-, owing to their willingness to form multiple bonds. The pattern with the early transition metals—in the 3*d* series up to Mn, and for the 4*d*, 5*d* metals up to Ru and Os—is that the maximum oxidation state corresponds to the number of "outer shell" electrons. The highest oxidation states of the 3*d* metals may depend upon complex formation (*e.g.*, the stabilization of Co^{3+} by ammonia) or upon the pH (thus MnO_4^{2-}(*aq*) is prone to disproportionation in acidic solution). Within the 3*d* series, there is considerable variation in relative stability of oxidation states, sometimes on moving from one metal to a neighbour; thus, for iron, Fe^{3+} is more stable than Fe^{2+}, especially in alkaline conditions, while the reverse is true for cobalt. The ability of transition metals to exhibit a wide range of oxidation states is marked with metals such as vanadium, where the standard potentials can be rather small, making a switch between states relatively easy.

(Cotton, S. A. (2011). Lanthanides: Comparison to 3d metals.
Encyclopedia of inorganic and Bioinorganic Chemistry.)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(*a*) ***Assertion and reason both are correct statements and reason is correct explanation for assertion.***

(*b*) ***Assertion and reason both are correct statements but reason is not correct explanation for assertion.***

(*c*) ***Assertion is correct statement but reason is wrong statement.***

(*d*) ***Assertion is wrong statement but reason is correct statement.***

1. Assertion : Highest oxidation state is exhibited by transition metal lying in the middle of the series.

Reason : The highest oxidation state exhibited corresponds to number of $(n-1)d$ electrons.

2. Assertion : Fe^{3+} is more stable than Fe^{2+}.

Reason : Fe^{3+} has $3d^5$ configuration while Fe^{2+} has $3d^6$ configuration.

3. Assertion : Vanadium had the ability to exhibit a wide range of oxidation states.

Reason : The standard potentials vanadium are rather small, making a switch between oxidation states relatively easy.

4. Assertion : Transition metals like Fe, Cr and Mn form oxyions.

Reason : Oxygen is highly electronegative and has a tendency to form multiple bonds.

5. Assertion : The highest oxidation states of the 3*d* metals depends only on electronic configuration of the metal.

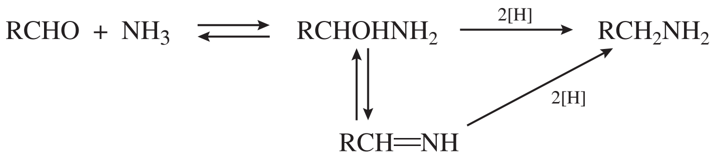
Reason : The number of electrons in the $(n-1)d$ and *ns* subshells determine the oxidation states exhibited by the metal.

Answers

1. (*c*) **2.** (*a*) **3.** (*a*) **4.** (*b*) **5.** (*d*)

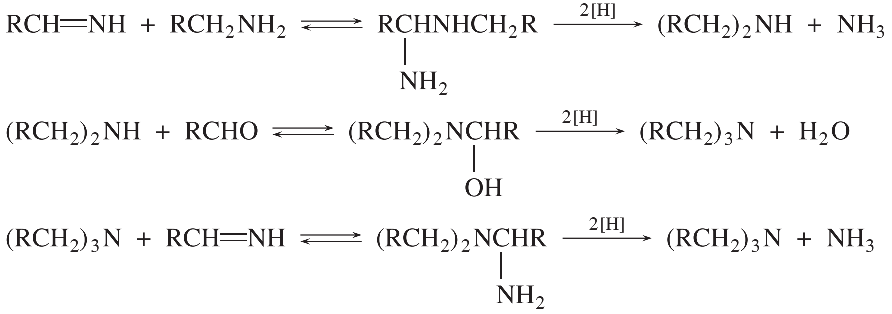
VII. ***Read the given passage and answer the questions that follow.***

Reductive alkylation is the term applied to the process of introducing alkyl groups into ammonia or a primary or secondary amine by means of an aldehyde or ketone in the presence of a reducing agent. The present discussion is limited to those reductive alkylations in which the reducing agent is hydrogen and a catalyst or "nascent" hydrogen, usually from a metal-acid combination; most of these reductive alkylations have been carried out with hydrogen and a catalyst. The principal variation excluded is that in which the reducing agent is formic acid or one of its derivatives; this modification is known as the Leuckart reaction. The process of reductive alkylation of ammonia consists in the addition of ammonia to a carbonyl compound and reduction of the addition compound or its dehydration product. The reaction usually is carried out in ethanol solution when the reduction is to be effected catalytically



$$\begin{tikzcd}
\mathrm{RCHO + NH_3} \arrow[r, shift left] & \mathrm{RCHOHNH_2} \arrow[l, shift left] \arrow[r, "{2[H]}"] \arrow[d, shift left] & \mathrm{RCH_2NH_2} \\
& \mathrm{RCH{=}NH} \arrow[u, shift left] \arrow[ur, "{2[H]}"'] &
\end{tikzcd}$$

