DIRECTORATE OF EDUCATION

GNCT of Delhi, Delhi Government

SUPPORT MATERIAL
(2021-2022)

Class : XII

CHEMISTRY

Under the Guidance of

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MESSAGE

I would like to congratulate the members of Core Academic Unit and the subject experts of the Directorate of Education, who inspite of dire situation due to Corona Pandemic, have provided their valuable contributions and support in preparing the Support Material for classes IX to XII.

The Support Material of different subjects, like previous years, have been reviewed/ updated in accordance with the latest changes made by CBSE so that the students of classes IX to XII can update and equip themselves with these changes. I feel that the consistent use of the Support Material will definitely help the students and teachers to enrich their potential and capabilities.

Department of Education has taken initiative to impart education to all its students through online mode, despite the emergency of Corona Pandemic which has led the world to an unprecedented health crises. This initiative has not only helped the students to overcome their stress and anxiety but also assisted them to continue their education in absence of formal education. The support material will ensure an uninterrupted learning while supplementing the Online Classes.

(H. Rajesh Prasad)

UDIT PRAKASH RAI, IAS
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MESSAGE

The main objective of the Directorate of Education is to provide quality education to all its students. Focusing on this objective, the Directorate is continuously in the endeavor to make available the best education material, for enriching and elevating the educational standard of its students. The expert faculty of various subjects undertook this responsibility and after deep discussions and persistent efforts, came up with Support Material to serve the purpose.

Every year the Support Material is revised/ updated to incorporate the latest changes made by CBSE in the syllabus of classes IX to XII. The contents of each lesson/chapter are explained in such a way that the students can easily comprehend the concept and get their doubts solved.

I am sure, that the continuous and conscientious use of this Support Material will lead to enhancement in the educational standard of the students, which would definitely be reflected in their performance.

I would also like to commend the entire team members for their contributions in the preparation of this incomparable material.

I wish all the students a bright future.

(UDIT PRAKASH RAI)

Dr. RITA SHARMA
Additional Director of Education
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सत्यमेव जयते

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D.O. No. PA/Addl.DE/Sch/21

Dated: 29.06.2021

MESSAGE

It gives me immense pleasure to present the revised edition of the Support Material. This material is the outcome of the tireless efforts of the subject experts, who have prepared it following profound study and extensive deliberations. It has been prepared keeping in mind the diverse educational level of the students and is in accordance with the most recent changes made by the Central Board of Secondary Education.

Each lesson/chapter, in the support material, has been explained in such a manner that students will not only be able to comprehend it on their own but also be able to find solution to their problems. At the end of each lesson / chapter, ample practice exercises have been given. The proper and consistent use of the support material will enable the students to attempt these exercises effectively and confidently. I am sure that students will take full advantage of this support material.

Before concluding my words, I would like to appreciate all the team members for their valuable contributions in preparing this unmatched material and also wish all the students a bright future.

(Rita Sharma)

DIRECTORATE OF EDUCATION

GNCT of Delhi, Delhi Government

SUPPORT MATERIAL

(2021-2022)

CHEMISTRY

Class : XII

NOT FOR SALE

PUBLISHED BY : DELHI BUREAU OF TEXTBOOKS

CHEMISTRY
CLASS-XII
2021-2022

LIST OF MEMBERS WHO REVIEWED AND REVISED SUPPORT MATERIAL OF CHEMISTRY

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भारत का संविधान

भाग 4क

नागरिकों के मूल कर्तव्य

अनुच्छेद 51क

मूल कर्तव्य – भारत के प्रत्येक नागरिक का यह कर्तव्य होगा कि वह –

1. संविधान का पालन करे और उसके आदर्शों, संस्थाओं, राष्ट्र ध्वज और राष्ट्रगान का आदर करें।
2. स्वतंत्रता के लिए हमारे राष्ट्रीय आंदोलन को प्रेरित करने वाले उच्च आदर्शों को हृदय में संजोए रखे और उनका पालन करे।
3. भारत की प्रभुता, एकता और अखंडता की रक्षा करे और उसे अक्षुण्ण रखे।
4. देश की रक्षा करे।
5. भारत के सभी लोगों में समरसता और समान भ्रातृत्व की भावना का निर्माण करे।
6. हमारी सामाजिक संस्कृति की गौरवशाली परंपरा का महत्त्व समझे और उसका निर्माण करे।
7. प्राकृतिक पर्यावरण की रक्षा और उसका संवर्धन करे।
8. वैज्ञानिक दृष्टिकोण और ज्ञानार्जन की भावना का विकास करे।
9. सार्वजनिक संपत्ति को सुरक्षित रखे।
10. व्यक्तिगत एवं सामूहिक गतिविधियों के सभी क्षेत्रों में उत्कर्ष की ओर बढ़ने का सतत् प्रयास करे।
11. माता–पिता या संरक्षक द्वारा 6 से 14 वर्ष के बच्चों हेतु प्राथमिक शिक्षा प्रदान करना (86वां संशोधन)।

CONSTITUTION OF INDIA

Part IV A (Article 51 A)

Fundamental Duties

Fundamental Duties : It shall be the duty of every citizen of India —

1. to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;
2. to cherish and follow the noble ideals which inspired our national struggle for freedom;
3. to uphold and protect the sovereignty, unity and integrity of India;
4. to defend the country and render national service when called upon to do so;
5. to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;
6. to value and preserve the rich heritage of our composite culture;
7. to protect and improve the natural environment including forests, lakes, rivers and wild life, and to have compassion for living creatures.
8. to develop the scientific temper, humanism and the spirit of inquiry and reform;
9. to safeguard public property and to adjure violence;
10. to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement.
11. who is a parent or guardian to provide opportunities for education to his child or, as the case may be, ward between the age of six and fourteen years.

भारत का संविधान

उद्देशिका

हम, भारत के लोग, भारत को एक **(सम्पूर्ण प्रभुत्व–सम्पन्न समाजवादी पंथनिरपेक्ष लोकतंत्रात्मक गणराज्य)** बनाने के लिए, तथा उसके समस्त नागरिकों को :

सामाजिक, आर्थिक और राजनैतिक **न्याय,**

विचार, अभिव्यक्ति, विश्वास, धर्म

और उपासना की **स्वतंत्रता,**

प्रतिष्ठा और अवसर की समता

प्राप्त करने के लिए,

तथा उन **सब में,**

व्यक्ति की गरिमा और **(राष्ट्र की एकता**

और अखंडता) सुनिश्चित करने वाली बंधुता

बढ़ाने के लिए

हम दृढ़संकल्प होकर इस संविधान को आत्मार्पित करते हैं।

THE CONSTITUTION OF INDIA

PREAMBLE

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a **(SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC)** and to secure to all its citizens :

JUSTICE, social, economic and political,

LIBERTY of thought, expression, belief, faith and worship,

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the **(unity an integrity of the Nation)**;

WE DO HEREBY GIVE TO OURSELVES THIS CONSTITUTION.

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Unit No.	Title	Page No
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UNIT VI	P-Block Elements	
UNIT VII	d- and f-Block Elements	
UNIT VIII	Coordination Compounds	
UNIT IX	Haloalkanes and Haloarenes	
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UNIT XI	Aldehydes, Ketones and Carboxylic Acids	
UNIT XII	Organic Compounds containing Nitrogen (Amines)	
UNIT XIII	Biomolecules	
	CBSE Sample Paper 2021-22 Term-I	
	Practice Paper Term-I	

SYLLABUS FOR SESSION 2021-22 CLASS XII Term-I

S.No.	UNIT	Periods	Marks
1	The Solid State	8	10
2	Solutions	8	
3	p-Block Elements	7	10
4	Haloalkanes and Haloarenes	9	15
5	Alcohols, Phenols and Ethers	9	
6	Biomolecules	8	
	TOTAL	49	35

The Solid State: 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.

Solutions: 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.

p-Block Elements: 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.

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: 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.

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

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

Alcohols, Phenols and Ethers: Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration.

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

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

Biomolecules: Carbohydrates - Classification (aldoses and ketoses), monosaccahrides (glucose and fructose), D-L configuration

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.

Nucleic Acids: DNA and RNA

SYLLABUS FOR SESSION 2021-22 CLASS XII Term-II

S.No.	UNIT	Periods	Marks
1	Electrochemistry	7	13
2	Chemical Kinetics	5	
3	Surface Chemistry	5	
4	d-and f-Block Elements	7	
5	Coordination Compounds	8	9
6	Aldehydes, Ketones and Carboxylic Acids	10	
7	Amines	7	13
	TOTAL	49	35

Electrochemistry: 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.

Chemical Kinetics: 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).

Surface Chemistry: Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, 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.

d-and f-Block Elements: 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.

Lanthanoids - Electronic configuration, oxidation states and lanthanoid contraction and its consequences.

Coordination Compounds: Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.

Aldehydes, Ketones and Carboxylic Acids: **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.

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

UNIT 1

The Solid State

Points to Remember

Solid State :

- Constituent particles have fixed positions and they can only oscillate about their mean position.

Classification of solids (on the basis of arrangement of consituent particles)

CRYSTALLINE SOLIDS

- Melt at a sharp and characteristic temperature
- When cut with a sharp edged tool, they split into two pieces and the newly generated surface are plain and smooth
- They have a definite and characteristic heat of fusion
- Anisotropic in nature
- True solids
- Long range order

AMORPHOUS SOLIDS

- Irregular shape
- Gradually soften over a range of temperature
- When cut with a sharp edged tool, they cut into two pieces with irregular surface.
- They do not have definite heat of fusion.
- Isotropic in nature.
- Pseudo solids or super cooled liquids.
- short range order

Classification of crystalline solids (on the basis of nature of intermolecular forces)

IONIC SOLIDS: Constituent particles are icons, coulombic or electrostatic forces exist between the ions, Insulators in solid state but conductors in molten state and in aqueous solutions. e.g. NaCl, MgO

METALLIC SOLIDS: Constituent particles are positive ions immersed in a sea of delocalized electrons. Interparticle forces are metallic bonds, conductors in solid states as well as in molten state. e.g. Cu, Fe, Mg.

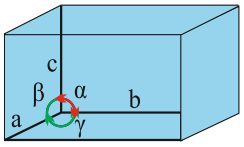
MOLECULAR SOLIDS: Constituent particles are molecules **Non-polar:** Dispersion or London forces e.g. Ar, CCl_4 **Polar :** Dipole-Dipole interaction between molecules e.g. HCl, SO_2 Hydrogen bonded: Hydrogen bonding exits e.g. H_2O (ice) Insulators (all types)

COVALENT SOLID OR NETWORK SOLID: Constituent particles are atoms and interparticle forces are covalent bonding. e.g. quartz, diamond.

Crystal Lattice: Regular arrangement of constituent particles of crystal in a three dimensional space.

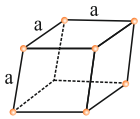
Unit Cell : Smallest portion of a regular of crystal lattice which when repeated over and again in different directions, generates the entire lattice.

Six Parameters of unit cell : Edge lengths: a,b,c (may or may not be mutually perpendicular); Angles between the edges: α, β, γ



TYPES OF UNIT CELL

PRIMITIVE
Constituent particles are present only at corners.



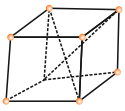
Primitive (or simple)

CENTRED
One or more constituent particles are present at positions other than corners.

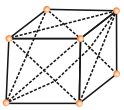
Body-centred particles are present at the corners and body-centre

Face-centred particles are present at the corners and centre of each face.

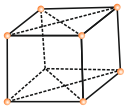
End-centred particles are present at the corners and centre of any two opposite faces.



Body centred



Face centred



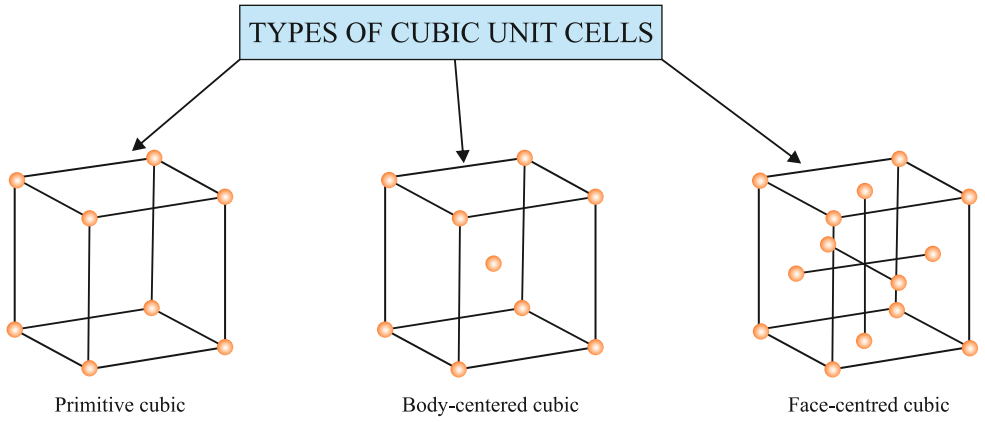
End centred

Crystal systems and Bravais Lattice

There are seven crystal systems and fourteen Bravais Lattice (Unit cell) corresponding to these seven crystal systems.

Crystal Class	Axial Distance	Axial Angles	Possible Type of Unit Cells	Examples
1. Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^0$	Primitive, body-centred face-centred	KCl, NaCl
2. Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^0$	Primitive, body-centred	SnO_2, TiO_2
3. Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^0$	Primitive, body-centred, face-centred, end-centred	KNO_3, $BaSO_4$
4. Hexagonal	$a=b\neq c$	$\alpha=\beta=90^0$ $\gamma=120^0$	Primitive	Mg, ZnO
5. Trigonal or Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq90^0$	Primitive	($CaCO_3$) Calcite, HgS (Cinnabar)
6. Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90^0$ $\beta\neq90^0$	Primitive and end-centred	Monoclinic sulphur $Na_2SO_4.10H_2O$
7. Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq90^0$	Primitive	$K_2Cr_2O_7$, H_3BO_3

- Most symmetrical crystal system : Cubic
- Most unsymmetrical crystal system : Triclinic

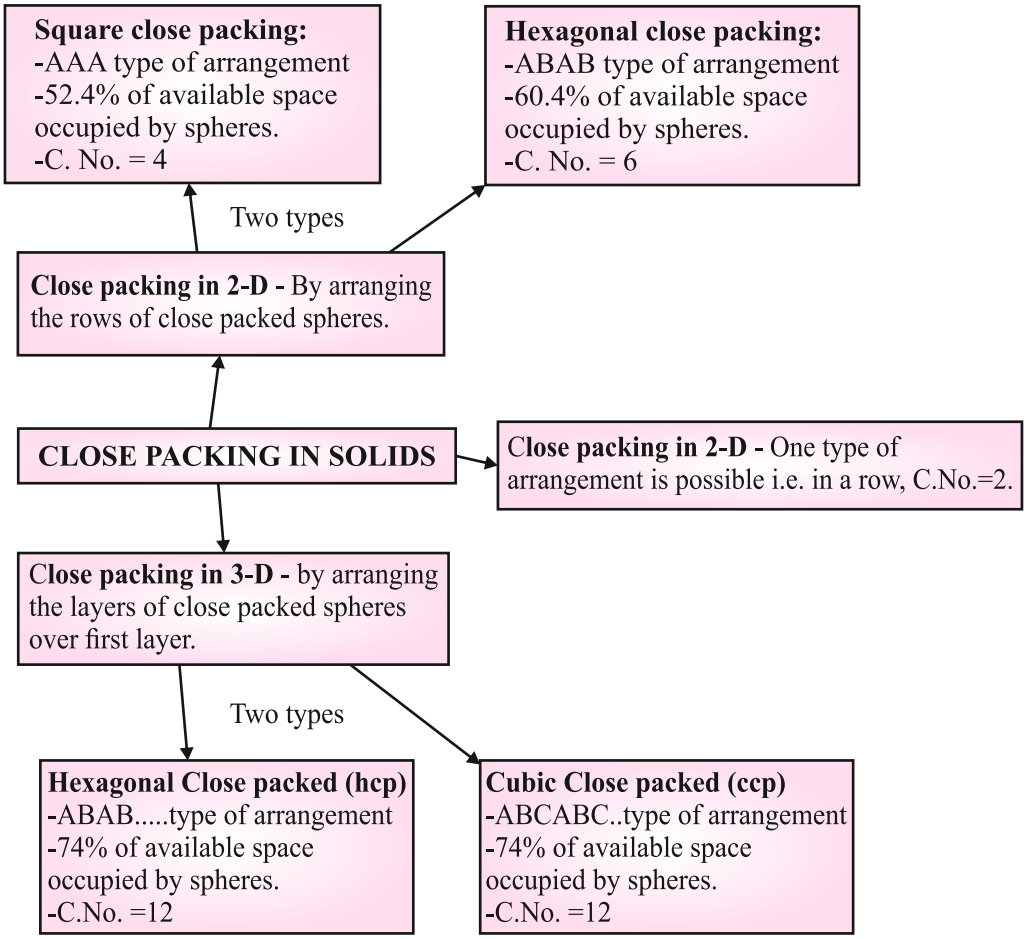


Number of atoms in different unit cells (z):

Contribution of particles at : Corner: 1/8, at face: 1/2, at body centre:1

- Simple cubic: 8x1/8=1
- Body-centred cubic: 8x1/8+1=2
- Face-centred cubic=8x1/8+6x1/2=4

PACKING IN SOLIDS:



VOIDS OR INTERSTITIAL SITES: Empty spaces left in the close packed structures.

1. In 2-D Packing: Trigonal voids are present.
2. In 3-D packing: Two types of voids

Tetrahedral void - Vacant space among four spheres having tetrahedral arrangement. C. No. = 4

Octahedral void- Double triangular void surrounded by six spheres C. No.= 6

Relation between the number of voids and the number of spheres in close packing

In close packing the number of spheres = N spheres

Number of octahedral voids= N

Total voids in ccp per unit cell= 4 (octahedral)+ 8 (tetrahedral) =12

Total voids in hcp per unit cell= 6 (octahedral)+ 12 (tetrahedral)= 18

Relationship between Edge length(a), Distance between nearest neighbours (d) Radius atom (r) and packing efficiency

S.No.	Unit Cell	Relationship between a and r	Relationship between a and d	Packing efficiency
1	Simple cubic	r = a/2	d = a	52.4%
2	Face centred cubic(fcc)	r = a/2 √ 2	d = a/ √ 2	74%
3	Body centred cubic (bcc)	r = √ 3a/4	d = √ 3a/2	68%

Density of the crystal (d)

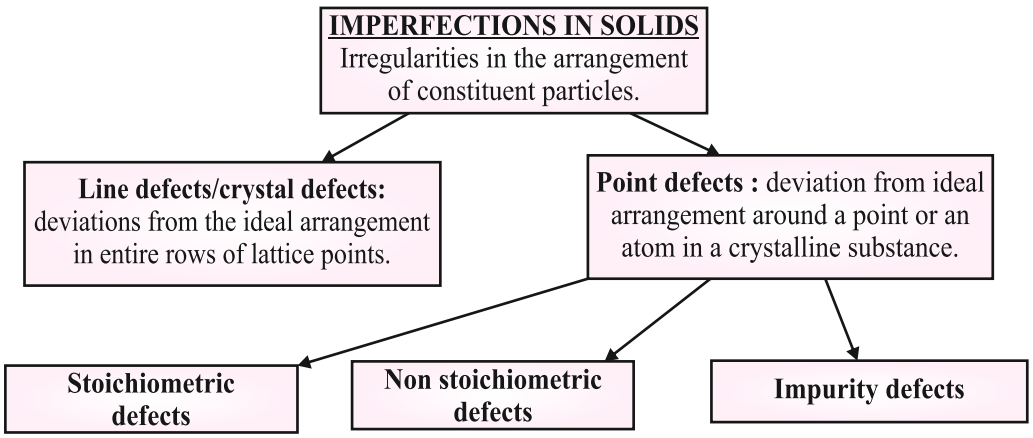
$$d = \frac{zM}{a^3 x\ N_A}\ g/cm^3$$

z = Number of particles present per unit cell

M = Molar mass of substance ($g\ mol^{-1}$)

a= Edge length of the unit cell (cm)

N_A = Avogadro number (6.02×10^{23})



Stoichiometric Defects: also known as Intrinsic or thermodynamic defects.

i) **Vacancy defect -** When some of the lattice sites are vacant; density decreases in this defect.

ii) **Interstitial defect -**When some constituent particles occupy an interstitial site. Density increases in this defect

For Ionic Solids : Electrical Neutrality should be maintained.

STOICHIOMETRIC DEFECTS IN SOLIDS

Schottky Defect

- Equal number of cations and anions are completely missing from crystal lattice
- Occurs in compounds having high coordination number and small difference in size of cations and anions.
- Density decreases e.g. NaCl, KCl

Frenkel Defect

- Cations are missing from lattice site and occupy interstitial sites.
- Occurs in compounds with low coordination number and large difference in size of cation and anions.
- Density remains the same e.g. AgI, AgCl, ZnS

- AgBr shows both Schottky as well as Frenkel defect.

NON-STOICHIOMETRIC DEFECTS

Metal Excess Defect

- Due to anionic vacancies - When crystals of alkali halides are healed in the vapour of alkali metal, some anions leave lattice sites in which electrons get trapped forming F - centre which impart colour to the crystals.

NaCl Crystals - Yellow colour
LiCl Crystals - Pink Colour
KCl Crystals-Violet/Lilac Colour
(Due to the excess of alkali (Na, Li & K) metal)

Due to the presence of extra cations at interstitial Sites:

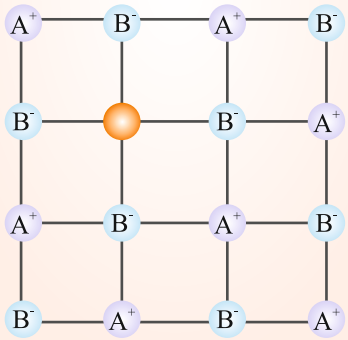
$ZnO \longrightarrow Zn^{2+} + 1/2O_2 + 2e^-$

White Yellow

Zn^{2+} ions and electrons move to interstitial sites.

Metal Deficiency Defect

It occurs when metal shows variable oxidation states. Few metal ions with lower oxidation states are missing from their site but metal ions with higher oxidation states are present at some sites thus balancing the charge. However, this leaves some cationic vacancies at the sites of metal ions. e.g. FeO exist as $Fe_{0.95}O$.



- **Impurity defect:** When foreign atoms are present at the lattice site in place of host atoms or at the vacant interstitial sites e.g. NaCl doped with $SrCl_2$ and AgCl doped with $CdCl_2$.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS:

1. Structure of a mixed oxide is ccp. Cubic unit cell of mixed oxide is composed of oxide ions. One Fourth of tetrahedral voids are occupied by divalent metal A and all the octahedral voids are occupied by monovalent metal B. Formula of oxide is
   (a) $A_2B_3O_4$ (b) AB_2O_2
   (c) ABO_2 (d) A_2BO_2
2. Number of tetrahedral voids in the unit cell of a face centred cubic lattice of similar atoms is
   (a) 4 (b) 6
   (c) 8 (d) 12
3. If an atom is placed on each lattice point, the number of atoms per unit cell for primitive, body - centered cubic and face-centred cubic lattice, respectively, are ?
   (a) 1, 1 and 4 (b) 1, 2 and 4
   (c) 1,4 and 2 (d) 1, 1 and 1
4. Percentages of free space in cubic close packed structure and in body centred packed structure are respectively
   (a) 48% and 36 % (b) 30% and 26 %
   (c) 26% and 32 % (d) 32% and 48 %
5. The correct order of the packing efficiency in different types of unit cells is.
   (a) *fcc*< *bcc*< simple cubic (b) *fcc*> *bcc*> simple cubic
   (c) *fcc*< *bcc*> simple cubic (d) *bcc*<*fcc*> simple cubic
6. Which of the following is not a characteristic of a crystalline solid?
   (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
7. Cations are present in the interstitial sites in .....
   (a) Frenkel defect (b) Vacancy defect
   (c) Schottky defect (d) Metal deficiency defect
8. The percentage of iron present as Fe(III) in $Fe_{0.93}O_{1.00}$ is
   (a) 8.3% (b) 9.6%
   (c) 11.5% (d) 17.7%

9. Which one of the following crystal habit is exhibited by match box.
   (a) Orthorhombic (b) Cubic
   (c) Trigonal (d) Monoclinic
10. Which of the following is/are not true about hexagonal close packing?
   (a) It is 26% empty space
   (b) ln this arrangement, third layer is identical to the first layer.
   (c) The coordination number in this arrangement is 6.
   (d) It is as closely packed as body centred cubic packing.
11. Which of the following is/are not true about hexagonal close packing?
   (a) It is 26% empty space
   (b) In this arrangement, third layer is identical to the first layer
   (c) The coordination number in this arrangement is 6
   (d) lt is as closely packed as body centred cubic packing
12. Monoclinic crystal has dimension
   (a) $a \neq b \neq c, \alpha = \gamma = 90°, \beta \# 90°$ (b) $a = b = c, \alpha = \beta = \gamma = 90°$
   (c) $a = b \neq c, \alpha = \beta = \gamma = 90°$ (d) $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$
13. Body centered cubic lattice has a coordination number of
   (a) 4 (b) 12
   (c) 8 (d) 6
14. The arrangement ABC ABC ABC.....is referred as
   (a) Octahedral close packing (b) Hexagonal close packing
   (c) Tetragonal close packing (d) Cubic close packing
15. Under which category iodine crystals are placed among the following
   (a) Ionic crystal (b) Metallic crystal
   (c) Molecular crystal (d) Covalent crystal
16. If NaCl is eloped with 10^{-3} mol % $SrCl_2$, then concentration of cation vacancies will be
   (a) $1 x 10^{-3}$ mol% (b) $3 x 10^{-3}$ mol%
   (c) $2 x 10^{-3}$ mol% (d) $4 x 10^{-3}$ mol%
17. The correct statement regarding F - centre is
   (a) Electron are held in the voids of crystals
   (b) F - centre produces colour to the crystals
   (c) Conductivity of the crystal increases due to F - centre
   (d) All of above

18. Which one of the following crystals does not exhibit Frenkel defect:-

(a) AgBr (b) AgCl

(c) KBr (d) ZnS

19. Amorphous substances show:-

(a) Short and long range order

(b) Short range order

(c) long range order

(d) Have no sharp m.p.

(a) A and C are correct (b) B and C are correct

(c) C and D are correct (d) B and D are correct

20. Graphite cannot be classified as_____.

(a) Conducting solid (b) Network solid

(c) Covalent solid (d) Ionic solid

II FILL IN THE BLANKS

1. Dry ice is an example of.....solid.
2. In diamond intermolecular forces are.....
3. Glass is an example of.....solids.
4. An atom at the corner of a unit cell makes.....contribution to a particular unit cell.
5. In an ionic crystal, the holes occupied by electrons are called.....
6. The conductivity of semiconductors.....with increase in temperature.
7. Silicon doped with gallium, behaves as.....type semiconductor.
8. If x is number of atoms per unit cell then number of tetrahedral voids in unit cell is .....
9. ln ccp arrangement of atoms,..... percent of the space available remains vacant.
10. n-type semiconductors are formed by doping with.....type impurity.

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement

(d) Assertion is wrong, but reason is correct statement

1. **ASSERTION:** ln close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.
   REASON: A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.
2. **ASSERTION:** The total number of atoms present in a simple cubic unit cell is one.
   REASON : Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.
3. **ASSERTION:** Graphite is a good conductor of electricity however diamond belongs to the category of insulators.
   REASON : Graphite is soft in nature on the other hand diamond is very hard and brittle.
4. **ASSERTION:** p-type semiconductors are good conductors of electricity due to metal excess defects.
   REASON: F-centres are created due to metal excess defects.
5. **ASSERTION:** Crystalline solids exhibit isotropy.
   REASON: The constituent particles in a crystalline solid are arranged in an orderly fashion.
6. **ASSERTION:** An excess of potassium ions makes KCl crystals appear violet in colour.
   REASON: An excess potassium ions in KCl creates F-centres in the crystal.
7. **ASSERTION:** Schottky defect is generally shown by the compounds with high coordination number.
   REASON: In Schottky defect equal number of anions and cations are missing from their lattice sites.
8. **ASSERTION:** Crystalline solids have sharp melting point.
   REASON: Crystalline solids have a regular arrangement of constituent particles.

IV ONE WORD ANSWER TYPE QUESTIONS

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?
2. Name a solid having both schottky and Frenkel defect?
3. Which one of the following is an example of molecular solid: CO_2 or SiO_2.
4. How many atoms are there in one unit cell of a body-centred cubic crystal?.
5. Which group of solids is electrical conductor as well as malleable and ductile?
6. What is the two-dimensional coordination number of a molecule in a square close-packed layer?
7. Which point defect in crystals of a solid decreases the density of the solid?
8. Name the non-stoichiometric point defect responsible for colour in alkali metal halides.
9. What is the packing efficiency of FCC?
10. Which stoichiometric defect (point defect) in crystals increases the density of a solid?

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. Some of the very old glass objects appear slightly milky instead of being transparent. Why?
2. How are unit cell and space lattice related?
3. What difference in behaviour between the glass and sodium chloride would you expect to observe if you break off piece of either cube?
4. Write a feature which will distinguish a metallic solid from an ionic solid.
5. Why Frenkel defect is not found in pure alkali metal halides?
6. Define F- centre.
7. 'Crystalline solids are anisotropic in nature' what do you understand by this statement?
8. What are primitive and non-primitive unit cells?
9. What kind of attractive forces are present in the molecular crystalline solids?
10. In spite of long range order in the arrangement of particles, why are the crystals usually not perfect?
11. What type of crystal defect is produced when sodium chloride is doped with $SrCl_2$?

12. Name the non-stoichiometric point defect responsible for colour in alkali metal halides.
13. What is the difference between hexagonal and monoclinic unit cells?
14. List two causes which lead to imperfections in solids.
15. Why are the solids containing F- centres paramagnetic?

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. Write two points of differences between crystalline and amorphous solids.
2. Silver crystallises in face-centred cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms). [Ans. $r = 141.4$ pm $= 141.4 \times 10^{-10}$ cm]
3. What is the difference between glass and quartz while both are made up from SiO_4^{4-} tetrahedral? Under what conditions could quartz be converted into glass?
4. In a compound, nitrogen atoms (N) make cubic dose packed lattice and metal atoms(M) occupy one third of the tetrahedral voids present. Determine the formula of the compound formed by M and N. [Ans. M_2N_3]
5. Why is FeO(s) not formed in stoichiometric composition?

   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]
6. How are the following properties of crystals affected by Schottky and frenkel defects?

   (i) Density (ii) Electrical conductivity.

Ans. (i) In **Frenkel defect** density of crystal remains same while in **Schottky defect** density of the crystal decreases.

(ii) Electrical conductivity of the crystal increases in both **Schottky defect** and **Frenkel defect.**

7. 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?

[ANS: z=4, FCC]

8. Account for the following:
   (i) Alkali metal halides cannot exhibit Frenkel defect.
   (ii) Zinc oxide on heating becomes yellow.
   (iii) Frenkel defect does not change the density of AgCl crystals.

9. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.0g?

[ANS : 1 g of NaCl contains= 2.57×10^{21} unit cells]

10. Experimentally it was found that a metal oxide has formula $M_{0.98}O_{1.00}$. M is present as M^{2+} and M^{3+} in its oxide. What percentage of metal is present as M^{3+}?

[ANS: 4.08%]

11. In a solid 'AB', 'A' atoms have ccp arrangement and B atoms occupy all the octahedral sites. If all the face centred atoms along one of the axes are removed, then what will be the resultant stoichiometry (formula) of the compound?

[ANS : A_3B_4]

12. An element crystallises in a fee lattice with unit cell edge of 250pm. Calculate its density if 300g of this element contain 2×10^{24} atoms.

[ANS : 38.4g/cm^3]

13. A metal having atomic mass 50g/mol has a body centred cubic crystal structure. The density of metal is 5.96g/cm^3. Find the volume of the unit cell.

[ANS : 2.786×10^{-23} cm^3]

14. Calculate packing efficiency in body centred cubic (BCC) lattice.

15. (i) Based on the nature of intermolecular forces, classify the following: Benzene, Silver.
   (ii) AgCl shows Frenkel defect while NaCl does not. Give reason.

16. ln a crystalline solid, having formula AB_2O_4, oxide ions are arranged in cubic close packed lattice while cations A are present in tetrahedral voids and cations B are present in octahedral voids.
   (i) What percentage of the tetrahedral voids is occupied by A?
   (ii) What percentage of the octahedral voids is occupied by B?

Ans. In a cubic close packed lattice of oxide ions there would be two tetrahedral voids and one octahedral void for each oxide ion.

For four oxide ions there would be eight tetrahedral and four octahedral voids, two are occupied by B.

(i) Percentage of tetrahedral voids occupied by A = 1/8 × 100 = 12.5%

(ii) Percentage of tetrahedral voids occupied by B = 2/4 × 100 = 50%

17. Mention the conditions causing Schottky defects and Frenkel defects.

18. How will you distinguish between the following pairs of terms:

(i) Tetrahedral and Octahedral voids.

(ii) Crystal lattice and Unit cell

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) Write the relationship between atomic radius (r) and edge length of cubic unit cell for (a) simple cubic unit cell (b) body-centred cubic unit cell (c) face centred cubic unit cell

(ii) What do you understand by the following types of stacking sequences:

(a) AB AB .....

(b) ABC ABC .....

2. In a cubic close packed structure of mixed oxides, the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one-half of octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxide?

Ans. In ccp, there is one octahedral and two tetrahedral voids corresponding to each atom constituting the lattice. Therefore,

Number of oxide ions=1

Number of tetrahedral voids per oxide ion in lattice= 1 × 2 = 2

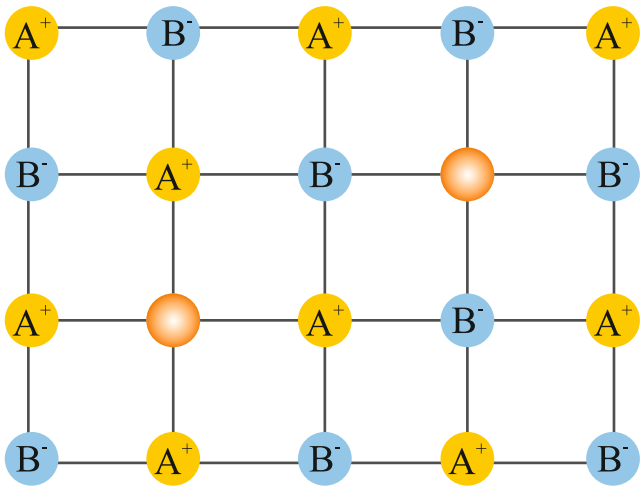
Number of divalent (A^{2+}) ions =(1/8) × 2 = 1/4

Number of octahedral voids per oxide ion in lattice= 1 × 1 = 1

Number of trivalent (B^{3+}) ions= 1 × (l/2)= 1/2

∴ Formula of solid= $A_{1/4} B_{1/2} O_1 = A B_2 O_4$.

3. Examine the illustration of a portion of the defective crystal given below and answer the following questions:



(i) What are these types of vacancy defects called?

(ii) What change in density is observed?

(iii) Name one ionic compound which can show this type of defect in the crystalline state?

(iv) How is the stoichiometry of the compound affected?

(v) State one condition for these defects to be shown by ionic crystals.

CASE STUDY BASED QUESTIONS

1. Read the passage given below and answer the questions that follow:

The geometrical from consisting of only a regular array of points in space is called a space lattice. Unit cell is the smallest three dimensional portion of crystal lattice which when repeated in different directions, generates the entire lattice. Unit cell may be simple (primitive unit cell) or centred unit cell. Centred unit cell may be Face centred, body centred or end-centred. There are seven basic primitive crystal systems and based on these seven primitive crystal systems there are 14 thre dimensional lattices known as Bravais lattice. A unit cell is characterized by six parameters namely Edge lengths - a,b,c and angle between the pair of edges : α,β,γ. Most symmetrical crystal system is cubic and most unsymmetrical crystal system is triclinic.

(A) In a tetragonal crystal:

(a) $a = b = c, \alpha = \beta = 90° \gamma \neq 90°$

(b) $a = b \neq c, \alpha = \beta = \gamma = 90°$

(c) $a \neq b \neq c, \alpha = \beta = \gamma = 90°$

(d) $a = b \neq c, \alpha = \beta = 90° \gamma = I\,20°$

(B) The number of atoms in bcc and fcc arrangement are respectively:

(a) 1,2 (b) 2,4

(c) 4,2 (d) 2,1

(C) The crystal system of a compound with unit cell dimensions a= 0.387, b= 0.387 c= 0.504 nm and α=β=90°,γ=l20° is:

(a) Cubic (b) Hexagonal

(c) Orthorhombic (d) Rhombohedral

(D) The packing fraction for a body centred cube is :

(a) 0.42 (b) 0.54

(c) 0.68 (d) 0.74

2. Read the passage given below and answer the question that follow:

The vacant spaces between particles in closed packed structure are known as voids. The closed packed structures have both octahedral and tetrahedral voids. Number of tetrahedral voids in a unit cell is double the number of atoms in unit cell and number of octahedral voids is equal to the number of atoms in unit cell. In ccp structure, there is one octahedral void al the centre of the body and twelve octahedral voids on the edges. Each one of which is common to four other unit cells. In ccp structure, there are eight tetrahedral Voids. These voids lie on the body diagonals. two tetrahedral voids are located at each body diagonal.

(A) The total number of octahedral voids in the face centred cubic unit cell is:

(a) 8 (b) 4

(c) 10 (d) 12

(B) The percentage of empty space in a face centred cubic arrangement is

(a) 74 (b) 26

(c) 68 (d) 32

(C) The anions (A) form hexagonal close packing and atoms (M) occupy only two-third of octahedral voids in it; then the general formula of the compound is:

(a) MA (b) A_2

(c) M_2A_3 (d) M_3A_2

(D) Coordination number of octahedral void is:

(a) 3 (b) 4

(c) 6 (d) 8

3. Read the passage given below and answer the questions that follow:

Packing refers to the arrangement of constituent units in such a way that the forces of attraction among the constituent particles is maximum and the constituents occupy the maximum available space. In two-dimensions, there are square close packing and hexagonal close packing. In three dimension, however, there are hexagonal close packing, cubic packing and body centred cubic packing. HCP and CCP have same packing efficiency and same coordination number of atoms.

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement

(d) Assertion is wrong, but reason is correct statement

(A) **ASSERTION:** Packing fraction of FCC and HCP unit cells are same.

REASON : Both FCC and HCP unit cells have same packing pattern i.e. ABC ABC ABC. .....

(B) **ASSERTION:** BCC arrangement is less closely packed than CCP arrangement.
REASON : In CCP arrangement, the two atoms at the corners of the unit cell are touching each other whereas in BCC arrangement. they are not touching each other.

(C) **ASSERTION :** In BCC arrangement coordination number is eight.
REASON: In BCC arrangement atoms occupy cubic voids.

(D) **ASSERTION** : In HCP coordination number of atom is 12.
REASON: Each atom touches six atoms in its own layer. three in layer above it and three atoms in layer below it.

ANSWERS

I. MULTIPLE CHOICE QUESTIONS

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

II. FILL IN THE BLANKS

1. Molecular solid 2. Covalent bonds 3. Amorphous 4. 1/8 5. F-centres
6. Increases 7. P 8. 2x 9. 26 10. donor

III. ASSERTION REASON TYPE QUESTIONS

1. (c) 2. (a) 3. (b) 4. (d) 5. (d) 6. (a) 7. (b) 8. (a)

IV. ONE WORD ANSWER TYPE QUESTIONS

1. Covalent 2. AgBr
3. CO_2 4. 2
5. Metallic solids 6. 4
7. Vacancy defect, Schottky defect
8. Metal excess defect (Anionic vacancies, F-centres)
9. -74%
10. Interstitial defect

CASE STUDY BASED QUESTIONS

PASSAGE: 1 :	(A)	b	(B)	b	(C)	b	(D)	c
PASSAGE: 2:	(A)	b	(B)	b	(C)	c	(D)	c
PASSAGE: 3	(A)	c	(B)	c	(C)	a	(D)	a

UNIT TEST
CHAPTER-1
THE SOLID STATE

TIME ALLOWED:1 HR. **M.M. : 20**

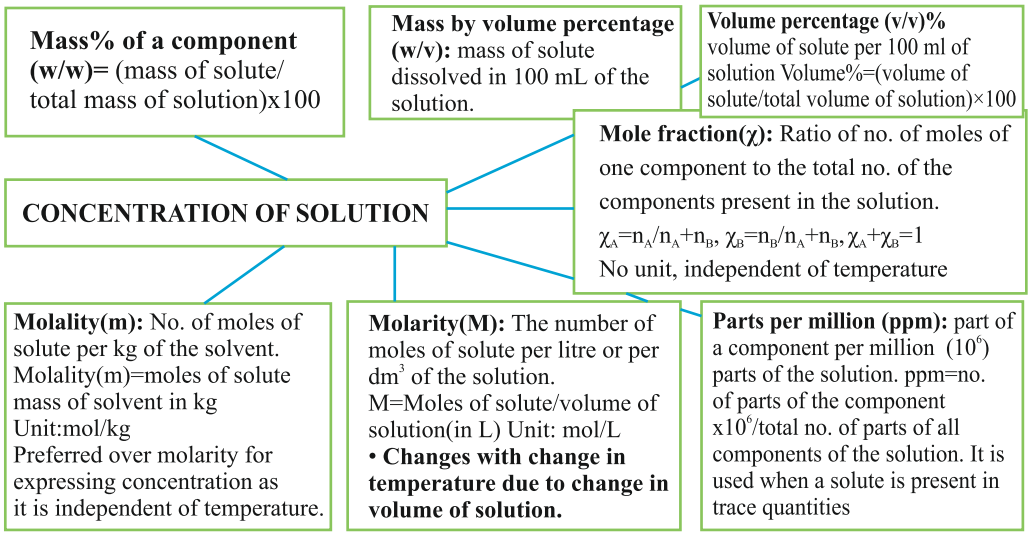
1. Which stoichiometric defect in crystal increases density of the solid? 1
2. A solid is hard, electrical insulator in solid as well as in molten state and melts at very high temperature. What type of solid is it? 1
3. A cubic solid is made of two elements P and Q Atoms of Q are at the corners of the cube and P at the body centre. What is the formula of the compound. 1
4. Non stoichiometric ZnO is yellow in colour, why? 1
5. Why Frenkel defect is not found in pure alkali metal halides? 1
6. Assign reason for the following:
   (i) Amorphous solids are isotropic in nature.
   (ii) The conductivity of metals decreases with increase in temperature. 2
7. In a solid, oxide ions are arranged in ccp. Cations A occupy $1/6^{th}$ of the tetrahedral voids and cations B occupy 1/3rd of the octahedral voids. What is the formula of the compound? 2
8. Define the following terms:
   (i) Primitive unit cells
   (ii) Void
   (iii) F-Centre 3
9. Calculate the efficiency of packing in case of a metal crystal for face centred-cubic (with the assumption that atoms are touching each other). 3
10. Calculate the density of copper which crystallises in a face centred cubic lattice structure. The radius of copper atom is 128pm. Given Atomic mass of copper= $63.5 gmol^{-1}$) 5

UNIT 2

Solutions

Points to Remember

- **SOLUTION:** A homogeneous mixture of two or more chemically non-reacting substances, whose composition can be varied within certain limits.
- A binary solution has two constituents one solute and one solvent.
- Solvent is the component present in largest amount and solute in smaller amount(in terms of moles).
- The solutions may be gaseous, liquid or solid depending upon the physical state of solvent.



HENRY'S LAW: The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution"

$p=K_H\chi$, K_H is Henry's law constant.

Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

Applications of Henry's Law

(i) **Carbonated beverages:** To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) **In deep sea diving.** To avoid bends, toxic effects of high concentration of nitrogen in the blood the tanks used by scuba divers are filled with air diluted with He.

(iii) **For climbers or people living at high altitude.** Concentration of O_2 in the blood and tissues is so low that they feel weak and are unable to think properly, a disease called anoxia.

RAOULT'S LAW

FOR A SOLUTION OF VOLATILE LIQUIDS:
The partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. If A and B are the two volatile components of solution then

$p_A = p_A^0 \chi_A$

$p_B = p_B^0 \chi_B$

Where p_A and p_B are partial vapour pressure of component 'B' respectively in solution. p_A^0 and p_B^0 are vapour pressure of pure components 'A' and 'B' respectively.

FOR A SOLUTION CONTAINING NON-VOLATILE SOLUTE: The vapour pressure of the solution is directly proportional to the mole fraction of the solvent.

$p_A = \chi_A$
$p_A = p_A^0 \chi_A$

Effect of adding non-volatile solute on vapour pressure of a liquid. The vapour pressure of a liquid decrease if some non-volatile solute is dissolved in it because some molecules of the solvent on the surface are replaced by the molecules of the non-volatile solute.

- **Raoults' law becomes a special case Henry's law** in which K_H becomes equal to P_A^0, i.e., vapour pressure of pure solvent.

TYPES OF LIQUID-LIQUID SOLUTIONS ON THE BASIS OF RAOULT'S LAW

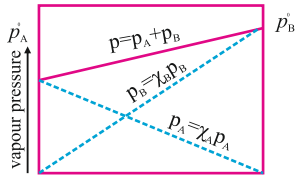
(Let A and B be the two liquids in solution.)

IDEAL SOLUTIONS

- Solutions which strictly obey Raoult's law over the entire range of concentration
- The interactions between solute and solvent are similar to those in pure components.

$P_A = P_B^0 \chi_A$ $P_B = P_B^0 \chi_B$
$\Delta H_{mix} = o$
$\Delta V_{mix} = o$

- Benzene + toluene, hexane + heptane, bromoethane + chloroethane



Graph for an ideal solution

NON-IDEAL SOLUTIONS

- Solutions which do not obey Raoult's law over the entire range of concentration
- The interactions between solute and solvent are different from those of pure components.

$P_A = P_B^0 \chi_A$ $P_B = P_B^0 \chi_B$
$\Delta H_{mix} \neq o$
$\Delta V_{mix} \neq o$

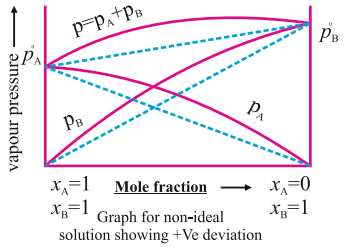
- Two types (i) Solutions showing positive deviations from Raoult's law.
  (ii) Solutions showing negative deviations from Raoult's law.

TYPES OF NON-IDEAL SOLUTIONS

NON-IDEAL SOLUTIONS SHOWING POSITIVE DEVIATION FROM RAOULT S LAW

- solute - solvent interactions are weaker than solute - solute and solvent - solvent interaction

$p_A > p_A^0 \chi_A$; $p_B > p_B^0 \chi_B$
$\Delta_{mix}H > 0$
$\Delta_{mix}V > 0$
e.g. Acetone and ethanol, Water and ethanol, Acetone and benzene.

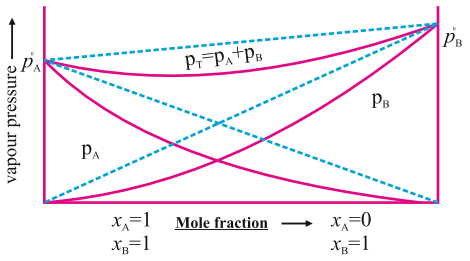


Graph for non-ideal solution showing +Ve deviation

NON-IDEAL SOLUTIONS SHOWING NEGATIVE DEVIATION FROM RAOULT S LAW

- solute - solvent interactions are stronger than solute - solute and solvent - solvent interaction

$p_A < p_A^0 \chi_A$; $p_B < p_B^0 \chi_B$
$\Delta_{mix}H < 0$
$\Delta_{mix}V < 0$
e.g. Acetone and aniline, Water and nitric acid, Water and HCl



AZEOTROPES

Liquid mixture, having the same composition, in liquid and vapour phase and boiling like a pure liquid is called a constant boiling mixture or an azeotropic mixture or an azeotrope.