Since the primary amine is formed in the presence of the aldehyde it may react in the same way as ammonia, yielding an addition compound, a Schiff's base ($RCH{=}NCH_2R$) and finally, a secondary amine. Similarly, the primary amine may react with the imine, forming an addition product which also is reduced to a secondary amine. Finally, the secondary amine may react with either the aldehyde or the imine to give products which are reduced to tertiary amines.



$$\mathrm{RCH{=}NH + RCH_2NH_2 \rightleftharpoons \underset{\displaystyle NH_2}{\underset{|}{RCHNHCH_2R}} \xrightarrow{2[H]} (RCH_2)_2NH + NH_3}$$

$$\mathrm{(RCH_2)_2NH + RCHO \rightleftharpoons \underset{\displaystyle OH}{\underset{|}{(RCH_2)_2NCHR}} \xrightarrow{2[H]} (RCH_2)_3N + H_2O}$$

$$\mathrm{(RCH_2)_3N + RCH{=}NH \rightleftharpoons \underset{\displaystyle NH_2}{\underset{|}{(RCH_2)_2NCHR}} \xrightarrow{2[H]} (RCH_2)_3N + NH_3}$$

Similar reactions may occur when the carbonyl compound employed is a ketone.

(**Source:** *Emerson, W. S. (2011). The Preparation of Amines by Reductive Alkylation. Organic Reactions, 174–255. doi:10.1002/0471264180.or004.03*)

1. Ethanal on reaction with ammonia forms an imine (X) which on reaction with nascent hydrogen gives (Y). Identify 'X' and 'Y'.

(*a*) X is $CH_3CH{=}NH$ and Y is CH_3NH_2
(*b*) X is $CH_3CHOHNH_2$ and Y is $CH_3CH_2NH_2$
(*c*) X is $CH_3CHOHNH_2$ and Y is CH_3NH_2
(*d*) X is $CH_3CH{=}NH$ and Y is $CH_3CH_2NH_2$

2. Acetaldehyde is reacted with ammonia followed by reduction in presence of hydrogen as a catalyst. The primary amine so formed further reacts with acetaldehyde. The Schiff's base formed during the reaction is:

(*a*) $CH_3CH{=}NHCH_3$
(*b*) $CH_3CH{=}NHCH_2CH_3$
(*c*) $CH_3{=}NHCH_2CH_3$
(*d*) $CH_3CH_2CH{=}NHCH_3$

3. The reaction of ammonia and its derivatives with aldehydes is called:

(*a*) Nucleophilic substitution reaction
(*b*) Electrophilic substitution reaction
(*c*) Nucleophilic addition reaction
(*d*) Electrophilic addition reaction

4. $(CH_3CH_2CH_2)_2NH + CH_3CH_2CHO \longrightarrow P \xrightarrow{[2H]} Q$
The compound Q is:

(*a*) $(CH_3CH_2CH_2)_3N$
(*b*) $(CH_3CH_2CH_2)_2N(CH_2CH_3)$
(*c*) $(CH_3CH_2)_3N$
(*d*) $(CH_3CH_2)_2NH$

5. Reductive alkylation of ammonia by means of an aldehyde in presence of hydrogen as reducing agents results in formation of:

(*a*) Primary amines
(*b*) Secondary amines
(*c*) Tertiary amines
(*d*) Mixture of all three amines

Answers

1. (*d*) **2.** (*b*) **3.** (*c*) **4.** (*a*) **5.** (*d*)

VIII. ***Read the given passage and answer the questions that follow.***

Some colloids are stable by their nature, *i.e*., gels, alloys, and solid foams. Gelatin and jellies are two common examples of a gel. The solid and liquid phases in a gel are interdispersed with both phases being continuous. In most systems, the major factor influencing the stability is the charge on the colloidal particles. If a particular ion is preferentially adsorbed on the surface of the particles, the particles in suspension will repel each other, thereby preventing the formation of aggregates that are larger than colloidal dimensions. The ion can be either positive or negative depending on the particular colloidal system, *i.e*., air bubbles accumulate negative ions, sulphur particles have a net negative charge in a sulphur sol, and the particles in a metal hydroxide sol are positively charged. Accumulation of charge on a surface is not an unusual phenomenon-dust is attracted to furniture surfaces by electrostatic forces. When salts are added to lyophobic colloidal systems the colloidal particles begin to form larger aggregates and a sediment forms as they settle. This phenomenon is called flocculation, and the suspension can be referred to as flocculated, or colloidally unstable. If the salt is removed, the suspension can usually be restored to its original state; this process is called deflocculation or peptization. The original and restored colloidal systems are called deflocculated, peptized, or stable sols.