MINIMUM BOILING AZEOTROPE

Minimum boiling azeotropes form when solutions exhibit positive deviation from Raoult's law. e.g. ethanol - water mixture.

MAXIMUM BOILING AZEOTROPE

Maximum boiling azeotropes form when solutions exhibit negative deviation from Raoult's law. e.g. nitric acid-water mixture.

COLLIGATIVE PROPERTIES

Physical properties of dilute solutions that depend upon the number of solute particles present in the solution irrespective of their nature.

RELATIVE LOWERING IN VAPOUR PRESSURE

$P_A^0 - P_A/P_A^0 = \chi_B$

P_A^0 = Vapour pressure of solvent, P_A = Vapour pressure of solution

Where $P_A^0 - P_A/P_A^0$ is relative lowering in vapour pressure. χ_B = mole fraction of solute

$\chi_B = n_B/n_A+n_B$

For dilute solution, $n^B << n^A$, hence n^B is neglected in the denominator.

$P_A^0 - P_A/P_A^0 = n_B/n_A$

$P_A^0 - P_A/P_A^0 = w_B/M_A/w_A M_B$

w_B = mass of solute

M_B = molar mass of solute

w_A = mass of solvent

M_B = molar mass of solvent

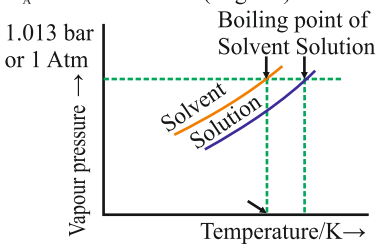
ELEVATION IN BOILING POINT (ΔT_b)

$\Delta T_b \propto m$, $\Delta T_b = k_b m$; m=molality

k_b = molal elevtion constant / Ebullioscopic constant. It is the elevation in boiling point when the molality of solution is unity. SI unit : K kg mol^{-1}

Elevation in boiling point and Molar mass of solute $M_B = k_b\ 1000 w_B/\Delta T_b W_A$

M_B=Molar mass of solute, w_B = mass of solute, w_A= mass of solvent (in gram)



COLLIGATIVE PROPERTIES

DEPRESSION IN FREEZING POINT (ΔT_f)

$\Delta T_f \propto m$, $\Delta T_f = K_f.m$

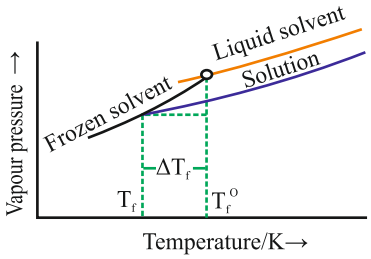
K_f = molal depression constant / Cryoscopic constant. It is the depression in freezing point when the molality of solution is unity. SI unit : K kg mol^{-1}

Depression in freezing point and Molar mass of solute

$M_B = k_f\ 1000 w_B/\Delta T_f w_A$

M_B= Molar mass of solute, w_B = mass of solute, W_A=mass of solvent (in gram)

APPLICATION : Ethylene glycol is used as antifreeze (causes depression in freezing point) in automobiles.



OSMOTIC PRESSURE (π)

The excess pressure that must be applied to a solution side to prevent osmosis i.e. to stop the passage of solvent molecules into it through semi-permeable membrane is called osmotic pressure.

$\pi \propto C$, $\pi \propto T$, $\pi = CRT$,

C = Molarity of solution, $C = n_B/V$, V=volume of solution (L), n_B=no. of moles of solute

$\pi V = n_B RT$

$\pi = w_B RT/M_B V$

R=0.0821L atm K^{-1} mol^{-1} ; T=Temperature in Kelvin

ISOTONIC SOLUTIONS

Two solutions having same osmotic pressure and same concentration are called isotonic solutions. Hypertonic solution have higher osmotic pressure and hypotonic solution have lower osmotic pressure than the other solution.

0.91% of sodium chloride is isotonic with fluid present inside human red blood cells.

REVERSE OSMOSIS- If a pressure higher than osmotic pressure is applied on the solution the solvent will flow from the solution into the pure solvent through the semi permeable membrance. It is used in the desalination of sea water.

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. The molality of 98% H_2SO_4 (density= 1.8 g/mL) by weight is:
   (a) 6 m (b) 18 m
   (c) 10 m (d) 4 m
2. Which of the following does not show positive deviation from Raoult's law?
   (a) benzene+ chloroform (b) benzene+ acetone
   (c) benzene+ ethanol (d) benzene+ CCl_4
3. Which solution will have least vapour pressure?
   (a) 1 M glucose (b) 2 M glucose
   (c) 3 M glucose (d) 4 M glucose
4. Which condition is not satisfied by an ideal solution?
   (a) $\Delta H_{mix} = 0$ (b) $\Delta V_{mix} = 0$
   (c) $\Delta P_{mix} = 0$ (d) $\Delta S_{mix} = 0$
5. Azeotrope mixture are:
   (a) mixture of two solids
   (b) those will boil at different temperature
   (c) those which can be fractionally distilled
   (d) constant boiling mixtures
6. Which is temperature independent term?
   (a) w/W% (b) v/V%
   (c) w/V% (d) Molarity
7. Solute when dissolve in water
   (a) increases the vapour pressure of water
   (b) decreases the boiling point of water
   (c) decrease the freezing point of water
   (d) All of the above
8. The plant cell will shrink when placed in:
   (a) water (b) a hypotonic solution
   (c) a hypertonic solution (d) an isotonic solution

9. Two aqueous solutions S_1 and S_2 are separated by a semi-permeable membrane. S_2 has lower vapour pressure than S1 of a non-volatile solute, Then
   a) more solvent will flow from S_1 to S_2
   b) more solvent will flow from S_2 to S_1
   c) solvent from S_1 and S_2 will flow at equal rates
   d) no flow will take place
10. Temperature dependent concentration term is :
   (a) M (b) m
   (c) *x* (d) All of these
11. Which of the fo1lowing solutions would have the highest osmotic pressure:
   (a) M/10 NaCl (b) M/10 Urea
   (c) M/10 $BaCl_2$ (d) M/10 Glucose
12. 0.5 M aqueous solution of glucose is isotonic with:
   (a) 0.5 M KCl solution (b) 0.5 M $CaCl_2$ solution
   (c) 0.5 M Urea solution (d) 1 M solution of sucrose
13. Which of the following is true for Henry's constant ?
   (a) lt decreases with temperature
   (b) It increases with temperature
   (c) Independent on temperature
   (d) It do not depend on nature of gases.
14. Which one is the best colligative property for determination of molecular mass of polymer?
   (a) osmotic pressure (b) elevation in boiling point
   (c) depression in freezing point (d) osmosis
15. An azeotropic solution of two liquids has boiling point lower than either of them when it
   a) shows negative deviation from Raoult's Law
   b) shows no deviation from Raoult's Law
   c) shows positive deviation from Raoult's Law
   d) is saturated

16. Henry's law constant K_H of CO_2 in water at 25°C is 3 x 10^{-2} mol/Latm^{-1}. Calculation the mass of CO_2 present in 100 L of soft drink bottled with a partial pressure of CO_2 of 4 atm at the same temperatrue.
    (a) 5.28 g (b) 12.0 g
    (c) 428 g (d) 528 g
17. If osmotic pressure of 1 M urea is π, what will be the osmotic pressure for 2 M urea?
    (a) π (b) 0.1π
    (c) 2π (d) 0.2π
18. The most likely an ideal solution is:
    (a) NaCI-H_2O (b) C_2H_5OH-C_6H_6
    (c) C_7H_{16} - H_2O (d) C_7H_{16}-C_8H_{18}
19. ΔH_{mix} for solution of $CHCl_3$ and CH_3COCH_3 is.
    (a) +ve (b) 0
    (c) -ve (d) None of these
20. The solutions A, B, C and D are respectively 0.1 M glucose, 0.05 M NaCl, 0.05 M $BaCl_2$ and 0.1 M $AlCl_3$. which one of the following pairs is isotonic?
    a) A & C b) B & C
    c) C & D d) A & B

II FILL IN THE BLANKS

1. The sum of mole fractions of all the components i a three component system is equal to
2. A Solution which distils without change in composition is called .....
3. Desalination of sea water is based on the phenomenon of.....
4. Relative lowering in vapour pressure is equal to the mole fraction of .....
5. The evaporation of aqueous solution of glucose causes its molarity to .....
6. The boiling point of sea water at 1atm pressure is that of distilled water.
7. The ratio of observed value of colligative property to the calculated value of colligative property is called .....
8. The most suitable colligative property to measure molecular mass of polymers is.....
9. People taking a lot of salt develop swelling or puffiness of their tissues. This disease is called.....
10. If observed molar mass of a solute is more than calculated molar mass, then the solute undergoes..... in solution.

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement

(d) Assertion is wrong, but reason is correct statement

1. Assertion: Molality is a better method to express concentration than molarity.
   Reason: Molality is defined in terms of mass of solvent and not volume of solution .
2. Assertion: Soda bottles are sealed under high pressure.
   Reason: High pressure increases the solubility of carbon dioxide gas in solution .
3. Assertion: Non-ideal solutions always form azeotropes.
   Reason: Boiling point of an azeotrope may be lower or higher than boiling points of both components.
4. Assertion: Benzene and hexane form an ideal solution.
   Reason : Both benzene and hexane are hydrocarbons.
5. Assertion: 1 molar NaCl solution has higher boiling point than one molar urea.
   Reason: NaCl dissociates into ions in solution .
6. Assertion: Two solutions having same osmotic pressures will also have same vapour pressures.
   Reason: Lowering of vapour pressure is not a colligative property .
7. Assert ion : Helium is mixed with nitrogen and oxygen in diving cylinders
   Reason: Helium has com paratively low value.
8. Assertfon: NaCl or $CaCl_2$ is used to clear snow on roads in the hills.
   Reason: The salts depress the freezing point of water.
9. Assert ion: Molar mass of acetic acid in benzene calculated using colligative property is almost double the actual value.
   Reason: Acetic acid dimerises in solution.
10. Assert ion: Vapour pressure of a solution is more that of the pure solvent.
    Reason: The solute particles occupy certain area of the surface of the solution which reduces the amount of vapour.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Which of the following is a dimension less quantity : molarity, molality or mole fraction?
2. Liquid 'Y' has higher vapour pressure than liquid 'X' . Which of them will have higher boiling point?
3. N_2 and O_2 gases have K_H values 76.48 kbar an d 34.86 kbar respectively at 293 K temperature. Which one of these will have more solubility in water?
4. Name for k_b is_____.
5. Mention the unit of ebullioscopic constant (molal boiling point elevation constant).
6. What type of deviation from Raoult's law is exhibited the solution forming minimum boiling azeotrope?
7. For reverse osmosis to take place external pressure applied must be lesser than or greater than osmotic pressure?
8. Name the law which can explain the solubility of gases in liquids at different pressures.
9. Out of molarity and molality which is preferred for expressing the concentration of solution?
10. A decrease in temperature is observed on mixing ethanol and acet one. What type of deviation from Raoult's law is this?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark Questions)

1. 10 cm^3 of a liquid A was mixed with 10 cm^3 of liquid B. The volume of the resulting solution was found to be 19.9 cm^3 . What do you conclude?
2. Will the molarity of a solution at 50°C be same, less or more than molarity at 25°C?
3. K_H value for Ar(g), CO_2(g), HCHO(g) and CH_4(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility?
4. The dissolution of NH_4Cl in water is endothermic process. What is the effect of temperature on its solubility?
5. Why is an increase in temperature observed on mixing chloroform with acetone?
6. Out of 1 M and 1 m NaOH aqueous solutions, which is more concentrated?
7. What is the similarity between Raoult's law and Henry' s law?

8. Out of two 0.1 molal solutions of glucose and of potassium chloride, which one will have a higher boiling point and why?
9. 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 their solutions?
10. What type of liquids form ideal solutions?
11. Mention the unit of cryoscopic constant.
12. Why is an increase in temperature observed on mixing chloroform with acetone?
13. Name the disease caused by low concentration of oxygen in the blood and tissues of people living at high altitude.
14. 10 cm^3 of a liquid A was mixed with 10 cm^3 of liquid B. The volume of the resulting solution was found to be 19.9 cm^3. What do you conclude?
15. What is meant by 5% Na_2CO_3 solution (*w*/W)?
16. Will the molarity of a solution at 50°C be same, less or more than molarity at 25°C?
17. What will be the mole fraction of C_2H_5OH in aqueous solution of C_2H_5OH when solution contain equal number of moles of water and C_2H_5OH?
18. Under what condition do non-ideal solutions show negative deviation?
19. What is an antifreeze?
20. Why is vapour pressure of glucose in water lower than that of water?

SHORT ANSWER TYPE QUESTIONS (2 or 3 Mark's Questions)

1. Why are aquatic species more comfortable in cold water than in warm water?
2. Why does sodium chloride solution freeze at lower temperature than water?
3. Red blood cells shrink when placed in saline water but swell in distilled water. Explain.
4. What are minimum and maximum boiling azeotropes?
5. Calculate the molarity of pure water ($d = 1$ g mL^{-1}). [Ans. 55.55M]

6. How many grams of KCl should be added to 1 kg of water to lower its freezing point to - 8.0°C ? (K_f = 1.86 K kg/mol)

[Ans. 160.18g]

7. A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What would be the molality of the solution? (Molar mass of glucose= 180 g mol^{-1})

[Ans. 0.617m]

8. Why soda water bottle kept at room temperature fizzes on opening?

9. Explain why on addition of 1 mole of NaCl to 1 litre of water, the boiling point of water increases, while on addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

10. components of a binary mixture of two liquids A and B were being separated by distillation. After some time separation of components stopped and composition of vapour phase becomes same as th at of liquid phase. Both the components started coming in the distillate. Explain reason.

11. Calculate the molar mass of the solute, 2.175 g of which when added to 39 g of benzene, decrease the vapour pressure of the benzene by 40 mm Hg. (Vapour pressure of pure benzene= 640 mm Hg). [Ans. 65.25gmol^{-1}]

12. A 10% (w/v) solution of cane sugar (mol wt. = 342) is isotonic with a 1% solution of substance X. What is the molecular weight of X?
(Hint : For isotonic solution $\pi_1=\pi_2$ so $C_1=C_2$) [Ans. 3l g/mol]

13. What is the effect of the following changes on the osmotic pressure of a solution containing non volatile solute?
    (i) Solvent is added to the solution
    (ii) solute is added to the solution
    (iii) Temperature

LONG ANSWER TYPE QUESTIONS (5 Marks's Questions)

1. (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 1.02gL^{-1}. (Molar mass of H_2SO_4 = 98 gL^{-1}).
   [Ans. 1.02 mol/L]

2. (i) When 2.56g of sulphur was dissolved in 100g of CS_2, the freezing point lowered by 0.383K. Calculate the formula of sulphur (S_x) . [K_f for CS_2= 3.83 $K_f gmo1^{-1}$, Atomic mass of sulphur= 32$gmo1^{-1}$]
   [Ans. x=8, formula= S_8]
   (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) 0.45% sodium chloride solution?

3. (i) Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?
   (ii) 2g of benzoic acid (C_6H_5COOH) dissolved in 25g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant for benzene is 4.9Kkg mol^{-1}. What is the percentage association of acid if it forms dimer in solution? [Ans. i=0.504, α.= 99.2%]

4. (a) Give reasons for the following:
   (i) At higher altitudes, people suffer from a disease called anoxia. In this disease, they become weak and cannot think clearly.
   (ii) When mercuric iodide is added to an aqueous solution of KI, the freezing point is raised.

(b) 0.6mL of acetic acid (CH_3COOH) having density 1.06g/mL, is dissolved in 1L of water, the depression in freezing point observer for this strength of acid was 0.0205°C. Calculate the van't Hoff factor. [Ans. i = 1.041]

5. (i) Define the following terms:

(a) Molarity (b) Molal elevation constant (K_b)

(ii) A solution containing 15g urea (molar mass= 60gmol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass =180gmolL^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. [Ans. Mass of glucose : 45g]

CASE STUDY BASED QUESTION

1. **Read the passage given below and answer the qu est ions that follow:**

Dissolution of solids in water can be accompanied by absorption or evolution of heat i.e. dissolution process may be exothermic or endothermic in nature but dissolution of gases in water is an exothermic process. Dissolution of a substance in water is either due to ion dipole interaction or by hydrogen bond format ion. Dissolution of gases in water is highly affected by pressure. The quantitative relationship between the solubility of gas in liquid and pressure is given by Henry's law in the form of mathematical relationship $p=K_H\chi_B$.

(A) **Dissolution of glucose in water can be explained by:**

(a) Hydrogen bond (b) ion-ion interaction

(c) vander Waals' force (d) ion- dipole interaction

(B) **Solubility of KCl in water increases with the rise in temperature. This means that enthalpy of dissolution of KCl in water:**

(a) =O (b) <O

(c) >O (d) unpredictable

(C) **The value of K_H for N_2 gas in water at 298K is 86.76k bar, the value of K_H for N_2 in water at 303K in kbar is :**

(a 86.76 (b) >86.7 6

(c) <86.76 (d) unpredictable

2. **Read the passage given below and answer the questions that follow:**

Many biological processes depend on osmosis, which is a spontaneous process by which the solvent molecules pass through a semi permeable membrane from a solution of higher concentration to a solution of higher concentration. The name osmosis is derived from the Greek word 'osmosis' which means 'to push'. It is also important to know that the semipermeable membrance selectivity allows certain molecules in the solution to pass through it but not others. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by a semipermeable membrane, solvent flow between one to the other one in either direction is same, i.e. the net solvent flow between the two isotonic solution is zero.

In the following questions a statement of assertion followed by a statement or reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements 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.

(A) **ASSERTION:** Among all the colligative properties, osmotic pressure measurement provides better method for determination of the molecular mass of the solute.

REASON: Osmotic pressure measurement cannot be carried at room temperature.

(B) **ASSERTION**: The osmotic pressure of 0.1 M urea solution is less than 0.1 M NaCl solution.

REASON : Osmotic pressure is not a colligative property.

(C) **ASSERTION** : The molecular mass of polymers cannot be calculated using the boiling point or freezing point method.

REASON : The boiling point method for determining the molecular mass is used for compounds stable at high temperature.

(D) **ASSERTION** : The elevation in boiling point for two isotonic solutions is same .

REASON : The boiling point depends upon concentration of solute.

3. **Read the passage given below and answer the questions that follow:**

The colligative property of a solution is a property that depends only on the number of solute particles present, not on their identity. An ideal solution is a solution in which all components obey Raoult's law (i.e., $P_A = x_A P^0_A$) throughout the composition range. The vapour pressure of a binary volatile mixture is $P = P^0_B + (P^0_A - P^0_B)\chi_A$. The composition of the vapour is given by $Y^A = x_A P_A^0 / P_B^0 + (P_A^0 - P_B^0)x_A$ and $Y_B = 1 - Y_A$. The total vapour pressure of a mixture is $P = P_A^0 P_B^0 / P_A^0 + (P_B^0 - P_A^0)Y_A$. Azeotrope is a mixture that boils without change in composition. In colligative properties, the elevation of boiling point is given by $\Delta T = kbm$ and the depression of freezing point by $\Delta T_f = k_f m$. During dissociation of ionic electrolytes, the van't Hoff factor equals, $i = 1 + (n-1)\alpha$.

During association of electrolytes, $I = 1 - \beta + \beta/n$

Here α and β are the degrees of dissociation and association, respectively, of electrolytes.

(A) **The vapour-phase compositions in two binary liquid mixtures follow:**

(a) Boyle's law (b) Dalton's law

(c) Raoult's law (d) Henry's law

(B) **The mole fraction of a solute is 0.4. The relative lowering of vapour pressure is :**

(a) 60% (b) 80%

(c) 40% (d) 20%

(C) **Which is not a colligative property?**

(a) Elevation in boiling point (b) Boiling point

(c) Depression in freezing point (d) Osmotic pressure

(D) **The most accurate method for the measurement of molar mass is:**

(a) osmotic pressure (b) ebullioscopy

(c) cryoscopy (d) Raoult's law

ANSWERS

I MULTIPLE CHOICE QUESTIONS

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

II FILL IN THE BLANKS

1.	One	2.	Azeotropic mixture
3.	Reverse osmosis	4.	Solute
5.	Increase	6.	Greater than
7.	van' t Hoff factor	8.	Osmotic pressure
9.	Edema	10.	Association

III ASSERTION REASON TYPE QUESTIONS

1.	(a)	2.	(a)	3.	(d)	4.	(c)
5.	(a)	6.	(d)	7.	(c)	8.	(a)
9.	(a)	10.	(d)				

IV ONE WORD ANSWER TYPE QUESTIONS

1.	Mole fraction	2.	X	3.	0_2
4.	3	5.	$Kkgmol^{-1}$	6.	Positive deviation
7.	Greater	8.	Henry's law	9.	Molality
10.	Positive				

CASE STUDY TYPE QUESTIONS:

PASSAGE: 1 (A) a (B) c (C) b

PASSAGE: 2 (A) c (B) c (C) a (D) c

PASSAGE : 3 (A) c (B) c (C) b (D) a

UNIT TEST
CHAPTER-2
SOLUTIONS

TIME ALLOWED:1 HR. **M.M. 20**

1. 250g fluoride is present in 1000 kg toothpaste sample, concertation of fluoride in ppm is 1

   (a) 250 ppm (b) 25 ppm

   (c) 2500 ppm (d) 4 ppm

2. At a given temperature, the osmotic pressure of a concentrated solution of a substance 1

   (a) is higher than that of a dilute solution.

   (b) is lower that of a dilute solution

   (c) is same as that of a dilute solution

   (d) cannot be compared with osmotic pressure of dilute solution.

3. The value of Henry's law constant K_H is: 1

   (a) Greater for gases with higher solubility

   (b) greater for gases with lower solubility

   (c) constant for all gases

   (d) not related with the solubility of gases

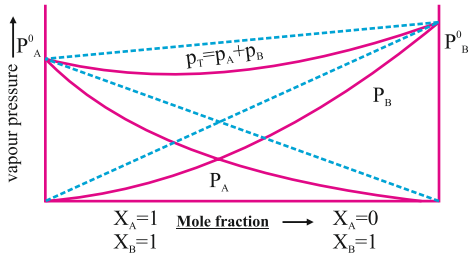
4. What type of deviation from Raoult's law is shown by the liquid mixture forming minimum boiling azeotrope? 1

5. Justify that relative lowering in vapour pressure is a colligative property. 1

6. Draw the graph between vapour pressure and temperature and explain the elevation in boiling point of a solvent in solution. 2

7. CCl_4 and water are immiscible whereas ethanol and water are miscible in all proportions. Explain . 2

8. The graphical representation of vapour pressures of two component system as a function of composition is given below. On the basis of graph answer the questions that follow: 3



(i) Are the A-B interactions weaker, stronger or of the same magnitude as A-A and B-B?

(ii) Name the type of deviation from Raoult's law exhibited by this solution.

(iii) Predict the sign of Δ_{mix} H for this system.

(iv) Predict the sign of Δ_{mix} V for this solution.

(v) Give one example of such a solution.

(vi) What type of azeotrope will this system form?

9. A solution containing 1.9g per 100 mL of KCl (molar mass=74.5 $gmol^{-1}$) is isotonic with a solution containing 3g per 100 mL of urea (molar mass=60$gmol^{-1}$). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature. 3

10. (i) Boiling point is not a colligative property but elevation in boiling point is a colligative property. Comment. 5

(ii) What happens when we place the red blood cell in distilled water?

(iii) State Raoult's law for a solution containing non-volatile solute.

(iv) Define Cryoscopic constant.

UNIT 3

Electrochemistry

Points to Remember

Galvanic cells: A galvanic cell is a device in which chemical energy is converted into electrical energy.e.g. Daniell cell.

- Daniell cell consists of two beakers containing $CuSO_4$ and $ZnSO_4$ solutions. A zinc rod is dipped into $ZnSO_4$ while a copper rod is dipped into $CuS0_4$ solution. In this cell zinc reacts with copper (II) ions and produces metallic copper and zinc (II) ion according to the reaction :

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Electrons flow from anode to cathode in the external circuit. The solutions of two beakers are connected by salt bridge.

Functions of salt bridge :

(i) It allows the flow of current by completing the electrical circuit.

(ii) It maintains electrical neutrality of the cell.

Electrode Potential

The potential difference that develops between the metal and its electrolyte is known as electrode potential.

(a) **Oxidation potential:** The tendency of an electrode to lose electrons or to get oxidised is called oxidation potential. For example, $M(s) \longrightarrow M^{n+}(aq) + ne^-$

(b) **Reduction potential:** The tendency of an electrode to gain electrons or to get reduced is called reduction potential. For example, $M^{n+}(aq) + ne^- \longrightarrow M(s)$

According to latest IUPAC convention, the half reactions are always written as reduction half reaction and their potentials are represented by reduction potentials

$$E^{o}_{ox} = - E^{o}_{red}$$

Cell potential of a cell

The potential difference between the two electrodes of galvanic cell is called the cell potential and is measured in volts.

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

- Half cell potential or electrode potential of M^{n+}/M cannot measured directly because a half cell whether oxidation or reduction half cell cannot work on its own we cannot determine the absolute electrode potential of an electrode. To solve this problem, a reference electrode standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) is used, its standard electrode potential (oxidation as well as reduction) is arbitrarily taken as zero.

Electrochemical series or e.m.f. series

Arrangement of different electrodes in the order (increasing or decreasing) of their standard electrode potentials.

Applications of the electrochemical series:

1. **To compare the relative oxidising and reducing powers:** substances with higher reduction potentials are stronger oxidising agents.
2. **Calculation of standard emf of electrochemical cell (E^{o}_{cell}) :**
   $E^{o}_{cell} = E^{o}_{Cathode} - E^{o}_{anode}$
3. **Comparison of the reactivity of metals:** A metal with smaller reduction potential has a strong tendency to get oxidised and can displace metals having greater reduction potential from the aqueous solution of their salts.
4. **To predict whether a metal displace hydrogen from acids :** Metals having a negative reduction potential value can displace hydrogen from acid.
5. **To predict the spontaneity of a redox reaction:** E_{cell} should be positive. If emf comes out to be negative, the direct reaction as given cannot take place, the reverse reaction may takes place.

Effect of opposing potential on the cell reaction

Consider a Daniell cell: $Zn_{(s)} / Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)}/Cu$

- When Eext < l.lV, Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
- When E_{ext} > 1.1 V, flow of current in this case occurs from zinc electrode to copper electrode, the cell now **ectrolytic cell.**

NERNST EQUATION FOR SINGLE ELECTRODE

For the electrode reaction $M^{n+}(aq) + ne^{-} \longrightarrow M(s)$

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

Concentration of pure solid [M] should be taken as unity

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]} \quad (\text{since } \log_e = 2.303 \log_{10})$$

At 298 K

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

Calculation of cell potential using Nernst Equation

$$E_{cel} = E^{o}_{cell} - \frac{2.303RT}{nF} \log_{10} \frac{[PRODUCTS]}{[REACTANTS]} \quad \text{At 298K}$$

$$E_{cel} = E^{o}_{cell} - \frac{0.059.}{n} \log_{10} \frac{[PRODUCTS]}{[REACTANTS]}$$

EQUILIBRIUM CONSTANT (Kc) FROM NERNST EQUATION

$$E^{o}_{cell} = \frac{2.303RT}{nF} \log_{10} K_c$$

$$E^{o}_{cell} = \frac{0.059}{n} \log_{10} K_c \quad \text{at 298 K}$$

GIBB'S ENERGY CHANGE AND CELL POTENTIAL

$$\Delta_r G = nF\, E_{cell}$$

$$\Delta_r G^{o} = -nF\, E^{o}_{cell}$$

For cell reaction to be spontaneous, ΔG^{o} must be negative, the value of E^{o} cell must be positive.

FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT

$$\Delta_r G^{o} = -2.303\, RT \log_{10} K_c$$

CONDUCTORS: Substances that allow the flow of electric current through them are called electrical conductors .

Metallic / electronic Conductor

- Flow of electricity due to movement of electrons
- No chemical change as there is no transfer of matter.
- Faraday's law is not followed
- Conduction decreases with temperature because kernels start vibrating faster which interfere in the flow of electrons.

Electrolytic conductor

- Flow of electricity due to movement of ions
- Ions are oxidised or reduced at the electrodes, hence involve transfer of matter .
- Faraday's law is followed
- Conduction increase with temperature because dissociation increases and viscosity decreases

FACTOR AFFECTING ELECTROLYTIC CONDUCTANCE

1. **Interionic interactions**: Greater the interionic interactions lesser is the mobility of the ions, hence lesser will be conductance.
2. **Solvation of ions:** More the salvation of the ions, the lesser will be the electrical conductivity.
3. **Viscosity of the solvent:** Higher the viscosity of the solvent, lesser is the mobility of ions.
4. **Temperature:** As the temperature of the electrolytic solution is increased, the kinetic energy of the ions in the solution increases, hence their mobility increases. This results in the increase of electrical conductance of the electrolytic solution.
5. **Effect of concentration of solution:** More the concentration of electrolytic solution smaller will be its electrical conductivity.

- Weak electrolyte ionise to a lesser extent in concentrated solution, on dilution ionisation increases which causes increase in conductivity.
- Strong electrolyte ionise completely. On dilution interionic attraction decreases, so mobility of ions increases, consequently conductance increases.

Electrolytic conduction

Resistance (R) : A measure of obstruction in the flow of current. Unit: ohm (Ω)

$R \propto \frac{l}{a}$ $R = \rho \frac{l}{a}$

p, constant of proportionality, known as specific resistance or resistivity.

Resistivity or specific resistance (ρ) :

$\rho = R \frac{a}{l}$

Resistivity may be defined as the resistance offered by the conductor of 1 m length with area of cross section equal to 1 m^2

Unit : ohm. m or Ω. m

Conductance (G): Conductance is a measure of the ease with which current flows through the conductor. It is reciprocal of electrical resistance.

$$G = 1/R$$

Units: ohm^{-1} or Ω^{-1} *i.e.*, Siemen (S), $1S = 1\Omega^{-1}$

Specific conductance or conductivity (k): conductivity is the reciprocal of resistivity.

$$k = 1/\rho = \frac{1}{R}\cdot\frac{l}{a}$$,l/a is known as cell constant (G*)

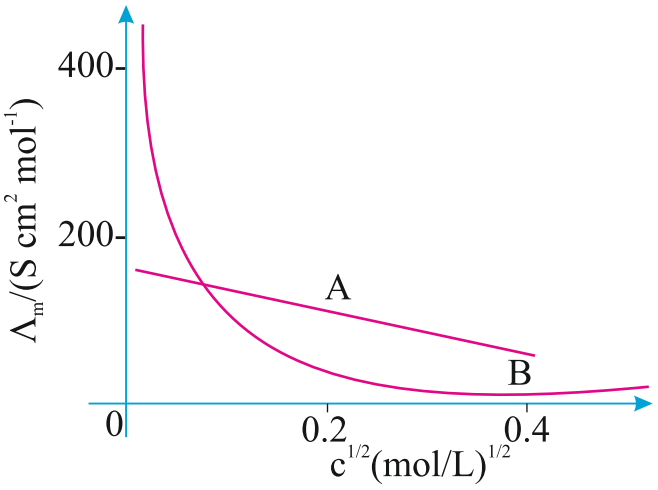
k = C. G* i.e . Conductivity= Conductance x cell constant

Units of k= ohm^{-1} cm^{-1} or Sl units are ohm^{-1} m^{-1} or S m^{-1}

- **Molar conductivity (Λm) -** of a solution is the conductance of all the ions produced from one mole of the electrolyte dissolved in a given volume of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them.

  Λ_m= k x 1000/Molarity, Unit: $ohm^{-1}cm^2 mol^{-1}$ (Scm^2mo1^{-1}) , Sl unit= Sm^2mo1^{-1}
- **Effect of dilution**. Conductance increases (because total no. of ions increase), conductivity decreases (because no. of ions per unit volume decreases), molar conductivity increase with dilution.
- **Variation of molar conductivity with concentration**. For a strong electrolyte, it is given by **Debye - Huckel - Onsager equation**: $\Lambda_m = \Lambda^O_m - A\sqrt{c}$ where A is a constant depending upon the nature of the solvent and temperature. Λ^O_m **is limiting molar conductivity and it is defined as the molar conductivity of electrolyte when concentration appproaches zero i.e. at infinite dilution.**

  <u>Graphical representation of the variation of Λ_m vs$\sqrt{c}$</u>



It can be seen that if we plot Λ_m against $c^{1/2}$, we obtain a straight linewith intercept equal to Λ^O m and slope equal to '-*A*'.

Reasons for increase of Λ_m with dilution. Molar conductivity of a strong electrolyte increases with dilution because interionic attractions decrease with dilution. Small deviations at higher concentration are due to large interionic attractions. Molar conductivity of a weak electrolyte increases with dilution because dissociation increases with dilution.

Inability to determine limiting molar conductivity experimentally for a weak electrolyte. Molar conductivity at infinite for a strong electrolyte can be found by extrapolation to zero concentration but that of weak electrolyte cannot be thus found.

KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

For e.g. $Al_2(SO_4)_3$ $\Lambda^0m[Al_2(SO_4)_3] = 2\Lambda^0m(Al^{3+}) + 3\lambda^0m(SO_4^{2-})$

Applications of Kohlrausch's Law

a) In calculation of limiting molar conductivity of weak electrolyte

b) In calculation of degree of dissociation, i.e., $\alpha = \Lambda^c_m/\Lambda^0_m$

c) In calculation of dissociation constant (K_c) by using value of a, $K_c = c\alpha^2/1-\alpha$

ELECTROLYTIC CELLS : The device in which conversion of electrical energy into chemical energy is done is known as electrolytic cell. An electrolytic cell consists of a vessel for electrolytic solution or molten electrolyte in which two metallic electrodes connected to a source of electric current are immersed.

PRODUCTS OF ELECTROLYSIS: If an electrolytic solution consists of more than two ions then during electrolysis all the ions are not discharged simultaneously but certain ions are liberated at the electrode in preference to the others. This is based on the principle of preferential discharged theory which states that the ion which requires least energy is discharged first.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. The potential of a hydrogen electrode at pH=10 is :

   (a) 0.591 V (b) 0.00 V

   (c) -0.591 V (d) -0.059 V

2. How many coulomb are required for the oxidation of 1 mol of H_2O_2 to O_2?

   (a) 9.65×10^4C (b) 93000 C

   (c) 1.93×10^5C (d) 19.3×10^2C

3. KCl is used in salt bridge because:

   (a) It forms a good jelly with agar -agar

   (b) It is a strong electrolyte

   (c) It is a good conductor of electricity

   (d) Migration factor of K^+ and Cl^- ions are almost equal

4. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^0cell will be respectively.

   (a) -ve, < 1, - ve (b) - ve, > 1, - ve

   (c) - ve, > 1, + ve (d) + ve, > 1, - ve

5. lf a salt bridge is removed between the half cells, the voltage:

   (a) drops to zero (b) does not change

   (c) increase gradually (d) increases rapidly

6. The process in which chemical change occurs on passing electricity is termed :

   (a) Ionisation (b) neutralisation

   (c) electrolysis (d) hydrolysis

7. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is:

   (a) 1F (b) 3F

   (c) 5F (d) 4F

8. The value of Λ_m^0 for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 $Ohm^{-1}cm^2 mol^{-1}$ respectively. Calculate Δ_m^0 for NH_4OH solution.

   (a) 215.5 $Ohm^{-1}cm^2 mol^{-1}$ (b) 251.5 $Ohm^{-1}cm^2 mol^{-1}$

   (c) 244.7 $Ohm^{-1}cm^2 mol^{-1}$ (d) 351.5 $Ohm^{-1}cm^2 mol^{-1}$

9. In a Galvanic cell the electrical work done is equal to :
   (a) Free energy change (b) mechanical work done
   (c) thermodynamic work done (d) all of the above
10. Zn cannot displace following ions from their aqueous solution :
   (a) Al^{3+} (b) cu^{2+}
   (c) Fe^{2+} (d) Na^{+}
11. Electrical work done is equal to :
   (a) $-n FE^{0}_{cell}$ (b) $n FE^{0}_{cell}$
   (c) $n E^{0}_{cell}$ (d) None of these
12. Which are not the following decrease with increase in concentration?
   (a) Conductance (b) Molar conductance
   (c) Conductivity (d) All of the above
13. The standard electrode potential values of three metallic cations, X, Y, Z are 0.52,-3.03 and -l.18V, respectively. The order of reducing power of the corresponding metals is
   (a) Y > Z > X (b) X > Y > Z
   (c) Z > Y > X (d) Z > X > Y
14. How is elctrical conductance of a conductor related with lenght and area of cross section of the conductor?
   (a) $G=k.l.a^{-1}$ (b) $G=l.a.k^{-1}$
   (c) $G=k.a.l^{-1}$ (d) $G=k.l.a^{-2}$
15. What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?
   (a) Copper will deposit at cathode. (b) Copper will dissolve at anode.
   (c) Oxygen will be released at anode. (d) Copper will deposit at anode.
16. The cell constant of a conductivity cell_____.
   (a) changes with change of electrolyte. (b) changes with change of concentration of electrolyte.
   (c) changes with temperature of electrolyte. (d) remains constant for a cell.
17. An electrochemical cell can behave like an electrolytic cell when
   (a) $E_{cell} = 0$ (b) $E_{cell} > E_{ext}$
   (c) $E_{ext} > E_{cell}$ (d) $E_{cell} = E_{ext}$
18. Which of the following statement is not correct about an inert electrode in a cell?
   (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.

19. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called
    (a) Cell potential
    (b) Cell emf
    (c) Potential difference
    (d) Cell voltage
20. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that :
    (a) this redox couple is a stronger reducing agent than the H^+/H_2 coupl e.
    (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.

II FILL IN THE BLANKS:

1. The conductance of a solution placed between two opposite faces of a centimetre cube is called..... .
2. Strong electrolytes give almost a linear plot of Λ_m versus..... .
3. In a galvanic cell, the electrons flow from ..... to.....through connecting wire.
4. The unit of resistivity is ..... .
5. For the spontaneous cell reaction, E^0 should be..... .
6. Conductivity of an electrolytic solution.....with increase in dilution.
7. The unit of cell constant is.....
8. An aqueous solution of copper nitrate.....be stored in iron vessel.
9. Protection of iron by coating with zinc is called .....
10. To deposit 2 mol of Ca from $CaCl_2$.....electricity is required .

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

1. **Assertion:** When aqueous sodium chloride solution is electrolysed, Oxygen gas is produced at the anode.
   Reason : It is due to the overpotential for oxidation of water to oxygen.
2. **Assertion:** Molar conductivity of an electrolyte increases with decrease in concentration.
   Reason: The mobility of ions decrease with increase in concentration.
3. **Assertion:** Reduction of 1 mole of Cu^{2+} ions require 2 faraday of charge.
   Reason: 1 Faraday is equal to the charge of 1 mole of electrons.
4. **Assertion:** Lechlanche cell gives constant voltage throughout its life.
   Reason: The overall reaction of button cell does not involve any ion in solution whose concentration can changering its life time.
5. **Assertion:** Coating iron with zinc prevents rusting.
   Reason: The coating of zinc prevents moist air to come in contact with the metal.
6. **Assertion:** More negative the electrode potential greater is the power to act as oxidising agent .
   Reason: As the electrode potential becomes more negative there is greater tendency to undergo oxidation.
7. **Assertion:** Secondary cells are cells which can be recharged after use.
   Reason: The products are electrolysed back to the initial reactants during recharge of the cell.
8. **Assertion :** Kohlrausch law helps to find the molar conductivity of weak electrolyte at infinite dilution.
   Reason : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.
9. **Assertion :** Fluorine is the best oxidising agent.
   Reason : Fluorine has highest reduction potential.
10. **Assertion:** Λ_m for weak electrolytes shows a sharp increase when the electrolyte solution is diluted.
    Reason: For weak electrolytes degree of dissociation increases with dilution of solution.

IV ONE WORD ANSWER TYPE QUESTIONS

1. How much charge in Faraday is required for the reduction of 1 mol Al^{3+} to Al?
2. What is the effect of increase of temperature on ionic conductance?
3. What flows in the internal circuit of a Galvanic cell?
4. Name of the reference electrode in determining the standard electrode potential.
5. Can E^0_{cell} for a cell reaction ever be equal to zero?
6. Reciprocal of resitivity.
7. How will pH of brine (aqueous NaCl solution) be affected when it is electrolysed?
8. What is the name given to the constant quantity of charge carried by one mole electrons?
9. Name of refrence electrode used for determination of E^0 instead of NHE/SHE.
10. What is the effect of presence of salt in water on the rate of rusting of iron?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Why is it not possible to measure single electrode potential ?

Ans. Because the half cell containing single electrode cannot work independently, as charge cannot flow on its own in a single electrode

Q. 2. Name the factors on which emf of a cell depends.

Ans. Emf of a cell depends on following factors

(a) Nature of reactants

(b) Concentration of solution in two half cells

(c) Temperature

Q. 3. What is the effect of temperature on the electrical conductance of metal ?

Ans. Temperature increases, electrical conductance decreases

Q. 4. What is the effect of temperature on the electrical conductance of electrolyte ?

Ans. Temperature increases, electrical conductance increases.

Q. 5. What is the relation between conductance and conductivity ?

Ans. $\Lambda^c_m = \frac{k}{C}$

Q. 6. Reduction potentials of 4 metals A, B, C and D are – 1.66 V, + 0.34 V, + 0.80 V and – 0.76 V. What is the order of their reducing power and reactivity ?

Ans. A > D > B > C

Q.7. Why Na cannot be obtained by the electrolysis of aqueous NaCl solution ?

Ans. Due to low reduction potential. Na^+ ions are not reduced at cathode. Instead. H^+ are reduced and H_2 is obtained

Q.8. What is the use of platinum foil in the hydrogen electrode ?

Ans. It is used for the in and out flow of electrons.

Q.9. Why Λ_m° for CH_3COOH cannot be determined experimentally ?

Ans. Molar conductivity of weak electrolytes keeps on increasing with dilution and does not become constant even at very large dilution.

Q.10. Why does the conductivity of a solution decrease with dilution ?

Ans. Conductivity of a solution is dependent on the number of ions per unit volume. On dilution. the number of ions per unit volume decreases. hence the conductivity decreases

Q.11. How does the pH of Aqulous NaCl solution be affected when it is electrolysed?

Ans. When Aqulous NaCl solution is electrolysed, H_2 is liberated at cathode, Cl_2 at anode and NaOH is formed in the solution Hence pH of solution increases

Q.12. Which reference electrode is used to measure the electrode potential of other electrodes?

Ans. Standard hydrogen electrode (SHE) whose electrode potential is taken as zero.

Q.13. Out of zinc and tin, which one protects iron better even after cracks and why ?

Ans. Zinc protects better because oxidation potential of zinc is greater but that of tin is less than that of iron.

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How can you increase the reduction potential of an electrode for the reaction :

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

Ans. Nernst equation is

$$E_{M^{n+}/M} = E^{\ominus}_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \text{ at } 298k$$

$E_{M^{n+}/M}$ can be increased by

(a) Increase in concentration of M^{n+} ions in solution

(b) By increasing the temperature

2. Calculate emf of the following cell at 298 K :

$$Mg(s) + 2Ag^+ (0.0001M) \rightarrow Mg^{2+} (0.130\ M) + 2Ag(s)$$

[Given : $E^{\circ}_{cell} = 3.17$ V]

Ans.

$$E = E^{\circ}_{cell} - \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17 - \frac{0.059}{2} \log \frac{.130}{(.0001)^2}$$

$$= 3.17 - 0.21 = 2.96V$$

3. How much electricity in term of Faraday is required to produce 40 gram of Al from Al_2O_3 ? (Atomic mass of Al = 27 g/mol)

Ans. $Al^{3+} + 3e^- \rightarrow Al$

27 gram of Al require electricity = 3F

40 gram of Al require electricity = $\frac{3F}{27} \times 40 = 4.44$ F

4. Calculate Λ°_m for $CaCl_2$ and $MgSO_4$ from the following data :
$\Lambda^0_m(Ca^{2+})$=119.0,Scm^2 mol^{-1}, Scm^2 mol^{-1}, Mg^{2+}=106.0, Cl^- = 76.3 and SO_4^{2-} = 160.0Scm^2 mol^{-1}

Ans. $\Lambda^{\circ}_{m(CaCl_2)} = \Lambda^{\circ}_{m(Ca^{2+})} + 2\Lambda^{\circ}_{m(Cl^-)}$ $= 119 + (2 \times 76.3) = 271.6$ S cm^2 mol^{-1}

$\Lambda^{\circ}_{m(MgSO_4)} = \Lambda^{\circ}_{m(Mg^{2+})} + 2\Lambda^{\circ}_{m(SO_4^{2-})}$ $= 106 + 160 = 266$ S cm^2 mol^{-1}

5. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

$H^+ + e^- \rightarrow \frac{1}{2}H_2$, $n = 1$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[H^+]} \qquad E = 0 - \frac{0.0591}{1} \times pH$$

E = - 0.0591 x 10 V E = - 0.591V

6. If a current of 0.5 amp flows through a metallic wire for 2 hours, how many electrons would flow through the wire ?

Ans. $q = I \times t = 0.5 \times 2 \times 60 \times 60 = 3600$ C

96500 Coulombs are equal to 6.022×10^{23} e

So, 3600 Coulombs $= \frac{6.022 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22}$ electrons

7. The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm^{-1}. Calculate molar conductivity.

Ans. Molar conductivity $= \frac{k \times 1000}{M} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}}$

$= 124.0$ S cm^2 mol^{-1}

8. The standard reduction potential for the Zn^{2+} (aq)/Zn (s) half cell is - 0.76V. Write the reactions occurring at the electrodes when coupled with standard hydrogen electrode (SHE).

Ans. At anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

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

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

9. Calculate the electrode potential of a copper wire dipped in 0.1M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 Volt.

Ans. The electrode reaction written as reduction potential is

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad n = 2$$

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34 - \frac{0.0591}{2}\log\frac{1}{0.1} = 0.3104 \text{ V}$$

10. Two metals A and B have reduction potential values – 0.76 V and + 0.34 V respectively. Which of these will liberate H_2 from dil. H_2SO_4?

Ans. Metal having higher oxidation potential will liberate H_2 from H_2SO_4. Thus, A will liberate H_2 from H_2SO_4.

11. E° values of MnO_4^-, Ce^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidizing agent.

Ans. $Cl^- < MnO_4^- < Ce^{4+}$

12. A solution of $CuSO_4$ is electrolysed for 10 mins. with a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

Ans.

$$I = 1.5 \text{ Ampere}$$

$$\text{Time} = 10 \times 60s = 600s$$

$$Q = I \times t$$

$$= 1.5 \times 600 = 900\ C$$

$$Cu^{2+} + 2e^- \rightarrow Cu\ (s)$$

2F amount of electricity deposit copper = 63.5 g

$$900\ C \text{ amount of electricity deposit copper} = \frac{63.5 \times 900}{2 \times 96500}$$

$$= 0.296 \text{ g}$$

13. Depict the galvanic cell in which the reaction

$$Zn\,(s) + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag\,(s)$$

takes place. Further show :

(a) Which of the electrode is negatively charged ?

(b) The carriers of the current in the cell.

(c) Individual reaction at each electrode.

Ans. $Zn\,(s)|Zn^{2+}\,(aq)\,||\,Ag^{+}\,(aq)|Ag\,(s)$

(a) Zn electrode (anode)

(b) Ions are carriers of the current in the cell.

(c) At anode

$$Zn\,(s) \longrightarrow Zn^{2+} + 2e$$

At cathode

$$Ag^{+} + e \rightarrow Ag\,(s)$$

14. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1} ?

Ans. Cell constant $= k \times R$

$= 0.146 \times 10^{-3} \times 1500$

$= 0.219\ cm^{-1}$

15. Determine the values of equilibrium constant K_c and $\Delta G^{\ominus}$ for the following reaction :

$$Ni\,(s) + 2Ag^{+}\,(aq) \rightarrow Ni^{2+}\,(aq) + 2Ag\,(s) \qquad E^{\ominus} = 1.05\ V$$

Ans. $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$n = 2,\ E^{\ominus}_{cell} = 1.05\ V$

$F = 96500\ C\ mol^{-1}$

$\Delta G^{\ominus} = -2 \times 1.05 \times 96500$

$= -202.650\ kJ$

$\Delta G^{\ominus} = -RT \ln K_c$

$$\ln K_c = \frac{\Delta G^{\ominus}}{RT} = \frac{-202.650 \times 10^{3}}{8.314 \times 298}$$

$K_c = 3.32 \times 10^{35}$

16. The K_{sp} for AgCl at 298 K is 1.0×10^{-10}. Calculate the electrode potential for Ag^+/Ag electrode immersed in 1.0M KCl solution. Given $E^{\theta}_{Ag^+/Ag} = 0.80$ V.

Ans. $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Cl^-] = 1.0\ M$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1\times10^{-10}}{1} = 1 \times 10^{-10}\ M$$

Now, $Ag^+ + e^- \rightarrow Ag(s)$

$$E = E^{\theta} - \frac{0.059}{1}\log\frac{1}{[Ag^+]} = 0.80 - \frac{0.059}{1}\log\frac{1}{10^{-10}}$$

$$= 0.80 - 0.059 \times 10 = 0.21\ V$$

17. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2 \text{ is } \Delta G = +960\ kJ,\ F = 96500\ C\ mol^{-1}.$$

Ans. $$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$$

$$n = \frac{6\times2}{3} = 4e^-$$

$$\Delta G = -nFE$$

$\Delta G = 960 \times 10^3\ J,\ n = 4,\ F = 96500\ C\ mol^{-1}$

$$960 \times 10^3 = -4 \times 96500 \times E$$

$$E = -2.487\ V$$

Minimum potential difference needed to reduce $Al_2O_3 = -2.487$ V

18. The cell in which the following reaction occurs :

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^0_{cell} = 0.236$ V.

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans. $n = 2$

$$\Delta G^0 = -nFE^0_{cell} = -2 \times 96500 \times 0.236\ J = -45.55\ kJ/mol$$

$$\Delta G^0 = -2.303\ RT \log K_c$$

$$\log K_c = \frac{\Delta G^0}{-2.303RT} = \frac{45.55 \times 10^3}{2.303 \times 8.314 \times 298} = 7.983$$

$$K_c = \text{antilog}\ (7.983) = 9.616 \times 10^7$$

19. 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 $\lambda^0(H^+) = 349.6$ S cm^2 mol^{-1}, $\lambda^0(HCOO^-) = 54.6$ S cm^2 mol^{-1}.

Ans. $\Lambda^0_m(HCOOH) = \lambda^0_m(H^+) + \lambda^0_m(HCOO^-)$

$= 349.6 + 54.6$ S cm^2 $mol^{-1} = 404.2$ S cm^2 mol^{-1}

$\Lambda^c_m = 46.1$ S cm^2 mol^{-1}

$HCOOH \rightleftharpoons HCOO^- + H^+$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^0_m} = \frac{46.1}{404.2} = 0.114$$

Initial conc	C mol L^{-1}	0	0
At equil.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114}$$

$$= 3.67 \times 10^{-4}$$

20. Calculate the potential of the following cell

Sn^{4+} (1.5 M) + Zn → Sn^{2+} (0.5) + Zn^{2+} (2M).

Given : $E^0_{Sn^{4+}/Sn^{2+}} = 0.13$V, $E^0_{Zn^{2+}/Zn} = -0.76$V

Will the cell potential increase or decrease, if the concentration of Sn^{4+} is increased?

Ans. $$E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log\frac{\left[Sn^{2+}\right]\left[Zn^{2+}\right]}{\left[Sn^{4+}\right]\left[Zn\right]}$$

$$= 0.89 - \frac{0.0591}{2}\log\frac{0.5\times 2}{1.5\times 1} \quad = 0.89 - \frac{0.0591}{2}\log\frac{1}{1.5} = 0.895\ V$$

On increasing the concentration of Sn^{2+}, EMF of the cell will increase.

21. $E^{\circ}(Cu^{2+}/Cu)$ and $E^{\circ}(Ag^{+}/Ag)$ is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is +ve. If the coucentration of Cu2+ is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag^{+}.

Ans. Cu is more reactive than silver, so that the cell is as Cu/Cu^{2+} (0.01M) || Ag^{+} (C)/Ag

or cell reaction $Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Cu^{2+}\right]\left[Ag\right]^{2}}{\left[Cu\right]\left[Ag^{+}\right]^{2}}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{(0.01)\times 1^{2}}{1\times\left[Ag^{+}\right]^{2}}$$

Or $[Ag^{+}] = 1.47 \times 10^{-9}$ M

22. Calculate the potential of the cell at 298 K :

Cd/Cd^{2+} (0.1M) || H^{+} (0.2M)/Pt, H_2 (0.5 atm)

Given E° for $Cd^{2+}/Cd = -0.403$ V. R = 8.314 J^{1} mol^{-1}. F = 96500 C mol^{-1}.

Ans. The cell reaction is $Cd + 2H^{+}$ (0.2M) $\rightarrow Cd^{2+}$ (0.1M) + H_2 (0.5 atm)

$$E^{\circ}_{cell} = 0 - (-0.403) = +0.403\ V$$

$$E_{cell} = 0.403 - \frac{2.303RT}{nF}\log\frac{\left[Cd^{2+}\right]\times P_{H_2}}{\left[Cd\right]\left[H^{+}\right]^{2}}$$

$$= 0.403 - \frac{2.303\times 8.314\times 298}{2\times 96500}\log\frac{0.1\times 0.5}{(0.2)^{2}}$$

$$E_{cell} = 0.403 - 0.003 = 0.40\ V$$

23. The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^{3} ohm. Calculate its resistivity, conductivity and molar conductivity.

Ans. Diameter = 1 cm, radius = 0.5 cm

$$\text{Area} = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \text{ cm}^2$$

$$\rho = \frac{R \times a}{l} = \frac{5.55 \times 10^3 \times 0.785}{50} = 87.135 \text{ ohm cm}$$

$$\text{Conductivity } (k) = \frac{1}{\rho} = \frac{1}{87.135} = 0.01148 \text{ ohm}^{-1} \text{ cm}^{-1} = 0.01148 \text{ ohm cm}$$

$$\text{Molar conductivity } \Lambda_m^m = \frac{k \times 1000}{M} = \frac{0.01148 \times 1000}{0.05} = 29.6 \text{ S cm}^2 \text{ mol}^{-1}$$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Conductivity of 0.00241M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ^o_m for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant ?

Ans.

$$\Lambda_m = \frac{k \times 1000}{M}$$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}} = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^m_m} = \frac{32.76}{390.5} = 8.39 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times \left(8.39 \times 10^{-2}\right)^2}{1 - 8.39 \times 10^{-2}} = 1.86 \times 10^{-5}$$

$$Cu^{2+} + 2e \rightarrow Cu\,(s)$$

2F of electricity deposit Cu = 63.5 g

$$1295.6 \text{ of electricity deposit Cu} = \frac{63.5 \times 1295.6}{2 \times 96500} = 0.426 \text{ g}$$

Q.2. (a) Define Kohlransh's law.

(b) Suggest a way to determine the Λ^o_m for CH_3COOH.

(c) The Λ^o_m for sodium acetate, HCl, NaCl are 91.0, 425.9 and 126.4 S cm^2 mol^{-1} respectively at 298 K. Calculate Λ^o_m for CH_3COOH.

Ans. (a) The molar conductivity at a infinite dilution for a given salt can be expressed as the sum of the individual contribution from the ions of electrolyte

(b) $\Lambda^o CH_3COOH = ?$

$$\Lambda^o CH_3COO^- + \Lambda^o H^+ = \Lambda^o CH_3COO + \Lambda^o Na^+ + \Lambda^o H^+ + \Lambda^o Cl^- - \Lambda^o Na^+ - \Lambda^o Cl^- \quad ...(i)$$

$$\Lambda^o_m CH_3COOH = \Lambda^o CH_3COONa + \Lambda^o HCl - \Lambda^o NaCl$$

(c) $\Lambda^o_m CH_3COOH = \Lambda^o CH_3COONa + \Lambda^o HCl - \Lambda^o NaCl$

$= 91.0 + 425.9 - 126.4$

$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$

Q.3. (i) Calculate E^0_{cell} for the following reaction at 298K:

$2Al(s) + 3Cu^{2+}(0.01M) \rightarrow 2Al^{3+}(0.01M) + 3Cu(s)$

Given Ecell= 1.98V [ANSWER: E^0_{cell}=1.9997V]

(ii) Using the E^0 values of A and B, predict which is better for coating the surface of iron and why?

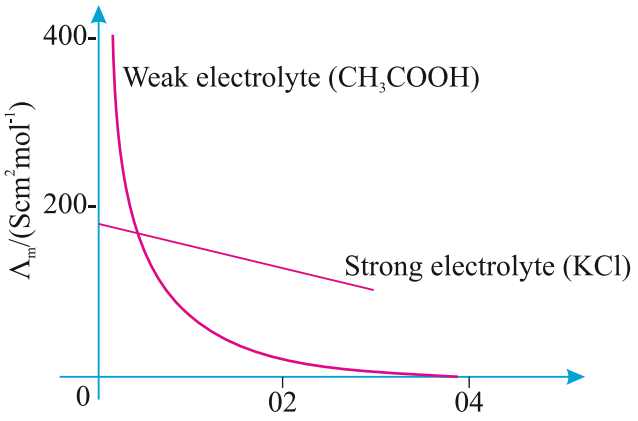
[$E^0_{Fe^{2+}/Fe}$=-2.37V, $E^0_{B2+/B}$=-0.14V]

CASE STUDY BASED QUESTIONS

1. **Read the passage given below and answer the questions that follow:**

The study of the conductivity of electrolyte solution is important for the development of electrochemical devices, for the characterisation of the dissociation equilibrium of weak electrolytes and for the understanding of charge transport by ions. The conductivity of electrolyte is measured for electrolyte solution with concentration in the range of 10^{-3} to 10^{-4}mol/L, as solution in this concentration range can be easily prepared. The variation in molar conductivity (Λ_m) of strong electrolyte with concentration is given by equation $\Lambda_m=\Lambda^0_m-A\sqrt{C}$

Where Λ^0_m is the molar conductivity at infinite dilution and Cis the concentration for solution. Following graph shows the, variation of molar conductivity with concentration for both weak and strong electrolytes.



Limiting molar conductivity cannot be determined by extrapolation of Λ_m versus$\sqrt{C}$ curve. Molar conductivity at infinite dilution can be calculated by sum of contributions of each ion. $\Lambda^0_m = \nu^+\lambda_0^+ + \nu\lambda_0^-$

Where λ_0^+ and λ_0^- are the limiting ionic conductivities of positive and negative ions respectively and v^+ and v^- are their stoichiometric coefficients in the salt molecular formula.

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.

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.

(A) **ASSERTION**: For CH_3COOH Λ^0_m cannot be determined experimentally.

REASON: CH_3COOH is a weak acid and Debye Huckel Onsager equation cannot be used. Extrapolation method cannot be employed.

(B) **ASSERTION** : The ratio of conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.

REASON : Conductivity of solution decreases with dilution whereas observed conductance increases with dilution.

(C) **ASSERTION** : Molar conductance of all electrolytes decrease with increasing concentration.

REASON : Lesser no. of ions are available per unit volume of solution at higher concentration.

(D) **ASSERTION** : 0.1 M NH_4OH at 25°C ha s lesser conductance than at 50 °C.

REASON : Conductance of a weak electrolyte decreases with increase in temperature.

2. **Read the passage given below and answer the questions that follow:**

In the Daniell cell, the copper electrode is the anode. The electrons leave the cell from the zinc and enter into the copper electrode. To complete the circuit a salt bridge (an inverted U-tube) is used. Salt bridge consists of a concentrated solution of agar-agar + KCl/ KNO_3/NH_4NO_3. The mobility of cations and anions are the same. The maximum electrical work is given by *W*e, max =ΔG. This ΔG is related to emf as ΔG =-n*FE*. The extent of reaction is measured by ΔG. The emf of a cell is determined by the Nernst equation,

$$E = E^0 - \frac{0.059}{n} \log Q.$$

The Nernst equation is also used to calculate the emf of concentration cell.

$M/M^+_{(aq)} \,||\, M^+_{(ar)}/M$. When a given cell is at equilibrium, $Q = K_{eq}$.

To calculate the standard electrode potential of a half cell like Ag/Ag^+, Cu/Cu^{2+}, one has to complete it with SHE e.g.

Pt/H2(g) /H+(aq) its $E^0 = 0$ (by convention). Front the emf study, we can calculate E^0, pH, valency, Keq, Ks, thermodynamic parameters, etc.

(A) An electrochemical cell stops working after some time because

(a) Electrode potential of both the electrodes becomes zero.

(b) Electrode potential of both the electrodes becomes equal.

(c) One of the electrode is eaten away.

(d) The reaction start s proceeding in opposite direction.

(B) **Which of the following statements is correct for a galvanic cell?**

(a) Reduction occurs at cathode. (b) Oxidation occurs at anode.

(c) Electrons flow from anode to cathode. (d) All statements are correct.

(C) **What is correct when net cell reaction is spontaneous?**

(a) E°_{cell} is negative (b) $E_{cell}>0$

(c) $E_{cell}=E^{0}_{cell}$ (d) $\Delta G<0$

(D) **The function of salt bridge is to:**

(a) allow ions to move from anode to cathode

(b) allow solutions from one half cell to the other half cell

(c) allow the current to flow through the cell and keep the solutions electrically neutral

(d) keep the level of solutions same.

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. d 2. c 3. d 4. c 5. a 6. c 7. b 8. b 9. a 10. a, d

11. a 12. a,b 13. a 14. a 15. a, b 16. a 17. c 18. d 19. c 20. b,d

II FILL IN THE BLANKS

1.	Conductivity	2.	$c^{1/2}$	3.	Anode to cathode
4.	ohm metre	5.	positive	6.	decreases
7.	m^{-1}	8.	can	9.	galvanisation

10. 4F

III ASSERTION REASON TYPE QUESTIONS

1. a 2. a 3. a. 4. d 5. c.

6. d. 7. a 8. a 9. a 10. a

IV ONE WORD ANSWER TYPE QUESTIONS

1. 3F 2. Increases 3. ions 4. Standard hydrogen electrode 5. No

6. Conductivity 7. increases 8. Faraday constant

9. Calomal electrode 10. increases

CASE STUDY TYPE QUESTIONS

PASSAGE: 1: (A) a (B) b (C) c (D) c

PASSAGE: 2: (A) b (B) d (C) b,d (D) c

UNIT TEST

CHAPTER-3

ELECTROCHEMISTRY

TIME ALLOWED :1 HR. **M.M. 20**

1. What does the negative sign in the expression $E^0_{zn2+/zn} = -0.76V$ mean? 1
2. Write unit of molar conductivity. 1
3. Suggest a way to determine the Λ_m° value of water. 1
4. Write the nernst equation of the following cell

   $Mg(s)/Mg^{2+}(0.001M) \| Cu^{2+}(0.001M)/Cu(s)$ 1
5. Why is it not possible to measure single electrode potential? 1
6. Calculate emf of the following cell 2

   $Cd/Cd^{2+}(0.10M) \| H^+(0.20M)/H_2(0.5\ atm)/Pt$

   (Given E^0 for $Cd^{2+}/Cd = -0.403V$)
7. Why on dilution Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually? 2
8. Conductivity of 2.5×10^{-4} M methanoic acid (HCOOH) is 5.25×10^{-5} Scm^{-1}. Calculate its molar conductivity and degree of dissociation. 3

   Given: $\lambda^0(H^+) = 349.5\ Scm^2mol^{-1}$ and $\lambda^0(HCOO^-) = 50.5\ Scm^2mol^{-1}$.
9. (i) The conductivity of an aqueous solution of NaCl in a cell is 92 ohm^{-1}, the resistance offered by the cell is 247.8 ohm. Calculate the cell constant. 3

   (ii) What is the effect of dilution on the conductivity of an electrolytic solution?
10. Calculate EMF and ΔG for the following cell at 298K:

    $Mg(s) | Mg^{2+}(0.01M) \| Ag^+(0.0001M) | Ag(s)$

    Given : $E^0_{Mg^{2+}/Mg} = -2.37V$, $E^0_{Ag^+/Ag} = +0.80V$ 5

UNIT 4

Chemical Kinetics

Points to Remember

RATE OF REACTION:-

For a reaction R→P

Rate of reaction = change of conc. of R or P / Time interval

Rate = -Δ[R]/Δt = Δ [P]/ Δt , This is average rate of reaction.

For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometiric coefficients.

For e.g. for a chemical reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$r_{avg} = -\Delta[N_2]\,\Delta t = -1/3\,(\Delta[H_2]/\Delta t) = \frac{1}{2}(\Delta[NH_3]/\Delta t)$

Units of rate of a reaction:- Concentration $time^{-1}$

- if concentration is in mol L^{-1} and time is in seconds then the units will be mol $L^{-1}s^{-1}$.
- In gaseous reaction, when the concentration of the gases is expressed in terms of their partial pressure, then the units will be atm s^{-1}.

INSTANTANEOUS RATE is defined as the rate of change in concentration of any one of reactant or product at a particular instant of time.

when $\Delta t \rightarrow 0$; $r_{inst} = -d[R]/dt = d[P]/dt$

Factors affecting rate of a reaction:

(a) **Nature of the reacting species:** Chemical reaction is a process in which new

(b) **Concentration of reactants:** The rate of reaction increases with increase in concentration of reactants.

(c) **Effect of temperature:** The rate of reaction is nearly double for every 10^0C rise in temperature.

(d) **Catalyst:** generally catalyst increases the rate of reaction.

(e) **Effect of radiations:** The rates of some reactions are enhanced due to absorption of radiation. These reactions are called photochemical reactions.

LAW OF MASS ACTION:

The rate of a chemical reaction is directly proportional to the product of the

molar concentrations of the reactants.

$aA+bB \rightarrow$ Products

According to law of mass action

Rate $\alpha [A]^a[B]^b$,

Rate $=k[A]^a[B]^b$

RATE CONSTANT OF A REACTION

at a given temperature may be defined as rate of the reaction when the molar concentration of each of the reactants is unity.

CHARACTERISTICS OF RATE CONSTANT

(i) Rate constant is a measure of the rate of the reaction.

(ii) Larger the value of k, faster is the reaction.

(iii) Different reactions have different values of k.

(iv) For a particular reaction, the rate constant is independent of concentration.

(v) At a particular temperature, the value of k is constant. However, it changes with temperature.

- **RATE LAW** is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation. It is determined experimentally.
- **ORDER OF A REACTION:** The sum of powers of the concentration of the reactants in the rate law expression is called the order of the chemical reaction.

  For the rate law expression

  Rate $= k[A]^x[b]^y$
- **UNITS OF RATE CONSTANTS:** Units of rate constant are different from reaction of different order : $(molL^{-1})^{1-n}$ $time^{-1}$ where 'n' is order of reaction. For gas phase reaction unit of rate constant is $(atm\ of\ bar)^{1-n}s^{-1}$

Reaction	Order ($\alpha+\beta$)	Units of rate constant
Zero order reaction	0	$\frac{molL^{-1}}{s}$-x$\frac{1}{(molL^{-1})^0}$=$molL^{-1}s^{-1}$
First order reaction	1	$\frac{molL^{-1}}{s}$ x $\frac{1}{(molL^{-1})^1}$ = s^{-1}
Second order reaction	2	$\frac{molL^{-1}}{s}$ x$\frac{1}{(molL^{-1})^2}$ =$mol^{-1}L^{-1}s^{-1}$

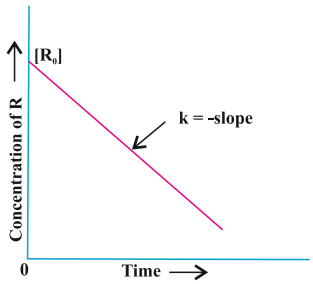
MECHANISM AND RATE LAW:

The reactions taking place in one step are called **elementary reactions.** When a sequence of elementary reactions, (called mechanism) gives us the products, the reactions are called **Complex reactions.** In complex reactions,

the rate of the reaction is determined by the slowest step in the sequence. The slowest step is called **rate determining step** in the proposed mechanism.

ZERO ORDER REACTION

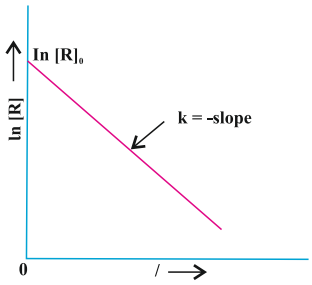
Integrated rate equation $k=[R]_0-[R]/t$

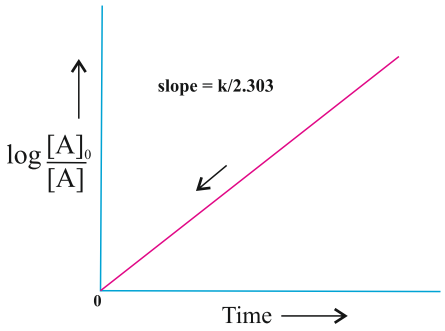


INTEGRATED RATE EQUATION FOR FIRST ORDER REACTION:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

where $[R]_0$ is initial concentration of reactants and [R] is concentration at time t.





For a typical first order gas phase reaction: $A(g) \rightarrow B(g) + C(g)$

$$\mathbf{k = \frac{2.303}{t} \log \frac{P_i}{(2P_i - P_t)}}$$

Where p_i is the initial pressure of A and P_t the total pressure at time 't'.

- **HALF-LIFE PERIOD** ($t_{1/2}$): The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

  For zero order reaction : $t_{1/2} = [R]_0/2k$

  For first order reaction : $t_{1/2} = 0.693/k$

For zero order reaction $t_{1/2} \alpha [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.

- Chemical reactions which are not truly of the first order but under certain conditions become first order reactions are called **PSEUDO FIRST ORDER REACTIONS.**

  e.g. A bimolecular reaction, in which one reactant is present in large excess and rate of reaction is independent of its concentration, the reaction follows first order kinetics.

  For example, ester hydrolysis, where water is taken in excess.

  $CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3COOH + CH_3CH_2OH$ is a bimolecular but first order reaction.

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. The initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is

(a) Zero (b) one (c) Fraction (d) none

2. Which of the following statements is correct?

(a) The rate of a reaction decreases with passage of time as the concentration of reactants descreases

(b) The rate of a reaction is same at any time during the reaction

(c) The rate of a reaction is independent of temperature change

(d) The rate of a reaction decreases with increase in concentration of reactants(s)

3. The rate constant of a reaction is $5.8 \times 10^{-21} s^{-1}$. The order of the reaction is.

(a) First order (b) zero order (c) Second order (d) Third order

4. A second order reaction between A and B is elementary reaction: A+B→Product rate law expression of this reaction will be:

(a) Rate=k[A][B] (b) Rate=$k[A]^0[B]^2$ (c) Rate=$k[A]^2[B]^0$ (d) Rate = $k[A]^{3/2}[B]^{1/2}$

5. Which of the following is pseudo first order reaction?

(a) $2H_2O_2 \rightarrow 2H_2O + O_2$

(b) $2O_3 \rightarrow 3O_2$

(c) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

(d) $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

6. A large increase in the rate of reaction for rise in temperature is due to:

(a) Increase in the number of collisions

(b) Increase in the number of activated molecules

(c) Lowering of activation energy

(d) Shortening of the mean free path.

7. Radioactive decay is an example of:

(a) first order (b) zero order (c) second order (d) 0.5 order

8. For a zero order reaction, the plot of concentration of reactant vs time is (intercept refers to concentration axis)

(a) linear with +ve slope and zero intercept

(b) linear with -ve slope and zero intercept

(c) linear with -ve slope and non-zero intercept

(d) linear with positive slope and none-zero inercept

9. The rate constant of nth order has units

(a) $litre^{1-n}mol^{n}s^{-1}$ (b) $mol^{1-n}litre^{1-n}s^{-1}$

(c) $mol^{1-n}litre^{n}s^{-1}$ (d) $mol^{1-n}lire^{n-1}s^{-1}$

10. A hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below:

$A_2 \rightarrow A+A$ (fast)

$A+B_2 \rightarrow AB+B$(slow)

$A+B \rightarrow AB$ (Fast)

The order of reaction is:

(a) 2 (b) 0 (c) 1½ (d) 1

11. In a first order, the concentration of the reactant reduced to 1/4 in 60 minutes. What will be its half life?

(a) 120 min (b) 40 min

(c)30 min (d) 25 min

12. For a complex reaction_____

(a) order of overall reaction is same as molecularity of the slowest step.

(b) order of overall reaction is less than the molecularity of the slowest step.

(c) order of overall reaction is greater than molecularity of the slowest step.

(d) molecularity of the slowest step is never zero or non integer.

13. Which of the reaction ends in infinite time?

(a) Zero order (b) First order

(c) Second order (d) Third order

14. Which one is correct for first order reaction.

(a) $t_{75\%}/t_{50\%}=1.5$ (b) $t_{75\%}/t_{50\%}=2$ (c) $t_{99.9\%}/t_{50\%}=10$ (d) $t_{99.9\%}/t_{50\%}=2$

15. The rate constant of a zero order reaction is :

(a) Independent upon initial concentration

(b) Inversely proportional to concentration

(c) Does not depend upon concentration

(d) None of these

16. For the elementary reaction M→N, the rate of dissappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is:

(a) 4 (b) 3 (c) 2 (d) 1

17. When initial concentration of a reactant is doubled in a reaction, its half life period is not affected. The order of the reaction is.

(a) Second

(b) more than zero but less than first

(c) Zero

(d) First

18. Which of the following influences the rate of reaction?

(a) Temperature

(b) Concentration

(c) Light

(d) All of these

19. Higher order(>3) reactions are rare due to

(a) shifting of equilibrium towards reactants due to elastic collisions

(b) loss of active species on collisions

(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved.

20. Half life period of a first order reaction is:

(a) directly proportional to the initial concentration of the reactant

(b) half of the rate constant

(c) same for all reactions

(d) independent of initial concentration of reactants

II FILL IN THE BLANKS

1. Hydrolysis of ethyl acetate in an acidic solution is an example of ..... order reaction.
2. If the activation energy of the reaction is low, it proceeds at ..... rate.
3. In a multi step reaction, the ..... step determines the rate of reaction.
4. For a first order reaction, the half life period is equal to .....
5. The order and molecularity of a complex reaction.....be same.
6. The inversion of cane sugar is a ..... reaction though its molecularity is.....
7. The difference of energy between activated complex and that of the reactants is called.....
8. The unit of first order rate constant when concentration is Measured in terms of pressure and time in minutes is.....
9. A first order reaction has $t_{1/2} = 6.93$min. The rate constant is .....
10. Increase in temperature increases the number of .....

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

1. **Assertion:** Hydrolysis of methyl ethanoate is a pseudo first order reaction.

Reason: Water is present in large excess and therefore its concentration remains constant throughout the reaction.

2. **Assertion:** The slowest elementary step in a complex reaction decides the rate of the reaction.

   Reason: The slowest elementary step always has the smallest molecularity.

3. **Assertion:** A catalyst increases the rate of a reaction.

   Reason: The catalyst increases the activation energy which in tum increases the rate of the reaction.

4. **Assertion:** Activation complex for the forward reaction reaction will have lower energy than that for the backward reaction in an exothermic reaction.

   Reason: Reactants have greater energy than products for an exothermic reaction.

5. **Assertion:** Increase in temperature increases rate of reaction.

   Reason: More colliding molecules will have energy greater than threshold energy.

6. **Assertion:** Unit of rate constant is independent of order of reaction.

   Reason: The power of concentration terms in the rate equation keep changing with change in order.

7. **Assertion:** The half life of a reaction is independent of initial concentration for a first order reaction.

IV ONE WORD ANSWER TYPE QUESTIONS

1. For reactions of which order the units of rate constant and rate of reaction are same?
2. What is the difference in energy between the energy of activated complex and the average energy of reactants called?
3. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?
4. What is the effect of catalyst on activation energy of reaction?
5. For a reaction half-life is observed to be independent of the initial concentration of the reactants. What is the order of reaction?
6. What is the effect of catalyst on Gibb's energy change (ΔG) of a reaction?
7. For which type of reaction, order and molecularity have the same value?
8. Identify the order of reaction from the following unit of rate constant: $Lmol^{-1}s^{-1}$
9. What is the effect of increase in surface area of reactants on rate of reaction?
10. E_1 and E_2 are the activation energies of the reactant and product respectively. If $E_2 > E_1$, predict the nature of reaction (Exothermic or Endothermic)?

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. The rate law for a reaction is Rate=K [A][B]$^{3/2}$

Can the reaction be an elementary process? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

2. For the reaction $2H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expression - $d[H_2]/dt$ and $d[NH_3]/dt$ inter-related?

Ans.-1/3 $d[H_2]/dt = 1/2\ d[NH_3]/dt$

3. Identify the order of a reaction from the following rate constant : $k=2.3x10^{-5}$ L mol^{-1} s^{-1}

Ans. Second order

4. For a chemical reaction half life period cannot depend on concentration of solution. What is order of reeaction?

Ans. First order reaction

5. What will be the effect of temperature on rate constant?

Ans. Rate constant of a reaction is nearly doubled with rise in temperature by 10^0C.

6. Why can't molecularity of any reaction be equal to zero?

Ans. Molecularity of a reaction means the number of molecules of the reactants taking place in an elementary reaction. Since at least one molecule must be present, so that molecularity will be atleast one.

7. Three-fourth of a reaction is completed in 32 minutes. What is the half life period of this reaction?

Ans. 16 minutes.

8. What is meant by an elementary reaction?

Ans. A reaction which takes place in one step is called an elementary reaction. For example: $H_2+I_2 \rightarrow 2HI$.

9. Give one example of a reaction where order and molecularity are equal?

Ans. $2HI \rightarrow H_2 + I_2$ (Order = Molecularity = 2)

10. For a reaction R→P, the rate becomes 2 time when the concentration of the reactant A is increased 4 times. What is the order of reaction ?

Ans. $r=k(a)^n \Rightarrow 2r = k(4a)^n \Rightarrow 2 = n=0.5$

11. Decomposition reaction of ammonia on Pt surface has rate constant = 2.5 x 10^{-1} mol L^{-1} sec^{-1}. What is order of reaction ?

Ans. Unit of k explain that it is zero order reaction.

12. Mention the unit of rate constant of first order reaction?

Ans. $Time^{-1}$ (s^{-1})

13. Give an example of a reaction having fractional order.

Ans. Decomposition of acetaldehyde (order = 1.5)

$CH_3CHO \rightarrow CH_4 + C O$

14. What is order of radioactive decay?

Ans. First order

15. 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 = 1/2 + 2 = 2.5

16. The rate constant of a zero order reaction in A is 0.003 mol L^{-1} sec^{-1}. How long will it take for the initial concentration of A to fall from 0.10M to 0.075 M?

Ans. $t = [R]_0 - [R]/k = 0.10 - 0.075/0.003 = 8.3$ second

17. In a reaction 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Average rate: $-\Delta[A]/2\Delta t = -½(0.4-0.5/10) = 5x10^{-3} M\ min^{-1}$

18. Why are reactions of higher order less in number ?

Ans. Reaction takes place due to collide of molecules. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are less.

19. State a condition under which a bimolecular reaction is kinetically first order reaction.

Ans. A bimolecular reaction becomes first order reaction when one of the reactants is in excess.

20. The rate constant of a reaction is $3x10^2$ min^{-1}. What is its order of reaction?

Ans. First order reaction.

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q. 1. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate activation energy.

Ans. $k_2/k_1 = 4$

$T_1 = 293\ K,\ T_2 = 313\ K$

$$\log\frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Thus, on calculating and substituting values, we get :

$E_a = 52.86\ KJ\ mol^{-1}$

Q. 2. If the decomposition of nitrogen oxide as

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

follows a first order kinetics.

(a) Calculate the rate constant for a 0.05M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s ?

(b) What concentration of N_2O_5 would give a rate of 2.45×10^{-5} mol L^{-1} s^{-1} ?

Ans. (a) Rate $= k[N_2O_5]$

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{1.5\times10^{-6}}{0.05}$$

$$k = 3.0 \times 10^{-5}$$

(b) Rate $= 2.45 \times 10^{-5}$ mol L^{-1} s^{-1}

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.45\times10^{-5}}{3.0\times10^{-5}} = 0.82\ M$$

Q. 3. Write the difference between order and molecularity of reaction.

Ans.

Order	Molecularity
1. It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneously collision in a reaction
2. It is determined experimentally.	2. It is a theoretical concept.
3. Order of reaction need not to be a whole number.	3. It is whole number only.
4. Order of reaction can be zero.	4. It can't be zero or fractional.

Q. 4. Consider the decomposition reaction :

$$2H_2O_2 \xrightarrow{OH^-/I^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below :

Step 1. $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ **(slow)**

Step 2. $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ **(fast)**

(a) Determine rate law expression.

(b) Determine the order of reaction.

Ans. (a) Rate $= K[H_2O_2][I^-]$ because second step is rate determining step.

(b) Order $= 1 + 1 = 2$

Q. 5. The decomposition of hydrocarbon follows the equation $K = (4.5 \times 10^{11}\ s^{-1})\ e^{-28000/T}$. Calculate E_a.

Ans. $k = (4.5 \times 10^{11}\ s^{-1})\ e^{-28000/T}$

Comparing the equation with Arrhenius equation,

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

$$\frac{E_a}{R} = 28000\ K$$

$$E_a = 28000 \times 8.314 = 232792\ J\ mol^{-1}$$

Q.7. For a first order reaction time taken for half of the reaction to complete is t_1 and ¾ of the reaction to complete is t_2. How are t_1 and t_2 related ?

Ans. $t_2 = 2t_1$ because for 3/4th of the reaction to complete time required is equal to two half lives.

Q.8. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction

$$R = [R]_0 - kt$$

For completion of the reaction $[R] = 0$

$$\therefore \quad kt = [R]_0 \qquad t = \frac{[R]_0}{k}$$

Q.9. The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

Ans. Suppose, order of reaction is n and the reaction is $A(g) \rightarrow$ Products

$$\text{Rate} = k[A]^n \qquad \text{...(i)}$$

When volume is doubled, molar conc. becomes half and rate of reaction gets halved.

$$\frac{\text{Rate}}{2} = k\left(\frac{A}{2}\right)^n \qquad \text{...(ii)}$$

Dividing equation (i) by equation (ii),

$$(2)^1 = (2)^n \qquad n = 1$$

Q.10. A reaction which is first order with respect to A has rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 ML^{-1} ?

Ans.

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$k = 6\ min^{-1}$, $[A]_0 = 0.5$, $[A] = 0.05$, $t = ?$

$$t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6}\log 10 = 0.3838\ min$$

Q.11. The conversion of the molecules X to Y follows second order kinetics. If the concentration of X is increased to three times, how will it affect the rate of formation of Y ?

Ans. 9 times

Q.12. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 gram of this reactant take to reduce to 3 grams ?

Ans. $t = 444$ seconds

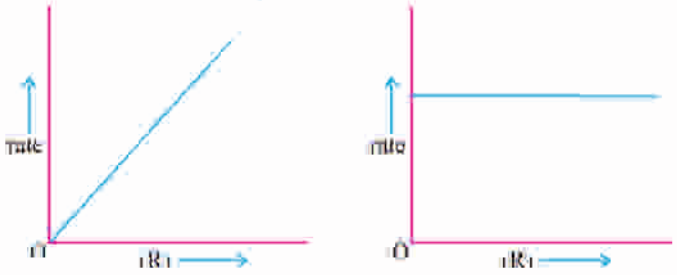
Q.13. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. If rate of formation of NO is 6×10^{-4} atm min^{-1}, calculate the rate of formation of H_2O.

Ans. 9.0×10^{-4} atm min^{-1}

Q.14. Consider a certain reaction A → Product 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. [A] = 0.135 M

Q.15. Explain with an example, what is a pseudo first order action ? The graphs (A and B) given below are plots of rate of reaction Vs concentration of the reactant Predict the order from the graphs



Q.16. The half life period of a first order reaction is 60 min. What % will be left after 240 mins. ?

Ans. 6.25%

Q.17. Time for half change for a first order reaction is 25 min. What time will be required for 99% reaction ?

Ans. 166.16 mins

Q.18. **The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.**

Ans.

$$K = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{t}\log\frac{[N_2O_5]_0}{[N_2O_5]_t} = \frac{2.303}{60}\log\frac{1.24\times10^{-2}}{0.2\times10^{-2}}$$

$$= \frac{2.303}{60}\log 6.2 = \frac{2.303}{60}\times 0.7924\ \text{min}^{-1} = 0.0304\ \text{min}^{-1}$$

Q.19. **The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :**

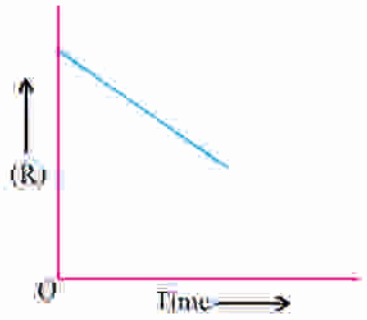
$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

S. No.	Time per second	Total pressure (atm)
1	0	0.5
2	100	0.512

Calculate rate constant.

Ans. 4.98×10^{-4} sec^{-1}

Q.20. **For a chemical reaction R → P, the variation in the concentration (R) vs time (*t*) plot is given :**



(a) **Predict the order of reaction.**

(b) **Write down its rate law.**

(c) **What is the slope of the curve?**

Q.21. In a pseudo first order reaction of hydrolysis of an ester in H_2O, the following results were obtained :

t/s	0	30	60	90
Ester (M/L)	0.55	0.31	0.17	0.085

(a) Calculate the average rate of reaction between the time interval 30 to 60 sec.

(b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Ans. (a) Average rate during 30-60 sec $= \dfrac{0.17 - 0.31}{60 - 30} = 4.67 \times 10^{-3}$ mol L^{-1} sec^{-1}

(b) $$k_{30} = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{30}\log\frac{0.55}{0.31}$$

$$k_{60} = \frac{2.303}{60}\log\frac{0.55}{0.17}$$

$$k_{90} = \frac{2.303}{90}\log\frac{0.55}{0.085}$$ Average K = 1.98×10^{-2} sec^{-1}

Q.22. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2 ? [K = 2.5×10^{-4}]

Ans. $2NH_3 \rightarrow N_2 + 3H_2$

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[NH_2]}{dt} + \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{d[NH_3]}{dt} = \text{rate} = k \times [NH_3]^0 = 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{1}{2} \times 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4} = 3.75 \times 10^{-44} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$\text{Rate} = -\frac{d[NH_3]}{dt} = k \times [NH_3]^0 = 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

Rate of production of $N_2 = 2.5 \times 10^{-4}$ mol L^{-1} sec^{-1}

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.1. (a) What are pseudo order reaction ? Give example.

(b) Rate coustant K of a reaction varies with temperature 'T' according to the equation :

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log k vs 1/T, a straight line with a slope of – 4250 K is obtained. Calculate E_a for the reaction.

Ans. (a) The chemical reaction which look like higher order reaction but in real they follow lower order kinetics.

For example,

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

excess

$$\text{Rate} = k[CH_3COOC_2H_5]$$

$$\text{Order} = 1$$

(b) $$\text{Slope} = \frac{E_a}{2.303R} = -4250\ K$$

So, $$E_a = -2.303 \times R \times \text{Slope} = -2.303 \times 8.314\ J\ K^{-1}\ mol^{-1} \times -4250$$

$$= 81375.3\ J\ mol^{-1} = 81.375\ kJ\ mol^{-1}$$

Q.2. **(a) Determine the units of rate constant for first and zero order reaction.**

(b) Show that time required for the completion of 99% of the first order reaction is twice the 90% of completion of the reaction.

Ans: (a) $k = (\text{mol})^{1-n} L^{n-1} s^{-1}$

For zero order $n = 0$

So, $k = (\text{mol})^{1-0} L^{0-1} s^{-1} = s^{-1}$ mol L^{-1}

For first order, $n = 1$

$k = (\text{mol})^{1-n} L^{n-1} s^{-1}$

So, $k = (\text{mol})^{1-1} L^{1-1} s^{-1}$

$\equiv s^{-1}$

(b) For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$[A]_0 \equiv a, \quad [A] = a - \frac{a \times 99}{100} \equiv 0.01\, a$

$$t(99\%) = \frac{2.303}{k} \log \frac{a}{0.01a} \qquad = \frac{2.303}{k} \log 100 \qquad = \frac{2.303}{k} \times 2$$

...(i)

For 90% completion of reaction.

$$[A] \equiv a - \frac{a \times 99}{100} = 0.1a$$

$$t(90\%) = \frac{2.303}{k} \log \frac{a}{0.1a} \qquad = \frac{2.303}{k} \times 1$$

...(ii)

Dividing equation (i) by equation (ii), we get

$t(99\%) = 2 \times t(90\%)$

Q.3. (a) Define rate constant of reaction

(b) A first order reaction takes 40 mins for 30% decomposition. Calculate $t_{1/2}$

Ans. (a) **Rate constant :** It is the rate of chemical reaction when the concentration of reactant taken as unity at a given temperature

(b) Let initial conc. $= a$

$$\text{Conc after 40 mins.} = a - \frac{a \times 30}{100}$$

$$= 0.70\, a$$

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

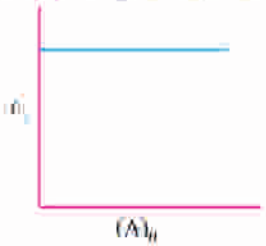
$$= \frac{2.303}{40} \log \frac{a}{0.70a} \quad = \frac{2.303}{40} \log \frac{1}{0.70}$$

$$= \frac{2.303}{40} \times 0.1549 \quad = 8.92 \times 10^{-3}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{8.92 \times 10^{-3}} \quad = 77.7 \text{ min}$$

Q.4. (a) Determine the order of reaction and also determine the units of rate constant.



(b) The following data were given for thermal decomposition of SO_2Cl_2 at a constant volume :

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Ans. (a) First order reaction

$$k = \text{mol}^{1-n}\, L^{n-1}\, S^{-1}$$

$$n = 1$$

$$k = (\text{mol})^{1-1} L^{1-1} S^{-1}$$

$$= S^{-1}$$

(b) $$k = \frac{2.303}{t} \log \frac{P_i}{(2P_i - P_t)}$$

$$= \frac{2.303}{100} \log \frac{0.5}{(2 \times 0.5 - 0.6)}$$

$$= \frac{2.303}{100} \log \frac{0.5}{0.4}$$

$$= \frac{2.303}{100} \times 0.969 = 2.23 \times 10^{-3}\, s^{-1}$$

Now, Rate $= P_{SO_2Cl_2}$

Pressure of SO_2Cl_2 when total pressure $= 0.65$ atm

$$P_{SO_2Cl_2} = 2P_i - P_t$$

$$= 2 \times 0.5 - 0.65 = 0.35 \text{ atm}$$

Rate $= 2.23 \times 10^{-3} \times 0.35 = 7.8 \times 10^{-4}$ atm S^{-1}

CASE STUDY BASED QUESTIONS

1. Read the passage given below and answer the questions that follow:

The rate of reaction is the change of concentration of reactant or product with time. The rate law for the reaction $aA+bB \rightarrow cC+dD$ the rate law is rate$=k[A]^a[B]^b$. The rate of reaction is calculated by knowing *k, a* and *b*. The rate laws are determined experimentally. During the collisions among two A and two B molecules, doubling the number of either type of molecule increases the number of collisions to eight. The species temporarily formed by the reactant molecules as a result of the collision before they form the product is called the *activated complex*. The temperatare-dependent rate constant is given by the Arrhenius equation. In many cases, the sum of a series of simple reactions are called elementary steps or elementary reactions because they represent the progress of the overall reaction at the molecular level. The sequence of elementary steps that leads to product formation is called the reaction mechanism. The number of molecules reacting in an elementary step determines the molecularity of a reaction.

(A) **On which of the following quantities does the rate constant of a reaction depend?**

(a) Concentrations of reactants (b) Nature of reactions

(c) Temperature (d) All the above

(B) **Instantaneous rate of reaction is measured from the:**

(a) graph of time versus concentration (b) molecularity of reaction

(c) integration method (d) reaction mechanism of a reaction

(C) **The order of reaction is always defined in terms of:**

(a) product concentration (b) rate constant of a reaction

(c) reactant concentration (d) ratio of the product concentration to the reactant concentration

(D) **The number of molecules reacting in an elementary step of a reaction may be:**

(a) 1 (b) l/2 (c) 12 (d) 5

2. Read the passage given below and answer the questions that follow:

The integrated rate equations can be fitted with kinetic data to determine the order of a reaction. The integrated rate equations for zero and first order reaction are:

Zero order : $[A] = -kt + [A]_o$

First order : $\log [A] = \frac{-kt}{2.303} + \log [A]_o$

These equations can also be used to calculate the half life periods of different reactions, which give the time during which the concentration of a reactant is reduced to half of its initial concentration i.e. at time $t_{1/2}$; $[A] = [A]_o$

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.

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.

(A) **ASSERTION:** For the first order reaction the units of rate constant are $time^{-1}$.

REASON: The rate of first order reaction remains constant throughout.

(B) **ASSERTION:** In zero order reaction, the cone. versus time graph is a straight line.

REASON: The rate of change of concentration per unit time in zero order reaction remains constant.

(C) **ASSERTION:** Half-life period is always independent of initial concentration.

REASON: Half-life period is inversely proportional to rate constant.

(D) **ASSERTION**: The slowest step in the reaction is rate determining step.

REASON: Order of a reaction is given by rate law expression.

ANSWERS

I MULTIPLE CHOICE QUESTION:

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

II FILL IN THE BLANKS:

1.	Pseudo first	2.	Fast	3.	Slowest
4.	0.693/k	5.	Cannot	6.	First, two
7.	Activation energy	8.	min^{-1}	9.	0.1 min^{-1}
10.	Effective collisions				

III ASSERTION REASON TYPE QUESTIONS:

1. (a) 2. (c) 3. (c) 4. (d) 5. (a) 6. (d) 7. (c) 8. (a) 9. (a) 10. (b)

IV ONE WORD ANSWER TYPE QUESTIONS:

1.	Zero order	2.	Activation energy	3.	First order reaction
4.	Decrease	5.	First order	6.	No effect
7.	Elementary reaction	8.	Second order	9.	Increase
10.	Endothermic				

CASE STUDY BASED QUESTIONS:

PASSAGE: 1: (A) c (B) a (C) c (D) a

PASSAGE: 2: (A) c (B) a (C) d (D) b

UNIT TEST

CHAPTER - 4

CHEMICAL KINETICS

TIME ALLOWED : 1 HR **M.M. : 20**

1. Which of the following statements is not correct for the catalyst? 1
   (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.
2. For the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ 1
   Which of the following expression is correct for the rate of the reaction?