Why does a small amount of salt have such a dramatic effect on the stability of a lyophobic colloidal system?

The answer lies in an understanding of the attractive and repulsive forces that exist between colloidal particles. Van der Waals forces are responsible for the attractions, while the repulsive forces are due to the surface charge on the particles. In a stable colloid, the repulsive forces are of greater magnitude than the attractive forces. The magnitude of the electrical repulsion is diminished by addition of ionized salt, which allows the dispersed particles to aggregate and flocculate. River deltas provide an example of this behaviour. A delta is formed at the mouth of a river because the colloidal clay particles are flocculated when the freshwater mixes with the salt water of the ocean.

(**Source:** *Sarquis, J. (1980). Colloidal systems. Journal of Chemical Education, 57(8), 602. doi:10.1021/ed057p602*)

1. **Gelatin is a ________________ colloidal system.**

   (*a*) Solid in solid (*b*) Solid in gas (*c*) Liquid in solid (*d*) Liquid in gas

2. **Colloidal solutions are stable due to:**

   (*a*) presence of charges on the colloidal particles (*b*) formation of aggregates by colloidal particles

   (*c*) preferential adsorption on the surface (*d*) preferential absorption on the surface

3. **Settling down of colloidal particles to form a suspension is called:**

   (*a*) flocculation (*b*) peptization (*c*) aggregation (*d*) deflocculation

4. **When van der Waals forces are greater than forces due to the surface charge on the particles,**

   (*a*) flocculation occurs. (*b*) the colloid is stable.

   (*c*) peptization takes place. (*d*) deflocculation occurs.

5. **The particles in suspension will repel each other, thereby preventing the formation of aggregates that are larger than colloidal dimensions. This statement explains:**

   (*a*) formation of delta (*b*) river water is a colloidal of clay particles

   (*c*) effect of salt on lyphobic colloid (*d*) phenomenon of flocculation

Answers

1. (*c*) **2.** (*c*) **3.** (*a*) **4.** (*a*) **5.** (*b*)

IX. ***Read the given passage and answer the questions that follow.***

Industrially widely applied esterification reactions are commonly catalysed using mineral liquid acids, such as sulphuric acid and *p*-toluenesulphonic acid. The catalytic activity of homogeneous catalysts is high. They suffer, however, from several drawbacks, such as their corrosive nature, the existence of side reactions, and the fact that the catalyst cannot be easily separated from the reaction mixture. The use of solid acid catalysts offers an alternative and has received a lot of attention in the past years. Solid acid catalysts are not corrosive and, coated onto a support, they can be easily reused. Examples of solid acid catalysts used in esterification reactions include ion-exchange resins, zeolites and superacids like sulphated zirconia and niobium acid.

Ion-exchange resins are the most common heterogeneous catalysts used and have proven to be effective in liquid phase esterification and etherification reactions. Because of their selective adsorption of reactants and swelling nature, these resins not only catalyse the esterification reaction but also affect the equilibrium conversion. Shortcomings include insufficient thermal resistance, which limits the reaction temperature to 120°C, preventing widespread use in industry. Zeolites, like Y, X, BEA, ZSM-5 and MCM-41 offer an interesting alternative and have proven to be efficient catalysts for esterification reactions. Zeolites have found wide application in oil refining, petrochemistry and in the production of fine chemicals. Their success is based on the possibility to prepare zeolites with strong Brønsted acidity that can be controlled within a certain range, combined with a good resistance to high reaction temperatures.

In this study, the activity of various commercial available solid acid catalysts is assessed with respect to the esterification of acetic acid with butanol. The ion-exchange resins Amberlyst 15 and Smopex-101, the acid zeolites H-ZSM-5, H-MOR, H-BETA and H-USY, and the solid superacids sulphated zirconia and niobium acid are selected. Comparative esterification experiments have been carried out using the homogeneous catalysts sulphuric acid, *p*-toluenesulphuric acid and a heteropolyacid (HPA).