(a) $\Delta[Br^-]/\Delta t=5\Delta[H^+]/\Delta t$ (b) $\Delta[Br^-]/\Delta t=6\Delta[H^+]/5\Delta t$

(c) $\Delta[Br^-]/\Delta t=5\Delta[H^+]/6\Delta t$ (d) $\Delta[Br^-]/\Delta t=6\Delta[H^+]/\Delta t$

3. For a zero order reaction will the molecularity be equal to zero? Explain. 1

ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

4. **ASSERTION:** The rate of reaction is the rate of change of concentration of a reaction or a product. 1

REASON: Rate of reaction remains constant during the course of reaction.

5. **ASSERTION:** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex reactions. 1

REASON: Reactant molecules undergo chemical change irrespective of their orientation during collision.

6. (i) Why does the rate of a reaction increase with increase in temperature? 2

(ii) Why is the probability of reaction with molecularity higher than three very rare?

7. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of reactant is reduced to half? What is the unit of rate constant for such a reaction? 2

8. After 24 hours, only 0.125 g out of the initial quantity of 1g of a radioactive isotope remains behind. What is its half-life period? 3

9. A first order reaction is 50% completed in 40 minutes at 300K and in 20 minutes at 320K. Calculate the activation energy of the reaction. 3

(Given: log2= 0.3010, log4=0.6021, R= 8.314$JK^{-1}mol^{-1}$)

10. (i) Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction? 5

(ii) Define instantaneous rate of reaction

(iii) Why H_2 and O_2 do not react at room temperature?

(iv) For which type of reactions, order and molecularity have the same value?

UNIT 5

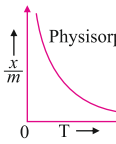
Surface Chemistry

Points to Remember

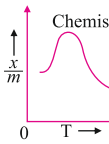
Surface Chemistry

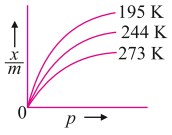
The branch of chemistry which deals with the phenomenom occurring at the surface

- **Absorption**
- **Adsorption**
  - **Physisorption**
  - **Chemisorption**
  - **Factors affecting adsorption of gases on**
    - **Nature of gas**
    - **Nature of adsorbent**
    - **Activation of adsorbent**
    - **Pressure**
      - **Adsorption Isobar**



    - **Temperature**
      - **Freundlich Adsorption Isotherm**





- **Catalysis**
  - **Homogeneous catalysis**
  - **Heterogeneous catalysis**
- **Colloids**
  - **Classification**
    - **a) Based on Physical State**
      - **Solid+Solid=Solid sol**
      - **Solid+Liquid = Sol**
      - **Solid+Gas=Aerosol**
      - **Liquid+Solid=Gel**
      - **Liquid+Liquid=Emulsion**
      - **Liquid+Gas=Aerosol**
      - **Gas+Solid=Solid Foam**
      - **Gas+Liquid=Foam**
    - **b) Based on Interaction of Dispersed Phase & Dispersion Medium**
      - **Lyophillic Colloid**
      - **Lyophobic colloid**
    - **c) Based on Types of Particles of Dispersed Phase**
      - **Multimolecular colloid**
      - **Marcromolecular colloid**
      - **Associated colloid**

- **Methods of preparation of Sol**
  - **Condensation Method**
    - **Chemical Reaction**
      - **Oxidation**
      - **Reduction**
      - **Hydrolysis**
      - **Double Decomposition**
    - **Excessive Cooling**
    - **Exchange of Solvent**
  - **Dispersion Method**
    - **Electrical Dispersion**
    - **Peptisation**

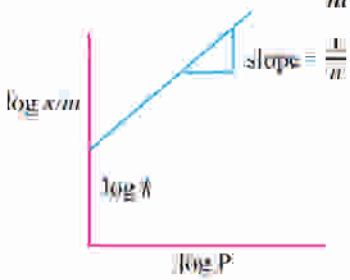
- **Properties of colloidal sol**
  - Trndall effect : scattering of light, path of light visible.
  - Show Colligative properties:
  - Brownian movement: Zig Zag movement of particles
  - Charge on the colloidal particles due to prefrential adsorption of ions, nature of charge is same on all particles
  - Electrophoresis : movement of colloidal particles towards oppositely charged electrode in presence of external field.
  - Electro-osmosis: movement of particles of dispersion medium in applied electric field.
  - Coagulation: Process of setting of colloidal particles

- **Purification of colloidal sol**
  - **Dialysis:** Process of removing impurities using SPM
  - **Electrodialysis:** When dialysis is carried out in electric field
  - **Ultrafiltration:** Using special filters which are permeable to ionic substances except colloidal particles

IMPORTANT FACTS

1. Adsorption occurs because of unbalanced forces acting inwards on the surface of the solid or a liquid.
2. The substance adsorbed is called **adsorbate** and substance on which adsorption takes place is **adsorbent.**
3. In physical adsorption, adsorbate is held to adsorbent by weak van der Waals forces. In chemisorptions, adsorbate is held to adsorbent by strong chemical bond.
4. Water vapours are adsorbed in silica gel but absorbed in $CaCl_2$.
5. If the concentration of adsorbate is more on the surface with respect to bulk, it is called **positive adsorption.** If it is less on the surface with respect to bulk, it is called **negative adsorption.**
6. Greater the surface area of the adsorbent, the more is the extent of adsorption.
7. Higher the critical temperature of a gas, greater is its extent of adsorption.
8. Physical adsorption is due to van der Waals forces and is reversible. Chemisorption involves the formation of compounds on the surface and is irreversible.
9. At constant temperature, adsorption generally increases with pressure. The lower the temperature, the greater is the effect of pressure.
10. **Frenudlich adsorption isotherm**

$$\frac{x}{m} = kP^{1/n} (n > 1) \qquad \text{i.e.,} \qquad \log\frac{x}{m} = \log k + \frac{1}{n}\log P$$



The plot of $\log x/m$ vs $\log P$ gives a straight line with slope $= 1/n$ and y-intercept $= \log k$

11. Adsorption is generally temperature dependent. Generally adsorption is **exothermic** and, therefore, adsorption decreases with the increase in temperature.
12. For adsorption from solution, pressure (P) is replaced by equilibrium concentration (C).
13. **Colloidal solutions** are intermediate between true solutions and suspensions. Their size ranges in the order 1 nm to 1000 nm.

14. A colloidal system consists of two phases the dispersed phase and dispersion phase

15. **Lyophilic sols :** There is strong attraction between dispersed phase and dispersion medium. These are formed by organic substances like gum, starch, protein etc. These are reversible and more stable.

16. **Lyophobic sols :** There is very little interaction between dispersed phase and dispersion medium and are formed by inorganic substances like metals, their sulphides etc. These are irreversible and less stable.

17. The stability of lyophilic sols is due to their greater hydration in the solution.

18. The colloidal systems show Brownian movement, Tyndall effect and electrophoresis.

19. Aggregate of ions in an associated colloidal sol is called **ionic micelle.** The concentration above which these are formed is called **critical micelle concentration** (CMC) and the temperature above which these are formed is called **Kraft temperature** (T_k).

20. Conversion of a freshly precipitated substance into colloidal sol by shaking with a suitable electrolyte is called **peptization.**

21. The movement of colloidal particles under the influence of an electric field is called **electrophoresis.**

22. The process of changing the colloidal particles in a sol into the insoluble precipitate by the addition of some suitable electrolytes is known as **coagulation.**

23. According to Hardy Schulze rule, greater the valency of the flocculating ion of the electrolyte, the faster is the coagulation.

24. The minimum number of millimoles of the electrolyte required for complete coagulation of one litre of a colloidal sol is called its **coagulation or flocculation value.**

25. **Emulsions** are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of (i) oil in water (o/w) and (ii) water in oil (w/o) type

26. The process of making emulsion is called emulsification.

27. To stabilize an emulsion, an emulsifying agent or emulsifier is added. Soap and detergents are most frequently used as **emulsifiers.**

28. The potential difference between the fixed layer and the diffused layer of opposite charges in colloids is called electrokinetic potential or zeta potential.

OBJECTIVE TYPE QUESTIONS (1 Mark)

I MULTIPLE CHOICE QUESTIONS

1. **Rate of physisorption increases with:**
   (a) decrease in temperature (b) increase in temperature
   (c) decrease in pressure (d) decrease in surface area

2. **The colloidal system consisting of a liquid adsorbate in a solid adsorbent is termed as:**
   (a) aerosol (b) foam
   (c) emulsion (d) Gel

3. **Which of the following has least coagulating value for positive sol?**
   (a) Cl^- (b) SO_4^{2-}
   (c) PO_4^{-3} (d) $[Fe(CN)_6]^{4-}$

4. **Which can adsorb larger volume of hydrogen gas?**
   (a) colloidal solution of platinum
   (b) finely divided nickel
   (c) finely divided platinum
   (d) colloidal $Fe(OH)_3$

5. **What is the emulsifer in milk?**
   (a) albumin (b) soap
   (c) gelatin (d) caesin

6. **Which one of the following gases will be adsorbed most easily?**
   (a) N_2 (b) H_2
   (c) O_2 (d) CO_2

7. **Cottrell precipitator works on the principle of:**
   (a) distribution law (b) addition of electrolyte
   (c) Le-chatelier principle (d) neutralisation of charge on colloids

8. **Which one of the following is correctly matched?**
   (a) Emulsion-smoke (b) Gel-butter
   (c) Aerosol-hair cream (d) Sol-whipped cream

9. **A colloidal solutions show:**
   (a) very high osmotic pressure (b) high osmotic pressure
   (c) low osmotic pressure (d) no osmotic pressure

10. Alums purify muddy water by:

(a) dialysis (b) adsorption

(c) absorption (d) coagulation

11. Which of the following is an example of associated colloid?

(a) soap in water (b) protein in water

(c) rubber in benzene (d) $AgNO_3$ in water

12. The coagulating power of an electrolyte for blood decrease in the order.

(a) Na^+, Al^{+3}, Ba^{+2} (b) PO_4^{-3}, SO_4^{-2}, Cl^-

(c) Al^{+3}, Ba^{+2}, Na^+ (d) Cl^-, SO_4^{-2}, PO_4^{-3}

13. A catalyst changes:

(a) Gibbs energy of reaction (b) Enthalpy of reaction

(c) Equilibrium constant (d) Activation energy of reaction

14. Bredig's are method can not be used for the preparation of colloidal sol of

(a) Cu (b) Au

(c) Ag (d) Na

15. Which is not a method of purification of colloidal solution?

(a) ultrafiltration (b) electrodialysis

(c) Bredig's arc method (d) dialysis

16. Match the column and choose correct option:

(A) Smoke	P. foam
(B) Butter	Q. emulsion
(C) Hair cream	R. aerosol
(D) Whipped cream	S. gel

(a) A–P, B–S, C–Q, D–R (b) A–R, B–Q, C–S, D–P

(c) A–R, B–S, C–Q, D–P (d) A–S, B–P, C–R, D–Q

17.

Column 1	Column 2
(A) Soap in water	P. Associated colloid
(B) Starch gelatin	Q. Lyoprilic colloid
(C) Gold sol	R. Collodion
(D) Cellulose nitrate in alcohol	S. Lyophobic colloid

(a) A–R, B–S, C–Q, D–P (b) A–P, B–Q, C–S, D–R

(c) A–R, B–S, C–P, D–Q (d) A–P, B–Q, C–R, D–S

II FILL IN THE BLANKS

1. Collodion is a 4% solution of.....in a alcohol or ether.
2. Starch is an example of ..... colloids .
3. The equation $x/m = kp^{1/n}$ is called.....equation.
4. In ..... sol, the interaction between dispersed phase and dispersion medium is strong.
5. Amongst As_2S_3, protein in water and soap in water, the example of multimolecular colloid is.....
6. .....sol are irreversible in nature.
7. The purification of a sol by using a cellophane bag is called .....
8. Cheese is an example of .....
9. Scattering of light by colloidal particles and making them visible is called.....
10. A catalyst increases th e rate of reaction by.....it s energy of activation.

III ASSERTION-REASON TYPE QUESTIONS

In each of the following questions, a statement of Assertion (A) is given followed by a corresponding statement of Reason (R) just below it. Of the statements, mark the correct answer as

(a) Both assertion and reason are correct, and reason is the correct explanation of the assertion .

(b) Both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is incorrect.

(d) Assertion is false but reason is correct.

1. **Assertion.** The conversion of fresh precipitate of colloidal state is called peptisation.

   Reason. It is caused by addition of common ions.

2. **Assertion.** Colloidal solutions are stable but colloidal particles do not settle down.

   Reason. Brownian movement counters the force of gravity actively on colloidal particles.

3. **Assertion.** The catalytic convertor in the car's exhaust converts polluting exhaust gases into non-toxic gases.

   Reason. Catalytic convertor contains a mixture of transition metals and their oxides embedded in the inner support.

4. **Assertion.** Micelles are formed by sur fact ant molecules above the critical micelle concentration

   Reason. The conductivity of a solution having sufficient molecules decreases sharply at the CMC

5. **Assertion.** Lyophilic colloids are more stable than lyophobic colloids.

   Reason. In lyophobic system, the dispersed particles are more solvated than in lyophilic system.

6. **Assertion :** Aqueous gold colloid is red in colour .

   Reason: The colour arises due to scattering of light by colloidal gold particles.

7. **Assertion.** Colloidal solutions do not show Brownian, motion.

   Reson. Brownian motion is responsible for stability of sols.

8. **Assertion:** A colloidal sol gets precipitated by the addition of an electrolyte.

   Reason : The rate of coagulation depends on the magnitude and sign of charge of the coagulating ions.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Which will be adsorb more readily on the surface of charcoal? NH_3 or CO_2.
2. Give an example of gel.
3. Name the temperature above which the formation of micelles takes place.
4. Give one example of' oil in water' type emulsion.
5. Name the process involved in tanning of animal hides.
6. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol :

   (i) NaCl (ii) Na_2SO_4 (iii) $K_4[Fe(CN)_6]$.

7. Is adsorption exothermic or endothermic in nature?
8. What name is given to the sol in which dispersion medium is water?
9. Give an example of associated colloid.
10. Name the phenomenon responsible for 'Blue colour of sky'?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Why does a gas mixed with another gas not form a colloidal system ?

[*Hint* Gaseous mixture is homogeneous]

Q. 2. Why are adsorbate particles attracted and retained on the surface of adsorbent ?

[*Hint* The unbalanced forces of the adsorbent are responsible for attracting adsorbate particles at adsorbent surface]

Q. 3. Explain the terms sorption and desorption.

[*Hint* Sorption is used to describe the process when adsorption and absorption take place simultaneously.

Desorption Removal of adsorbate from the surface of adsorbent]

Q. 4. "Chemisorption is highly specific." Illustrate with an example.

[*Hint* As it involves chemical bonding between adsorbent and adsorbate]

Q. 5. "Adsorbents in finely divided form are more effective." Why ?

[*Hint* Due to their more surface area in finely divided form]

Q. 6. Name two compounds used as adsorbent for controlling humidity.

Ans. Silica gel, Alumina gel

Q.7. 'Generally high temperature is favourable for chemisorption.' Why ?

[*Hint* To provide energy of activation.]

Q.8. Why gas masks are used by miners in coal mines while working ?

[*Hint* To absorb poisonous gases.]

Q.9. Write the chemical reaction involved in the preparation of sulphur sol.

[*Hint* $SO_2 + 2H_2S \xrightarrow{\text{oxidation}} 3S_{(sol)} + 2H_2O$]

Q.10. What are the physical states of dispersed phase and dispersion medium in foam rubber ?

[*Hint* Dispersed phase Gas, Dispersion medium Solid]

Q.11. What is the composition of colloidion solution ?

[*Hint* 4% solution of nitrocellulose in a mixture of alcohol and ether]

Q.12. Why do colloidal particles show Brownian movement ?

[*Hint* Due to unbalanced bombardment of the dispersed phase particles by the molecules of the dispersion medium.]

Q.13. State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface.

[*Hint* ΔS = –ve]

Q.14. Why does sky appear blue to us ?

[*Hint* Due to scattering of blue light by dust particles and water suspended in air.]

Q.15. What happens when hydrated ferric oxide and arsenious sulphide sols are mixed in almost equal proportions ?

[*Hint* Mutual precipitation/coagulation took place.]

Q.16. Gelatin is generally added to ice-cream. Why ?

[*Hint* Ice-cream is water in oil type emulsion and gelatin acts as emulsifier.]

Q.17. How is lake test for aluminium ion based upon adsorption ?

[*Hint* $Al_2O_3.xH_2O$ has the capacity to adsorb the colour of blue litmus from the solution.]

Q.18. Mention the two conditions for the formation of micelles.

[*Hint* CMC and T_k.]

Q.19. How is Brownian movement responsible for the stability of sols ?

[*Hint* Stirring effect due to Brownian movement does not allow the particles to settle down.]

Q.20. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol : (i) KCl, (ii) $CaSO_4$, (iii) $K_4[Fe(CN)_6]$?

[*Hint* $K_4[Fe(CN)_6]$]

Q.21. State the purpose of impregnating the filter paper with colloidion solution.

[*Hint* To reduce pore size of filter paper so that colloidal particles cannot pass through.]

Q.22. Explain the terms : (i) CMC, (ii) Kraft temperature (T_k).

[*Hint* CMC Concentration above which micelle formation took place

Kraft Temperature It is the temperature above the micelle formation took place.]

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

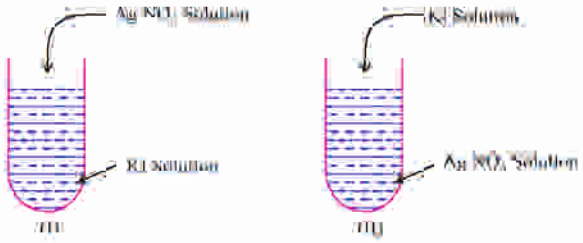
Q. 1. Explain the effect of temperature on the extent of physical and chemical adsorption.

[*Hint* Physical adsorption decreases with increase of temperature, while chemical adsorption increases with increase of temperature.]

Q. 2. Define the term peptization and mention its cause.

[*Hint* It is the process of converting a ppts into a colloidal sol by shaking it with small amount of electrolyte with dispersion medium. Ppts adsorb one of the ions of the electrolyte on its surface.]

Q. 3. What will be the charge on colloidal solutions in the following cases ?



Give reasons for the origin of charge.

Ans. (i) I^- ions are adsorbed on AgI, forming negatively charged colloid

(ii) Ag^+ ions are adsorbed on AgI, forming positively charged colloid

Reason for origin of charge is the preferential adsorption of common ions of the electrolyte present in excess.

Q.4. Mention two examples of emulsifying agents for o/w emulsions and w/o emulsions.

[*Hint* For o/w emulsions Proteins, gums, soaps

For w/o emulsions Fatty acids, long chain alcohols, lampblack.]

Q.5. A small amount of silica gel and a small amount of anhydrous calcium chloride are placed separately in two beakers containing water vapour. Name the phenomenon that takes place in both the beakers.

[*Hint* Silica gel Adsorption, Anhydrous $CaCl_2$ Absorption, as it forms $CaCl_2.2H_2O$]

Q.6. Write the differences between adsorption and absorption.

[*Hint* Adsorption is surface, while absorption is bulk phenomenon.]

Q.7. How can physisorption be distinguished from chemisorptions ?

[*Hint* Physisorption arises because of van der Waal's forces, not specific and reversible while chemisorptions is caused by chemical bond formation, highly specific and irreversible.]

Q.8. In what ways these are different : (a) a sol and a gel (b) a gel and an emulsion ?

[*Hint*

(a) For a sol : Dispersed phase : Solid, Dispersion medium : Liquid

For a gel : Dispersed phase : Liquid, Dispersion medium : Solid

(b) For a gel : Dispersed phase : Liquid, Dispersion medium : Solid

For an emulsion : Dispersed phase : Liquid, Dispersion medium : Liquid]

Q.9. State "Hardy Schulze Rule" with one example.

[*Hint* It states that greater the valency of the flocculating ion of the electrolyte, the faster is the coagulation.]

Q.10. What is an emulsifying agent ? What role does it play in forming an emulsion ?

[*Hint* Those agents which stabilize emulsions. It acts as binding agent between two immiscible liquid phases.]

Q.11. Define the terms :

(a) Helmholtz electrical double layer

(b) Zeta potential

[*Hint* (a) The combination of the two layers of opposite charges around the colloidal particles. *E.g.*, AgI/I⁻ K⁺

(b) The potential difference between the fixed layer and diffused layer of opposite charges is called zeta potential.]

Q.12. Mention the two necessary conditions for the observation of Tyndall effect.

[*Hint* (a) The size of dispersed phase particles is not much smaller the wavelength of light used.

(b) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.]

Q.13. Account for the following :

(a) Artificial rain can be caused by spraying electrified sand on the clouds.

(b) Electrical precipitation of smoke.

Q.14. Write chemical equations for the preparation of sols :

(a) Gold sol by reduction

(b) Hydrated ferric oxide sol by hydrolysis.

[*Hint* (a) $2AuCl_3 + 3SnCl_2 \xrightarrow{\text{Reduction}} 2Au\ (sol) + 3SnCl_4$

(b) $FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol)\ (Or\ Fe_2O_3 \cdot xH_2O) + 3HCl$]

Q.15. How can the two emulsions can be distinguished :

(a) oil in water type (o/w) and

(b) water in oil type (w/o)

[*Hint* (a) By dilution test

(b) By dye test]

Q.16. Leather gets hardened after tanning. Why ?

Ans. Animal hide is colloidal in nature and has positively charged particles. When it is soaked in tannin which has negatively charged colloidal particles, it results in mutual coagulation. This results in the hardening of leather.

Q.17. Why are some medicines more effective in the colloidal form ?

Ans. Medicines are more effective in the colloidal form because of large surface area and are easily assimilated in this form.

Q.18. What happens when dialysis is prolonged ?

Ans. When dialysis is prolonged the traces of electrolyte which stabilises the colloids are removed completely. This makes the colloid unstable and therefore coagulation takes place.

Q. 19. How are the following colloids different from each other in respect of dispersion medium and dispersed medium ? Give one example of each type.

(a) An aerosol (b) A hydrosol (c) An emulsion

[*Hint*

	D.P.	D.M.	Example
(a)	Solid/liquid	Gas	Smoke, dust, fog, cloud
(b)	Solid	Water	Muddy water
(c)	Liquid	Liquid	Milk, hair cream]

Q. 20. What happens :

(a) By persistent dialysis of a sol.

(b) When river water meets the sea water.

(c) When alum is applied on cuts during bleeding.

[*Hint* (a) Coagulation of sol takes place.

(b) Delta formation takes place due to coagulation of river water.

(c) Clot is formed due to coagulation of blood which stops further bleeding.]

Q. 21. Distinguish between multimolecular, macromolecular and associated colloids with the help of one example of each.

[*Hint* (i) Multimolecular colloids formed by aggregation of small atoms or molecules. Example, gold sol, sulphur sol

(ii) Macromolecular colloids formed by dispersing macromolecules having colloidal size in proper dispersion medium. Example, protein, starch colloid.

(iii) Associated colloids are formed by aggregation of particles at higher concentration to colloidal range. Example, micelles.]

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.1 **(i) Comment on the statement that "colloid is not a substance but state of a substance."**

(ii) Write short notes on the following :

(a) Tyndall Effect

(b) Brownian Movement

(c) Hardy Schulze Rule

Ans. (i) The given statement is true. This is because the statement may exist as a colloid under certain conditions and as a crystalloid under certain other conditions. e.g., NaCl in water behaves as a crystalloid while in benzene, behaves as a colloid (called associated colloid). It is the size of the particles which matters i.e., the state in which the substance exist. If the size of the particles lies in the range 1 nm to 1000 nm it is in the colloid state.

(ii) (a) Tyndall Effect : Scattering of light by colloidal particles by which part of beam becomes clearly visible. This effect is known as tyndall effect.

(b) Brownian Movement: Zig-zag motion of colloidal particles.

(c) Hardy Schulze Rule: Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

e.g. $Na^{+} < Ca^{++} < Al^{3+}$ For negatively charged sol

$Cl^{-} < CO_3^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$ For positive sol

CASE STUDY BASED QUESTIONS

1. Read the passage given below and answer the following questions:

Earlier the term 'Colloids' was used for a category of substances . However later the term colloidal state was preferred. The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension. Colloid science is the science of both large molecules and finely subdivided multiphase systems. It is the system of more than one phase that colloid and surface science meet. Colloid science is interdisciplinary in many respects; its field of interest overlaps physics, biology, materials science , and several other disciplines. The knowledge of colloid chemistry is required in various aspects of chemistry.

Colloidal dispersions have been classified into different types depending upon the physical state of the dispersed phase and dispersion medium or the nature of interaction between them or the nature of colloidal particles. They are prepared in the industry or in the laboratory by a number of methods and then purified. Their properties have also been studied in detail.

The following questions are multiple choice questions. Choose the most appropriate answer:

(A) The dispersed phase and dispersion medium in soap lather are respectively

(a) gas and liquid (b) liquid and gas

(c) solid and gas (d) solid and liquid

(B) Which of the following are lyophillic colloids?

(a) Gold sol (b) As_2S_3 sol

(c) Starch sol (d) $Fe(OH)_3$ sol

(C) Lyophilic sols are more stable than lyophobic sols because

(a) The colloidal particles have positive charge

(b) The colloidal particles have no charge

(c) The colloidal particles are solvated

(d) There is strong electrostatic repulsion

(D) The formation of micelles takes place only above

(a) Inversion temperature (b) Kraft temperature

(c) Critical temperature (d) Boyle ' s temperature

2. Read the passage given below and answer the following questions:

Colloidal particles are electrically charged- posit ive or negative. The dispersion medium has an equal and opposite charge making the. system neutral as a whole. Owing to the similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. This is why a sol is stable and particles do not settle down . But coagulation is the process of destabilizing (reducing the charge) particles, while the coagulant is the material used to accomplish coagulation. Floculation is applied on the process of collision of particles to form a bigger size particle which is easy to be removed by a simple technique like sedimentation or filtration. This coagulant may be natural or chemical in nature. Natural coagulants have been used domestically at household level for centuries in traditional water treatment in many rural areas. These natural coagulants are added to the turbid water to remove the turbidity. Most urban communities particularly in developing countries collect water from a natural water body in the catchment , whether a stream, a river, or an underground aquifer which is not clean . Currently, the need of clean water for everyday activities inspires many researchers to render the coagulation and flocculation processes more efficient. Many scientists have been trying to purify and to treat polluted and turbid water using different chemical coagulants like Alum.

The following questions are multiple choice questions. Choose the most appropriate answer:

(A) Tanning of leather is

(a) colouring of leather by chemicals

(b) drying process to make the leather hard

(c) polishing of leather to make it look attractive

(d) hardening of leather by coagulation

(B) Which of the following electrolytes will have maximum coagulating value for AgI/Ag^{+} sol?

(a) Na_2S (b) Na_3PO_4

(c) Na_2SO_4 (d) NaCl

(C) Which of the following colloids cannot be coagulated easily?

(a) Lyophobic colloids (b) Irreversible colloids

(c) Extrinsic colloids (d) Lyophilic colloids

(D) Which one of the following does not involve coagulation?

(a) Formation of delta region (b) Treatment of drinking water by potash alum

(c) Blue colour of sky (d) Clotting of blood by the use of ferric chloride

3. Read the passage and answer the following questions:

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Quantitative studies on adsorption have been made by Freundlich and Langmuir. They have put mathematical expressions relating x/m (mass of the adsorbate adsorbed per gram of the adsorbent) with equilibrium pressure, p if the adsorbate were a gas and with equilibrium concentration, C, if the adsorbate were a solute from an aq. Solution. They authenticated their expressions by suitable plots.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated char coal, synthetic resins and

water purification. Among these methods, adsorption is currently considered to be very suitable for waste water treatment because of its simplicity and cost effectiveness. Adsorption is commonly used technique for the removal of metal ions from various industrial effluents. Activated carbon is the most widely used adsorbent. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It can remove a wide variety of toxic metals. Some widely used adsorbents for adsorption of metal ions include activated carbon, clay minerals.

The following questions are multiple choice questions. Choose the most appropriate answer:

(A) In physisorption, adsorbent does not show specificity for any particular gas because_____.

(a) involved van der Waals' forces are universal.

(b) gases involved behave like ideal gases .

(c) enthalpy of adsorption is low .

(d) it is a reversible process.

(B) **Which of the following statements is correct for the spontaneous adsorption of a gas?**

(a) ΔS is negative and, therefore, ΔH should be highly positive

(b) ΔS is negative and, there fo re, ΔH should be highly negative

(c) ΔS is positive and, therefore, ΔH should be negative

(d) ΔS is positive and, therefore, ΔH should also be highly positive

(C) **A small amount of silica gel and that of anhydrous $CaCl_2$ are placed separately in two corners of a room containing water vapour. What phenomena will occur in these two cases?**

(a) Adsorption in both

(b) Absorption in both

(c) Adsorption on silica gel and absorption on $CaCl_2$

(d) Absorption on silica gel and adsorption on $CaCl_2$

(D) **On the basis of the data given below predict which of the following gases shows least adsorption of 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

ANSWER

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

II. 1. Cellulose nitrate 2. Lyophillic colloids 3. Freundlich isotherm 4. Lyophillic 5. As_2S_3 6. Lyophobic 7. Dialysis 8. Gel 9. Tyndall effect 10. Lowering

III 1. (b) 2. (a) 3. (a) 4. (b) 5. (c) 6. (a) 7. (d) 8. (a)

IV. 1. NH_3 2. Butter or any other suitable example 3. Kraft Temperature (Tk) 4. Milk/Vanishing cream 5. Mutual Coagulation 6. $K_4[Fe(CN)_6]$ 7. Exothermic 8. Hydrosol 9. Soap 10. Scattering of light

CASE STUDY TYPE QUESTIONS :

PASSAGE: 1 : (A) a (B) c (C) c (D) b

PASSAGE: 2: (A) d (B) b (C) d (D) c

PASSAGE: 3: (A) a (B) b (C) c (D) d

PASSAGE: 4: (A) a (B) c (C) d (D) b

UNIT TEST

CHAPTER-5

SURFACE CHEMISTRY

TIME 1 HR. **MM : 20**

1. How does positive adsorption differ from negative adsorption? (1)
2. Why is finely divided substance more effective as an adsorbent? (1)
3. What is Kraft temperature (T_k) and CMC? (1)
4. What is the principle of Dialysis? (1)
5. What is the cause of Brownian movement? (1)
6. Differentiate oil-in-water (o/w type) and water-in-oil (w/o type) emulsions. (2)
7. What is sorption? How does it differ from adsorption? (2)
8. State Hardy Schulze rule. (2)
9. Write the difference between (3)

   (a) aerosol and hydrosol (b) physisorption and chemisorption
10. Distinguish between miltimolecular, macromolecular and associated colloids with the help of one example of each. (3)
11. Write a short note on the following: (3)

    (a) Tyndal effect (b) Coagulation (c) Peptisation

UNIT 6

p-Block Elements

Points to Remember

Anomalous behavior of first element in the p-block elements is attributed to small size, large (charge/radius) ratio, high ionization enthalpy, high electronegativity and unavailability of d-orbitals in its valence shell.

Consequences :

1. The first element in p-block element has four valence orbitals i.e., one 2s and three 2p. Hence maximum covalency of the first element is limited to four. The other elements of the p-block have vacant d-orbitals in their valence shell, e.g., three 3p and five three 3d orbitals. Hence, these elements show maximum covalency greater than four. Following questions can be answered :

   (i) Nitrogen (N) does not form pentahalide while P forms PCl_5, PF_5 and PF_6^-. Why ?

   (ii) Sulphur (S) forms SF_6 but oxygen does not form OF_6. Why ?

   (iii) Though nitrogen forms pentoxide but it does not form pentachloride. Why ?

   (iv) Fluorine forms only one oxoacid while other halogens form a number of oxoacids. Why ?

2. The first member of p-block elements displays greater ability to form pπ-pπ bond(s) with itself, (e.g., C = C, C = C, N ≡ N, N = N) and with the other elements of second period, for example, C = O, C = N, N = O compared to the subsequent members of the group.

   This is because p-orbitals of the heavier members are so large and diffuse that they cannot have effective sideways overlapping. Heavier members can form pπ-dπ bonds with oxygen.

   Now, the following question can be explained using the above mentioned reasoning :

   (i) Oxygen exists as O_2 but sulphur as S_8. Why ?

3. Due to small size and high electronegativity and presence of lone pair(s) of electrons, elements N, O, F when bonded to hydrogen atom, forms hydrogen bonds which are stronger than other intermolecular forces. This results in exceptionally high m.p. and b.p. of the compounds having N -H/O-H/F-H bonds.

Isostructural species have same number of bond pairs and lone pairs if present around the central atom in a molecule/ion. Thus, they have the same geometry/ shape/structure and the same hybridisation scheme. For example, ICl_4^-/XeF_4, BrO_3^-/XeO_3, BH_4^-/NH_4^+ are the pairs of isostructural species. Inert pair effect : Due to poor shielding effect of intervening d and/or f-electrons, the effective nuclear charge increases. This increased nuclear charge holds the ns^2 electrons of heavier elements strongly and the tendency of ns^2 electrons to take part in bonding is more and more restricted down the group. Consequently, more stable lower oxidation state which is two units less than higher oxidation state, becomes more and more stable than the higher oxidation state. Following questions can be explained with the help of inert pair effect :

(i) For N and P, + 5 oxidation state is more stable than + 3 oxidation state but for Bi + 3 oxidation state is more stable than + 5. Explain why ?

(ii) $NaBiO_3$ is a strong oxidizing agent. Why ?

[Hint : Bi (V) is least stable.]

(iii) In group 16, stability of +6 oxidation state decreases and the stability of +4 oxidation state increases down the group. Why ?

(iv) SO_3 acts as reducing agent. Explain why ?

(v) Why is BrO_4^- a stronger oxidizing agent than ClO_4^- ?

[Hint : It is because + 7 oxidation state is less stable in BrO_4^- due to which Br-O bond becomes weaker.]

(vi) $AsCl_5$ is less stable than $SbCl_5$.

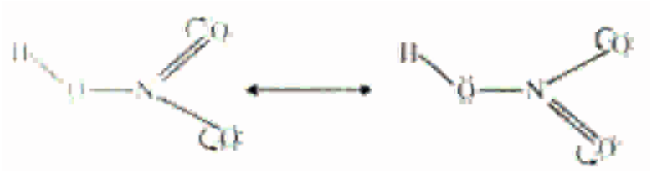
[Hint : More effective nuclear charge in As than Sb.]

(vii) The stability of highest oxidation state of 4p element is less than those of 3p and 5p elements of the same group. Why ?

Bond length : Resonance averages bond lengths. The two oxygen-oxygen bond lengths are identical in the 03 molecule because it is resonance hybrid of following two canonical forms.



In case of HNO_3, two nitrogen-oxygen bonds are identical and smaller than the third nitrogen-oxygen bond. This is because the third N-OH bond is not involved in resonance.

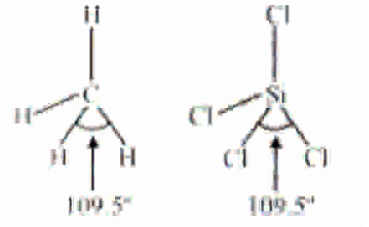


Now the following questions can be explained on the basis of this concept :

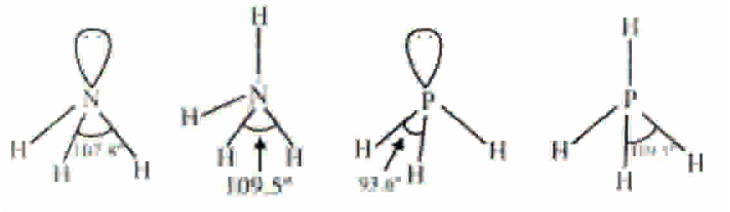
(i) In SO_2, the two sulphur-oxygen bonds are identical. Explain why ?

(ii) In NO_3^- ion, all the three N-O bonds are identical. Why ?

Bond angle : In regular structures (where no lone pairs are present in the valence shell of the central atom in a molecule/ion), the bond angle does not depend upon the size/electronegativity of the central or terminal atoms.



In presence of lone pair(s) on the central tom, the geometry is distorted and the bond angle is changed.



Comparison of HNH and HPH bond angles Since N is more electronegative than P, the bonding electron pair of N — H bond will shift more towards N atom than the bonding electron pair of P — H bond would shift towards P atom.

This results in more bond pair-bond pair repulsion in NH_3 molecule than PH_3 molecule. Because of more L.P-B.P repulsion, the N-H bonds are pushed closer to a lesser extent than in PH_3. Consequently, HNH bond angle is greater than HPH angle.

Now, the following questions can be explained using the above mentioned concept :

(i) Bond angle in PH_4^+ ion is higher than in PH_3. Why ?

(ii) H-O-H bond in H_2O is greater than H-S-H angle in H_2S. Why ?

Boiling and melting points of hydrides depends upon the molar mass (or surface area) of molecules. More the molar mass, the higher is the m.p. and b.p. Hydrides forming intermolecular hydrogen bonds have exceptionally high m.p. and b.p. since intermolecular hydrogen bonds are stronger than the van der Waals forces. Increasing order of melting point and boiling point of hydrides is as given below :

$PH_3 < AsH_3 < SbH_3 < NH_3$ Melting point

$PH_3 < AsH_3 < SbH_3 < SbH_3$ Boiling point

$H_2S < H_2Se < H_2Te < H_2O$ Melting point and boiling point

$HCl < HBr < HI < HF$ Boiling point

$HCl < HBr < HF < HI$ Melting point

(i) NH_3 has higher boiling point than PH_3.

(ii) H_2O is liquid and H_2S is gas or H_2S is more volatile than H_2O.

Thermal stability, reducing power and acid strength of hydrides depend upon bond dissociation enthalpy of E - H bond (E = group 15, group 16, and group 17 clement). Due to the increase in size down the group, bond dissociation enthalpy of E-H bond decreases. Consequently, while thermal stability decreases down the group, reducing power and acid strength of hydrides increases down the group.

The following questions can be explained using the above concepts. Explain why :

(i) HF is weaker acid than HCl.

(ii) Among hydrogen halides, HI is the strongest reducing agent.

(iii) H_2Te is more acidic than H_2S.

(iv) NH_3 is mild reducing agent while BiH3 is the strongest reducing agent among the group-15 hydrides.

(v) H_2S is weaker reducing agent than H_2Te.

Basic nature of hydrides EH_3 of group 15 elements

All the hydrides EH_3 of group 15 elements has one lone pair of electrons. In ammonia, the lone pair of electrons is present in sp3 hybrid orbital of the N-atom. The sp^3 hybrid orbital is directional and further N is more electronegative than H, the bond pair of N — H is shifted towards N atom which further increases the electron density on N atom. In PH_3, the lone pair of electrons is present in large and more diffuse 3s orbital which is non-directional. As a result, PH_3 is less basic than NH_3 and basic character decreases down the group. NH_3 donates electron pair more readily than PH_3. $(SiH_3)_3N$ has less Lewis basic nature than that of $(CH_3)_3N$ because lone pair of electrons in p-orbital of N atom in $(SiH_3)_3N$ is transferred to the vacant d-orbital of Si atom forming dπ-pπ bond.

Covalent/Ionic Character of Halides

Pentahalides are more covalent than trihalides since the element (E) in higher oxidation state (+ 5) in pentahalides has more polarizing power than element (E) in lower oxidation state (+3) in trihalides, similarly, $Snc1_4$, $Pbc1_2$, $Sbc1_3$ and UF_4 respectively. Compounds having more ionic character have more m.p. and b.p. than the compounds having more covalent character.

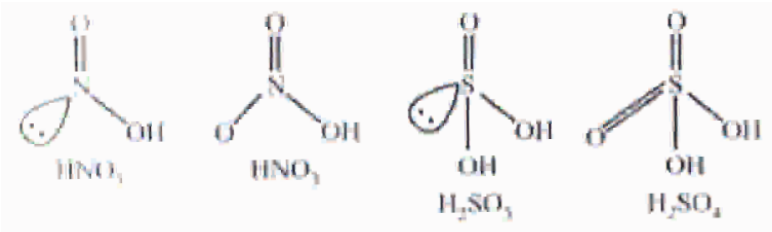
Following questions can be explained by using this concept. Explain why :

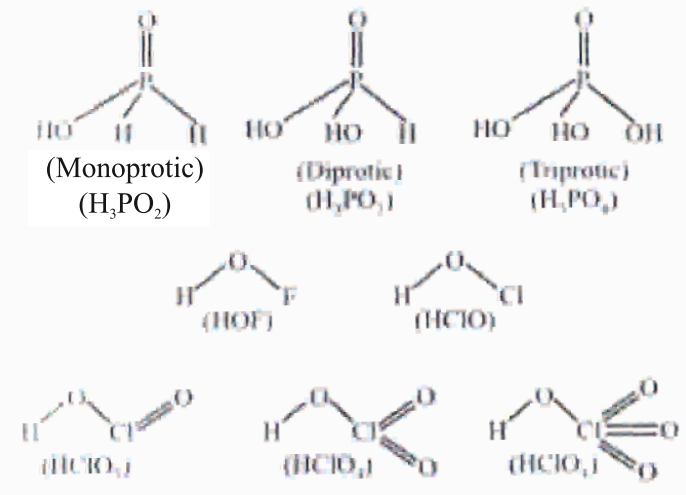
(i) $SnCl_2$ has more b.p. than $SnCl_4$

(ii) $SbCl_5$ is more covalent than $SbCl_3$

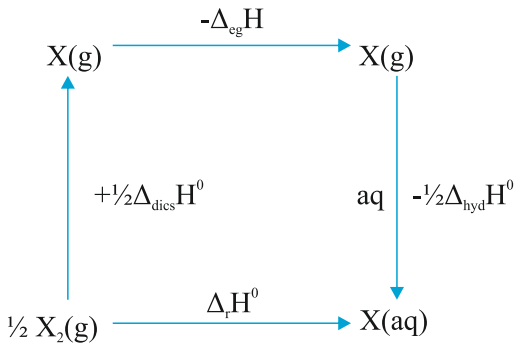
(iii) PCl_5 has lower boiling point than that of PCl_3

Oxoacids of N, P and halogens :





Oxidising Power of Halogens



The more negative the value of $\Delta_r H^0 = 1/2\Delta_{diss} H^0 - \Delta_{eg} H^0 - \Delta_{hyd} H^0$ the higher will be oxidizing property of the halogen and more positive will be standard reduction potential E^0_{red} of the halogen. Following questions can be explained on the basis of parameters, like $\Delta_{diss} H°$, $\Delta_{eg} H°$ and $\Delta_{hyd} H°$.

(i) Why does F_2 have exceptionally low bond dissociation enthalpy ?

(ii) Although electron gain enthalpy of fluorine (F) is less negative as compared to chlorine (Cl), Fluorine gas (F_2) is a stronger oxidizing agent than Cl_2 gas. Why ? Some Important Reactions

Group 18 Elements:

Group 18 consists of six elements: Helium, Neon, Argon, Krypton, Xenon and Radon. All these are gases and chemically unreactive. 2 They form very few compounds, they have stable closed shell electronic configuration ($1s^2$ (He), ns^6np^6), because of this they are termed as noble/inert gases. Initially they were also called rare gases.

Occurrence:

All the noble gases except Radon occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.

ATOMIC and PHYSICAL PROPERTIES

1. **Electronic configuration:** All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$. Many of the properties of noble gases including their inactive nature are ascribed to their closed shell electronic configuration.
2. **lonisation enthalpy :** Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increase in atomic size.
3. **Atnmie radii (van der waals radii)** : Atomic radii increase down the group with increase in atomic number.

4. **Electron gain enthalpy:** Since noble gases have stable electronic configurations, they have a little tendency to gain electron only at the expense of energy and therefore, have large positive values of electron gain enthalpy.

Physical properties

- All the noble gases are monoatomic.
- They are colourless, odourless and tasteless.
- They are sparingly soluble in water.
- They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces. Down the group melting point/boiling point increases as magnitude of dispersion forces increases with increase of atomic mass.
- Helium has the lowest boiling point (4.2K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Chemical Properties:

- In general, noble gases are least reactive.

Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases have stable closed shell electronic configuration helium ($1s^2$) and other members have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Discovery of Noble gases compound

- In March 1962, **Neil Bartlett** observed the reaction of a noble gas.
- He was studying properties of PtF_6 (red gas, boiling point:342.29K),one of the strongest oxidising agent which can ionise 0_2 and prepared a red compound which is formulated as $O_2^+PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ/mol) was almost identical with that of xenon (1170 (kJ/mol).

- He made efforts to prepare same type of compound with Xe and was successful in preparing another compound $Xe^{+}PtF_6^{-}$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

(a) **Xenon - fluorine compounds:**

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$Xe\,(g) + F_2\,(g) \text{ (xenon in excess)} \xrightarrow{673K,\ 1bar} XeF_2(s)$$

$$Xe\,(g) + F_2\,(g) \text{ (1:5 ratio)} \xrightarrow{873K,\ 7bar} XeF_4(s)$$

$$Xe\,(g) + 3F_2\,(g) \text{ (1:20 ratio)} \xrightarrow{573K,\ 60\text{-}70bar} XeF_6(s)$$

- XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K. O_2F_2 in this reaction act as fluorinating agent.

  $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

- XeF_2 , XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They arc powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

  $2XeF_2\,(s) + 2H_2O(l) \rightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$

- The structures of the three xenon fluorides can be deduced from VSEPR and these arc shown in XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase. The position of lone pair is not fixed due to very strong repulsions between 6 bond pairs and a lone pair on xenon.

- Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$XeF_2 + PF_5 \rightarrow [XeF]+[PF_6]^-$; $XeF_4 + SbF_5 \rightarrow [XeF_3]+[SbF_6]$

$XeF_2 + MF \rightarrow M^+[XeF_7]^-$ (M = Na, K, Rb or Cs)

(b) **Xenon-Oxygen compounds**

Hydrolysis of XeF_4 and XeF_6 with water gives $Xe0_3$.

$6XeF_4 + 12\,H_2O \rightarrow 4Xe + 2XeO_3 + 24\,HF + 3\,O_2$

$XeF_6 + 3\,H_2O \rightarrow XeO_3 + 6\,HF$

- Partial hydrolysis of XeF_6 gives oxyfluorides, XeO_2F_2 and $XeOF_4$.
- $Xe0F_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.
- $Xe0_3$ is a colourless explosive solid and has a pyramidal molecular structure.

Uses of Noble Gases

- **Helium** is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors . It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.
- **Neon** is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.
- **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. It is also used in the laboratory for handling substances that are air-sensitive.