The weight-based activity of the heterogeneous catalysts tested is maximum for Smopex101. The following table gives the activity of different catalysts in the esterification reaction between acetic acid and butanol at 75°C.

Activity of the different catalysts, acid and butanol, 75°C

Catalyst	An
Homogeneous	
No catalyst	—
Sulphuric acid	0.9
p-Toluenesulphuric acid	1.7
HPA	5.5
Ion-exchange	
Amberlyst 15	1.9
Smopex-101	1.8
Zeolite	
H-USY-20	2.8
H-ZSM-5-12.5	2.8
H-BETA-12.5	2.8

Here: k_{obs}: observed reaction rate constant ($m^3\ mol^{-1}\ s^{-1}$) k_c catalysed reaction rate constant ($m^3\ mol^{-1}\ g\ cat^{-1}\ s^{-1}$)

Please note: k_c = k obs/amount (in g)

(**Source:** *PETERS, T., BENES, N., HOLMEN, A., & KEURENTJES, J. (2006). Comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol. Applied Catalysis A: General, 297(2), 182–188. doi:10.1016/j.apcata.2005.09.00*)

1. **Which of the following are heterogeneous catalysts for esterification reaction:**

(*a*) sulphuric acid and *p*-toluenesulphonic acid
(*b*) sulphuric acid and niobium acid
(*c*) *p*-toluenesulphonic acid and niobium acid
(*d*) niobium acid and sulphated zirconia

2. **Unit for observed rate constant for esterification reaction is $m^3\ mol^{-1}\ s^{-1}$, so the reaction is:**

(*a*) zero order
(*b*) first order
(*c*) second order
(*d*) third order

3. **The catalytic activity of homogeneous catalysts is high. The weight based activity of HPA is less than which of the following heterogenous catalysts?**

(*a*) Smopex-101
(*b*) Amberlyst-15
(*c*) sulphated ZrO_2
(*d*) H-USY-20

4. **The weight-based activity of the heterogeneous catalysts tested decreases in the following order:**

(*a*) Smopex-101 > Amberlyst 15 > sulphated ZrO_2 > H-USY-20 >H-BETA-12.5 > HMOR-45 > Nb_2O_5 > H-ZSM-5-12
(*b*) Smopex-101 > Amberlyst 15 > sulphated ZrO_2 > H-USY-20 > H-BETA-12.5 > HMOR-45 > H-ZSM-5-12 > Nb_2O_5

(*c*) Smopex-101 > Amberlyst 15 > sulphated ZrO_2 > H-USY-20 > H-BETA-12.5 > Nb_2O_5 > H-MOR-45 > H-ZSM-5-12

(*d*) Smopex-101 > Sulphated ZrO_2 > Amberlyst 15 > H-USY-20 > H-BETA-12.5 > HMOR-45 > H-ZSM-5-12 > Nb_2O_5

5. Catalysts used in oil refining industry are:

(*a*) ion exchange resins (*b*) superacids (*c*) zeolites (*d*) mineral liquid acids

Answers

1. (*d*) **2.** (*c*) **3.** (*a*) **4.** (*a*) **5.** (*c*)

X. Read the given passage and answer the questions that follow.

Biopolymers are polymers that are generated from renewable natural sources, are often biodegradable and nontoxic. They can be produced by biological systems (*i.e.*, microorganisms, plants and animals), or chemically synthesized from biological materials (*e.g.*, sugars, starch, natural fats or oils, etc.). Two strategies are applied in converting these raw materials into biodegradable polymers: extraction of the native polymer from a plant or animal tissue, and a chemical or biotechnological route of monomer polymerization. Biodegradable biopolymers (BDP) are an alternative to petroleum-based polymers (traditional plastics). Some BDP degrade in only a few weeks, while the degradation of others takes several months. In principle the properties relevant for application as well as biodegradability are determined by the molecular structure. According to the American Society for Testing and Materials, biopolymers are degradable polymers in which degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.

Polylactic acid (PLA) is an example of biopolymer. It is a thermoplastic polyester. Generally, there are two major routes to produce polylactic acid from the lactic acid ($CH_3CH(OH)^{-}COOH$) monomer. The first route involves condensation–water removal by the use of solvent under high vacuum and temperature. This approach produces a low to intermediate molar mass polymer. An alternative method is to remove water under milder conditions, without solvent, to produce a cyclic intermediate dimer, referred to as lactide. This intermediate is readily purified by vacuum distillation. Ring opening polymerization of the dimer is accomplished under heat, again without the need for solvent. By controlling the purity of the dimer it is possible to produce a wide range of molar masses. PLA is a good material for production of clothing, carpet tiles, interior and outdoor furnishing, geotextiles, bags, filtration systems, etc.

The primary biodegradability of PLA was tested using hydrolysis tests at various composting temperatures and pH. It was demonstrated that composting is a useful method for PLA biodegradation. The degradation rate is very slow in ambient temperatures. A 2017 study found that at 25°C in sea water, PLA showed no degradation over a year. As a result, it is poorly degraded in landfills and household composts, but is effectively digested in hotter industrial composts.

(**Source:** *Flieger, M., Kantorová, M., Prell, A., Řezanka, T., & Votruba, J.(2003). Biodegradable plastics from renewable sources. Folia Microbiologica, 48(1), 27–44. doi:10.1007/bf02931273*)

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(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

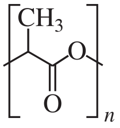
(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. Assertion : Biodegradable polymers degrade in few weeks.

Reason : Microorganisms bring about degradation of biopolymers.

2. Assertion : Lactic acid on polymerisation forms



Reason : PLA is used in producing geotextiles.

3. Assertion : Lactic acid undergoes condensation polymerisation
Reason : Lactic acid is a bifunctional monomeric unit.
4. Assertion : The degradation of PLA is very slow in ambient temperature.
Reason : PLA is a thermoplastic.
5. Assertion : PLA is poorly degraded in landfills.
Reason : The degradation rate of PLA is very slow in ambient temperatures.

Answers

1. (*d*) **2.** (*b*) **3.** (*a*) **4.** (*b*) **5.** (*a*)

XI. ***Read the given passage and answer the questions that follow.***

In the last 10 years much has been learned about the molecular structure of elemental sulfur. It is now known that many different types of rings are sufficiently metastable to exist at room temperature for several days. It is known that at high temperature, the equilibrium composition allows for a variety of rings and chains to exist in comparable concentration, and it is known that at the boiling point and above, the vapour as well as the liquid contains small species with three, four, and five atoms.

The sulfur atom has the same number of valence electrons as oxygen. Thus, sulfur atoms S_2 and S_3 have physical and chemical properties analogous to those of oxygen and ozone. S_2 has a ground state of 38 $\sigma 3s^2\ \sigma^* 3s^2\ \sigma 3p_z^2\ \pi 3p_x^2 = 3p_y^2\ \pi^* 3p_x^1 = \pi^* 3p_y^1$. S_3, thiozone has a well known uv spectrum, and has a bent structure, analogous to its isovalent molecules O_3, SO_2, and S_2O. The chemistry of the two elements, sulphur and oxygen, differs because sulfur has a pronounced tendency for catenation. The most frequently quoted explanation is based on the electron structure of the atom. Sulfur has low-lying unoccupied 3*d* orbitals, and it is widely believed that the 4*s* and 3*d* orbitals of sulfur participate in bonding in a manner similar to the participation of 2*s* and 2*p* orbitals in carbon.

(**Source:** *Meyer, B (1976). Elemental sulfur. Chemical Reviews, 76(3), 367–388. doi:10.1021/cr60301a003*)

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(*d*) ***Assertion is wrong statement but reason is correct statement.***

1. Assertion : Sulphur belongs to same period in the periodic table as oxygen.
Reason : S_2 has properties analogous to O_2.
2. Assertion : Thiozone has bent structure like ozone.
Reason : Ozone has a lone pair which makes the molecule bent.
3. Assertion : S_2 is paramagnetic in nature.
Reason : The electrons in $\pi^* 3p_x$ and $\pi^* 3p_y$ orbitals in S_2 are unpaired.
4. Assertion : Sulphur has a greater tendency for catenation than oxygen.
Reason : 3*d* and 4*s* orbitals of sulphur have same energy.

Answers

1. (*d*) **2.** (*b*) **3.** (*a*) **4.** (*c*)

XII. ***Read the given passage and answer the questions that follow.***

Adenosine triphosphate (ATP) is the energy-carrying molecule found in the cells of all living things. ATP captures chemical energy obtained from the breakdown of food molecules and releases it to fuel other cellular processes. ATP is a nucleotide that consists of three main structures: the nitrogenous base, adenine; the sugar, ribose; and a chain of three phosphate groups bound to ribose. The phosphate tail of ATP is the actual power source which the cell taps. Available energy is contained in the bonds between the phosphates and is released when they are broken, which occurs through the addition of a water molecule (a process called hydrolysis). Usually only the outer phosphate is removed from ATP to yield energy; when this occurs ATP is converted to adenosine diphosphate (ADP), the form of the nucleotide having only two phosphates.