CHEMICAL REACTIONS

1. $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
2. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
3. $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + SO_4^{2-} + 4H^+ + 2Mn^{2+}$
4. $2F_2\,(g) + 2H_2O\,(l) \rightarrow 4H^+\,(aq) + 4F^-\,(aq) + O_2\,(g)$
5. $X_2(g) + H_2O(l) \rightarrow HX\,(aq) + HXO\,(aq)$ (X=Cl, Br)
6. $4I^-(aq) + 4H^+\,(aq) + O_2 \rightarrow 2I_2\,(s) + 2H_2O\,(l)$
7. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

8. $2NaOH\ (Dil) + X_2 \xrightarrow{Cold} NaX + NaOX + H_2O$

9. $6NaOH\ (Conc) + 3X_2 \xrightarrow{heat} 5NaX + NaXO_3 + 3H_2O\ (X_2=Cl_2, Br_2, I_2)$

10. $2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

11. $NaCl + H_2SO_4 \xrightarrow{heat} NaHSO_4 + HCl$

12. $XeF_2 + PF_5 \rightarrow [XeF]^+[PF6]^-$

13. $XeF_6 + MF \rightarrow M^+[XeF_7]^-\ (M=Na, K, Rb \text{ or } Cs)$

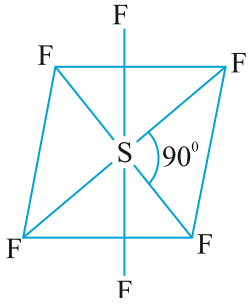
14. $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

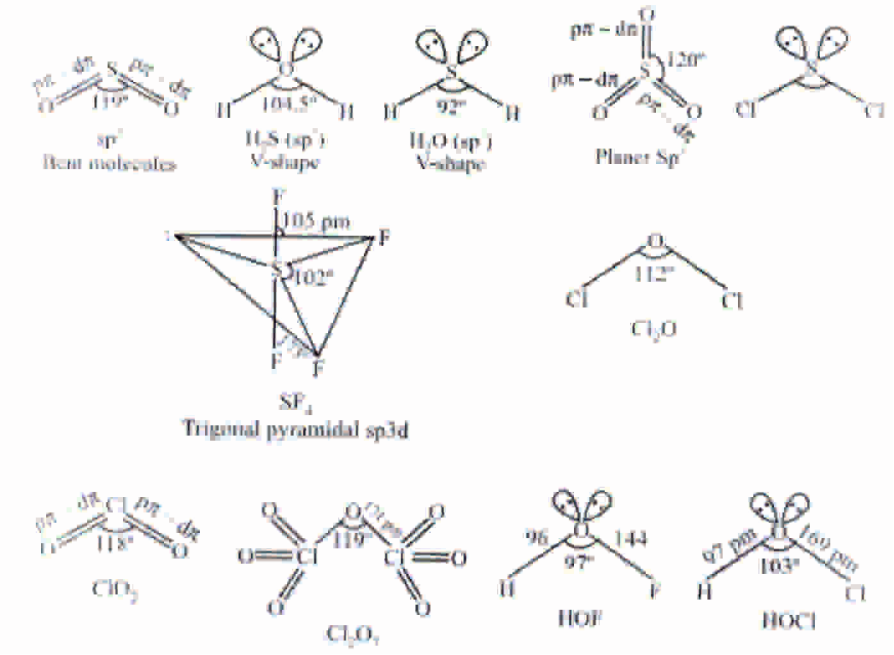
15. $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

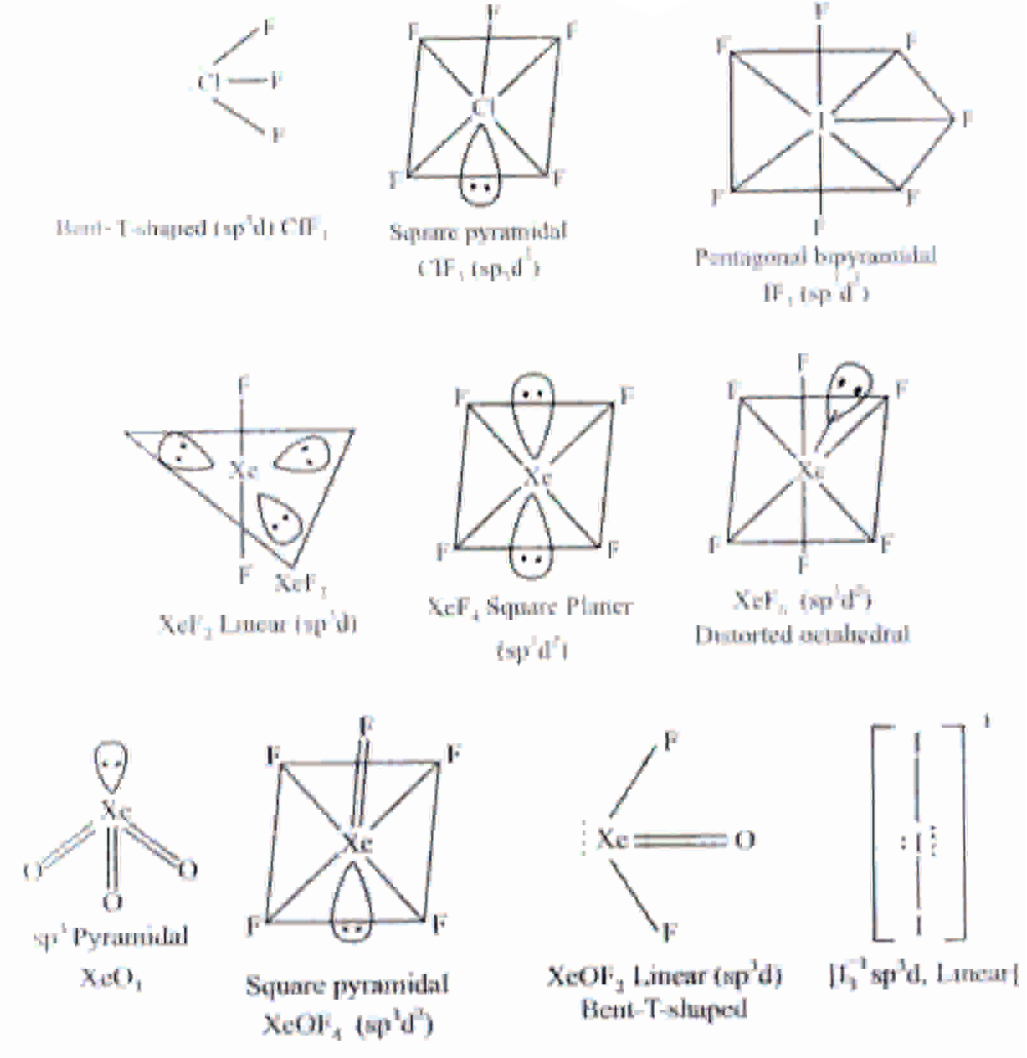
16. $XeF_6 + H_2O \rightarrow XeOF_3 + 2HF$

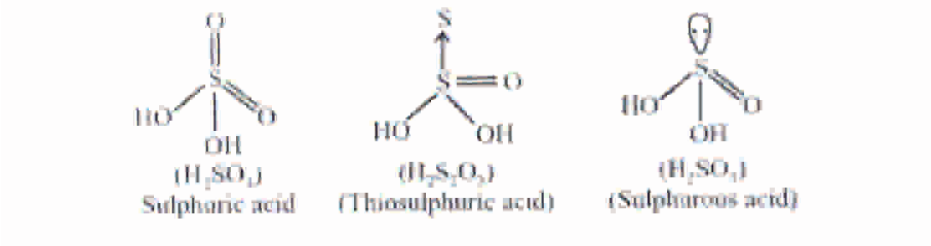
17. $XeF_6 + 2H_2O \rightarrow XeO_2F_3 + 4HF$

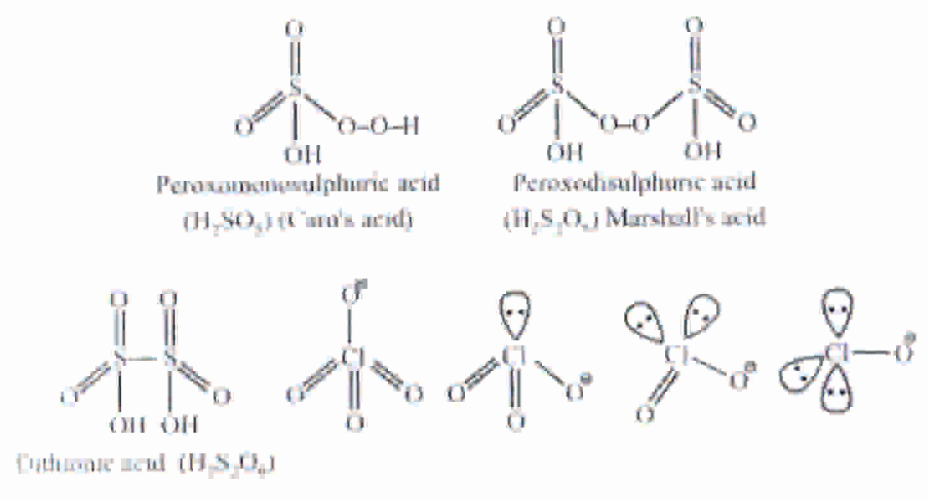
STRUCTURES OF COMPOUNDS






Bent-T-shaped (sp^3d) ClF_3
Square pyramidal
(ClF_5 (sp^3d^2))
Pentagonal bipyramidal
(IF_7 (sp^3d^3))
XeF_2 Linear (sp^3d)
XeF_4 Square Planer
(sp^3d^2)
XeF_6 (sp^3d^3)
Distorted octahedral
sp^3 Pyramidal
XeO_3
Square pyramidal
$XeOF_4$ (sp^3d^2)
$XeOF_2$ Linear (sp^3d)
Bent-T-shaped
[I_3^- sp^3d, Linear]


(H_2SO_4)
Sulphuric acid
($H_2S_2O_3$)
(Thiosulphuric acid)
(H_2SO_3)
(Sulphurous acid)



OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. On addition of cone. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodise salt, violet fumes come out. This is because

   (a) H_2SO_4 reduces HI to I_2 (b) HI is of violet colour

   (c) Hl gets oxidised to I_2 (d) HI changes to H103

2. Affinity for hydrogen decreases in the group from fluorine to iodine which of the halogen acids should have highest bond dissociation enthalpy?

   (a) HF (b) HCl

   (c) HBr (d) HI

3. Which of the following are permonoacids of sulphur?

   (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 $H_2S_2O_7$

4. In the preparation of compounds of Xe, Bartlett had taken $O_2^+PtF_6^-$ as a base compound. This is because

(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.

5. Reduction potentials of same ions are given below. Arrange them in decreasing Order of oxidising power. Ion ClO_4^- IO_4^- BrO_4^-

Reduction potential E°/V E-=1.1 9V E-=1.65V E-=1.74V

(a) $ClO_4^- > IO_4^- > BrO_4^-$

(b) $IO_4^- > BrO_4^- > ClO_4^-$

(c) $BrO_4^- > IO_4^- > ClO_4^-$

(d) $BrO_4^- > ClO_4^- > IO_4^-$

6. Bond angle in H_2O (104.5°) is higher than the bond angle of H_2S (921.1^0). The difference is due to



(a) O is diatomic and S is tetra-atomic

(b) difference in electronegativity of S and O

(c) difference in oxidation states of S and O

(d) difference in shapes of hybrid orbitals of S and 0

7. Arrange the following hydrides of group 16 elements in order of increasing stalility.

(a) $H_2S < H_2O < H_2Te > H_2Se$ (b) $H_2O < H_2Te < H_2Se < H_2S$

(c) $H_2O < H_2S < H_2Se < H_2Te$ (d) $H_2Te < H_2Se < H_2S < H_2O$

8. The hybridisation of sulphur in sulphur tetrafluroide is

(a) sp^3d (b) sp^3d^2

(c) sp^3d^3 (d) sp^3

9. On heating $KClO_3$, we get

(a) $KClO_3 + O_2$ (b) $KCl + O_2$

(c) $KCl + O_3$ (d) $KCl + O_2 + O_3$

10. The correct order of acidic strength is:

(a) $K_2O > CaO > MgO$ (b) $CO_2 > N_2O_5 > SO_3$

(c) $Na_2O > MgO > Al_2O_3$ (d) $Cl_2O_7 > SO_2 > P_4O_{10}$

11. Which one is not a property of ozone?

(a) it acts an oxidising agent in dry state (b) oxidation of KI into KIO_2

(c) PbS is oxidised to $PbSO_4$ (d) Hg is oxidised to Hg_2O

12. The oxyacid of sulphur that contains a Ione pair of electrons on sulphur is:

(a) sulphurous acid (b) sulphuric acid

(c) peroxodisulphuric acid (d) pyrosulphuric acid

13. The oxidation state of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$-follows the order:

(a) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$ (b) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

(c) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$ (d) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

14. The correct order of increasing electro gain enthalpy of halogens is:

(a) $I < Br < Cl$ (b) $Br < I < Cl$

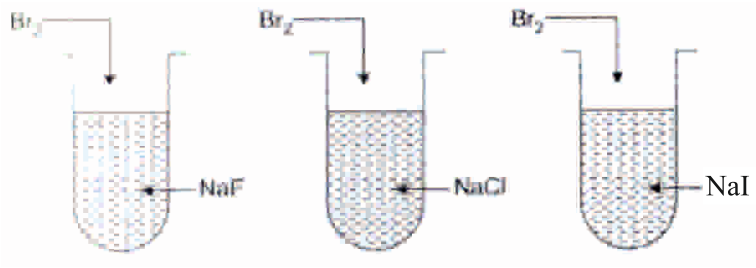
(c) $Cl < Br < I$ (d) $I < Cl < Br$

15. Which is the correct arrangement of the compounds based on their bond strength?

(a) $HF > HCl > HBr > HI$ (b) $HI > HBr > HCl > HF$

(c) $HCl > HF > HBr > HI$ (d) $HF > HBr > HCl > HI$

16. What is the correct operation when Br2 is treated with NaF, NaCl and Nal taken in three test tukes lavelled (X), (Y) and (Z)?



(a) F_2 is liberated in (X) and Cl_2 in (Y)

(b) Only I_2 is liberated in (Z).

(c) Only Cl_2 is liberated in (Y)

(d) Only F_2 is liberated in (X)

17. Which of the following increasing order is not correct as mentioned in the property with it?

(a) $HClO < HClO_2 < HClO_3 < HClO_4$ (thermal stability)

(b) $HClO_4 < HClO_3 < HClO_2 < HClO$ (oxidising power)

(c) $F^- < Cl^- < Br^- < I^-$ (reducing nature)

(d) $HIO_4 < ICl < I_2 < HI$ (oxidation number of iodine)

18. Complete the following reactions by filling the appropriate choice:

(A) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + (i) + (ii)$

(B) $XeF_6 + 3H_2O$ (iii) + 6HF

	(i)	(ii)	(iii)
(a)	F_2	H_2O	$XeOF_4$
(b)	24 HF	$3O_2$	XeO_3
(c)	2 HF	$2H_2O$	XeO
(d)	HF	H_2O	Xe_2O_3

19. Among the following molecules (i) XeO_3, (ii) $XeOF_4$, (iii) XeF_6 those having same number of lone pairs on Xe are:

(a) (i) and (ii) only (b) (i) and (iii) only

(c) (ii) and (iii) only (d) (i), (ii) and (iii)

20. Compound with the geometry square pyramidal and sp^3d^2 hybridisation is:

(a) $XeOF_2$ (b) $XeOF_4$

(c) XeO_4 (d) XeO_2F_2

21. Bond dissociation enthalpy of E-H (E = element) bonds is given below. Which of the compounds will act as strongest reducing agent?

Compound	NH_3	PH_3	AsH_3	SbH_3
Δdiss (E—H)/kJ mol-1	389	322	297	255

(a) NH_3 (b) PH_3 (c) AsH_3 (d) SbH_3

22. Which of the following statements is wrong?

(a) Single N–N bond is stronger than the single P–P bond.

(b) PH_3 can act as a ligand in the formation of coordination compound with transition elements.

(c) NO_2 is paramagnetic in nature.

(d) Covalency of nitrogen in N_2O_5 is four.

23. A brown ring is formed in the ring test for NO^-_3 ion. It is due to the formation of

(a) $[Fe(H_2O)_5(NO)]^{2+}$ (b) $FeSO_4.NO_2$

(c) $[Fe(H_2O)_4(NO)_2]^{2-}$ (d) $FeSO_4.HNO_3$

24. Which of the following properties is not shown by NO?

(a) Its bond order is 2.5. (b) It is diamagnetic in the gaseous state.

(c) It is a neutral oxide. (d) It combines with oxygen to form nitrogen dioxide.

25. In the preparation of HNO_3, we get NO gas by catalytic oxidation of ammonia. The moles of NO produced by the oxidation of two moles of NH_3 will be_____.

(a) 2 (b) 3

(c) 4 (d) 6

II ASSERTION AND REASON TYPE QUESTIONS

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong but reason is correct statement.

1. **ASSERTION :** PCl_5 is covalent in gaseous and liquid states but ionic in solid state.
   REASON : $PC1_5$ exists as tetrahedral PCl_4^+ cation and octahedral PCl_6^- anion.
2. **ASSERTION :** The moisture present in NH_3 cannot be removed by P_2O_5 or conc. H_2SO_4. It can be dried by CaO.
   REASON: NH_3 has high heat of vapourisation and cause intense cooling on being vapourised.
3. **ASSERTION :** SF_4 is hydrolysed but SF_6 is not.
   REASON: SF_4 has see saw shape but SF_6 has octahedral shape.
4. **ASSERTION :** Bond energy of Cl -Cl bond is more than F-F bond.
   REASON : Shorter the bond length, more the bond strength and more is the bond energy.
5. **ASSERTION :** N_2 is less reactive than P_4.
   REASON : Nitrogen has more electron gain enthalpy than phosphorus.
6. **ASSERTION :** HNO_3 makes iron passive.
   REASON : HNO_3 forms a protective layer of ferric nitrate on the surface of iron.
7. **ASSERTION:** HI cannot be prepared by the reaction of KI with concentrated H_2SO_4.
   REASON : HI has lowest H-X bond strength among halogen acids.
8. **ASSERTION :** Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2.
   REASON : Oxygen forms pπ-pπ multiple bond due to small size and small bond length but pπ-pπ bonding is not possible in sulphur.

9. **ASSERTION :** 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 : MnO_2 oxidises HCl to chlorine gas which is greenish yellow.

10. **ASSERTION :** SF_6 cannot be hydrolysed but SF_4 can be.
REASON : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. In group 15 elements, there is considerable increase in covalent radius from N to P but small increase from As to Bi. Why ?
[Hint : Due to completely filled d- and/or f-orbitals in As, Sb and Bi.]

Q.2. The tendency to exhibit - 3 oxidation state, decreased down the group in group 15 elements. Explain.
[Hint : Due to increase in size and decrease in electronegativity down the groups.]

Q.3. Maximum covalence of nitrogen is '4' but the heavier elements of group 15 show covalence greater than '4'. Why ?
[Hint : Nitrogen is not having vacant d-orbitals in its octet, hence cannot expand its octet, while heavier members have vacant d-orbitals to expand their octet.]

Q.4. Nitrogen exists as a diatomic molecule with a triple bond between the two atoms, whereas the heavier elements of the group do not exist as E_2 at room temperature. Assign a reason.
[Hint : p-p multiple bonds are formed by N due to its small size.]

Q.5. The ionization enthalpies of group 15 elements are higher than those of corresponding members of group 14 and 16 elements. Assign the reason.
[Hint : Due to their stable electronic configuration ($ns^2 np^3$).]

Q.6. The boiling point of PH_3 is lesser than NH_3. Why ?
[Hint : NH_3 molecules are stabilized by intermolecular H-bonding, while PH_3 by weak van der Waals's forces.]

Q.7. NO_2 dimerises to form N_2O_4 . Why ?
[Hint : Due to presence of odd electron on N.]

Q.8. Draw the structure of N_2O_5 molecule.

Q.9. How does ammonia solution react with Ag^+ (aq) ? Write the balanced chemical equation.

[Hint : $Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$]

Q.10. Why does NH_3 forms intermolecular hydrogen bonds whereas PH_3 does not ?

[Hint : Due to strong cicctroncgativity, small size of nitrogen atom and presence of lone pair of electrons on N atom.]

Q.11. Write disproportionation reaction of H_3PO_3 ? [Hint : $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$]

Q.12. How does NH_3 acts as a complexing agent ? [Hint : Metal hydroxides are dissolved in excess of NH_4OH. Ammonia acts as a Lewis base. It can donate electron pair to central metal atom or ion.]

Q.13. Write the reaction of PCl_5 with heavy water. [Hint : $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$]

Q.14. What is laughing gas ? How is it prepared ? [Hint : N_2O, $NH_4NO_3 \rightarrow 3\ N_2O + 2H_2O$]

Q.15. Why is white phosphorus kept under water ?

[Hint : Due to high angular strain, it is highly reactive and catches fire in air, hence kept under water.]

Q.16. "Hydrophosphorus acid is a good reducing agent." Justify with an example.

[Hint : $4AgNO_3 + H_3PO_2 + 2H_2O \rightarrow 4Ag + 4HNO_3 + H_3PO_4$]

Q.17. Draw the structure of $H_4P_2O_7$ and find out its basicity.

[Hint : As four - OH groups are present, hence basicity is 4.]

Q.18. Why is Bi (V) a stronger oxidant than Sb (V) ?

[Hint : Due to inert pair effect; + 3 oxidation state is more stable than + 5 oxidation state in Bi.]

Q.19. How many P-O - P bonds are there in cyclotrimetaphosphoric acid ? [Hint : 3 bonds]

Q.20. Give reason : In the solid state, PCl_5 behaves as an ionic species. [Hint : It exists as an ionic solid $[PCl_4]^+[PCl_6]^-$]

Q.21. Give reason : $BiCl_3$ is less covalent than PCl_3 .

[Hint : Due to more polarization power of P^{3+} ion than Bi^{3+} ion.]

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Complete the following reactions :

Q.1. (i) $(NH_4)_2Cr_2O_7 \xrightarrow{heat}$

(ii) $NH_4Cl(aq) + NaNO_2(aq) \rightarrow$

Q.2. (i) $NH_2CONH_2 + H_2O \rightarrow$

(ii) $FeCl_3(aq) + NH_4OH(aq) \rightarrow$

Q.3. (i) $Ca_3P_2 + H_2O(l) \rightarrow$

(ii) $I_2 + HNO_3(conc.) \rightarrow$

Q.4. (i) $Ba(N_3)_2 \xrightarrow{heat}$

(ii) $4H_3PO_3 \xrightarrow{heat}$

Q.5. (i) $PH_4I + KOH \rightarrow$

(ii) $HgCl_2 + PH_3 \rightarrow$

Q.6. (i) $PCl_3 + 3H_2O \rightarrow$

(ii) $PCl_5 + H_2O \rightarrow$

Q.7. (i) $NO_3^- + Fe^2 + H^+ \rightarrow$

(ii) $Zn + HNO_3(dil.) \rightarrow$

Q.8. (i) $Zn + HNO_3(conc.) \rightarrow$

(ii) $P_4 + HNO_3(conc.) \rightarrow$

Q.9. (i) $NH_3 + O_2 \xrightarrow[500K,\ 9\ bar]{Pt/Rh}$

(ii) $P_4 + NaOH + H_2O \rightarrow$

Q.10. (i) $NH_3(excess) + Cl_2 \rightarrow$

(ii) $NH_3 + Cl_2(excess)$

Q.11. (i) $P_4 + HNO_3(conc.) \rightarrow$

(ii) $Cu + HNO_3(conc.) \rightarrow$

Q.12. Arrange the following in the decreasing order of their basicity. Assign the reason :

$PH_3, NH_3, SbH_3 AsH_3, BiH_3$.

[Hint : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$]

Q.13. An unknown salt X reacts with hot conc. H_2SO_4 to produce a brown coloured gas which intensifies on addition on copper turnings. On adding dilute ferrous sulphate solution to an aqueous solution of X and then carefully adding conc. H_2SO_4 along the sides of the test tube, a brown complex Y is formed at the interface between the solution and H_2SO_4 . Identify X and Y and write the chemical equation involved in the reaction.

[Hint : $X = NO_3^-$ salt,] [$Y = [Fe(H_2O)_5 (NO)]^{2+}$]

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

$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5 (NO)]^{2+}] + H_2O$ (Brown complex)

Q.14. Explain each of the following : (i) The bond angles (O-N-O) are not of the same value in NO_2^- and NO_2^+. (ii) BiH_3 is the strongest reducing agent amongst all the hydrides of group 15 elements. (iii) Ammonia has greater affinity for protons than phosphine.

[Hint : (i) Due to presence of lone pair of electron on N in NO_2^- (ii) Bi-H bond dissociation enthalpy is least and releases hydrogen most easily. (iii) NH_3 is stronger Lewis base than PH_3]

Q.15. Write balanced equation for the following reactions : (i) Zn is treated with dilute HNO_3. (ii) Copper metal with conc. HNO_3 . (iii) Iodine is treated with conc. HNO_3.

[Hint : (i) $4Zn + 10HNO_3 (dil.) \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$

(ii) $3Cu + 8HNO_3 (dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(iii) $I_2 + 10HNO_3 (conc.) \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$]

Q.16. A transluscent 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 NaOH liberates a highly poisonous gas (C) having a rotten fish smell. (A) with excess of chlorine forms (D) which hydrolyses to form compound (E). Identify the compounds (A) to (E).

[Hint : A : White phosphorus, B : Red phosphorus, C : PH_3, D : PCl_5 , E : H_3PO_4]

Q.17. Assign the appropriate reason for the following : (i) Nitrogen exists as diatomic molecule and phosphorus as P_4 at room temperature. Why ? (ii) Why does R_3 P =O exist but R_3 N = O does not ? (R= an alkyl group). (iii) Why is N_2 unreactive at room temperature ?

[Hint : (i) Due to its small size and high electronegativity, N forms pπ-pπ multiple bond (N = N) whereas P does not form pπ-pπ bonds but forms P-P single bond.

(ii) In R_3 N = O, N should have a covalence of 5 so the compound R_3 N = O does not exist since maximum covalence shown by N cannot exceed 4.]

GROUP 16 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. Explain why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis ?

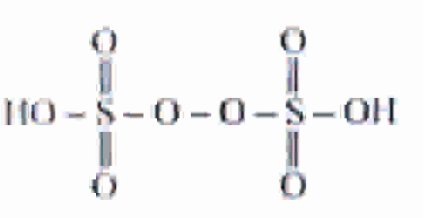
[Hint : Water molecule cannot attack 'S' atom due to steric hinderance and 'S' atom is also coordinately saturated in SF_6 molecule.]

Q.2. In group 16, the stability of + 6 oxidation state decreases and that of + 4 oxidation state increases down the group. Why ?

[Hint : Due to inert pair effect.]

Q.3. Draw the structure of $H_2S_2O_8$ and find the number of S-S bond. if any.

[Hint :



Number of S-S bond ⇨ 0.]

Q.4. What happens when sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt ?

[Hint : It converts Fe^{3+} ions to Fe^{2+} ions. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$]

Q.5. All the bonds in SF_4 are not equivalent. Why ?

[Hint : It is having see-saw shape. (4BP + 1LP)]

Q.6. O_3 acts as a powerful oxidizing agent. Why ?

[Hint : Due to the ease with which it liberates atoms of nascent oxygen.] $O_3 \rightarrow O_2 + [O]$

Q.7. Which one of the following is not oxidized by O_3? State the reason : KI, $FeSO_4$, K_2MnO_4, $KMnO_4$

[Hint : $KMnO_4$, since Mn is showing maximum oxidation state of + 7.]

Q.8. Why does oxygen not show an oxidation state of + 4 and + 6 ?

[Hint : Due to absence of vacant d-orbitals in the octet of oxygen.]

Q.9. Oxygen and sulphur in vapour phases are paramagnetic in nature. Explain why?

[Hint : Due to presence of unpaired electrons in anti-bonding molecular orbitals in them.]

Q.10. Thermal stability of hydrides of group 16 elements decreases down the group. Why?

[Hint : Because down the group E - H bond dissociation enthalpy decreases.]

Q.11. Why are the two S - O bonds in SO_2 molecule have equal strength ?

[Hint : Due to resonance, two S - O bonds have partial double bond character, hence have equal strength.]

Q.12. $Ka_2 << Ka_1$ for H_2SO_4 in water, why ?

[Hint : $H_2SO_4\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + HSO_4^-\,(aq)$; $Ka_1 > 10$

$HSO_4^-\,(aq) + H_2O \rightarrow H_3O^+\,(aq) + SO_4^{2-}(aq)$; $Ka_2 = 10^{-2}$ Ka_2 is less than Ka_1 because HSO_4^- ion has much less tendency to donate a proton.]

Q.13. H_2O is a liquid while inspite of a higher molecular mass, H_2S is a gas. Explain.

[Hint : H_2O molecules are stabilized by intermolecular hydrogen bonding, while H_2S by weak van der Waal's forces.]

Q.14. The electron gain enthalpy with negative sign for oxygen (-141 KI mol^{-1}) is numerically less than that for sulphur (-200 KJ mol^{-1}). Give reason.

[Hint : Due to smaller size of oxygen than sulphur electron-electron repulsion is more in oxygen than sulphur.]

Q.15. Dioxygen O_2 is a gas while sulphur (S_8) is a solid. Why ?

[Hint : Because oxygen is smaller in size hence have capacity to form pπ-pπ multiple bond, exists as dioxygen (O_2), whereas due to bigger size sulphur do not form multiple bond and exist as S_8.]

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q.1. Write the chemical equations of the following reactions : (a) Sucrose is heated with conc. H_2SO_4. (b) Sodium nitrate is heated with conc. H_2SO_4.

[Hint : (a) $C_{12}H_{22}O_{11} + \text{Conc. } H_2SO_4 \rightarrow 12C + 11H_2O$

(b) $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$]

Q. 2. Complete the following reactions :

(a) $PbS + O_3 \rightarrow$

(b) $KI + H_2O + O_3 \rightarrow$

(c) $MnO^{-1}_4 + SO_2 \rightarrow H_2O$

(d) $S_8 + H_2SO_4\,(\text{Conc.}) \rightarrow$

Q.3. Explain why : (a) H_2S is more acidic than H_2O. (b) Two S - O bonds in SO_2 are identical. (c) SF_6 is inert and stable but SF_4 is reactive. (d) Sulphur has greater tendency for catenation than oxygen.

[Hint : (iii) Because six F atoms protect the sulphur atom from attack by any reagent due to steric hindrance but four F atoms in SF_4 cannot offer much steric hindrance, hence reactive.]

Q.4. How is O_3 estimated quantitatively ?

[Hint : O_3 reacts with an excess of KI solution buffered with a borate buffer, I_2 is liberated which is titrated against standard solution of sodium thiosulphate.]

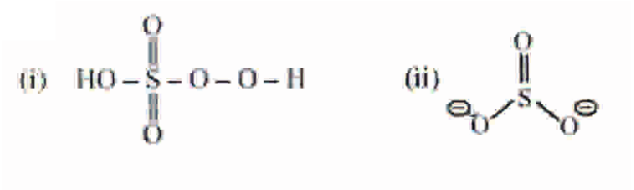
$2I^-(aq) + H_2O(1) + O_2(g) \rightarrow I_2(s) + O_2(g) + 2OH^-(aq)$

Q.5. Explain why O_3 is thermodynamically less stable than O_2 ?

[Hint : Because O_3 is endothermic compound/decomposition of O_3 is exothermic and ΔG is negative/decomposition of O_3 is spontaneous.]

Q.6. Draw the structure of : (i) H_2SO_5 (ii) SO_3^{2-}

[Hint:]



Q.7. (i) How does O_3 react with lead sulphide ? Write chemical equation. (ii) What happens when SO_2 is passed in acidified $KMnO_4$ solution ? (iii) SO_2 behaves with lime water similar to CO_2. Explain why ?

[Hint : (i) $PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$

(ii) It decolourises acidified $KMnO_4$ solution.

$SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

(iii) It turns lime water milky due to the formation of insoluble $CaSO_3$.

$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$

(Milkiness)

Q.8. Complete the reactions :

(i) $CaF_2 + H_2SO_4(Conc.) \rightarrow$

(ii) $C_{12}H_{22}O_{11} + H_2SO_4(Conc.)$

(iii) $SO_2 + MnO_4^- + H_2O \rightarrow$

Q.9. An amorphous solid 'A' burns in air to form a gas 'B' which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aq. $KMnO_4$ solution. Identify the solid 'A' and the gas 'B' and write the reaction involved.

[Hint : A = S_8; B= SO_2 (g)] (i) How is SO_2 prepared in laboratory ? (ii) What happens when SO_2 is passed through water and reacts with NaOH ? Write balanced equation. (iii) Write its any two uses.

[Hint :(I) $Na_2SO_3(s) + H_2SO_4(aq) \rightarrow SO_2(g) + Na_2SO_4(aq) + H_2O(l)$

(ii) $2NaOH + SO_2(g) \rightarrow Na_2SO_3(aq) + H_2O$

$Na_2SO_3(aq) + SO_2 + H_2O \rightarrow 2NaHSO_3(aq)$

(iii) It is used as bleaching agent and disinfectant.

Q.10. Assign reason for the following :

(i) Sulphur in vapour state exhibits paramagnetism.

(ii) H_2O is less acidic than H_2Te.

(iii) In spite of having same electronegativity, oxygen forms hydrogen bond while chlorine does not.

[Hint : (iii) Due to bigger size of Cl.]

GROUP 17 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1Mark)

Q.1. Explain why fluorine forms only one oxoacid, HOF.

[Hint : Because of unavailability of d-orbitals in its valence shell.]

Q.2. Why HF is the weakest acid and HI is the strongest ?

[Hint : K_a (HF) = 7 x 10^{-4} ; K_a (HI) = 7 x 10^{-11} Intermolecular H-bonds in H - F and high bond dissociation enthalpy of H - F makes it weakest and weak bond in H - I makes it strongest.]

Q.3. Explain why halogens are strong oxidizing agents.

[Hint : High electronegativity and more negative electron gain enthalpies of halogens.]

Q.4. I_2 is more soluble in KI than in water. Why ?

[Hint : $KI + I_2 \rightarrow KI_3$]

Q.5. What is cause of bleaching action of chlorine water ? Explain it with chemical equation.

[Hint : Formation of nascent oxygen.]

Q.6. Electron gain enthalpy of fluorine (F) is less negative than that of chlorine (Cl). Why ?

[Hint : Due to small size of F atom and compact 2p orbitals there are strong interelectronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience more repulsion in F than in Cl.]

Q.7. Why can't we prepare HBr by heating KBr with sulphuric acid ?

[Hint : As HBr readily reduces H_2SO_4 forming Br_2.]

Q.8. Explain why : ICl is more reactive than I_2 ?

[Hint : Because I - Cl bond is weaker than I - I bond.]

Q.9. Which oxide of iodine is used for the estimation of carbon mono oxide ?

[Hint : I_2O_5]

Q.10. Arrange the following oxoacids of chlorine in increasing order of acid strength :

HOCl, HOClO, $HOClO_2$, $HOClO_3$

[Hint : HOCl < HOClO < $HOClO_2$ < $HOClO_3$]

Q.11. Why does fluorine not play the role of a central atom in interhalogen compounds?

[Hint : Due to smallest size of F. and high electronegativity]

Q.12. Fluorine exhibit only - 1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain why ?

[Hint : Due to absence of vacant d-orbitals in the octet of F.]

Q.13. ClF_3 exists but FCl_3 does not. Why ?

[Hint : Because F does not show oxidation state other than - 1.]

Q.14. Despite lower value of its electron enthalpy with negative sign, fluorine is a stronger oxidizing agent than chlorine. Explain.

[Hint : Due to its low bond dissociation enthalpy (F-F bond) and high hydration enthalpy of F^-.]

Q.15. ClF_3 molecule has a bent T-shaped structure and not a trigonal planar structure. Explain.

[Hint : Due to presence of 2LP and 3BP.]

Q.16. What happens when NaCl is heated with H_2SO_4 in the presence of MnO_2 ?

[Hint : $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$]

Q.17. With what neutral molecule ClO^- is isoelectronic ?

[Hint : ClF or OF_2.]

Q.18. Why HF acid is stored in wax coated glass bottle ?

[Hint : HF is corrosive, hence HF attacks glass surface.]

Q.19. Bond dissociation enthalpy of F_2 is less than that of Cl_2. Explain why ?

[Hint : F_2 is having higher electron-electron repulsion due to its smaller size, as compared to Cl_2.]

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q.1. (i) Interhalogen compounds are more reactive than halogens except F_2. Why?

(ii) Give one important use of ClF_3.

[Hint : (i) Because X - X bond in interhalogens is weaker than X - X bond in halogens except F - F bond. (ii) ClF_3 is used for the production of UF_6.]

Q.2. (i) Write the composition of bleaching powder. (ii) What happens when NaCl is heated with cone. H_2SO_4 in the presence of MnO_2. Write the chemical equation.

[Hint : (I) $Ca(OCl)_2$. $CaCl_2.Ca(OH)_2.2H_2O$]

Q.3. A colourless pungent smelling gas, which easily liquefies to a colourless liquid and freezes to a white crystalline solid, gives dense white fumes with ammonia. Identify the gas and write the chemical equation for its laboratory preparation.

[Hint : $NaCl + H_2SO_4$ (cone.) $\rightarrow NaHSO_4 + HCl$]

Q.4. NO_2 readily dimenise, whereas ClO_2 does not. Why ?

[Hint : Due to bigger size of Cl than N.]

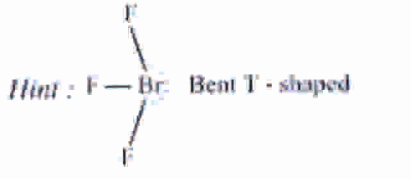
Q.5. Compare the oxidizing powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy, electron gain enthalpy of halogens and hydration enthalpy of halide ions.

[Hint : It is due to low enthalpy of dissociation of F - F bond and high hydration enthalpy of F^-.]

Q.6. Which fluorinating agent are oftenly used instead of F_2 ? Write chemical equation showing their use as flurorinating agents.

[Hint $U(s) + 3ClF_3(1) \rightarrow UF_6(g) + 3ClF(g)$]

Q.7. Draw the structure of BrF_3.



Complete the following reactions :

Q.8. (i) $Al_2O_3(s) + NaOH(aq) + H_2O(1) \rightarrow$ (ii) $HCl + O_2 \rightarrow$

Q.9. (I) $Ca(OH)_2 + Cl_2 \rightarrow$ (ii) N_2 (excess) $+ Cl_2 \rightarrow$

Q.10. (i) $Na_2SO_3 + Cl_2 + H_2O \rightarrow$ (ii) $N_2 + Cl_2$ (excess) $\rightarrow$

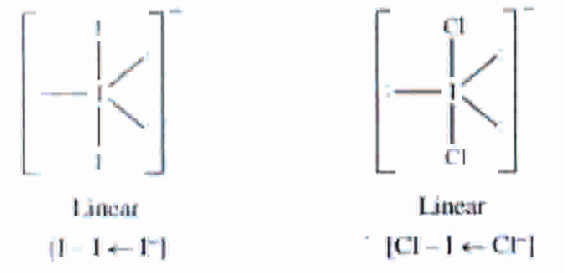
Q.11. (i) $C1_2 + NaOH$ (cold & dil.) $\rightarrow$ (ii) $Cl_2 + NaOH$ (hot & cone.) $\rightarrow$

Q.12. (i) $Fe + HCl \rightarrow$ (ii) $Cl_2 + F_2$ (excess) $\rightarrow$

Q.13. (i) $U + ClF_3 \rightarrow$ (ii) $FeSO_4 + H_2SO_4 + Cl_2 \rightarrow$

Q.14. Draw the structure of : (a) I_3^- (b) ICl_2^-

Hint :



Q.15. Give appropriate reason for each of the following : (i) Metal fluorides are more ionic than metal chlorides. (ii) Perchloric acid is stronger than sulphuric acid. (iii) Addition of chlorine to KI solution gives it a brown colour but excess of Cl_2 makes it colourless.

[Hint : (i) According to Fajan's Rule, bigger ions are more polarized than the smaller ions by a particular cation. (ii) $C1O_4^-$ is more resonance stabilized than SO_4^{2-} since dispersal of negative charge is more effective in $C1)_4^-$ as compared with SO_4^{2-}. (iii) $2KI + Cl_2 \rightarrow 2KCl + I_2$

$5Cl_2$ (excess) $+ I_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$ (colourless)

Q.16. X_2 is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in H_2O to give a solution which turns blue litmus red. When X_2 is passed through NaBr solution, Br_2 is obtained. (i) Identify X_2, name the group to which it belongs. (ii) What arc the products obtained when X_2 reacts with H_2O ? Write chemical equation. (iii) What happens when X_2 reacts with hot and conc. NaOH ? Give equation. [Hint : (i) Cl_2, 17 group.

(ii) $Cl_2(g) + 2H_2O(1) \rightarrow HCl(aq) + HOCl$ (aq)

(iii) $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

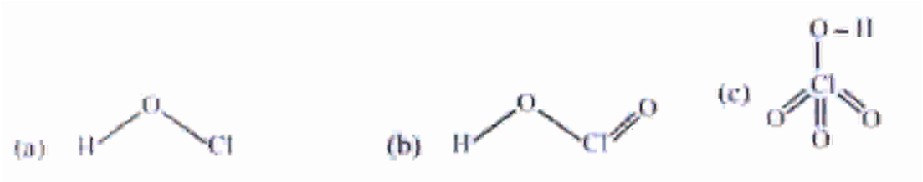
Q.17. Arrange the following in the order of the property indicated for each set : (I) F_2, Cl_2, Br_2, I_2 (Increasing bond dissocation energy) (ii) HF, HCl, HBr, HI (decreasing acid strength)

[Hint : (i) F_2 has exceptionally low bond dissociation enthalpy. Lone pairs in F_2 molecule arc much closer to each other than in Cl_2 molecule. Stronger electron-electron repulsions among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low, $I_2 < F_2 < Br_2 < Cl_2$

(ii) Acid strength depends upon H - X bond dissociation enthalpy. As the size of 'X' atom increases, bond dissociation enthalpy of H-X decreases. HI>HBr>HCl> HF

Q.18. Draw the structure of : (i) Hypochlorous acid (ii) Chlorous acid (iii) Perchlorie acid

[Hint :



Q.19. Which is more acidic among $HClO_4$ and HIO_4 ? Why

[Hint : $HClO_4$ is more acidic than HIO_4. Because Cl is more electronegative than Br, due to which ClO_3 group have more tendency to withdraw electrons of O-H bond towards itself as compared to BrO_3 group.]

GROUP 18 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. What inspired N. Barlett for carrying out reaction between Xe and PtF_6 ?

[Hint : Almost same ionization enthalpy of oxygen and Xe.]

Q.2. Predict the shape and the bond angle (90° or more or less) in the following case : XeF_2 and the angle .... $F \rightarrow \ddot{x}\ddot{e}\rightarrow F$

[Hint : Linear, 180°]

Q.3. Structure of Xenon fluoride cannot be explained by valence bond approach. Why ?

[Hint : Due to fully filled octet of Xe.]

Q.4. Why do some noble gases form compounds with fluorine and oxygen only ?

[Hint : Due to high electronegativity of F and oxygen.]

Q.5. XeF_2 has a straight linear structure and not a bent angular structure. Why ?

[Hint : In XeF_2, 2 bond pairs and 3 lone pairs are present hence linear structure.]

Q.6. Why do noble gases have very low boiling point ?

[Hint : Because noble gases are stabilized by weak van der Waal's forces.]

Q.7. Write the chemical equation involved in the preparation of XeF_4.

[Hint : $Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$] Ratio 1 : 5

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q.1. Suggest reason why only known binary compounds of noble gases are fluorides and oxides of Xenon and to a Jesse extent of Kryton.

[Hint : F and O are most electronegative elements Kr and Xe both have low ionization enthalpies as compared to He and Ne.]

Q.2. (i) Hydrolysis of XeF_6 is not regarded as a redox reaction. Why ? (ii) Write a chemical equation to represent the oxidizing nature of XeF_4.

[Hint : (i) Because oxidation number of Xe do not change during hydrolysis of XeF_6. (ii) $XeF_4 + 2H_2 \rightarrow Xe + 4HF$]

Q.3. Write chemical equations when : (i) XeF_2 is hydrolysed. (ii) PtF_6 and Xenon are mixed together.

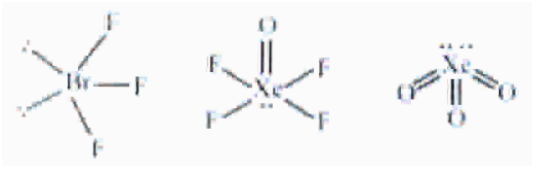
[Hint : (i) $2XeF_2(s) + 2H_2O(1) \rightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

(ii) $Xe + PtF_6 \rightarrow Xe^+[PtF_6]^-$]

Q.4. Complete the reactions : (i) $XeF_6 + H_2O \rightarrow$ (ii) $XeF_6 + H_2O \rightarrow$

Q. 5. Draw the structure of BrF_3, $XeOF_4$, XeO_3 using VSEPR theory.

[Hint :



Q.6. Account for the following : (i) XeF_2 has linear structure and not a bent structure. (ii) The majority of known noble gas compounds are those of Xenon. Why ?

[Hint : (ii) Xe has low ionization enthalpy as compared to other noble gases.]

Q.7. Write the chemical reactions :

(i) $XeF_2(s) + H_2O(1) \rightarrow$

(ii) $XeF_4 + O_2F_2 \rightarrow$

Q.8. Assign reason to the following : (i) Noble gases have large positive values of electron gain enthalpy. (ii) Helium is used by scuba divers. (iii) No chemical compound of helium is known.

[Hint : (i) Due to their electron configuration. (ii) Due to its less solubility in blood. (iii) Due to its high ionization enthalpy.]

Q.9. Draw the structure of : (i) $XeOF_4$ (ii) XeF_6 (iii) XeO_3

[Hint :

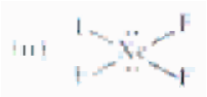


Q.10. Complete the reactions : (i) $XeF_2 + NaF \rightarrow$ (ii) $XeF_4 + SbF_5 \rightarrow$ (iii) $XeF_4 + H_2O$

Q.11. (i) How is XeO_3 prepared from XeF_6 ? Write the chemical equation for the reaction.

(ii) Draw the structure of XeF_4.

[Hint : (i) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$ Or $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$



CASE STUDY BASED QUESTIONS

1. **Read the passage given below and answer the following questions.**

Phosphorus forms a number of oxyacids in which oxidation states of P ranges from +1 to +5. The number of-OH groups attached to phosphorus determines the basicity of the oxyacid and the presence of P-H bond is responsible for the reducing nature.

(A) The oxyacid of phosphorus in which phosphorus has the lowest oxidation state is :

(a) hypophosphorus acid (b) orthophosphoric acid

(c) pyrophosphoric acid (d) metaphosphoric acid

(B) 1 mole each of H_3PO_2, H_3PO_3 and H_3PO_4 will neutralise respectively x mole of NaOH, y mole of $Ca(OH)_2$ and z mole of $Al(OH)_3$. (assuming all as strong electrolytes), x, y, z are in the ratio of

(a) 3 : 15 : 1 (b) 1 : 2 : 3

(c) 3 : 2 : 1 (d) 1 : 1 : 1

(C) The number of P-O-P and P-O-H bonds present respectively in pyrophosphoric acid molecule

(a) 1, 2 (b) 1, 4

(c) 2, 4 (d) 1, 3

(D) Oxidation state of phosphorus in metaphosphoric acid is:

(a) 1 (b) 3

(c) 5 (d) 4

2. Read the passage and answer the following questions.

Study the passage given below and answer the questions. The hydrides of oxygen family are H_2O, H_2S, H_2Se, H_2Te and H_2Po. The acidic nature, thermal stability and reducing character of these hydrides depend on the strength of M-H bond. H_2S is widely used in laboratory in qualitative analysis.

(A) Hydrogen sulphide reacts with lead acetate forming a black compound which reacts with hydrogen peroxide to form another compound. The colour of the compound is :

(a) black (b) yellow

(c) white (d) pink

(B) The reaction in the Kipp's apparatus stops on closing the outlet because:

(a) the acid gets weak

(b) a protective film is formed on iron sulphide

(c) gas starts coming out from the top

(d) the contact between the sulphide and the acid is broken by the pressure of the gas collected in the free surface of the middle chamber

(C) The boiling points of hydrides of group 16 are in the order:

(a) $H_2O > H_2Te > H_2S > H_2Se$ (b) $H_2O > H_2S > H_2Se > H_2Te$

(c) $H_2O > H_2Te > H_2Se > H_2S$ (d) None of the above

(D) Thc strongest reducing agent out of H_2O , H_2S , H_2Se , H_2Te

(a) H_2O (b) H_2S

(c) H_2Se (d) H_2Te

3. Read the given passage and answer the following questions :

The common oxidation states of elements of group 15 are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group. Further due to inert pair effect, the stability of +5 oxidation state decreases while that of +3 oxidation state increase down the group. Nitrogen is restricted to a maximum covalency of 4 while heavier elements expand their co-valencey upto 6 due to vacant of d-abitals. All the elements of group 15 from hydrides of the type EH_3 (Where E=N,P,As, Sb, Bi). The stability of hydrides decreases.