The importance of ATP (adenosine triphosphate) as the main source of chemical energy in living matter and its involvement in cellular processes has long been recognized. The primary mechanism whereby higher organisms, including humans, generate ATP is through mitochondrial oxidative phosphorylation. For the majority of organs, the main metabolic fuel is glucose, which in the presence of oxygen undergoes complete combustion to CO_2 and H_2O:

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

The free energy (ΔG) liberated in this exergonic (ΔG is negative) reaction is partially trapped as ATP in two consecutive processes: glycolysis (cytosol) and oxidative phosphorylation (mitochondria). The first produces 2 mol of ATP per mol of glucose, and the second 36 mol of ATP per mol of glucose. Thus, oxidative phosphorylation yields 17-18 times as much useful energy in the form of ATP as can be obtained from the same amount of glucose by glycolysis alone.

The efficiency of glucose metabolism is the ratio of amount of energy produced when 1 mol of glucose oxidised in cell to the enthalpy of combustion of glucose. The energy lost in the process is in the form of heat. This heat is responsible for keeping us warm.

(**Source:** *Erecińska, M., & Silver, I.A. (1989). ATP and Brain Function. Journal of Cerebral Blood Flow & Metabolism, 9(1), 2–19. https://doi.org/10.1038/jcbfm.1989.2 and https://www.britannica.com/science/adenosine-triphosphate)*

1. Cellular oxidation of glucose is a:

(*a*) spontaneous and endothermic process
(*b*) non spontaneous and exothermic process
(*c*) non spontaneous and endothermic process
(*d*) spontaneous and exothermic process

2. What is the efficiency of glucose metabolism if 1 mole of glucose gives 38 ATP energy? (Given: The enthalpy of combustion of glucose is 686 k cal, 1 ATP = 7.3 k cal)

(*a*) 100% (*b*) 38% (*c*) 62% (*d*) 80%

3. Which of the following statement is true?

(*a*) ATP is a nucleoside made up of nitrogenous base adenine and ribose sugar .
(*b*) ATP consists the nitrogenous base, adenine and the sugar, deoxyribose.
(*c*) ATP is a nucleotide which contains a chain of three phosphate groups bound to ribose sugar.
(*d*) The nitrogenous base of ATP is the actual power source.

4. Nearly 95% of the energy released during cellular respiration is due to:

(*a*) glycolysis occurring in cytosol
(*b*) oxidative phosphorylation occurring in cytosol
(*c*) glycolysis in occurring mitochondria
(*d*) oxidative phosphorylation occurring in mitochondria

5. Which of the following statements is correct:

(*a*) ATP is a nucleotide which has three phosphate groups while ADP is a nucleoside which three phosphate groups.
(*b*) ADP contains a nitrogenous bases adenine, ribose sugar and two phosphate groups bound to ribose.
(*c*) ADP is the main source of chemical energy in living matter.
(*d*) ATP and ADP are nucleosides which differ in number of phosphate groups.

Answers

1. (*d*)

2. (*b*)

(Glucose catabolism yields a TOTAL of 38 ATP. 38 ATP × 7.3 kcal/mol ATP = 262 kcal. Glucose has 686 kcal. Thus the efficiency of glucose metabolism is 262/686 × 100 = 38%.)

3. (*c*) **4.** (*d*) **5.** (*b*)

XIII. ***Read the given passage and answer the questions that follow.***

The transition metals when exposed to oxygen at low and intermediate temperatures form thin, protective oxide films of up to some thousands of Angstroms in thickness. Transition metal oxides lie between the extremes of ionic and covalent binary compounds formed by elements from the left or right side of the periodic table. They range from metallic to semiconducting and deviate by both large and small degrees from stoichiometry. Since d electron bonding levels are involved, the cations exist in various valence states and hence give rise to a large number of oxides. The crystal structures are often classified by considering a cubic or hexagonal close-packed lattice of one set of ions with the other set of ions filling the octahedral or tetrahedral interstices. The actual oxide structures, however, generally show departures from such regular arrays due in part to distortions caused by packing of ions of different size and to ligand field effects. These distortions depend not only on the number of *d*-electrons but also on the valence and the position of the transition metal in a period or group.