1 Maximum co-valency of Nitrogen is -

(a) 3 (b) 4

(c) 5 (d) 6

2 Common oxidation state of group 15 elements is-

(a) -3,+3,+5 (b) -4,+4,3

(c) 5,-3,1 (d) 6,2,3

3 Correct among the following hydrides, the correct decreasing order of basic strength is

(a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(b) $NH_3 < PH_3 < AsH_3 < SbH_3$

(c) $NH_3 > AsH_3 > SbH_3 > BiH_3$

(d) $SbH_3 > AsH_3 > BiH_3 > PH_3 > NH_3$

4 Correct order of reducing character of hydrides of Group 15 is -

(a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(b) $NH_3 < PH_3 < AsH_3 < SbH_3$

(c) $NH_3 > AsH_3 > SbH_3 > BiH_3$

(d) $SbH_3 > AsH_3 > BiH_3 > PH_3 > NH_3$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (a) How is XeF_6 prepared from the XeF_4 ? Write the chemical equation for the reaction.

(b) Deduce the structure of XeF_6 using VSEPR theory.

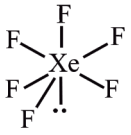
(c) How does XeF_2 reacts with PF_5 ?

(d) Give one use each of helium and neon.

(e) Write the chemical equation for the hydrolysis of XeF_4.

[*Hint :* (a) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

(b) Distorted octahedral (6BP + 1LP)



(c) $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$

(d) He is used in filling balloons/used by scuba divers.

Ne is used in discharge tubes, advertisement display purposes.

(e) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$]

Q.2. A greenish yellow gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate solution gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with the evolution of a colourless gas 'Y'. Identify gases 'X' and 'Y'.

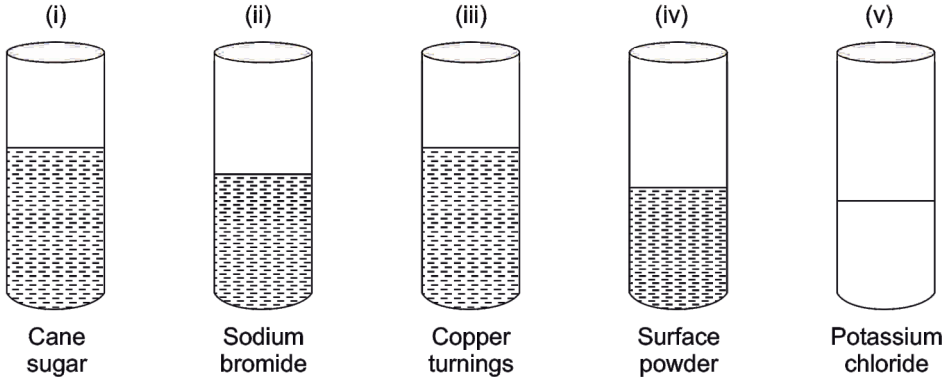
[Hint:]

$$\underset{X}{Cl_2} + H_2O \longrightarrow HCl + HClO$$

$$AgNO_3 + HCl \longrightarrow \underset{\text{(whiteppt.)}}{AgCl} + HNO_3$$

$$Mg + 2HCl \longrightarrow \underset{(Y)}{MgCl_2} + H_2$$

Q.3. Concentrated sulphuric acid is added followed by heating in each of the following test types labelled (i) to (v)



Identify in which of the above test tubes, the following changes will be observed. Support your answer with the help of a chemical equation.

(a) formation of black substance

(b) evolution of brown gas

(c) evolution of colourless gas

(d) formation of brown substance which on dilution becomes blue.

(e) disappearance of yellow powder along with the evolution of a colourless gas.

[*Hint*]

(a) $C_{12}H_{22}O_{11} \xrightarrow{Conc.H_2SO_4} \underset{(Black\ mass)}{12C} + 11H_2O$

(b) $2NaBr + 3H_2SO_4 \xrightarrow{heat} 2NaHSO_4 + SO_2 + Br_2 + 2H_2O$

(c) $KCl + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HCl(g)$

(d) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(e) $S_8 + 16H_2SO_4 \longrightarrow 24SO_2 + 16H_2O$

Q.4.An aqueous solution of gas 'A' gave the following data (reactions):

(a) It decolourised an acidified $KMnO_4$ solution.

(b) On boiling with H_2O_2 followed by cooling and then adding an aqueous solution of $BaCl_2$, a white precipitate insoluble in dilute HCl was obtained.

(c) On passing H_2S through the solution of the gas, white turbidity was obtained. Identify the gas and give equations for gas steps (i), (ii), and (iii).

Ans. (i) $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow \underset{(Colourless)}{K_2SO_4} + \underset{(Colourless)}{2MnSO_4} + 2H_2SO_4$

(ii) $H_2O_2 + SO_2 \xrightarrow{Boil} H_2SO_4$

$H_2SO_4 + BaCl_2 \longrightarrow \underset{(white\ ppt.)}{BaSO_4} + 2HCl$

(iii) $\underset{'A'}{SO_2} + 2H_2S \longrightarrow \underset{(turbidity)}{3S} + 2H_2O$

Q.5. An element 'A' exist as a yellow solid in standard stae. It forms a voilet hydride 'B' which is a foul smelling gas and is extensively used in qualitative analysis of salts. When reated with oxygen. 'B' forms an oxide 'C' which is a colourless and pungent smelling gas. The gas when passed through acidified $kMnO_4$ solution, decolourises it, 'C' gets oxidised to another oxide 'D' in the presence of heterogenous catalyst. Identifier A, B, C, D and also give the chemical equation of reaction 'C' with acidified $KmnO_4$ solution and for conversion of 'C' into 'D'.

Solution:

(iii) $\underset{(A)}{S_8(s)} + 8H_2(g) \xrightarrow{heat} \underset{(B)}{8H_2S(g)}$

$\underset{(B)}{2H_2S(g)} + 3O_2(g) \xrightarrow{\Delta} \underset{(C)}{2SO_2(g)} + 2H_2O(g)$

$\underset{(C)}{2SO_2(g)} + O_2(g) \xrightarrow{Pt.} \underset{(D)}{2SO_3(g)}$

Overall : $\underset{(voilet)}{2KMnO_4} + 5SO_2 + 2H_2O \longrightarrow \underset{(colourless)}{K_2SO_4} + \underset{(colourless)}{2MnSO_4} + 2H_2SO_4$

from NH_3 to BiH_3. Reducing character of hydrides increases. Basicity of hydrides also decrease from NH_3 to BiH_3.

ANSWERS

I MULTIPLE CHOICE TYPE QUESTIONS

1. (c) 2. (a) 3. (a) 4. (c) 5. (c) 6. (b) 7. (d) 8. (a) 9. (b) 10. (d) 11. (b) 12. (a) 13. (b)
14. (a) 15. (a) 16. (b) 17. (d) 18. (b) 19. (d) 20. (b) 21. (d) 22. (a) 23. (a) 24. (b) 25.(a)

II ASSERTION AND REASON

1. (b) 2. (b) 3. (b) 4. (c) 5. (c) 6. (c) 7. (b) 8. (a) 9. (a) 10. (a)

CASE STUDY BASED QUESTIONS

PASSAGE I (A) (a) (B) (d) (C) (b) (D) (c)

PASSAGE II (A) (a) (B) (d) (C) (c) (D) (d)

PASSAGE III (A) (b) (B) (a) (C) (a) (D) (b)

UNIT TEST
CHAPTER-6
p- BLOCK ELEMENTS

MAXIMUM MARKS : 20 **TIME : 1 HRS**

1. Draw shape of BrF_5 (1)
2. Nitrogen does not form pentahalides. Why? (1)
3. Draw the structure of SO_2 molecule. Comment on the nature of two S-O bonds formed in it. Are the two S-O bonds in this molecule equal? (1)
4. The value of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen. Why? (1)
5. Elements of group 16 generally show lower value of first ionisation enthalpy compared to the elements in the corresponding periods of group 15. (1)
6. (i) Draw the structure of XeF_6.
   (ii) Give reason: Hydrogen iodide is a stronger acid than hydrogen fluoride in aqueous solution. (2)
7. Despite lower value of its electron gain enthalpy with negative sign, fluorine is a stronger oxidising agent than chlorine. Explain. (2)
8. Complete the following chemical reaction equations: (2)
   (I) I_2+Conc. $HNO_3 \rightarrow$ (ii) $HgCl_2 + PH_3 \rightarrow$
9. Explain the following observations: (3)
   (i) The molecules NH_3 and NF_3 have dipole moments which arc of opposite direction.
   (ii) All the bonds in PCl_5 molecule are not equivalent.
   (iii) Ozone acts as an oxidising agent.
10. Draw the structures of (3)
    (i) ClF_3 (ii) XeF_4 (iii) XeO_2F_2
11. A white waxy, translucent solid, M, insoluble in water but soluble in CS_2, glows in dark, M dissolves in NaOH in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of Q.
    (a) Identify M, N and Q, write the chemical equations of the reactions involved.
    (b) M exists in the form of discrete tetrahedral molecules. Draw its structure.
    (c) M on heating at 573 K is changed into other less reactive form R, which is non poisonous, insoluble in water as well as in CS_2 and does not glow in dark. Identify R and draw its structure. (5)

UNIT 7

d- and f- Block Elements

Points to Remember

Element having partially filled d-subshell in their elemental or common oxidation state.

Zn, Cd and Hg not considered as transition elements as not having partially filled d - subshell in their elemental or common oxidation state.

General Electronic configuration of the d-block elements is $(n-1)\,d^{1-10}ns^{-2}$.

Outer Electronic Configurations of four d-block series elements.

1st Series										
	Sc	T1	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series										
	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

General Properties of the Transition Elements

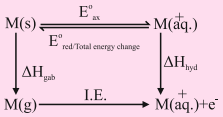
Atomic and Ionic Radii : In a given transition series, from left to right net nuclear charge as well as screening effect increase. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then screeninh effect counter balance nuclear charge due to which atomic size becomes almost constant for next five elements of the series. Size of 4d and 5d series elements is almost same due to lanthanoid contraction.

Enthalpies of Atomisation: Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms.

Ionisation Enthalpies : ● In a series from left to rigth, ionization enthalphy increases due to increase in nucleae charge.

● The irregular trend in the first ionization enthalphy of the 3d metals, though of little chemical significance, considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

Standard Electrode Potentials:



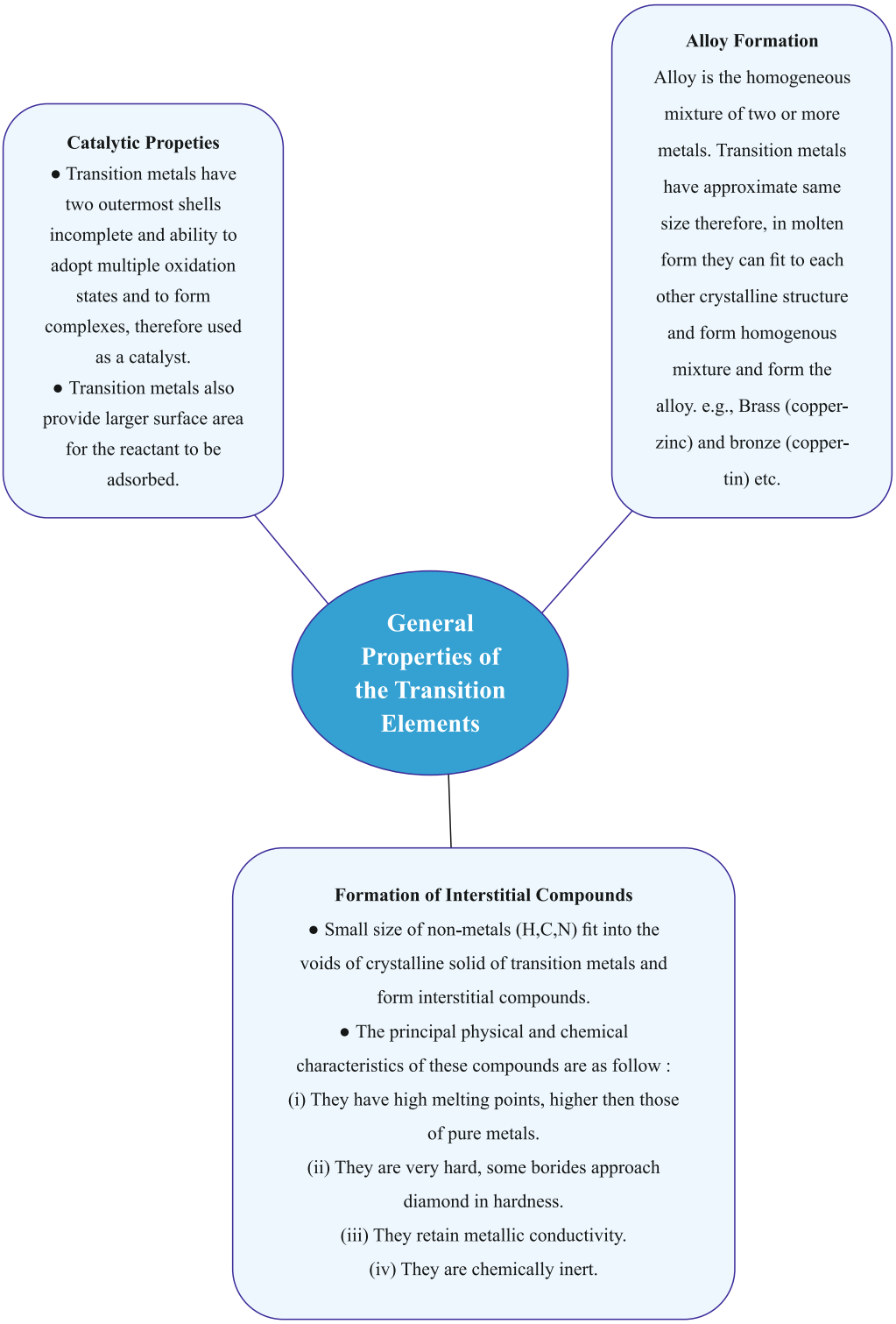
Total energy change E°red. = DHsub + I.E. + DHhyd. Thus, we can find the total energy change for a particular oxidation state of a metal in its aqueous solution.
The irregularity is due to irregular variation of ionisation energies and the sublimation energies of the atoms and the hydration energies of the divalent ions of the members of first transition series. Greater the value of negative electrode potential, greater will be the stability of M+2 state.

Oxidation States : Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are Sc(+3), Ti(+4), V(+5), Cr(+3,+6), Mn(+2,+7), Fe(+2,+3), Co(+2,+3), Ni(+2), Cu(+2), Zn(+2)
● The transition elements in their lower oxidation states (+2 and +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent. ● Only Os and Ru show + 8 oxidation states in their compounds. ● Ni and Fe in Ni(CO)4 and Fe (CO)5 show zero oxidation state.

Magnetic Properties :
● When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moments associated with its spin angular momentum.
● The magnetic moment is determined by the number of unpaired electrons.
Magnetic moment = nn+()
2
where, n=number of unpaired electron. If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

Formation of Complex Compounds
● Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of elements from ligands.
● They have vacant d-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

Formation of Coloured
● The d-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy d-orbitals is excited to a higher energy d-orbital, the energy of required wavelenght is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.
● In V_2O_5, V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.


Alloy Formation
Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogenous mixture and form the alloy. e.g., Brass (copper-zinc) and bronze (copper-tin) etc.
Catalytic Propeties
● Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.
● Transition metals also provide larger surface area for the reactant to be adsorbed.
General Properties of the Transition Elements
Formation of Interstitial Compounds
● Small size of non-metals (H,C,N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.
● The principal physical and chemical characteristics of these compounds are as follow :
(i) They have high melting points, higher then those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

Some important Compounds of Transition Elements

Preparation

Ore- Ferrochrome or chromate ($FeO.Cr_2O_3$) or ($FeCr_2O_4$)

$FeO.Cr_2O_3+8Na_2CO_3+7O_2 \rightarrow 8Na_2CrO_4+2Fe_2O_3+8CO$ (yellow)

$2Na_2CrO_4+2H^+ \rightarrow Na2Cr_2O_2+2Na^++H_2O$ (orange)

$Na_2Cr_2O_2+2KCl \rightarrow K_2Cr_2O_2+2NaCl$

Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

Propeties

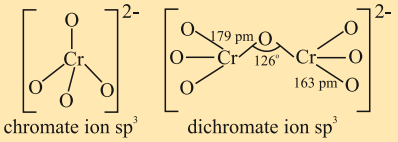
Sodium and potassium dichromates are strong oxidizing agents, thus, acidified, K2Cr2O7 will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

$Cr_2O_7^{2-}+14H^++61^- \rightarrow 2Cr^{3+}+7H_2O+3I_2$

$Cr_2O_7^{2-}+3H_2S+8H^+ \rightarrow 2Cr^{3+}+3S+7H_2O$

$Cr_2O_7^{2-}+14H^++3Sn^{2+} \rightarrow 3Sn^{4+}+2Cr^{3+}+7H_2O$

Potassium Dichromate ($K_2Cr_2O_7$)



chromate ion sp^3

dichromate ion sp^3

Uses

(a) K2Cr2O7 is used as oxidizing agent in volumetric analysis.

(b) It is used in mordant dyes, leather industry, photography (for hardening of film).

(c) It is used in chromyl chloride test.

(d) It is used in cleaning glassware.

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Ore

Preparation

$2MnO_2+4KOH+O_2 \rightarrow 2K_2MnO_4+2H_2O$
(green)

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

Commercial preparation

$MnO_2 \xrightarrow[\text{with air on } KNO_3]{\text{Fused with KOH oxidised}} \underset{\text{Manganous ion}}{MnO_4^{2-}}$

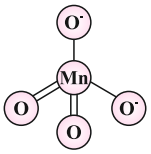
$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} \underset{\substack{\text{Permanganous ion}\\ \text{(purple)}}}{MnO_4^{-}}$

Uses

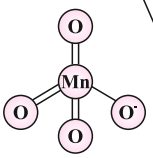
(a) In laborator preparation of Cl2.

(b) KMnO4 is used as an oxidizing agent, disinfectant.

(c) In making Baeyer's reagent.



Tetrahendral manganate (green) ion



Tetrahendral permanganate (purple) ion

 # Potassium Permanganate $KMnO_4$

NOTE :

K2Cr2O7 and KMnO4 are coloured due to charge transfer complex formation.

PROPERTIES:

$KMnO_4$ acts as strong oxidizing agent.

(a) In presence of dilute H_2SO_4, $KMnO_4$ is reduces to manganous salt.

$MnO_4^-+8H^++5e^- \rightarrow Mn^{2+}+4H_2O$

Acidic $KMnO_4$ solution oxidizes oxalates to CO_2, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

$C_2O_4^{2-} \rightarrow CO_2+2e^-$

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

$NO_2^- \rightarrow NO_3^-+2e^-$

$2I^- \rightarrow I_2+2e^-$

To acidufy $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as oxidizing agent.

(b) in alkaline medium, $KMmO_4$ is reduced to insoluble MnO_2.

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

Alkaline or neutral $KMnO_4$ solution oxidizes I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.

 # Not in CBSE syllabus 2021-22. Important for compititive examinations only.

The Inner Transition Elements (f-Block)

The f-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

LANTHANOIDS:

General configuration [Xe] 4f1-14, 5fd0-1, 6s2.

- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La3+ nor Lu3+ ion shows any colour but the rest do so.
- The lanthanoid ions other than the f 0 type (La3+ and Ce4+) and the f14 type (Yb2+ and Lu3+) are all paramagnetic. The paramagnetism arises to maximum in neodymium.
- Oxidation states→Ce4+; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common+3 state. The Eovalue foe Ce^{4+}/Ce^{3+} is +1.47 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu^{2+} os formed by losing the two s-electrons and its f^{7} configuration accounts for the formation of this ion. However, Eu2+ is a strong reducing agent changing to the common + 3state. Similarly, Yb2+ which has f14 configuration is a reductant, Tb4+ has half-filled f-orbitals and is an oxidant.
- Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigratte and gas lighters, toys, tank and tracer bullets.

#

ACTINOIDS:

- General configuration [Rn] $5f^{1-14}$,$6d^{0-2}$, $7S^{2}$.
- Actinoids exhibit a range of oxidation states due to comparable energies of 5f, 6d and 7s orbitals. The genral oxidation state of actinoids is + 3.
- All the actinoids are strong reducing agents and very reactive.
- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc. like lanthanoids.
- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.

 # Not in CBSE syllabus 2021-22. Important for compititive examinations only.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE TYPE QUESTIONS

1. One of the characteristics of transition metals to form the complex ion is:
   (a) Having unpaired electron in d-subshell
   (b) Having paired electrons in d-subshells
   (c) Providing empty d-orbitals
   (d) Having small charge/size ratio
2. The correct electronic configuration of copper atom is:
   (a) $3d^{10}4s^{1}$ (b) $3d^{10}4s^{2}$
   (c) $3d^{9}4s^{2}$ (d) $3d^{5}4s^{2}4p^{4}$
3. Maximum number of unpaired electrons are in :
   (a) Cr (b) Mn
   (c) Fe^{2+} (d) Co
4. Manganese exhibits maximum oxidation state in:
   (a) K_2MnO_4 (b) $KMnO_4$
   (c) MnO_2 (d) Mn_3O_4
5. General electronic configuration of d-block elements is :
   (a) $(n-1)d^{1-10}ns^{0-2}$ (b) $(n-1)d^{1-10}ns^{1-2}$
   (c) $(n-1)d^{1-10}ns^{0}$ (d) $(n-1)d^{1-10}ns^{1}$
6. Electronic configuration of d-block element 'x' in +3 oxidation state in [Ar] $3d^5$, Atomic number of 'x' is :
   (a) 25 (b) 26
   (c) 27 (d) 24
7. CrO_3 dissolves in aqueous NaOH to give:
   (a) $CrO4^{2-}$ (b) $Cr(OH)_3$
   (c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$
8. The electronic configuration of gadolinium (At. No 64) is:
   (a) $[Xe]\,4f^{8}\,5d^{O}\,6s^{2}$ (b) $[Xe]\,4f^{7}\,5d^{2}\,6s^{2}$
   (c) $[Xe]\,4f^{3}\,5d^{5}\,6s^{2}$ (d) $[Xe]\,4f^{6}\,5d^{2}\,6s^{2}$

9. Electronic configuration of a transition element in + 3 oxidation state is [Ar] $3d^5$. What is is atomic number?

(a) 25 (b) 26

(c) 27 (d) 24

10. 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.

(a) Mn_2O_7 (b) MnO_2

(c) Mn_5O_4 (d) Mn_2O_3

11. Which of the following oxidation state is common for all lanthanoids?

(a) +2 (b) +3

(c) +4 (d) +5

12. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after same time because:

(a) CO_2 is formed as the products

(b) Reaction is exothermic

(c) MnO_4^- catalysis the reaction

(d) Mn^{2+} acts as autocatalyst

13. $KMnO_4$ acts as 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:

(a) 2 5 (b) 3 5

(c) 4 5 (d) 1 5

14. Which of the following is amphotric oxide? Mn_2O_7, CrO_3, Cr_2O_3, CrO_3, V_2O_5, V_2O_4.

(a) V_2O_5, Cr_2O_3 (b) Mn_2O_7, CrO_3

(c) CrO_3, V_2O_5 (d) V_2O_5, V_2O_4

15. The magnetic moment is associated with its spin angular momentum. Spin only magnetic moment value of Cr^{3+} ion is.....

(a) 2.87 B,M (b) 3.87 B.M

(c) 3.47 B.M (d) 357 B.M

16. Generally transition elements and their salts are coloured due to the product of unpaired electrons in metal ions. Which of the following compounds are coloured?

(a) $KMnO_4$ (b) $ZnSO_4$

(c) $Ticl_4$ (d) Cu_2C1_2

17. 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?

(a) CO^{2+},Cr^{2+} (b) Cr^{2+},Mn^{2+}

(c) Mn^{2+},CO^{2+} (d) CO^{2+},Cr^{3+}

18. Which of the following actionoids show oxidation states upto + 7?

(a) Am (b) Pu

(c) U (d) Th

19. Which of the following ions show highest spin only magnetic moment value?

(a) Ti^{3+} (b) Mn^{2+}

(c) Fe^{2+} (d) CO^{3+}

II FILL IN THE BLANKS

1. Hybridisation of Cr in Chromate ion is.....
2. Maximum oxidation state exhibited by Mn is.....
3. Electronic configuration of Cr^{+} is.....
4. Theoretical magnetic moment of Ti^{3+} ion is.....
5. The equivalent weight of $K_2Cr_2O_7$ in acidic medium is.....
6. Last element in the actinide series is.....
7. The general electronic configuration of d — block elements is.....
8. The colour of $KMnO_4$ is due to.....
9. Out of Sc^{2+} and Sc^{3+} ion, ... is paramagnetic.
10. The oxidation state of Mn in K_2MnO_4 is .....

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(i) Both assertion and reason are True, and reason is the correct explanation of the assertion.

(ii) Both assertion and reason are True, but reson is not the correct explanation of the assertion.

(iii) Assertion is true, but reason is false.

(iv) Assertion is false, reason is true.

1. **ASSERTION** : Sc does not show variable oxidation states.
   REASON : Sc has only one electron in the 3d subshell.
2. **ASSERTION :** Separation of Zr and Hf is difficult.
   REASON: Because Zr and Hf lie in the same period of the periodic table.
3. **ASSERTION :** Actinoids form relatively less stable complexes as compared to lanthanoids.
   REASON: Actinoids can utilise their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.
4. **ASSERTION :** Cu cannot liberate hydrogen from acids.
   REASON: Because it has positive electrode potential.
5. **ASSERTION :** The highest oxidation state of osmium is + 8.
   REASON: Osmium is a 5d-block element.

IV ONE WORD QUESTION ANSWERS

1. Which element in 3d series shows highest number of oxidation states? (Mn)
2. Out of Cuprous and Cupric ions which is coloured? (Cupric)
3. Out of Zn and Cr which is having higher first ionisation enthalpy? (Zn)
4. Give general Electronic Configuration of actinoids. ($5f^{1-14}\ 6d^{0-1}\ 7s^2$)
5. Name the element of 3d series which does not exhibit variable oxidation state. (Sc)

6. What is the equivalent weight of $KMnO_4$ in alkaline medium. (58 g)
7. What is the maximum oxidation state shown by actinoids. (7)
8. Out of $Cucl_2$ and Cu_2cl_2 which is more stable? ($CuCl_2$)
9. Name one ore of Cr. (chromite ore)
10. What is the cause of similar size of Zr and Hf . (Lanthanoid Contraction)

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. Explain $CuSO_4.5H_2O$ is blue while $CuSO_4$ is colourless ?

Ans. Because water molecules act as ligands and results in crystal field splitting of d-orbitals of Cu^{2+} ion.

Q. 2. Which element among 3d series exhibit highest oxidation state ?

Ans. Mn

Q.3. In 3d series (Sc to Zn), the enthalpy of atomization of Zn is low. Why ?

Ans. Due to absence of unpaired electrons.

Q.4. Which element among 3d series exhibit only one oxidation state ?

Ans. Sc

Q.5. Why is the 3rd ionization energy of Mn (Z = 25) is unexpectedly high ?

Ans. Due to half-filled electronic configuration.

Q.6. Define alloy.

Ans. Alloys are homogeneous solid solutions of two or more metals.

Q.7. Transition metals show zero oxidation state with ligands like CO. Explain.

Ans. CO form synergic bonding with metal ion.

Q.8. Why can't HCl acid be used to acidify $KMnO_4$ solution ?

Ans. Because $KMnO_4$ oxidize HCl into Cl_2.

Q. 9. Name one ore of Mn and Cr.

Ans. Mn : MnO_2 Cr : $FeCr_2O_4$

Q.10. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their + 3 state ?

Ans. Mn^{+2} has half-filled electronic configuration.

Q.11. Why do transition metal (elements) show variable oxidation states ?

Ans. Due to presence of vacant d-orbitals.

Q.12. Write any uses of pyrophoric alloy.

Ans. Making bullets, shells and ligher flints.

Q.13. Which is more basic - $La(OH)_3$ or $Lu(OH)_3$? Why ?

Ans. $La(OH)_3$, due to lanthanide contraction, lower size, more covalent character, least basic.

Q.14. Find out number of Cr - O - Cr bond/bonds in $Cr_2O_7^{2-}$ ion.

Ans. 1

Q.15. Why is Ce^{4+} in aqueous solution a good oxidizing agent ?

Ans. Because Ce^{4+} is most stable in Ce^{+3} state in aqueous solution.

Q.16. Why do Zr and Hf exhibit similar properties ?

Ans. Due to lanthanide contraction.

Q.17. What is lanthanoid contraction ?

Ans. The regular slow decrease in the atomic or ionic radii of lanthanoids with increasing atomic number.

Q.18. Why is Cu (Z = 29) considered a transition metal ?

Ans. Due to its partially filled d-orbital in Cu^{2+} state.

Q.19. Arrange the given in increasing order of acidic character : CrO_3, CrO, Cr_2O_3.

Ans. $CrO_3 < CrO < Cr_2O_3$

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

Q. 1. Chromium is typical hard metal while mercury is a liquid. Explain why ?

Ans. Cr has five unpaired d-electrons. Hence metallic bonds are strong. In Hg, there is absence of 'unpaired electrons and size is larger.

Q.2. Why $KMnO_4$ is used in cleaning surgical instruments in hospitals ?

Ans. This is because $KMnO_4$ has a germicidal action.

Q.3. Most of the transition metals do not displace hydrogen from dilute acids, why ?

Ans. Due to their -ve reduction potential.

Q.4. Explain why Cu^{+} is not stable in aqueous solution ?

Ans. Due to less negative Δhyd of Cu^{+}/it cannot compensate 2nd ionization potential of Cu.

Q.5. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

Ans. Oxygen and fluoride have small size and high electronegativity. They can oxidise the metal.

Q.6. Write electronic configuration of Cu^{+2} and Co^{+2}.

Ans. $Cu^{2+} = [Ar]\ 3d^{9}\ 4s^{o}$ Co^{2+} - $[Ar]\ 3d^{7}$

Q.7. Briefly explain why electronic configuration of lanthanoids are not known with certainty ?

Ans. 4f/5d subshells are very close in energy. +ve electrons can jump from 4f to 5d or vice-versa.

Q.8. Why Zn, Cd, Hg are soft and have low melting point ?

Ans. Due to weak interatomic attraction/absence of unpaired electrons.

Q.9. Which of the following is/are transition element and why ? Zn, Cd, Ag, Fe, Ni

Ans. Fe, Ni, Ag

Q.10. What are interstitial compounds ? Give example.

Ans. When small atoms like C, H, B and N occupy interstitial site in their lattice. Example : TiC.

Q.11. Why is first ionization energy of 5d elements higher than those of 3d and 4d elements ?

Q.12. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% lanthanoid and 5% iron and traces of S, C, Ca and AI. Used in lighter flint, bullet tips etc.

Q.13. The following two reactions of HNO_3 with Zn are given :

(a) $Zn + \text{conc. } HNO_3 \rightarrow Zn(NO_3)_2 + X + H_2O$

(b) $Zn + \text{dil. } HNO_3 \rightarrow Zn(NO_3)_2 + Y + H_2O$ Identify X and Y.

Ans. $X = NO_2$ $Y = N_2O$

Q.14. Out of Fe and Cu, which one would exhibit higher melting point ?

Ans. Fe, due to large number of unpaired d-electrons/more interatomic attraction.

Q.15. Sc, the first member of first transition series does not exhibit variableoxidation state. Why ?

Ans. Due to noble gas electronic configuration in + 3 oxidation state no other oxidation state is stable.

Q.16. (a) Deduce the number of 3d electrons in the following ions : Cu^{2+}, Sc^{3+}

(b) Why do transition metals form alloy ?

(c) Why Zn^{2+} salts are white ?

Ans. (a) Cu^{+2} : 9 electrons : Sc^{3+} : 0 electron

(b) Transition metals have similar atomic radii.

(c) Absence of unpaired electron.

Q.17. (a) Why is separation of lanthanoid elements difficult ?

(b) Transition metal exhibit higher enthalpies of atomization. Explain why ?

(c) Why the transition metals have ability to form complexes?

Ans. (a) Due to lanthanide contraction, the size of these elements is nearly same.

(b) Transition metal contain large number of unpaired electrons, and they have strong interatomic attractions.

(c) Due to their small size and large nuclear charge.

Q.18. (a) Use Hund's rule to derive the electronic configuration of Ce^{3+} ions and calculate its magnetic moment.

(b) Is lanthanum a f-block element ?

Ans. (a) $Ce(58) = [Xe]\, 4f^1 5d^1 6s^2$; $Ce^{3+} = 4f^1$, μ=1.73 BM $\mu=\sqrt{n(n+2)}$

(b) No, it is a d-block element.

Q.19. Account for the following :

(a) Silver chloride dissolves in excess of NH_3.

(b) Cuprous chloride is diamagnetic while cupric chloride is paramagnetic.

(c) in CrO_4^{2-} ion, all the Cr-O bond length are equal.

Ans. (a) AgCl forms a soluble complex with NH_3. $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

(b) Cu^+ : $3d^{10}\ 4s^o$ - All electrons are paired. Cu^{2+} : $3d^9$ - Here, one unpaired electron is present.

(c) Due to resonance.

Q.20. The E^o values in respect of electrodes of Cr, Mn and iron are : Cr^{3+}/Cr^{2+} = - 0.4 V Mn^{3+}/Mn^{2+} = + 1.5 V Fe^{3+}/Fe^{2+} = + 0.8 V Compare the feasibilities of further oxidation of these ions.

Ans. Cr^{+3} is more stable than Cr^{2+}. Mn^{2+} is more stable than Mn^{3+}. Fe^{3+} is more stable than Fe^{2+}. Order of feasibility of + 2 oxidation state is : $Mn^{2+} > Fe^{2+} > Cr^{2+}$

Q.21. Write any three properties of interstitial compounds.

Ans. (a) They are chemically inert.

(b) They retain metallic conductivity.

(c) They have high melting point than their pure metals.

(d) These are harder and more corrosion resistant.

Q.22. Account for the following :

(a) All Scandium salts are white.

(b) The first ionization energy of the 5d series are higher than 3d and 4d transition elements in respective groups.

(c) Ce^{3+} can be easily oxidized to Ce^{4+}.

Ans. (a) Sc has only + 3 oxidation state, there is no unpaired electron.

(b) Due to lanthanide contraction, effective nuclear charge increase.

(c) Due to gain noble gas electron configuration.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (a) What is meant by disproportionation of an oxidation state ? Give one example.

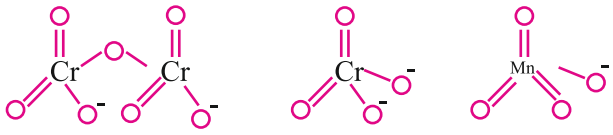
(b) Draw the structures of $Cr_2O_7^{2-}$, CrO_4^{-2}, MnO_4^-.

(c) What is the effect of lanthoids contraction beyond lanthanoid ?

Ans. (a) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.

$2Cu^+ \rightarrow Cu^{2+} + Cu$

(b)



(c) Size of respective 4d and 5d series elements becomes comparable from fourth group onwards (e.g., Zr and Hf).

2. 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 4d and 5d block elements.

(v) Trends in acidic character of lanthanoid oxides.

Ans. (i) As the size decreases covalent character increases. Therefore, La_2O_3 is more ionic and Lu_2O_3 is more covalent.

(ii) As the size decreases from La to Lu, stability of oxosalts also decreases.

(iii) Stability of complexes increases as the size of lanthanoids decreases.

(iv) Radii of 4d and 5d block elements will be almost same.

(v) Acidic character of Oxides increases from La to Lu.

3. (a) Answer the following questions:

(i) Which element of the first transition series has highest second ionisation enthalpy?

(ii) Which element of the first transition series has highest third ionisation enthalpy?

(iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Identify the metal and justify your answer.

(i) Carbonyl $M(CO)_5$

(ii) MO_3F

Ans. (a)

(i) Cu, because the electronic configuration of Cu is 3d104s1. So second electron needs to be removed from completely filled d-orbital.

(ii) Zn [Hint : As above.

(iii) Zn [Hint : No unpaired electron for metallic bonding]

(b) (i) $Fe(CO)_5$ [Hint : EAN rule]

(ii) MnO_3F [Hint : Mn shows + 7 oxidation state; d-electrons are not involved in bonding.]

4. (i) How would you account for the following?

(a) The oxidising power of oxo-anions are in the order $VO^{2+} < Cr_2O_7^{2-} < MnO^{4-}$

(b) The third ionisation enthalpy of manganese (Z = 25) is exceptionally high.

(c) Cr^{3+} is a stronger reducing agent than Fe^{2+}.

(ii) Give reasons for the following:

(a) Mn^{3+} is a good oxidising agent.

(b) $E^{o}(M^{2+}/M)$ values are not regular for first row transition metals (3d-series).

(c) Although 'F' is more electronegative than 'O' the highest Mn fluoride is MnF_4, where as the highest oxide is Mn_2O_7 reducing agent than Fe^{2+}.

Ans (i) (a) It is due to the fact that V in its lower oxidation state is less stable than Cr which in turn is less stable than Mn. Thus, MnO_4^- has a great tendency to get reduced and hence, behave as a good oxidising agent. Similary VO^{2+} has the least oxidising power.

(b) The third ionisation enthalpy of Mn is very high due to the fact that the third electron has to be removed from stable half-filled configuration, i.e., $3d^5$.

(c) Cr^{2+} is stronger reducing agent than Fe^{2+} because $d^4 \rightarrow d^3$ transition occurs in case of Cr^{2+} to Cr^{3+} while $d^6 \rightarrow d^5$ transition occurs in case of Fe^{2+} to Fe^{3+}. In a medium like water d^3 is more stable as compared to d^5.

(ii) (a) Mn3+ (3d4) is a good electron acceptor as the resulting species is more stable ($3d^5$).

(b) The $E^{o}(M^{2+}/M)$ values are not regular which can be explained from the irregular variation of ionisation enthalpies ($\Delta iH_1 + \Delta iH_2$) and also the sublimation enthalpies which are relatively much less for Mn and V.

(c) Due to multiple bond formation ability of oxygen, Mn can form Mn_2O_7.

5. The elements of 3d-transition series are given as:

SC, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following :

(i) Write the element which shows maximum number of oxidation states. Give reason.

(ii) Which element has the highest melting point?

(iii) Which element shows only + 3 oxidation state?

(iv) Which element is a strong oxidizing agent in + 3 oxidation state and why?

Ans (i) Mn. It has maximum unpaired electrons.

(ii) Cr

(iii) Sc

(iv) Manganese. Mn^{3+} to Mn^{2+} results in the stable half filled (d^5) configuration.

CASE STUDY BASED QUESTION

1. Read the passage and answer the following questions.

Potassium dichromate is one of the crystalline inorganic chemical reagents. Hexavalent chromium compounds are harmful to health. $K_2Cr_2O_7$ is widely used in laboratories and industry as an oxidizing agent because it is not deliquescent. Potassium dichromate looks very bright and red-orange color. In this work different amount of acidic (HCl) and alkaline (NaOH) solutions were added to stoke solutions of K_2CrO_4 and $K_2Cr_2O_7$ to show the effect of pH values on their spectra.

The results of UV-Visible spectroscopy shows that, the Changing of solution pH value when drops of HCI were added led to shift wavelength of K_2CrO_4 spectrum while no change has been occurred in $K_2Cr_2O_7$ spectrum. However, Changing PH values solution by adding drops of NaOH led to change in wavelength red shift for $K_2Cr_2O_7$ while no changes has been occurred in spectrum of K_2CrO_4.

Title of Research Article: Effect of the Acidic and Alkaline Solutions on K_2CrO_4 and $K_2Cr_2O_7$ by Ultraviolet and Visible Measurement Mohammad Radi Mohammad, Hasanain Saad Azeez* Al-Mustansiriyah Journal of Science ISSN: 1814-635X (print), ISSN:2521-3520 (online) Volume 30, Issue 1, 2019, 221-224

(A) The hybridization of Cr in dichromate ion is :

(a) d^2sp^3 (b) sp^3

(c) dsp^2 (d) sp^3d

(B) Colour of potassium dichromate is :

(a) purple (b) green

(c) yellow (d) orange

(C) Chemical formula of ferrochrome is :

(a) $FeCrO_2$ (b) $FeO.Cr_2O_3$

(c) Fe_2CrO_4 (d) None of these

(D) On increasing pH of dichromate, it converts in :

(a) CrO_4^{2-} (b) $Cr_2O_4^{2-}$

(c) CrO_4^{-1} (d) CrO_3

1. Read the passage and answer the following questions.

Heavy rare earth elements crystallize into hexagonally close packed (h.c.p.) structures and share a common outer electronic configuration, differing only in the number of 4 felectrons they have. These chemically inert 4f electrons set up localized magnetic moments, which are coupled via an indirect exchange interaction involving the conduction electrons. This leads to the formation of a wide variety of magnetic structures, the periodicities of which are often incommensurate with the underlying crystal lattice. Such incommensurate ordering is associated with a 'webbed' topology of the momentum space surface separating the occupied and unoccupied electron states (the Fermi surface). The shape of this surface—and hence the magnetic structure—for the heavy rare earth elements is known to depend on the ratio of the interplanar spacing c and the interatomic, intraplanar spacing a of the h.c.p. lattice. A theoretical understanding of this problem is, however, far from complete. Here, using gadolinium as a prototype for all the heavy rare earth elements, we generate a unified magnetit phase diagram, which unequivocally links the magnetic structures of the heavy rare earths to their lattice parameters.

In addition to verifying the importance of the c/o ratio, we find that the atomic unit cell volume plays a separate, distinct role in determining the magnetic properties: we show that the trend from ferromagnetism to incommensurate ordering as atomic number increases is connected to the concomitant decrease in unit cell volume. This

volume decrease occurs because of the so-called lanthanide contraction, where the addition of electrons to the poorly shielding 4f orbitals leads to an increase in effective nuclear charge and, correspondingly, a decrease in ionic radii.

Lanthanide contraction and magnetism in the heavy rare earth elements.

Hughes, I., Dane, M., Ernst, A. et al.

Nature 446,650-653 (2007). https://doi.org/10.1038/nature05668

(A) Rare earth elements are also called :

(a) Actinides (d) Lanthanides

(c) Alkali metals (d) None of these

(B) Radioactive lanthanide is :

(a) Pm (b) Ce

(c) Nd (d) Er

(C) Cause of lanthanide contractions is :

(a) poor shielding of 5f orbitals (b) poor shielding of 4f orbitals

(c) poor shielding of 6f orbitals (d) All of these

(D) The common oxidation state of lanthanides is :

(a) +4 (b) +3

(c) +2 (d) +1

ANSWERS

I. MULTIPLE CHOICE TYPE QUESTIONS

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

II FILL IN THE BLANKS

1. sp^3 2. +7
3. $[Ar]3d^5 4s^1$ 4. 1.732
5. 49g 6. lawrencium
7. (n-1)d1-10 ns O-2 8. charge transfer complex
9. Sc^{2+} 10. 6

III ASSERTION REASON TYPE QUESTIONS

1) (ii) 2) (ii) 3) (iii) 4) (i) 5) (ii)

CASE STUDY BASED QUESTIONS

PASSAGE I

(A) b (B) d

(C) b (D) a

PASSAGE II

(A) b (B) a

(C) b (D) b

UNIT TEST
CHAPTER-7

Maximum marks: 20 **Time Allowed: 1 Hour**

1. Which element among 3d-transition elements, exhibit the highest oxidation state? (1)
2. Mention two consequences of Lanthanoid Contraction. (1)
3. Calculate the magnetic moment of Cu^{2+} (Z = 29) on the basis of "spin-only" formula. (1)
4. Name a transition element which does not exhibit variable oxidation state in 3d series. (1)
5. Write the general electronic configuration of d-block elements. (1)
6. Write complete chemical equations for: (a) Oxidation of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium (b) Oxidation of Mn^{2+} by MnO_4^- in neutral or faintly alkaline medium. (2)
7. Account for the following: (a) Copper shows its inability to liberate hydrogen gas from the dilute acids. (b) Scandium (Z = 21) does not exhibit variable oxidation states. (2)
8. Explain lanthanoid contraction with its consequences. (2)
9. Assign reasons for the following: (3)

(a) Majority of transition metals form complexes.

(b) Ce^{3+} can be easily oxidised to Ce^{4+}.

(c) Actinoids display a variety of oxidation states.

10. Describe the preparation of potassium permanganate ($KMnO_4$). Write the chemical equations involved in the synthesis. (3)
11. Explain giving reasons: (3)

(a) Zn, Cd and Hg are not considered as transition metals.

(b) Elements in the middle of transition series have higher melting points.

(c) The decrease in atomic size of transition elements in a series is very small.

UNIT 8

Coordination Compounds

Points to Remember

Introduction : Complex compounds or coordination compounds are those molecular compounds which retain their identify in solid as well as in solution are known as complex compounds.

Example,

$K_4[Fe(CN)_6] + H_2O \rightarrow 4K^+ (ar) + [Fe(CN)_6]^{4-} (aq)$

Types of Complex

(I) Anionic complex

$K_3[Fe(C_2O_2)_3] \rightarrow 4K^+ + [Fe(C_2O_4)_3]^{3-}$

Anionic complex

(ii) Cationic complex

$[CoCl_2(en)_2]\ Cl \rightarrow [CoCl_2(en)_2]^+ + Cl^-$

Cationic complex

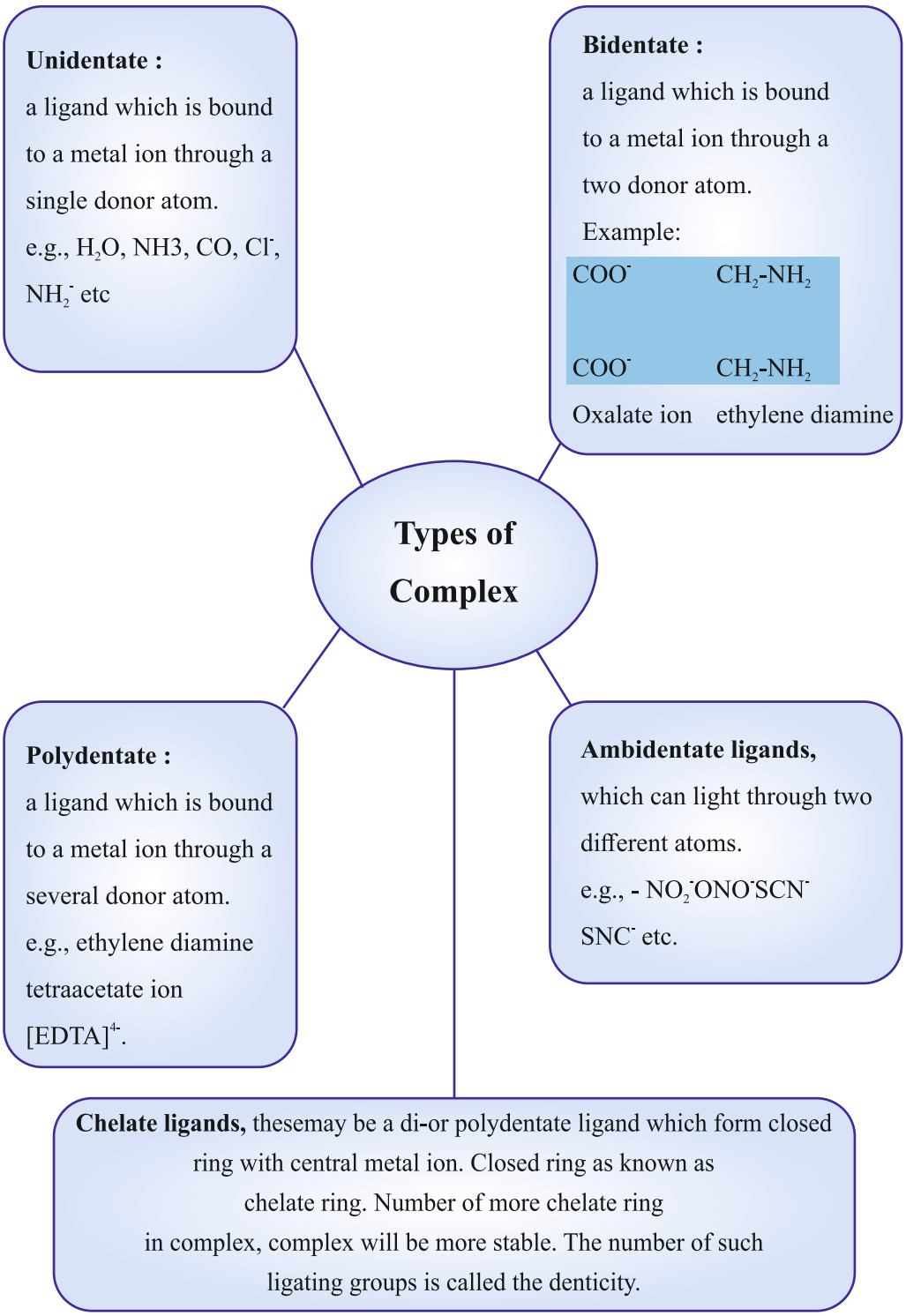
(iii) Neutral complex

$[Ni(CO)_4]$

neutral complex

Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.