(**Source:** *Smeltzer, W.W., & Young, D.J. (1975). Oxidation properties of transition metals. Progress in Solid State Chemistry, 10, 17-54.*)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(*a*) ***Assertion and reason both are correct statements and reason is correct explanation for assertion.***
(*b*) ***Assertion and reason both are correct statements but reason is not correct explanation for assertion.***
(*c*) ***Assertion is correct statement but reason is wrong statement.***
(*d*) ***Assertion is wrong statement but reason is correct statement.***

1. **Assertion** : Cations of transition elements occur in various valence states
   Reason : Large number of oxides of transition elements are possible.
2. **Assertion** : Crystal structure of oxides of transition metals often show defects.
   Reason : Ligand field effect cause distortions in crystal structures.
3. **Assertion** : Transition metals form protective oxide films.
   Reason : Oxides of transition metals are always stoichiometric.
4. **Assertion** : CrO crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by chromium ions.
   Reason : Transition metal oxide may be hexagonal close-packed lattice of oxide ions with metal ions filling the octahedral voids.

Answers

1. (*b*) **2.** (*a*) **3.** (*c*) **4.** (*d*)

XIV. ***Read the given passage and answer the questions that follow.***

The *d*-block elements are the 40 elements contained in the four rows of ten columns (3-12) in the periodic table. As all the *d* block elements are metallic, the term *d*-block metals is synonymous. This set of *d*-block elements is also often identified as the transition metals, but sometimes the group 12 elements (zinc, cadmium, mercury) are excluded from the transition metals as the transition elements are defined as those with partly filled *d* or *f* subshells in their compounds. Inclusion of the elements zinc, cadmium and mercury is necessary as some properties of the group 12 elements are appropriate logically to include with a discussion of transition metal chemistry.

The term transition element or transition metal appeared to derive from early studies of periodicity such as the Mendeleev periodic table of the elements. His horizontal table of the elements was an attempt to group the elements together so that the chemistry of elements might be explained and predicated. In this table there are eight groups labeled I-VIII with each subdivided into A and B subgroups. Mendeleev recognized that certain properties of elements in Group VIII are related to those of some of the elements in Group VII and those at the start of the next row Group I. In that sense, these elements might be described as possessing properties transitional from one row of the table to the next.

(**Source:** *Winter, M. J. (2015). d-block Chemistry (Vol. 27). Oxford University Press, USA.*)

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

- (*a*) *Assertion and reason both are correct statements and reason is correct explanation for assertion.*
- (*b*) *Assertion and reason both are correct statements but reason is not correct explanation for assertion.*
- (*c*) *Assertion is correct statement but reason is wrong statement.*
- (*d*) *Assertion is wrong statement but reason is correct statement.*

1. Assertion : Group 12 elements are not considered as transition metals.

Reason : Transition metals are those which have incompletely filled d subshell in their compounds.

2. Assertion : All *d* block elements are metallic in nature.

Reason : The *d*-block elements belong to Group 3-12 of the periodic table.

3. Assertion : Group VII elements of Mendeleev periodic table are transition elements.

Reason : Group I –VIII in Mendleev periodic table is divided into two subgroups, A and B.

4. Assertion : Nickel is a transition element that belongs to group 10 and period 4 of the modern periodic table.

Reason : Electronic configuration of Nickel is $[\mathrm{Ar}]_{18}\ 3d^8\ 4s^2$.

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*a*)

XV. *Read the given passage and answer the questions that follow.*

EVIDENCE FOR THE FIBROUS NATURE OF DNA

The basic chemical formula of DNA is now well established. As shown in Figure 1 it consists of a very long chain, the backbone of which is made up of alternate sugar and phosphate groups, joined together in regular 3′-5′ phosphate di-ester linkages. To each sugar is attached a nitrogenous base, only four different kinds of which are commonly found in DNA. Two of these---adenine and guanine--- are purines, and the other two thymine and cytosine-are pyrimidines. A fifth base, 5-methyl cytosine, occurs in smaller amounts in certain organisms, and a sixth, 5-hydroxy-methyl-cytosine, is found instead of cytosine in the T even phages. It should be noted that the chain is unbranched, a consequence of the regular internucleotide linkage. On the other hand the sequence of the different nucleotides is, as far as can be ascertained, completely irregular. Thus, DNA has some features which are regular, and some which are irregular. A similar conception of the DNA molecule as a long thin fiber is obtained from physicochemical analysis involving sedimentation, diffusion, light scattering, and viscosity measurements. These techniques indicate that DNA is a very asymmetrical structure approximately 20 A wide and many thousands of angstroms long. Estimates of its molecular weight currently center between 5×10^6 and 10^7 (approximately 3×10^4 nucleotides). Surprisingly each of these measurements tend to suggest that the DNA is relatively rigid, a puzzling finding in view of the large number of single bonds (5 per nucleotide) in the phosphate-sugar back bone. Recently these indirect inferences have been confirmed by electron microscopy.