Types of Complex
Unidentate :
a ligand which is bound to a metal ion through a single donor atom.
e.g., H_2O, NH3, CO, Cl^-, NH_2^- etc
Bidentate :
a ligand which is bound to a metal ion through a two donor atom.
Example:
COO^- CH_2-NH_2
COO^- CH_2-NH_2
Oxalate ion ethylene diamine
Polydentate :
a ligand which is bound to a metal ion through a several donor atom.
e.g., ethylene diamine tetraacetate ion $[EDTA]^{4-}$.
Ambidentate ligands,
which can light through two different atoms.
e.g., - NO_2^- ONO^- SCN^- SNC^- etc.
Chelate ligands, thesemay be a di-or polydentate ligand which form closed ring with central metal ion. Closed ring as known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

Homoleptic Complexes	Homoleptic Complexes
Complexes in which a metal is bound to only one kind of donor groups known as homoleptic.	Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic.
e.g., $[Co(NH)_6]^{3+}$	e.g., $[Co(NH_3)_4Cl_2]^{+}$

Nomenclature of Coordination Compounds

Neutral Complex
$[Pt(NH_3)_2Cl(NO_2)]$
Diammine chloronitrito-N-platinum (II)
(I) Name Of ligands in an alphabetical order
(II) Central metal atom and oxidation state

Anionic Complex
$K_3[Fe(CN)_6]$
Postassium hexacyaanoferrate (III)
(I) Name of ionisable metal and oxidation state
(II)Name of ligand in an alphabetical order
(III) Central metal atom + ate and oxidation state

Cationic Complex

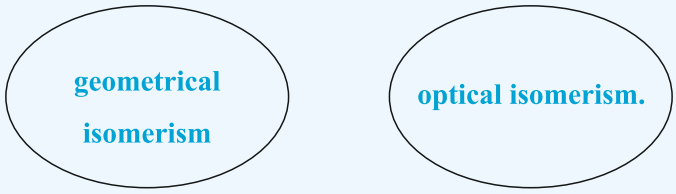
$[Cr(NH_3)_3(H_2O)_3]Cl_2$
triamminetriaquachromium (III) Chloride
1. Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.
2. Central metal atom and oxidation state indicated by Roman numeral in parenthesis.
3.Name of ionisable anion.

Isomerism in Coordination Compounds

Note: Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types :



Optical Isomerism

- it arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called dextro (d) and laevo (l).
- Optical isomerism is common in octahedral complexes but at least one didentate ligand should be present.

e.g., $[Co(en)_3]^{3+}$,$[PtCl_2(en)_2]^{2+}$etc.

 # Not in CBSE syllabus 2021-22. Important for compititive examinations only.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), The two ligands X may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer.
e.g., $[Pt(NH_3)_2Cl_2]$

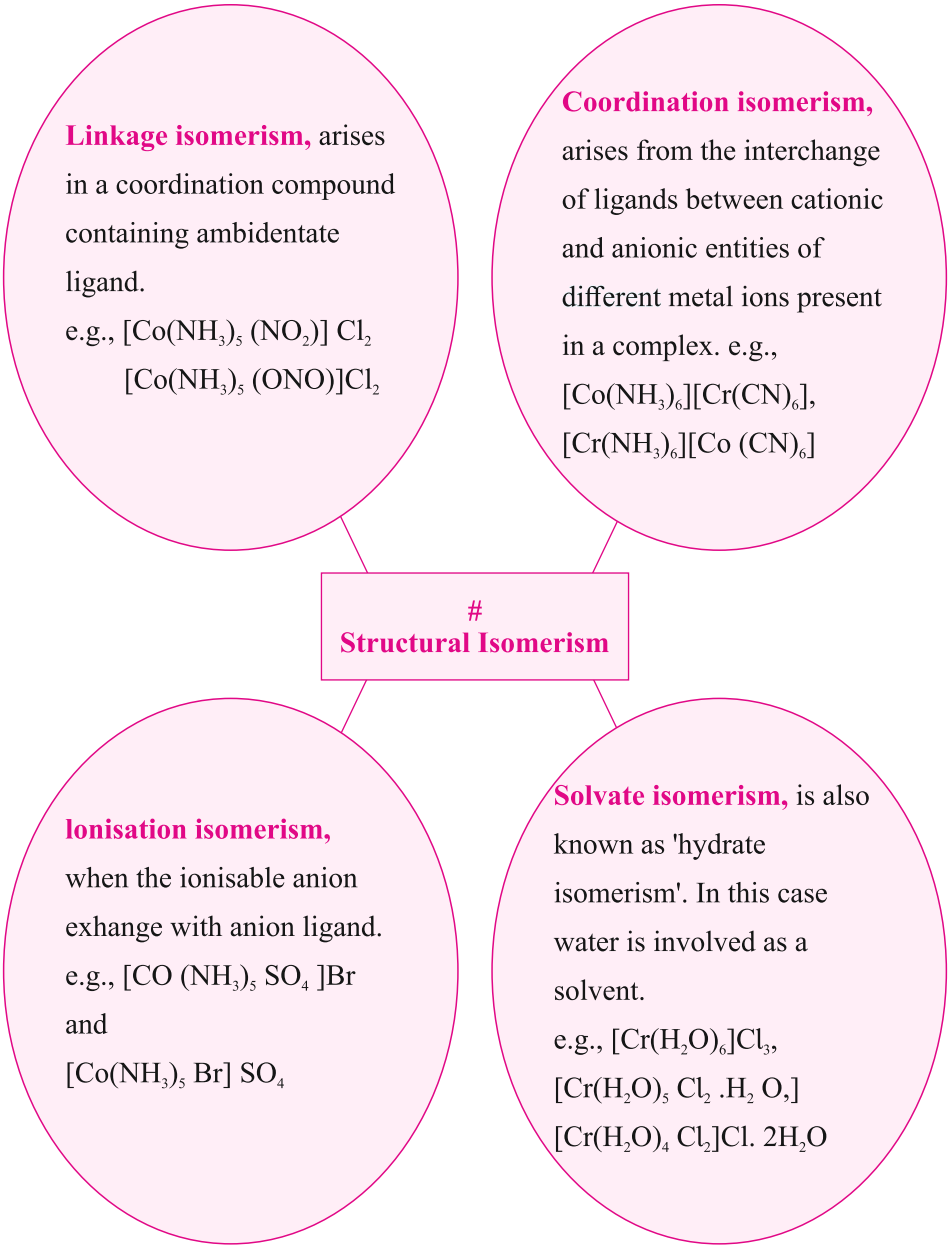
Square planar complex of the type [MABXL](where A, B, X, L are unidentates) shows three isomers - two cis and one trans. Such isomerism is not possible for terahedral geometry.
e.g., $[Pt(NH_3)(Br)(Cl)(Py)]$

Octahedral complexes of formula $[MX_2A_2]$ where X are unidentates and A are didentate and form cis and trans isomers.
e.g., $[CoCl_2(en)_2]$

Octahedral complexes of formula $[MX2\ L4]_1$ in which the two ligands X may be oriented cis or trans to each other.
e.g., $[Co(NH_3)_4\ Cl_2]^+$

Octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3\ (NO_2)_3]$. If threee donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the merodional (mer) isomer.

 # Not in CBSE syllabus 2021-22. Important for compititive examinations only.



 # Not in CBSE syllabus 2021-22. Important for compititive examinations only.

Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies - primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non- ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands from inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

(i) **Six ligands (unidentate) (octahedral entity)** Generally central atom belongs 3d series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

Inner orbital complexes,

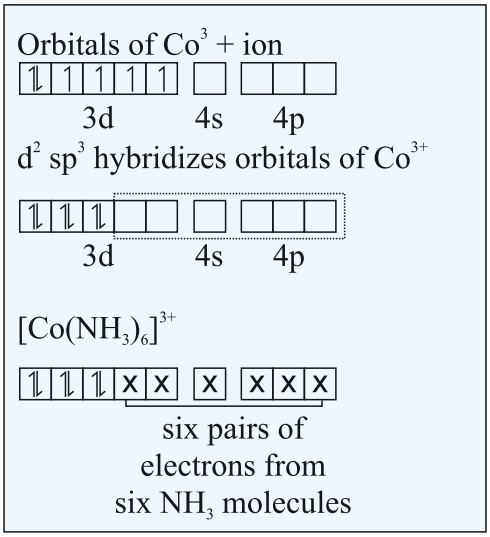
Which are formed due to participation of (n-1)d orbitals in hybridisation is ($d^2 sp^3$) and shape of complex will be octahedral.

Outer orbital complexes,

Which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2).

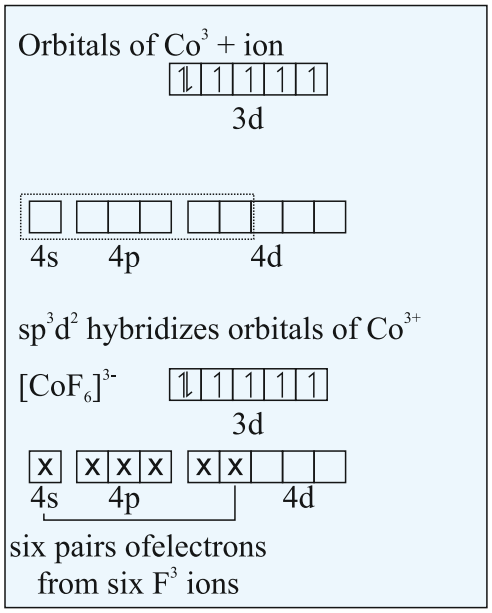
Generally halides (F_1^-,Cl_1^-,Br_1^-,I^-,), SCN^-,S^{2-} From outer orbital complexes and other ligands from inner orbital complexes.

e.g., Inner orbital complex, $[Co(NH_3)_6]^{3+}$



All electrons are paired therefore, complex will be diamagnetic in nature.

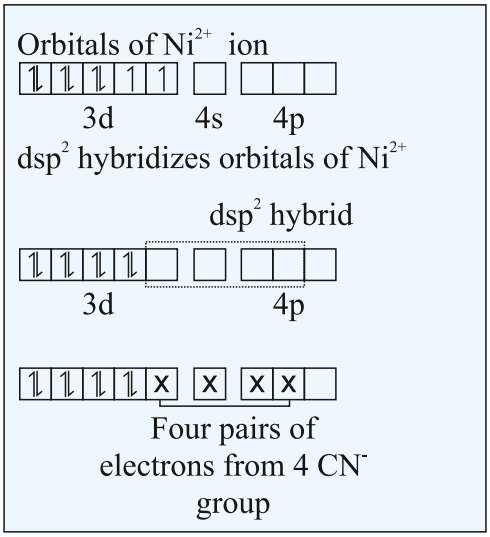
e.g., Outer orbital complex, $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

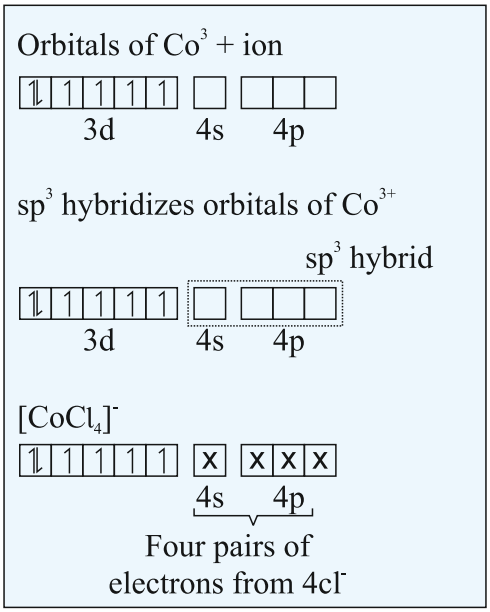
Complexes with coordination number: 4

1. **$[Ni(CN)_4]^{2-}$**



All electrons are paired. Complex will be diamagnetic in nature.

2. **$[CoCl_4]^-$**

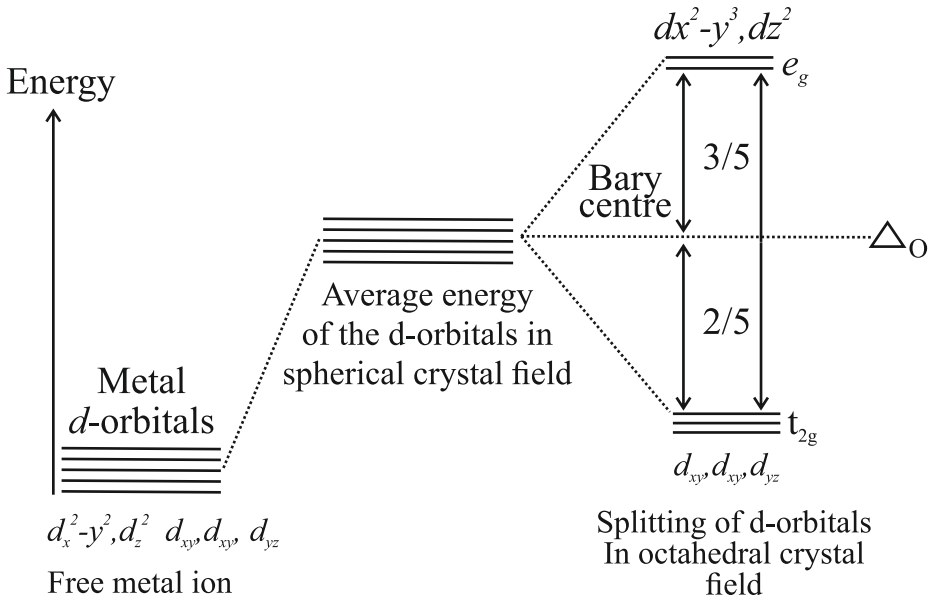


Complex has unpaired electrons. Complex will be paramagnetic in nature.

Crystal Field Theory

The five d-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory. The five d-orbitals in a gaseous metal atom/ion have same energy.

(i) Crystal field splitting in octahedral coordination entities



● Energy separation is denoted by Δo (the subscript o is for octahedral).

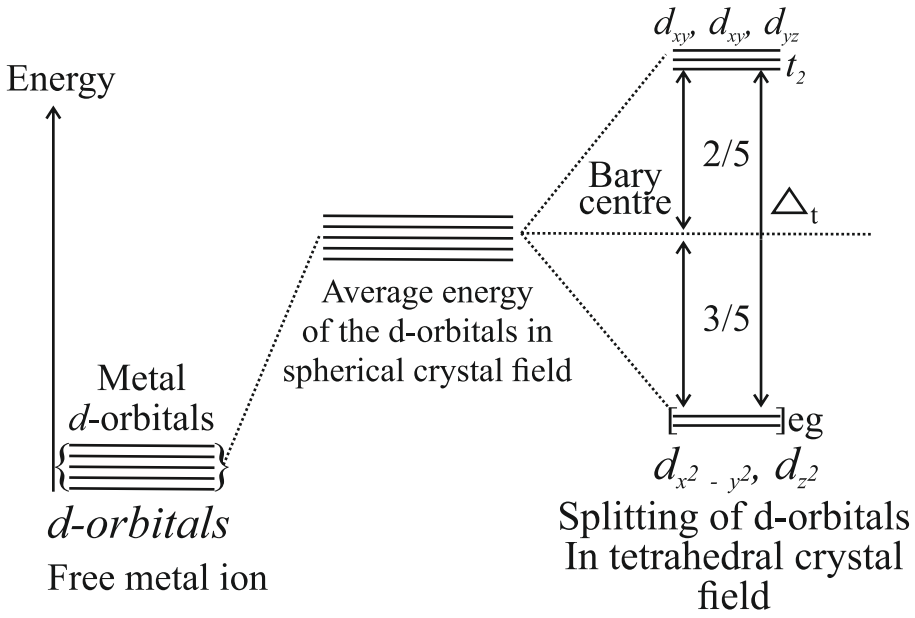
● The energy of the two eg orbitals (higher energy orbitals) will increase by (3/5)Δo. and that of the three t_{2g} (lower energy orbitals) will decrease by (2/5) Δo.

● If Δo < p, the fourth electron enters one of the eg, orbitals giving the configuration t_{2g} eg^1 . Ligands for which Δo < p are known as weak field ligands and form high spin complexes.

● If $\Delta o < p$, it becomes more energeticallly favourable for the fourth electron to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^o$.

Ligands which produce this effect are known as strong field ligands which produce this effect are known as strong field ligands which produce this effect are known as strong field ligands and from low spin complexes, where p represents the energy required for electron pairing in a single orbital.

(ii) Crystal field splitting in tetrahedral coordination entities.



● In tetrahedral coordination entities, $\Delta t = (4/9)\Delta o$.

Consequently the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

● Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

- In complex compounds d-orbitals split in two sets t_{2g} and eg These have different energies. The difference in energies lies in visible region and electron jump from ground state t_{2g} level to higher state eg level. This is known as d-d transition and it is responsible for colour of coordination compounds.
- d-d transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured. On the other hand, the ions d^0 and d^{10} configuration do not show d-d transition. 9. Importance and Applications of Coordination Compounds.
- Hardness of water is estimated by simple titration with Na_2 EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.
- Some important extraction processes of metals, like those of silver and gold make use of complex formation.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium.

Supplementary List of Ligands

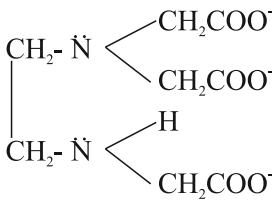
Ligand	F^-	$C1^-$	Br^-	I^-	OH^-	CN^-	O^{2-}	O_2^{2-}	O_2^-	CO_3^{2-}	PH_3
Name	fluoro	chloro	bromo	iodo	hydroxo	cyano	oxo	peroxo	superoxo	carbonato	phosphine
Ligand	SO_4^{2-}	NO_2^-	ONO	SCN^{-1}	NCS	CH_3COO^-	C_5H_5N	S^{2-}	$S_2O_3^{2-}$	NO_3	SO_3^{2-}
Name	sulphato	nitro	aitrito	thiocyanato	isothiocyanato	aeetate	pyridine (Py)	sulphido	thiosulphato	nitrato	sulphito
Ligand	NC^-	$(C_6H_5)_3P$	CS	NH_2^-	NH^{2-}	H_2NCSNH_2	$C_2O_4^{2-}$	H_2O	NH_3	CO	NO
Name	isocyano	triphenyl phosphine	thiocarbonyl	amido	imido	thiourea (tu)	oxalate (ox)	aqua	ammine	carbonyl	nitrosyl

$H_2N\text{-}CH_2\text{-}NH_2$

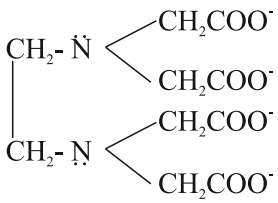
Ethylenediamine (en)

$H_2NCH_2CH_2NHCH_2CH_2NH_2$

Diethylenetriamine(diene)



Ethylenediaminetriacetate ion $EDTA^{3-}$



Ethylenediaminetriacetate ion $EDTA^{3-}$

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Which of the following compounds formed by Cu^{2+} ions is most stable?
   (a) $Cu^{2+}+4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$; Log K=11.6
   (b) $Cu^{2+}+4CN^- \rightarrow [Cu(CN_4]^{2-}$; Log K=27.3
   (c) $Cu^{2+}+2en \rightarrow [Cu(en)_2]^{2+}$; Log K=15.4
   (d) $Cu^{2+}+4H_2O \rightarrow [Cu(H_2O)_4]^{2+}$; Log K=8.9
2. The colour of the coordination compounds depends on the crystals field splitting. What will be the correct order of absorption of warleinth of light in the visible region for the complenes $[CO(NH_3)_6]^{3+}$; $[CO(CN)_0]^{3-}$; $[CO(H_2O)_6]^{3+}$.
   (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) $[CO(CN)_6]^{3-} > [CO(NH_3)_6]^{3+} > [CO(H_2O)_6]^{3-}$
3. 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.
   (a) 1 : 3 electrolyte (b) 1 : 2 electrolyte
   (c) 1 : 1 electrolyte (d) 3 : 1 electrolyte
4. The correct IUPAC name of $[Pt(NH_3)_2\ Cl_2]$ is
   (a) Diamminedichloridoplatinum (II)
   (b) Diamminedichlorideplatinum (IV)
   (c) Diamminedichlorideplatinum (0)
   (d) Diamminedichlorideplatinum (IV)
5. This stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complen species?
   (a) $[Fe\ (CO)_5\ ]$ (b) $[Fe(CN)_6\ ]^{3-}$
   (c) $[Fe(C_2\ O_4\ )_3\ ]^{3+}$ (d) $[Fe(H_2O)_6\ ]^{3+}$
6. The CFSE for octahedral $[CaCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[COCl_4]^{2-}$ will be:
   (a) 18,000 cm-1 (b) 16,000 cm^{-1}
   (c) 8,000 cm-1 (d) 20,000 cm^{-1}

7. Which of the following species is not impected to be a ligand?
   (a) NO (b) NH_4^+
   (c) $NH_2CH_2NH_2$ (d) CO
8. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is:
   (a) Platinum diaminechloritrite
   (b) Chloronitrito-N-ammine platinum(II)
   (c) Diamminechloridonitrite-N-platinum (II)
   (d) Diamminechlornitrite-N-platinate(II)
9. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?
   (a) $[CONH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{3-}$
   (c) $[Fe(CN)_6]^{4-}$ (d) $[Fe(CN)_6]^{3-}$
10. Which of the following options are correct for [Fe(CN)6]3- complex?
   (a) sp^3 hybridisation (b) sp^3d^2 hybridisation
   (c) paramagnetic (d) diamagnetic

II FILL IN THE BLANKS

1. The IUPAC name of linkage isomer of $[Co(NH_3)_5NO_2]C1_2$ is.....
2. The oxidation state of Ni in $K_2[Ni(CN)_4]$ is.....(2)
3. The metal present in vitamin B_{12} is.....(Cobalt)
4. NO is named as.....(Nitrosyl)
5. Octahedral crystal field splitting the three d orbitals having lower energy are collectively called.....(t_{2g})
6. The number of isomers of $[Pt(NH_3)_2Cl_2]$ are.....(4)
7. In complex $[Fe(H_2O)_6]^{3+}$ number of unpaired electrons are.....(5)
8. Number of ions produced per mole of the complex $[Co(NH_3)_5Cl]Cl_2$..... are (3)
9. Out of cis and trans isomer of $[RhCl(en)_2]^+$, ...isomer shows optical activity.(cis)
10. Triethylenetetraammine is.....ligand. (tetradendate)

III ASSERTION REASON TYPE QUESTIONS

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both assertion and reason are True, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are True, but reason is not the correct explanation of the assertion.

(c) Assertion is True, but reason is False.

(d) Both assertion and reason are False.

1. **ASSERTION:** Toxic metal ions are removed by the chelating ligands.
   REASON: Chelate complens tend to be move stable.
2. **ASSERTION:** $[(Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   REASON: Because it has $d^2 sp^3$ type hybridisation.
3. **ASSERTION:** Carbon monoxide forms low spin complexes with metals.
   REASON: Carbon monoxide is neutral oxide.
4. **ASSERTION:** Carbon monoxide is a deadly poison.
   REASON: CO can form strong complexes with haemoglobin.
5. **ASSERTION :** Tetrahedral complexes cannot exhibit geometrical isomerism.
   REASON: Tetrahedral complexes are chiral in nature.
6. **ASSERTION:** An octahedral complex with two bidentate ligands is always optically active.
   REASON: The cis - isomer of the octahedral complex is chiral.
7. **ASSERTION:** Ionisation isomerism is shown by complexes having ambidentate ligands.
   REASON: Ambidentate ligands have two possible ligating centres.
8. **ASSERTION:** $[Fe(CN)_6]^{3-}$ is more paramagnetic than$[FeF_6]^{3-}$.
   REASON: $[FeF_6]^{3-}$ has more number of unpaired electrons.
9. **ASSERTION:** $[Co(NH_3)_6]^{3+}$ is an inner orbital complex.
   REASON: $[Co(NH_3)_6]^{3+}$ forms an octahedral complex.

IV ONE WORD TYPE QUESTION ANSWERS

1. What is the oxidation state of Ni in $[Ni(Co)_4]$? (0)
2. Write IUPAC name of $[Ni(CN)_4]^{2-}$.(tetracynatonickelate(II) ion)
3. What is the hybridisation of Co in the complex $[CoF_6]^{3-}$?(sp^3d^2)
4. Write the chemical formula of potassiumtrioxalatochromate(III).
   ($K_3[Cr(C_2O_4)_3]$)
5. Haemoglobin is the complex of which transition element?(Iron)

6. Give an example of hexadendate ligand.(EDTA)
7. Out of NH_3 and H_2O which is strong field ligand?(NH_3)
8. Write electronic configuration of complex $[Fe(CN)_6]^{4-}$.($t_{2g}^6 e_g^1$)
9. What is the coordination number of Cr in $[Cr(en)_2Cl_2]Cl]Cl$
10. How many geometrical isomers are possible for $[Cr(ox)_3]^{3-}$?(0)

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q.1. What is ambidentate ligand ? Give one example.

Ans. Monodentate ligands contain more than one coordinating atoms. Example, CN^-.

Q.2 Write the IUPAC name of $[PtC1_2(en)_2(NO_3)_2]$.

Ans. Dichloridobis (ethylenediammine) nitratoplatinum (IV)

Q.3. What is a chelate ligand ? Give one example.

Ans. The ligand which contain from two or more donar sites simutaneously to form cyclic complaces. Example, ethane-1-2 diammine.

Q.4. How many geometrical isomers are possible for the $[Ni(NH_3)_4]^{2+}$?

Ans. Not possible because all 4 ligands are same.

Q.5. Define coordination polyhedron.

Ans. The spatial arrangement of the ligand with the central metal ion.

Q.6. Give the chemical formula of potassium hexacyano ferrate (II).

Ans. $K_4[Fe(CN)_6]$.

Q.7. Name the metal present in : (i) Chlorophyll (ii) cis platin

Ans. (i) Mg (ii) Pt

Q.8. The chemical formula of Wilkinson's catalyst is :

Ans. $[(PH_3P)_3RhCl]$

Q.9. Which of the two is more stable — $K_4[Fe(CN)_6]$ Or $K_3[Fe(CN)_6$

Ans. $K_4[Fe(CN)_6]$ because Fe has d^6 configuration in this case.

Q.10. Arrange the following complexes in order of increasing electrical conductivity : $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4]Cl_3$

Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_4]Cl_3$

More number of ions < more electrical conductivity

Q.11. Give an example of the role of coordination compounds in biological system.

Ans. Haemoglobin, the red pigment of blood acts as oxygen carrier. It is a coordination compound of iron.

Q.12. Why is CO a stronger ligand than Cl^- ? Or Give reason for : CO is a stronger complexing reagent than NH_3.

Ans. CO is a stronger ligand than Cl^- due to back bonding between its empty p-orbitals and filled d-orbitals of central metal ion which in turn increases Δo value.

Q.13. What do you understand by denticity of a ligand?

Ans. Denticity of a ligand is the number of coordinating or ligating groups sites present in a ligand.

Q.14. What is the coordination number of central metal ion in $[Fe(C_2O_4)_3]^{3-}$?

Ans. Coordination number = Number of ligands x Denticity = 3 x 2 = 6

Q.15 Name two properties of the central metal atom/ion which enable it to form stable complex entities.

Ans. (a) Small size of metal ion

(b) High charge on the metal ion.

Q.16 Write the IUPAC name of the complex $[Cr(en)_3][Co(CN)_6]$.

Ans. Tris (ethane- 1, 2-diamine) chromium(III) hexacyanidocobaltate(III)

Q.17. A blue coloured solution of $[CoCl_4]^{2-}$ ion changes to pink on reaction with $HgCl_2$. Why ?

Ans. $CoCl_4^{2-} + HgCl_2 \text{-}\!\!\rightarrow Co[HgCl_4] + 2Cl^-$

[Blue] [Pink]

SHORT ANSWER TYPE QUESTION (2 or 3 Marks)

Q.1. Explain the following : (i) NH_3 act as a ligand but NH_4^+ does not. (ii) CN^- is a ambidentate ligand.

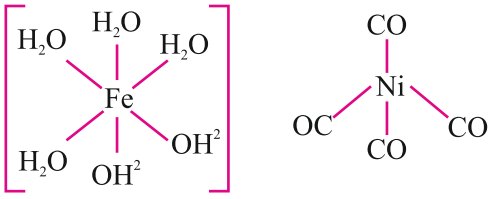
Ans. (i) NH_3 has one lone pair while NH_4^+ does not. (ii) Because it has two donor atoms in a monodentate ligand.

Q. 2. Mention the main postulates of Werner theory.

Ans. (i) Metal ion has two types of valency. (ii) Primary valency and secondary valency. (iii) Secondary valency is equal to coordination number.

Q. 3. Draw the structure of : (i) $[Ni(CO)_4]$ (ii) $[Fe(H_2O)_6]^{3+}$

Ans.



Q.4. How does EDTA help as a cure for lead poisoning ?

Ans. Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble compled lead-EDTA is eliminated in urine.

Q.5. Define homoleptic and heteroleptic complexes.

Ans. Homoleptic : When metal atom/ion is linked with one type of ligands. Example, $[Ni(CO)_4]$. Heteroleptic : With the more than one kind of ligands. Example, $[Co(NH_3)_4 Cl_2]^+$.

Q.6. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why ?

Ans. In $[NiCl_4]^{2-}$, Ni has $3d^8\ 4s^0$ configuration, Cl^- can't pair up while in $[Ni(CO)_4]$, Ni has $3d_8\ 4s_2$ configuration, CO pair up electrons

Q.7. The oxidation number of cobalt in the complex : (i) $K[Co(CO)_4]$ (ii) $[Co(C_2O_4)_3]^{3-}$

Ans. (i) - 1 (ii) + 3

Q.8. What are t_{2g} and e_g orbitals ?

Ans. In a free transition metal ion, the d-orbitals are degenerate. When it form complex, the degeneracy is split and d-orbitals split into t_{2g} and e_g orbitals.

Q.9. What is the solution in which photographic film is washed ? What reaction takes place ?

Ans. Hypo solution. $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Q.10. What is spectrochemical series ?

Ans. The arrangement of ligands in order of their increasing crystal field splitting field strength.

Q.12. What are the assumptions of Crystal Field theory.

Ans. (i) Ligand act as a point charge. (ii) Metal ion has electrostatic attraction force with the ligand. (Or any other)

Q.11. $CuSO_4$ is colourless while $CuSO_4 .5H_2O$ is coloured. Why ?

Ans. $CuSO_4$ does not has any ligand, so splitting of d-orbital take place while $CuSO_4$ $5H_2O$ has water ligand.

Q.12. What is the difference between inner and outer orbital complexes ?

Ans. Inner sphere complex : When d-orbital of inner shell take part in hybridisation. Outer sphere complex : When d-orbital of outermost shell take part in hybridisation.

Q.13. How is stability of coordination compound determined in aqueous solution ?

Ans. By using stability constant. More stability constant, more stability.

Q.14. In a complex ion $[Co(NH_3)_5\ NO_2]Cl_2$, (i) Identify the ligand. (ii) Oxidation number of metal ion.

Ans. (i) $NH_3\ NO_2$. (ii) + 3

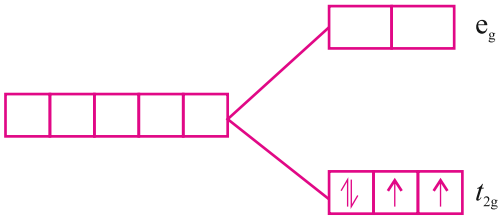
Q.15. Explain how the nature of ligand affects the stability of complex ion.

Ans. Strong ligand : More stability Weak ligand : Less stability

LONG ANSWER QUESTIONS (5 Marks)

Q.1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta o > p$: (i) Draw the diagram showing d-orbital splitting during this complex formation. (ii) What type of hybridisation will M^{n+} have ? (iii) Name the type of isomerism exhibited by this complex. (iv) Write the electronic configuration of metal M^{n+}.

Ans. (i) If $\Delta o > p$ then



(ii) $d^2 sp^3$

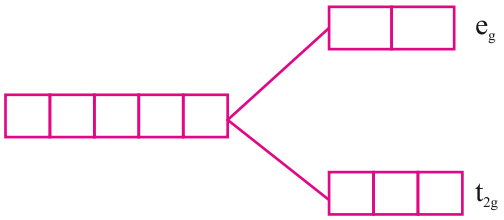
(iii) [M(AA)3 type complex show optical isomerism.

(iv) $t_{2g}^{\ 4} e_g^{\ o}$

Q.2. (i) Discuss the nature of bonding in metal carbonyls. (ii) Draw figure to show the splitting of d-orbitals in an octahedral crystal field and write electronic configuration of M^{2+} ion when : (a) $p > \Delta o$ (b) $\Delta o > p$

Ans. (i) The metal carbon bond in metal carbonyls possess both σ and π character. The M-C σ bond if formed by the M←C≡O while M-Cπ it bond if formed by the donation of a pair of electron from filled d-orbital of metal to antibonding π* orbital of CO.

(ii)



(a) $t_{2g}^3 e_g^2$ (b) $t_{2g}^5 e_g^0$

Q. 3. (I) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution. Why ?

(ii) A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio of 1 : 4.0.1M solution of this complex was found to be freeze at - 0.372º C. What is the formula of the complex ? $K_f = 1.86^{\circ}C/M$

Ans. (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN^- and H_2O has different crystal field splitting energy.

(ii) $\Delta T_f = i.K_f.\ m$, $i = 2$ means complex dissociate into two ions. Hence the formula is $[Co(NH_3)_4 Cl_2]Cl$.

Q.4. A metal ion M^{n+} having d4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta o > P$:

(i) Explain a 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 $\Delta o > P$, pairing will occur in the t_{2g} orbitals and eg 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.

Q.5. $CoSO_4Cl.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with AgNO3 to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with BaCl2 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'.

Ans. (i) A = $[Co(NH_3)_5SO_4]Cl$ B = $[Co(NH_3)_5Cl]SO_4$

(ii) Ionisation iosmerism

(iii) (A) = Pentaamminesulphatocobalt(III) chloride

(B) = Pentaamminechloridocobalt(1II) sulphate

CASE STUDY BASED QUESTION

1. Read the passage and answer the following question.

According to the VBT , the metal atom or ion under the influence of ligands can use its (n-1) d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. The geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex. The paramagnetic octahedral complex, $ICoF_6]^{3-}$ uses outer orbital (4d) in hybridisation (sp^3d^2). It is thus called outer orbital or high spin or spin free complex.

Source : NCERT

(A) Number of unpaired electrons present in $[CoF_6]^{3-}$ are :

(a) 4 (b) 3

(c) 2 (d) 1

(B) Paramagnetic complex is :

(a) $[Ni(CN)_4]^{2-}$ (b) $[Ni(Cl)_4]^{2-}$

(c) $[Ni(CO)_4]$ (d) All of these

(C) Outer orbital complex is :

(a) $[CoF_6]^{3-}$ (b) $[Co(NH_3)_6]^{3+}$

(c) $[Ni(CN)_4]^{2-}$ (d) None of these

(D) Inner orbital complex involves :

(a) nd orbitals (b) (n-1)d orbitals

(c) ns orbitals (d) None of these

2. <u>Read the passage and answer the following question.</u>

The degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Flo (the subscript o is for octahedral) . Thus, the energy of the two eg orbitals will increase by (3/5) Δo and that of the three t_{2g} will decrease by (2/5)Δo. The crystal field splitting, Δo, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals.

(A) The cause of removal of degeneracy of the d orbitals in coordination compunds is :

(a) Due to higher nuclear charge

(b) Due to ligand electron-metal electron repulsions

(c) Atomic size

(d) None of these

(B) The crystal field splitting is :

(a) The splitting of the degenerate levels due to the presence of ligands in a definite geometry.

(b) splitting of f- orbitals

(c) splitting of p- orbitals

(d) all of these

(C) Energy of two e_g orbitals in octahedral complexes increased by :

(a) $3/5\,\Delta o$ (b) $2/5\,\Delta o$

(c) $1/5\,\Delta o$ (d) $5/3\,\Delta o$

(D) Correct relation is :

(a) $\Delta_t = 9/4\Delta o$ (a) $\Delta_t = 4/9\Delta o$

(c) $\Delta_t = 2\Delta o$ (d) $\Delta_t = 5\Delta o$

3. <u>Read the passage and answer the following question.</u>

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins. When a ligand is bound to a metal ion through a single donor atom, as with Cl^- H_2O or NH_3, the ligand is said to be unidentate. When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be didentate and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate.

Ethylenediaminetetraacetate ion $(EDTA)^{4-}$ is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion. When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelate ligand. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Ligand which can ligate through two different atoms is called ambidentate ligand. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

(A) Ambidentate ligand is :

(a) CN^- (b) CO

(c) NH_3 (d) H_2O

(B) Total number of donor sites in EDTA are :

(a) 6 (b) 4

(c) 5 (d) 3

(C) Which has maximum denticity :

(a) NC^- (b) $C_2O_4^{2-}$

(c) NH_3 (d) H_2O

(D) Chelating ligand is :

(a) EDTA (b) NH_3

(c) CN^- (d) H_2O

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (b) 2. (c) 3. (b) 4. (a) 5. (c) 6. (a) 7. (b) 8. (c) 9. (a) 10. (c)

II FILL IN THE BLANKS

1. (pentaamminenitrito-O-Cobalt(III)chloride)
2. (2)
3. (CobaIt)
4. (Nitrosyl)
5. (t_{2g})
6. (4)
7. (5)
8. (3)
9. (cis)
10. (tetradendate)

III ASSERTION REASON TYPE QUESTIONS

1. (i) 2. (ii) 3. (ii) 4. (i) 5. (iii) 6. (iv) 7. (iv) 8. (iv) 9. (ii)

IV ONE WORD QUESTION ANSWERS

1. (0)
2. (tetracynatonickelate(II) ion)
3. $[CoF_6)^{3-}$, (sp^3d^2)
4. $(K_3[Cr(C_2O_4)_3]$
5. (Iron)
6. (EDTA)
7. (NH_3)
8. (t_{2g}^6, e_g^0)
9. (6)
10. (0)

CASE STUDY

PASSAGE I

(A) a (B) b

(C) a (D) b

PASSAGE II

(A) b (B) a

(C) a (D) b

PASSAGE III

(A) a (B) a

(C) b (D) a

UNIT 9

Haloalkanes and Haloarenes

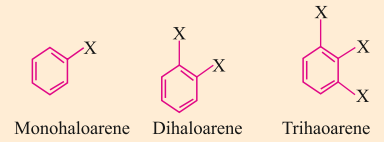
Points to Remember

Classification

• No. of halogen atoms

C_2H_5X Monohaloakane

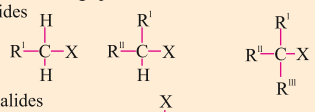
CH_2X-CH_2X Dihaloalkane



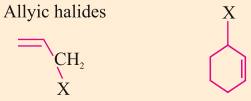
Monohaloarene Dihaloarene Trihaoarene

• Compounds containing sp^3 C-X bond

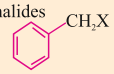
(a) Alkyl halides



(b) Allyic halides

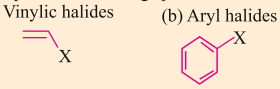


(c) Benzylic halides



Compounds containing sp^2 C-X bond

(a) Vinylic halides (b) Aryl halides



Nomenclatute

Common name : Alkyl group followed by halides. Dihalogen derivatves of arenes, prefix o-, p-are used

IUPAC name : Numerals are used for position of halogen.

Nature of C-X bond :

Carbon-halgoen bond is polarised due to more electronegativity of halogen

Preperation

From alcohol:

$R\text{-}OH + HCl \xrightarrow{ZnCl_2} R\text{-}Cl + H_2O$

$3R\text{-}OH + PX_3 \longrightarrow 3R\text{-}X + H_3PO_4$

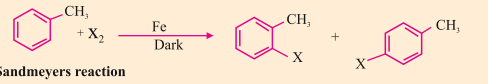
$R\text{-}OH + PCl_3 \longrightarrow R\text{-}Cl + POCl_3 + HCl$

From hydrocarbons:

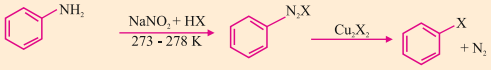
(a) By free redical halogenation

$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

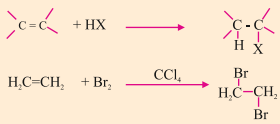
(b) By electrophilic substitution



(c) Sandmeyers reaction



(d) From alkanes



(e) Halogen exchange

R-X + NaI → R-I + NaX

R-X + AgF→RF+AgX

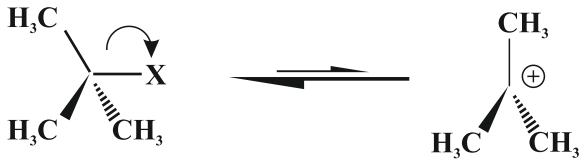
Properties and Reactions of Haloakanes and Haloarenes

Nucleophilic Substitution Reaction

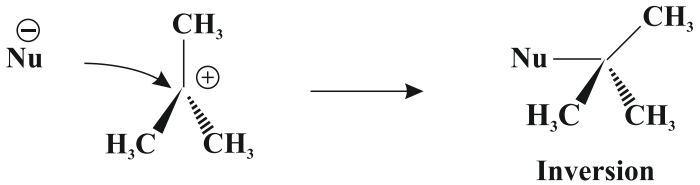
Mechanisms of S_N1 and S_N2:

S_N1

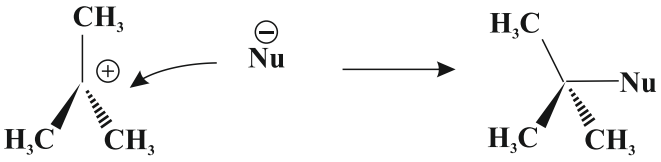
Step - 1



Step 2

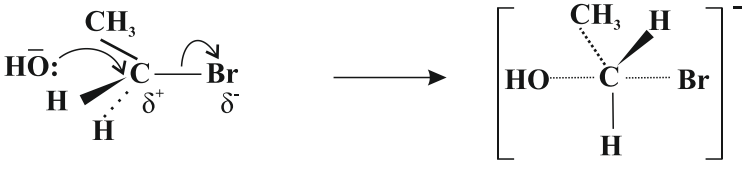


Inversion



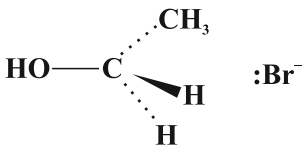
Retention

S_N2



Transition state

Reaction occurs when bromoethane is added to a dilute NaOH solution.



	S_N1	S_N2
Carbon (sp^3) Electrophile	Favored by 3^0 alkyl halides or benzylic, or allylic can also react by an S_N1 mechanism	Favored by $-CH_3$ and 1^0 alkyl halides 2^0, benzylic, or allylic can also react by an S_N2 mechanism
Nucleophile	Nature of the nucleophile has no affect on rate. In general, S_N1 use neutral, weak nucleophiles	Favored by more reactive nucleophiles $RS^- > NC^- > RO^- > HO^- > Cl^-$
Solvent Effect	Favored by polar, protic solvents.	Favored by polar, aprotic solvents.

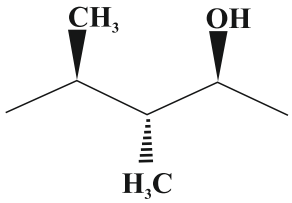
IMPORTANT POINTS

- In haloarenes electrophilic substitution reaction occurs at o-& p-position.
- Haloarenes cannot exhibit nucleophilic substitution reaction due to
  (i) Partial double bond charecter of C-X bond.
  (ii) Benzene ring is electron rich.
  (iii) Phenyl carbocation is not stable.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

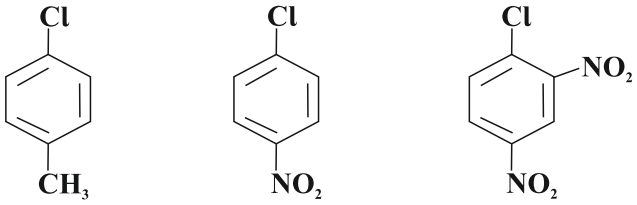
1. The Number of chiral carbons in given molecule is/are-



(a) 1 (b) 2

(c) 3 (d) 4

2. The correct increasing order of rate of reaction towards nucleophilic substitution for following is:



a **b** **c**

(a) a < b < c (b) a < c < b

(c) b < a < c (d) c < b < a

3. Which of the following molecules is chiral?

(a) 2-Bromobutane (b) 1-Bromobutane

(c) 2-Bromopropane (d) 2-Bromopropan-2-ol

4. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows.....

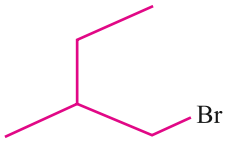
(a) S_N1 mechanism

(b) S_N2 mechanism

(c) Either S_N1 or S_N2 mechanism depending on temperature

(d) E_1 mechanism

5. Which is the correct IUPAC name for following molecule?



(a) 1-Bromo-2-ethylpropane

(b) 1-Bromo-2-ethy1-2-methylethane

(c) 1 -Bromo-2-methylbutane

(d) 2-Methyl-1-bromobutane

6. The correct increasing order of boiling points of the following compounds is-

(a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane

(b) Bromobenzene < 1 -Bromoethane < 1 -Bromopropane < 1 -Bromobutane

(c) 1 -Bromopropane < 1 -Bromobutane < 1 -Bromoethane < Bromobenzene

(d) 1-Brormoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

7. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of _____or_____.