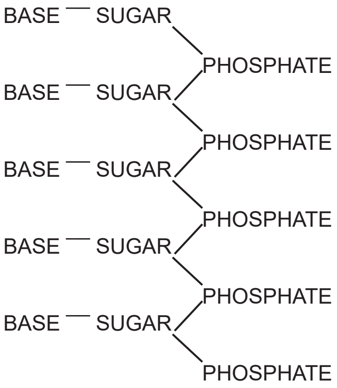

Figure 1: Chemical formula (diagrammatic) of a single chain of deoxyribonucleic acid

(**Source:** *Watson, J. D., & Crick, F. H. (1953, January). The structure of DNA. In Cold Spring Harbor symposia on quantitative biology (Vol. 18, pp. 123-131). Cold Spring Harbor Laboratory Press.*)

1. Purines present in DNA are:

(*a*) adenine and thymine (*b*) guanine and thymine

(*c*) cytosine and thymine (*d*) adenine and guanine

2. DNA molecule has ____________ internucleotide linkage and ____________ sequence of the different nucleotides

(*a*) regular, regular (*b*) regular, irregular (c) irregular, regular (*d*) irregular, irregular

3. DNA has a ____________ backbone.

(*a*) phosphate-purine (*b*) pyrimidines-sugar (*c*) phosphate-sugar (*d*) purine-pyrimidine

4. Out of the four different kinds of nitrogenous bases which are commonly found in DNA, ____________ has been replaced in some organisms.

(*a*) adenine (*b*) guanine (*c*) cytosine (*d*) thymine

Answers

1. (*d*) **2.** (*b*) **3.** (*c*) **4.** (*c*)

XVI. ***Read the given passage and answer the questions that follow.***

Polysaccharides may be very large molecules. Starch, glycogen, cellulose, and chitin are examples of polysaccharides. Starch is the stored form of sugars in plants and is made up of amylose and amylopectin (both polymers of glucose). Amylose is soluble in water and can be hydrolyzed into glucose units breaking glycosidic bonds, by the enzymes α-amylase and β-amylase. It is straight chain polymer. Amylopectin is a branched chain polymer of several D-glucose molecules. 80% of amylopectin is present in starch. Plants are able to synthesize glucose, and the excess glucose is stored as starch in different plant parts, including roots and seeds. The starch that is consumed by animals is broken down into smaller molecules, such as glucose. The cells can then absorb the glucose.

Glycogen is the storage form of glucose in humans and other vertebrates, and is made up of monomers of glucose. It is structurally quite similar to amylopectin. Glycogen is the animal equivalent of starch. It is stored in liver and skeletal muscles.

Cellulose is one of the most abundant natural biopolymers. The cell walls of plants are mostly made of cellulose, which provides structural support to the cell. Wood and paper are mostly cellulosic in nature. Like amylose, cellulose is a linear polymer of glucose. Cellulose is made up of glucose monomers that are linked by bonds between particular carbon atoms in the glucose molecule. Every other glucose monomer in cellulose is flipped over and packed tightly as extended long chains. This gives cellulose its rigidity and high tensile strength—which is so important to plant cells. Cellulose passing through our digestive system is called dietary fibre.

(**Source:** *https://chem.libretexts.org*)

1. In animals, Glycogen is stored in:

(*a*) Liver (*b*) Spleen (*c*) Lungs (*d*) Small Intestine

2. Amylose is:

(*a*) straight chain, water insoluble component of starch, which constitutes 20% of it.

(*b*) straight chain, water soluble component of starch, which constitutes 20% of it.

(*c*) branched chain, water insoluble component of starch, which constitutes 80% of it.

(*d*) branched chain, water soluble component of starch, which constitutes 80% of it.

3. Which biopolymer breaks down to release glucose, whenever glucose levels drop in our body:

(*a*) starch (*b*) cellulose (*c*) chitin (*d*) glycogen

4. The linkages which join monosaccharides to form long chain polysaccharides:

(*a*) Peptide linkage (*b*) Disulphide bonds (*c*) Hydrogen bonds (*d*) Glycosidic linkage

5. Cellulose on complete hydrolysis yields:

(*a*) amylose (*b*) amylopectin (*c*) glucose (*d*) amylose and amylopectin

Answers

1. (*a*) **2.** (*b*) **3.** (*d*) **4.** (*d*) **5.** (*c*)