(a) CaF_2, CaF_2 (b) CoF_2, Hg_2F_2

(c) Hg_2F_2, CaF_2 (d) NaF, CaF_2

8. Which of the following haloalkanes reacts with aqueous KOH most easily?

(a) 1-Bromobutane (b) 2-Bromobutane

(c) 2-Bromo-2-methylpropane (d) 2-Chlorobutane

9. Toluene reacts with halogen in the presence of $FeCl_3$ giving *ortho* and *para* compounds. The reaction is :

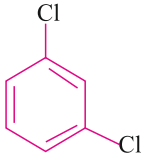
(a) electrophilic elimination (b) electrophilic substitution

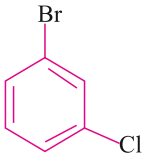
(c) free radical addition (d) nucleophilic substitution

10. Arrange the following compounds in the increasing order of their densities.

(A) 

(B) 

(C) 

(D) 

(a) (A) < (B) < (C) < (D) (b) (A) < (C) < (D) < (B)

(c) (D) < (C) < (B) < (A) (d) (B) < (D) < (C) < (A)

11. Chlorobezene is formed by reaction of chlorine with benzene in presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction ?

(a) Cl^- (b) Cl^+

(c) $AlCl_3$ (d) $AlCl_4^-$

12. Which of the following statement is correct ?

(a) Benzyl halides arc more reactive than vinyl and aryl halides.

(b) Vinyl halides are more reactive than alkyl halides.

(c) Aryl halides are less reactive than alkyl halides.

(d) Aryl halides are more reactive than benzyl halides

13. A new carbon-carbon bond is possible in the following reaction:

(a) $C_6H_6\,CH_2$-Cl (anhy. $AlCl_3$) $\rightarrow$

(b) $CH_3CH_2Br + CH_3CH_3NH_2 \rightarrow$

(c) CH_3-Br + CH_3CH_2-ONa $\rightarrow$

(d) CH_3CH_2-Br + KOH (alc.) $\rightarrow$

14. Alcoholic $AgNO_3$ does not give precipitate with-

(a) $C_6H_5CH_2Cl$ (b) $C_6H_5CH_2Cl$

(c) C_6H_5Cl (d) CH_3-CHCl-CH_3

15. Reaction intermediate of E_1 reaction is-

(a) Benzyne (b) Carbocation

(c) Carbanion (d) Free radical

II FILL IN THE BLANKS

1. Chlorobenzene may be converted into diphenyl by.....reaction.
2. The mixture containing two enantiomers in equal amount, having zero optical rotation is called.....
3. Reaction of bromopropane with magnesium metal in dry ether forms the category of compounds called.....
4. The major product of Friedel-Crafts acetylation of chlorobenzene is.....
5. Polyhalogen compound having antiseptic property is
6. Alkyl halides are..... in water but.....in organic solvents.
7. Bimolecular nucleophilic substitution of optically active haloalkanes leads to the .....of the configuration.

8. The molecules which rotates the plane-polarized light in clockwise direction are called.....

9. Halogens.....the aromatic ring towards electrophilic substitution due to -I effect of halogens.

III ASSERTION REASON TYPE QUESTIONS

In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices:

(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 :** S_N2 reaction is accompanied by the inversion of configuration.
   REASON: S_N2 reaction occur in two step.

2. **ASSERTION :** Treatment of chloroethane with saturated solution of AgCN give ethylisocyanide as major product.
   REASON : Cyanide ion (CN^-) is an ambidentate nucleophile.

3. **ASSERTION :** The boiling points of alkyl halides decreases in the order :
   RI> RBr > RC1> RF
   REASON : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

4. **ASSERTION :** tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.
   REASON : 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 :** Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.
   REASON : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

6. **ASSERTION :** In monohaloarenes, further electrophilic substitution occurs at *ortho* and *para* positions.
   REASON : Halogen is a ring deactivator.

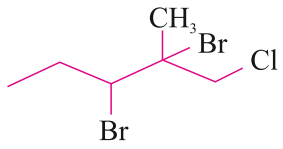
7. **ASSERTION :** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
   REASON : Oxidising agent oxidises I_2 into HI.
8. **ASSERTION:** The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.
   REASON: Vinyl group is electron donating group.
9. **ASSERTION:** Silver nitrite gives nitro alkane when it reacts with an alkyl halide.
   REASON: Silver nitrite is an ionic compound.
10. **ASSERTION:** Chloroform is generally stored in brown bottles which are filled to brims.
    REASON : $CHC1_3$ get oxidised to phosgene in atmosphere.
11. **ASSERTION:** Neopentyl chloride undergoes S_N2 reaction easily.
    REASON: Neopentyl chloride is a tertiary halide.
12. **ASSERTION :** It is difficult to replace chlorine by -OH in chlorobenzene in comparison to that in chloroethane.
    REASON : Chlorine-carbon (C-Cl) bond in chlorobenzene has a partial double bond character due to resonance.
13. **ASSERTION:** 2-Bromobutane reacts with aqueous KOH forming racemic mixture.
    REASON: 2-Bromobutane forms secondary carbocation which leads to bimolecular substitution reaction.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Name the category of nucleophiles to which CN^-, NO_2^- belongs, which may attack through two different sites.
2. Name the reaction which converts aniline into chlorobenzene.
3. Which isomer of dichlorobenzene has highest boiling point?
4. If elimination takes place according to Zaitsev (Saytzeff) rule then from which carbon removal of -H takes place?
5. Which mechanism Ph_3C-Cl follows when it reacts with aqueous NaOH?
6. Name the instrument used to measure optical rotation.
7. Name the category of the molecules related by non-superimposable mirror images of each other.
8. Which gas is formed by the reaction of chloroform with oxygen in presence of light?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

1. Give IUPAC name of:



Ans : 1-Chloro-2,3-dibromo-2-methylpentane

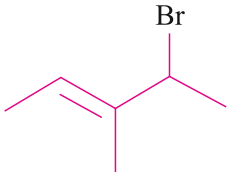
2. Identify A and B in each of the following process :

$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow{H_2/Ni} B$

Ans : A: CH_3-CH_2-CN; B:$CH_3CH_2CH_2NH_2$

3. Draw the structure of 4-bromo-3-methylpent-2-ene.

Ans:



4. Why Grignard reagent should be prepared under anhydrous condition?

Ans: It reacts with water and converts into corresponding hydrocarbon.
($RMgX+H_2O \rightarrow RH+MgX(OH)$)

5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Ans: It is slowly oxidised by air in presence of light to form $COC1_2$(Phosgene) which is a poisonous gas. ($CHCl_3+\frac{1}{2}O_2 \rightarrow COCl_2+2HCl$)

6. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure?

Ans: CH_3-$\underset{\displaystyle Cl}{\underset{|}{CH}}$-$CH_2$-$CH_3$

7. An organic compound 'A' on treatment with KCN gave 'B' which on hydrolysis with dil. HCl gave acetic acid. Identify A.

Ans: CH_3Cl

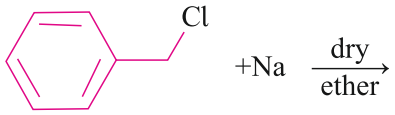
8. Arrange the following in order of their increasing reactivity in nucleophilic substitution reaction : CH_3F, CH_3I, CH_3Br, CH_3Cl

Ans: CH_3F, CH_3Cl, CH_3Br, CH_3I

9. Allyl chloride is more reactive than n-propyl chloride toward nucleophilic substitution reaction. Why?

Ans: Due to more stability of allyl carbocation than n-propyl carbocation.

10. Complete the reaction:



Ans: $PhCH_2CH_2Ph$ (Wurtz reaction)

11. Give one chemical test to distinguish between chlorobenzene and benzyl chloride?

Ans: $AgNO_3$ test, benzyl chloride gives white precipitate.

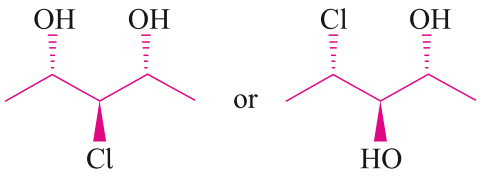
12. The presence of nitro group ($-NO_2$) at *ortho* or *para* position increase the reactivity of haloarenes toward nucleophilic substitution. Explain.

Ans: Nitro group withdraws electrons by -R, -I effect resulting the formation of more stable carbocation formed.

13. For the prepration of alkyl chloride form alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

Ans: The by-products are gaseous SO_2 and HCl which can be easily removed to give pure haloalkane.

14. Which of the following molecule is optically active?



Ans: b is optically active

15. The dipole moment of chlorobenzene is lower than cyclohexyl chloride. Why?

Ans: Due to sp^2 hybridised carbon in chlorobenzene which is more electronegative and reduces polarity of C-Cl bond.

16. Which compound will be formed by reaction of (+)-2-chlorobutane with KOH?

Ans: (+)-butan-2-ol

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. 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 acid, HI which is then oxidised by it to I_2.

2. 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) With OH^- ion, CH_3I will react faster than CH_3Br, as iodide is a better leaving group.

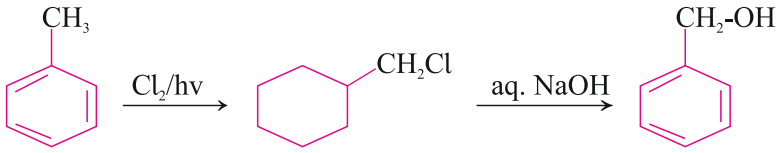
(ii) CH_3Cl as it is primary haloalkanes with less steric hindrance.

3. Carry out the following conversions in not more than two steps :

(i) Toluene to Benzyl alcohol

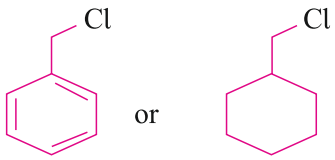
(ii) Benzyl alcohol to phenylethanenitrile

Ans: (i)



(ii) Benzyl alcohol +HCl (in presence of $ZnCl_2$)⟶ Benzyl chloride + KCN⟶ Phenylethanenitrile

4. Which of the following compounds would undergo S_N1 Reaction faster and why ?



a b

Ans: **a** will be more reactive due to higher stability of benzyl carbocation.

6. Complete the following reaction :

(i) $C_6H_5N_2Cl + KI \rightarrow$

(ii) $CH_2=CH_2 + Br_2 \rightarrow$

(iii) $CH_3CH_2OH + SOCl_2 \rightarrow$

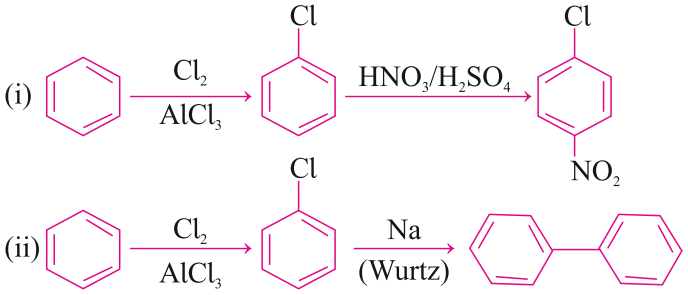
Ans: (i) C_6H_5I, (ii) $CH_2Br\text{-}CH_2Br$, (iii) CH_3CH_2Cl

7. Convert :

(i) Benzene to — nitrochlorobenzene

(ii) Benzene to diphenyl

Ans:



8. What happen when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

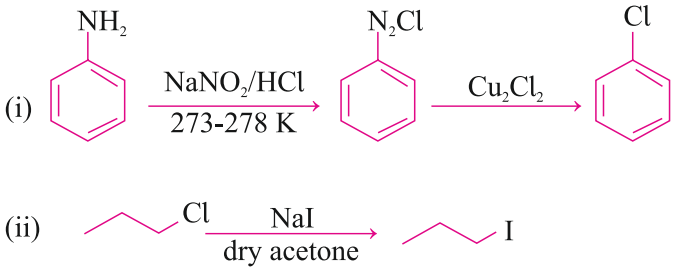
Ans: (i) l-Bromopropane is formed (Anti-Markonikov addition)

(ii) Toluene is formed (Friedel-Crafts Alkylation)

9. Write short note on :

(i) Sandmeyer reaction (ii) Finkelstein reaction

Ans:



10. Name the reagent used to convert:

(i) 2-Chloropropane to 2 nitropropane

(ii) Chloroethane to butane

Ans: (i) $AgNO_2$ (ii) Na / dry ether

11. Give reasons :

(i) Boiling point of alkyl bromide is higher than alkyl chloride.

(ii) Alkyl halides are better solvents than aryl halides.

Ans: (i) High magnitude of van der Waals forces in alkyl bromides.

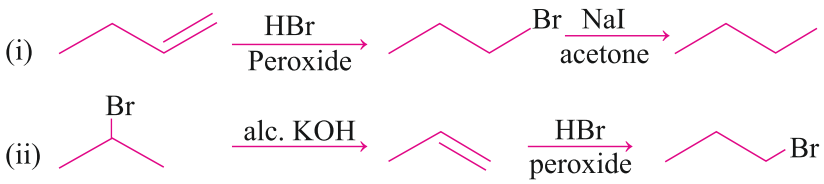
(ii) C - X is more polar in alkyl halides.

12. Carry out the following conversion :

(i) But-l-ene to n-Butyl iodide

(ii) 2-Bromopropane to 1-Bromopropane

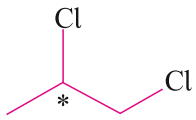
Ans:



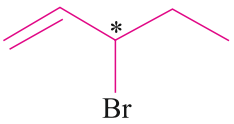
13. Identify and indicate the presence of center of chirality (if any) in the following molecules. How many stereoisomers are possible for those containing chiral center?

(i) 1,2- Dichloropropane (ii) 3- Bromopent-l-ene

Ans:



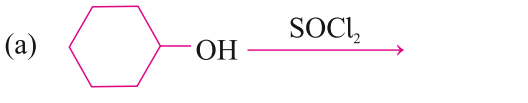
1,2-Dichloropropane



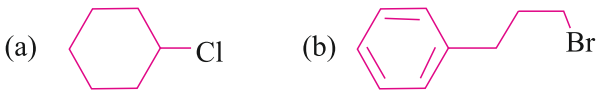
3-Bromopent-1-ene

[*marked carbon are chiral centres]

14. Complete the reactions:



Ans :



15. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanide as the chief product. Explain

Ans : KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C-C bond is more stable than C-N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

16. An organic compound **A** react with PCl_5 to give compound **B**, compound **B** react with Na /ether to give n-butane . What are compounds **A** and **B** ?

Ans : **A** = C_2H_5OH, **B** = C_2H_5Cl

17. 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.

Ans: In aqueous medium i.e., water, KOH will produce strong nucleophile OH^- which will bring about the substitution of alkyl halides to form alcohols. At the same time, the OH^- ions will be highly hydrated also. They will not be able to abstract a proton (H^+) from the β-carbon atom to form alkenes.

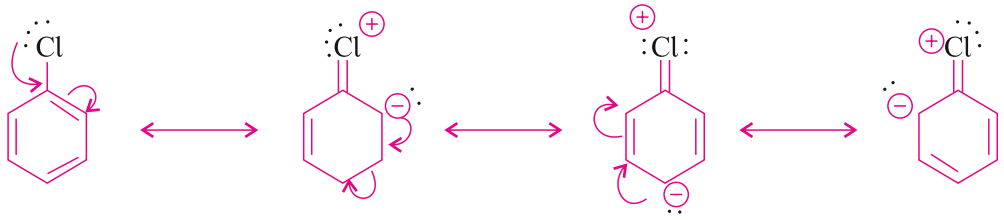
In alcoholic KOH, the solution will also contain ethoxide ions ($C_2H_5O^-$) in addition to OH^- ions. They being a stronger base than OH^- ions, will abstract a H^+ ion from the β-carbon atom giving alkene as the product as a result of dehydrohalogenation.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Haloarencs are extremely less reactive towards nucleophilic substitution reactions. Explain.

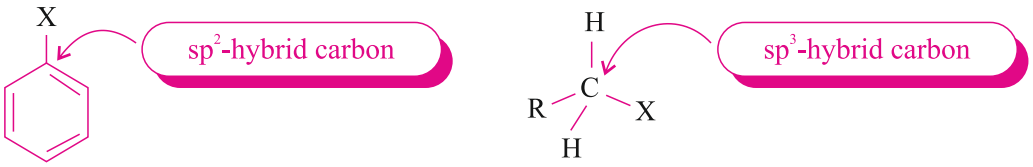
Ans: Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C-X bond: In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.



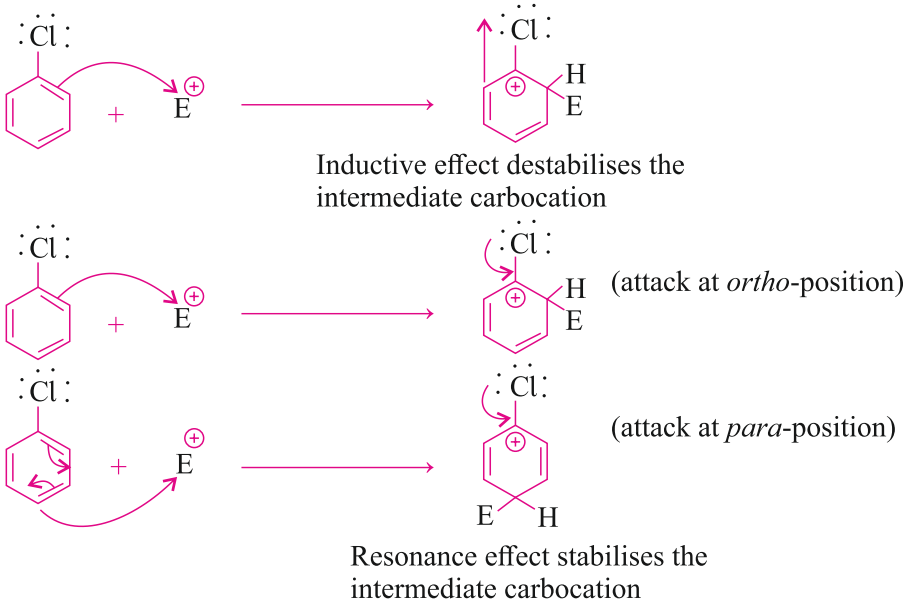
The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp^3-hybridised carbon in haloalkane with less s-character. Thus, C-Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(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 arenes.

2. Although chlorine is an electron withdrawing group, yet it is *ortho*- and *para*-directing in electrophilic aromatic substitution reaction. Explain.

Ans: Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.



Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para*-positions and hence makes the deactivation less for *ortho*- and *para*-attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

3. A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

Ans: (A) 1 -Bromo-2-methylpropane

(B) 2-Methylprop-1-ene

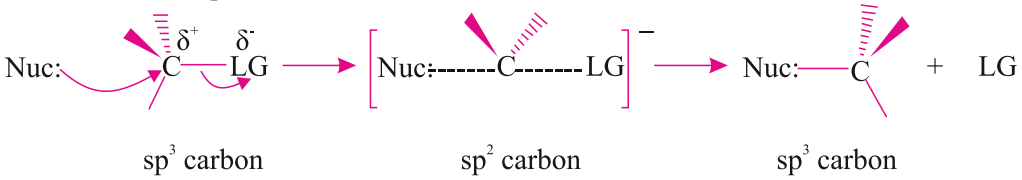
(C) tert-butylbromide

(D) 2,5-Dimethylhexane

CASE STUDY BASED QUESTIONS

1. Read the passage and answer the following questions:

The bimolecular nucleophilic substitution (S_N2) reactions are among the fundamental and most important organic reactions. Traditionally, the mechanism of the S_N2 reactions is studied using qualitative transition state theory. The functionalized sp^3 hybridized carbon in a substrate molecule functions as an electrophilic center. This electrophilicity is considered due to a partial positive charge created on carbon by the electronegative functional group. A nuelcophile (Nuc-) attacks the sp^3 hybridized carbon from the opposite side of the leaving group (-LG). This nucleophilic attack results in a transition state in which the carbon atom becomes sp^2 hybridized with the C-LG bond partially broken and the Nuc-C bond partially formed. Finally, the C-LG bond is broken completely coincident with formation of the Nuc-C bond, giving the nucleophilic substitution product.



Reference : Xiaoping Sun, **Mechanistic Studies of Nucleophilic Substitution and β-Elimination Reactions**, *Symmetry* **2010**, 2(1), 201-212;https://doi.org/10.3390/sym2010201

(A) Which of the following undergoes S_N2 reaction fastest?

(a) Chloropropane (b) Bromopropanc

(c) Iodopropane (d) Chlorobenzene

(B) S_N2 reaction accompanied by.....of the configuration.

(a) Retention (b) Inversion

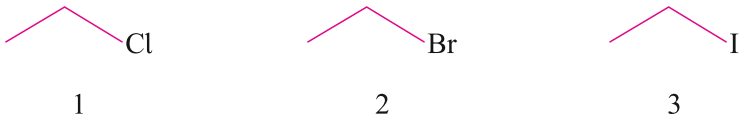
(c) Racemisation (d) Tautomerism

(C) Reaction of-2-of $(CH_3)_3$ C-Cl with aq. NaOH gives:

(a) $(CH_3)_3$ CH-OH (b) $(CH_3)_2$ CH-OH

(c) (a) and (b) (d) But-2-ene

(D) The correct order of rate of reaction in S_N2 for following molecules are:



(I) 1>2>3 (ii) 2 > 1 > 3

(iii) 1 > 3 > 2 (iv) 3 > 2 > 1

2. **Read the passage and answer the following questions:**

Halogenation of alcohols is a useful reaction as alcohol-starting materials are cheap and large varieties are commercially available. Many procedures are known that convert alcohols to halides however, they can involve harsh conditions and hazardous chemicals. For example, the chlorination of alcohols is traditionally performed using HCl gas or thionyl chloride, both of which are hazardous to human health and often produce many side reactions. Although improvements have been made upon these halogenation reactions, further green methodology is desired. On a laboratory scale, ammonium halide salts (NH_4X) arc solid reagents, which means they are easy to handle and measure.

Discovering a mild, neutral, highly selective and environmentally friendly system for catalytic dehydroxyhalogenation is desirable but it is not a trivial task. Compromises in the journey towards an ideal sustainable process have to be made. This is exhibited by some of the trends found in the literature regarding chlorination of alcohols. Some reports involve the use of tripbenylphosphine (PPh_3) as a superstoichiometric additive in dehydroxychlorination reactions.

Reference : Petten, C.F., Kalviri, H.A. & Kelton, F.M. **Halodehydroxylation of alcohols to yield benzylic and alkyl halides in ionic liquids**. *Sustain Chem Process* 3, 16 (2015). https://doi.org/ 1 0.1186/s40508-015-0043-4

(A) Which of the following reaction may be used for the formation of 2-Fluorobutane?

(a) Finkelstein Reaction (b) Swarts Reaction

(c) Sandmeyer Reaction (d) S_N2 Reaction

(B) For the reaction, R-OH + HX → R-X + H_2O the rate of reaction will be highest with the-

(a) Ethanol (b) Propan-l-ol

(c) Propan-2-ol (d) 2-Methylbutan-2-ol

(C) When primary, secondary and tertiary alcohols reacts with Lucas' reagent (HCl + $ZnCl_2$), the incorrect observation is-

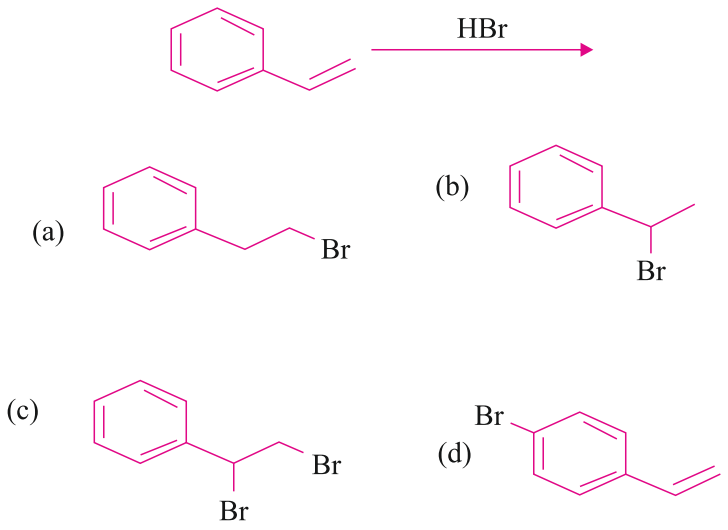
(a) Primary alcohol gives turbidity immediately.

(b) Secondary alcohols gives turbidity in 5-10 minutes.

(c) Tertiary alcohols are most reactive.

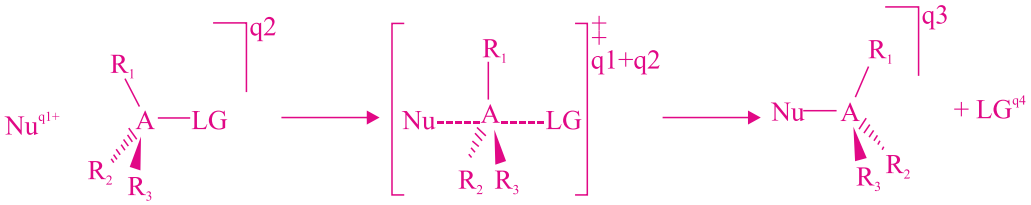
(d) Reaction follows S_N1 pathway.

(D) The correct product of following reaction is-

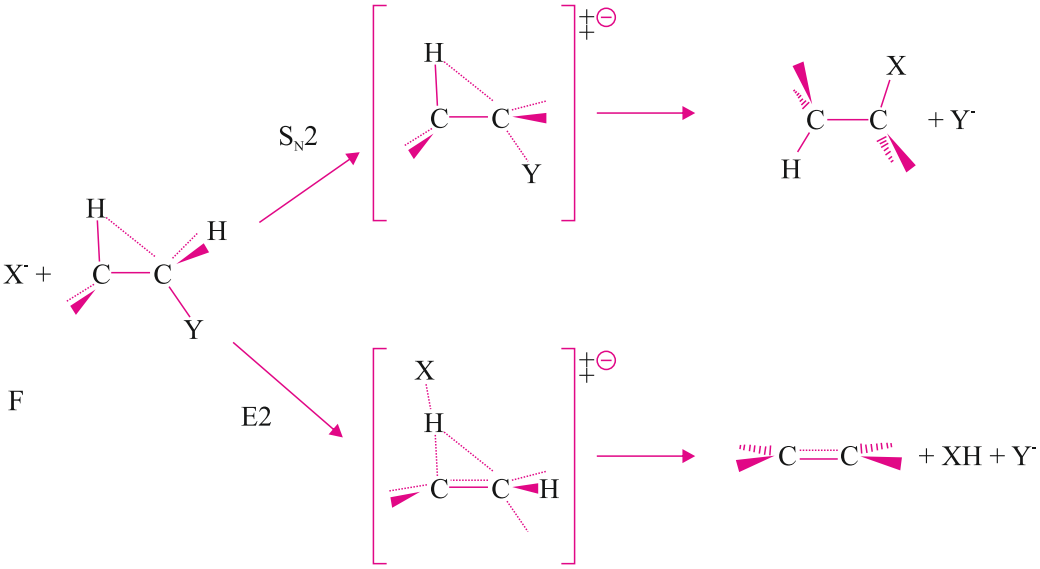


3. **Read the passage and answer the following questions:**

Bimolecular nucleophilic substitution (S_N2) reactions constitute one of the most widely-used organic chemistry reactions, both in chemistry and biology. The general reaction scheme is summarized in Scheme I, where a nucleophile Nu^q attacks the central atom A and simultaneously a leaving group LG is displaced. The reaction can proceed for either anionic species (typically ql=q4<0), neutral (radical) species (typically ql=q2=q3+q4=0), or cationic species (typically q2=q3>0), together with a wide range of nucleophiles, leaving groups and central atoms. The number and nature of the substituents around the central atom play a major role in determining reactivity.



S_N2 substitution is, in principle, always in competition with base induced elimination (E2), and the two pathways may occur as unwanted side reactions of each other.



Reference : T.A. Hamlin, M. Swart, F. M. Bickelhaupt, **Nucleophilic Substitution (S_N2): Dependence on Nucleophile, Leaving Group, Central Atom, Substituents, and Solvent** *ChemPhysChem* 2018, 19, 1315.

(A) Which of the following molecule leads to fastest reaction according to S_N2 mechanism.

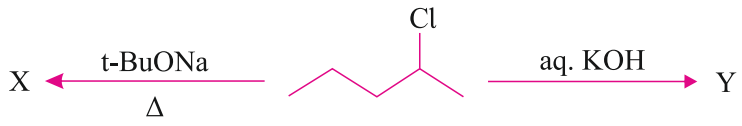
(a) 1-Chloropropane

(b) 2-Chloropropane

(c) 2-Chlorotoluene

(d) Chlorophenylmethane

(B) In given reactions, X and Y are respectively-



(a) Pent-l-ene, Pent-2-ene

(b) Pent-2-ene, Pentan-2-ol

(c) Pentan-2-ol, Pent-2-ene

(d) Pent- I -ene, Pentan-2-ol

(C) Which of the following haloalkane reacts with nucleophile forming racemic mixture?

(a) 1 -Chloropropane (b) Chlorobenzene

(c) 2-Chlorobutane (d) 3 -Chlorobutane

(D) Which of the following statement is incorrect about S_N2 reaction?

(a) It takes place in single step.

(b) It is accompanied by the inversion of configuration.

(c) Stability of carbocation determines the rate of reaction.

(d) lodopropane undergoes S_N2 faster than Chloropropanc.

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. b 2. a 3. a 4. a 5. c 6. d 7. b 8. a 9. b 10. a 11. b 12. a 13. a 14. c 15. b

II FILL IN THE BLANKS

1. Fittig reaction.
2. Racemic mixture.
3. Grignard reagent.
4. *p*-chloroacetophenone.
5. Iodoform.
6. Insoluble, soluble.
7. Inversion.
8. Dextrorotatory.
9. deactivates

III ASSERTION REASON TYPE QUESTIONS

1. C	2. B	3. B
4. D	5. A	6. B
7. D	8. C	9. C
10. A	11. D	12. A
13. C		

IV ONE WORD TYPE QUESTIONS

1. Ambident nucleophile.
2. Sandmeyer reaction.
3. para-diehlorobenzene.
4. β-carbon.
5. S_N1.
6. Polarimeter.
7. Enantiomers.
8. Phosgene

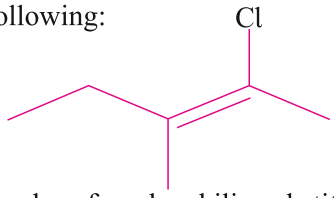
CASE STUDY BASED QUESTIONS

1. (A) - (c) (B) - (b) (C) - (a) (D) - (a)
2. (A) - (b) (B) - (d) (C) - (a) (D) - (b)
3. (A) - (a) (B) - (b) (C) - (c) (D) - (c)

UNIT TEST
CHAPTER-9
HALOALKANES AND HALOARENES

Maximum Marks : 20 **Time Allowed : 1 Hr**

1. Write IUPAC name of following: 1



2. The correct ascending order of nucleophilic substitution reactions for following molecules is- 1

   (I) Chlorobenzene (II) 4-Nitrochlorobenzene

   (III) 4-Chlorotoluene

   (a) I,II,III (b) I,III,II

   (c) III,I,II d) III,II,I

3. How will you convert aniline into iodobenzene? 1

4. Chlorobenzene on reaction with Chloromethane in presence of Zinc chloride forms- 1

   (a) *o*-dichlorobenzene

   (b) *o*-chlorotoluene

   (c) *p*-chlorotoluene

   (d) *o*-chlorotoluene and *p*-chlorotoluene

5. A solution of a molecule (X) rotates plane polarised light 32° clockwise. Which of the following is incorrect? 1

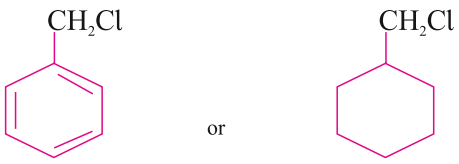
   (a) X is optically active

   (b) X is dextrorotatory

   (c) X has all achiral carbons

   (d) X forms non-superimposable

6. Which of the following undergoes S_N2 reaction faster and Why? 2



7. How will you synthesize following from aniline? Write chemical equations. 2
   (i) Chlorobenzene (ii) Iodobenzcne
8. Explain following giving examples: 2
   (i) raccmic mixture (ii) enantiomers
9. What happens when: 3
   (i) Bromoethane reacts with sodium ethoxide
   (ii) Chloroethanc reacts with AgCN.
   (iii) 2-Bromo-2-methylbutane is heated with ethanolic KOH.
10. Explain following: 3
   (i) Aryl chlorides and bromides can be easily prepared by electrophilic substitution of aromatic hydrocarbons with chlorine and bromine respectively in the presence of Lewis acid catalysts but for preparation of aryl iodides presence of an oxidising agent is required.
   (ii) Grignard reagent is kept under anhydrous conditions.
   (iii) Reactions through S_N2 mechanisms are accompanied by inversion of configuration.
11. Convert the following: 3
   (i) Ethanol to iodoethane
   (ii) Toluene to benzyl alcohol
   (iii) Benzene to diphenyl.

UNIT 10

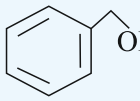
Alcohols, Phenols and Ethers

Points to Remember

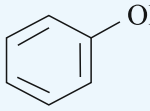
Classification of Alcohols:

(a) Containg sp^3 C-OH bond, $\dot{C}H_2\dot{O}H$ (1^0), > CH-OH(2^0), $\rangle$C - OH (3^0)

Allylic: CH_2 =CH-CH_2.OH

Benzylic: 

(b) Containg sp^2 C-OH bond, Vinylic CH_2=CH-OH

Phenols: 

Classification of ethers:

Simple/Symmetric: alkyl/aryl groups attached to oxygen are same e.g. $CH_3CH_2OCH_2CH_3$

Mixed/Unsymmetric: two different alkyl/aryl groups attached to oxygen e.g. $CH_3OCH_2CH_3$

Classification and Nomenclature of Alcohols and ethers

Nomenclature:

Alcohols: Common names (alkyl group + alcohol)

IUPAC (alkan+ol, substituting -e by - ol e.g. ethanol)

Phenols: Common names (as derivatives of phenol with position like ortho-, meta-,para-)

IUPAC (derivatives of phenols with numbers like 1,2-, 1,3-e.g.

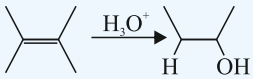
2-Nitrophenol or o-nitrophenol)

Ethers: Common names (alkyl/aryl groups in alphabetical order followed by ether e.g. ethyl methyl ether) IUPAC (In alkyl/aryl group-e is replaced by oxy followed by parent hydrocarbon e.g. methoxyethane)

Preparation of Alcohols

1. From alkenes:

a) By acid catalyzed hydration



b) By hydroboration-Oxidation

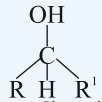
$3CH_3\text{-}CH{=}CH_2 + (H\text{-}BH_2)_2 \rightarrow (CH_3\text{-}CH_2\text{-}CH_2)_3B$

$\xrightarrow[H_2O]{H_2O_2, OH^-}$ $3CH_3\text{-}CH_2\text{-}OH + B(OH)_3$

2. From carbonyl compounds

a) By reduction of aldehydes and ketones

$R\text{-}CHO + H_2 \xrightarrow{Pd} RCH_2OH$

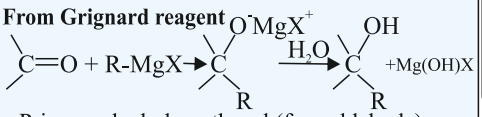
$R\text{-}CO\text{-}R \xrightarrow{NaBH_4}$ 

b) By reduction of carboxylic acids and esters

$RCOOH \xrightarrow[H_2O]{i)\ LiAlH_4} RCH_2OH$

$RCOOH \xrightarrow[H^+]{R^1\text{-}OH} RCOOR' \xrightarrow[Pd]{H_2} RCH_2OH + R'\text{-}OH$

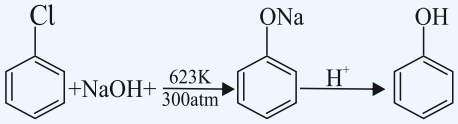
3. From Grignard reagent



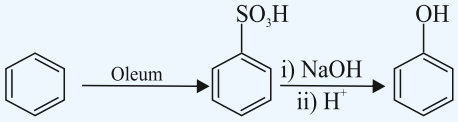
For Primary alcohol, methanal (formaldehyde)
Secondary, aldehydes other than methanal
Tertiary, Ketones are used with appropriate
Grignard reagent

Preparation of Phenol

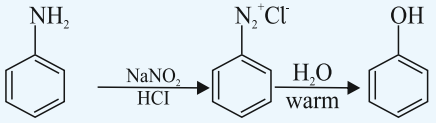
1. From Haloalkanes



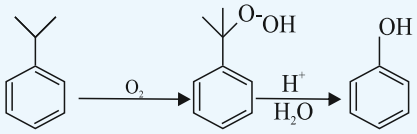
2. From Benzene sulphonic acid



3. From Diazonium salts



4. From Cumene



Preparation of Alcohols, Phenols and Ethers

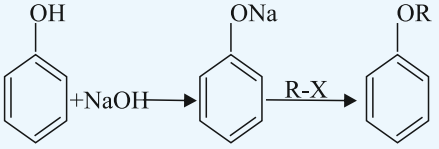
Preparation of Ethers

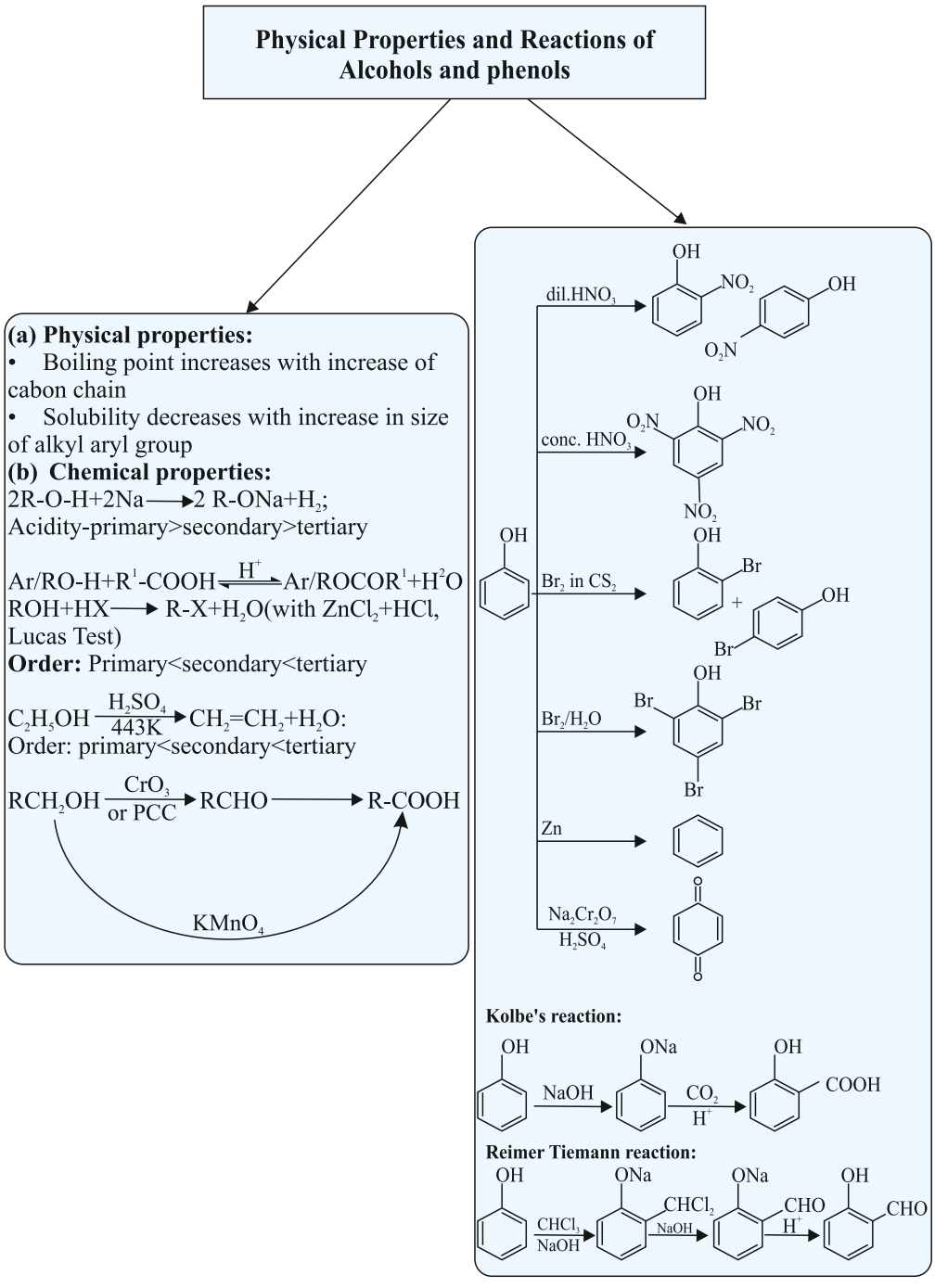
1. By dehydration of alcohols

$CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} CH_3CH_2OCH_2CH_3$

2. Williamsons Synthesis

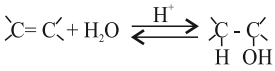
$RX + R'\text{-}ONa \longrightarrow R\text{-}O\text{-}R^1$

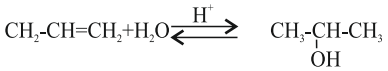



Physical Properties and Reactions of Alcohols and phenols
(a) Physical properties:
• Boiling point increases with increase of cabon chain
• Solubility decreases with increase in size of alkyl aryl group
(b) Chemical properties:
2R-O-H+2Na ⟶ 2 R-ONa+H2;
Acidity-primary>secondary>tertiary
Ar/RO-H+R1-COOH ⇌ Ar/ROCOR1+H2O
ROH+HX ⟶ R-X+H2O(with ZnCl2+HCl, Lucas Test)
Order: Primary<secondary<tertiary
C2H5OH —H2SO4, 443K→ CH2=CH2+H2O:
Order: primary<secondary<tertiary
RCH2OH —CrO3 or PCC→ RCHO ⟶ R-COOH
KMnO4
dil.HNO3
conc. HNO3
Br2 in CS2
Br2/H2O
Zn
Na2Cr2O7
H2SO4
Kolbe's reaction:
NaOH
CO2
H+
COOH
Reimer Tiemann reaction:
CHCl3
NaOH
CHCl2
NaOH
CHO
H+
CHO

Mechanisms:

a) Hydration of Alkenes

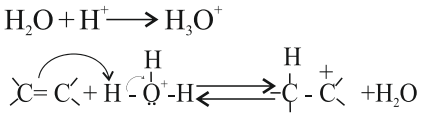




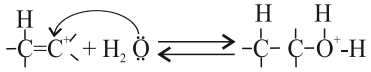
Mechanism of hydration of ethene

The mechanism of the reaction involves the following three steps:

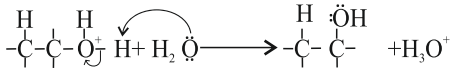
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.



Step 2: **Nucleophilic attack of water on carbocation.**

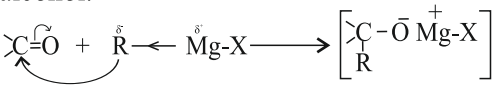


Step 3: **Deprotonation to form an alcohol.**

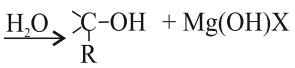


b) Reaction of Grignard reagent

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



Adduct ...(i)

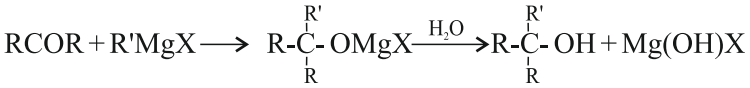


...(ii)

The overall reactions using different aldehydes and ketones in dry ether medium are as follows:

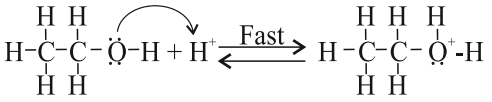






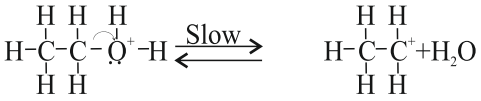
c) Dehydration of Alcohols

Step 1: **Formation of protonated alcohol.**

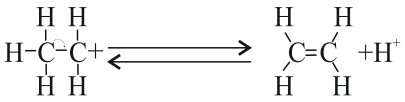


Ethanol — Protonated alcohol (Ethyl oxonium ion)

Step 2: **Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.**



Step 2: **Formation of ethene by elimination of a proton.**



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.

d) Dehydration of alcohol at 413K to form alkene

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

(i) $CH_3\text{-}CH_2\text{-}\ddot{O}\text{-}H + H^+ \rightarrow CH_3\text{-}CH_2\text{-}{}^{+}\ddot{O}\text{-}H$

(ii) $CH_3CH_2\text{-}\ddot{O}(H) + CH_3\text{-}CH_2\text{-}O^{+}(H)(H) \rightarrow CH_3CH_2\text{-}\overset{+}{O}(H)\text{-}CH_2CH_3 + H_2O$

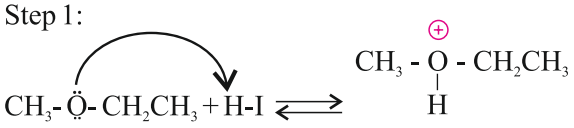
(iii) $CH_3CH_2\text{-}\overset{+}{O}(H)\text{-}CH_2CH_3 \rightarrow CH_3CH_2\text{-O-}CH_2CH_3 + H^+$

Acidic dehydration of alcohols, to give an alkene is also associated with substitution reaction to give an ether.

c) Reaction of ethers with HI

The reaction of an ether with concentrated HI starts with with protonation of ether molecule.

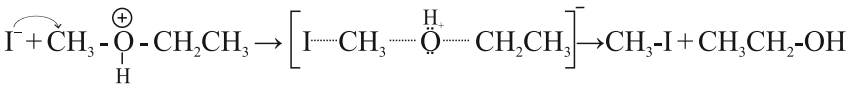
Step 1:



Step 2:

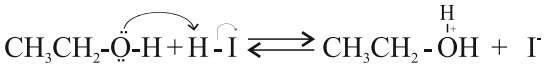
Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaccs an alcohol molecule by S_N2 mechanism.

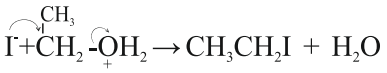
Thus, in the cleavage of mixed ethers with two different alkyl groups. The alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).



When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step 3:





OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Arrange the following compound in decreasing order of boiling point?

   (i) Propan-1-ol

   (if) Butan-2-ol

   (iii) Butan-1-ol

   (iv) Pentan-1-ol

   (a) i>iii>ii>iv (b) i>ii>iii>iv

   (c) iv>iii>ii>i (d) iv>ii>iii>i

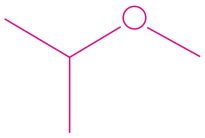
2. What is the correct order of reactivity of alcohols in the following reaction?

   $R - OH + HCl \xrightarrow{ZnCl_2} R - Cl + H_2O$

   (a) 1°>2°>3° (b) 1°>3°>2°

   (c) 3°> 10 > 2° (d) 3° > 2° > 1°

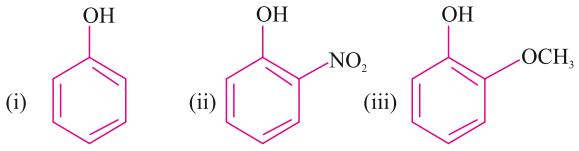
3. IUPAC name of the compound :



   (a) 1-methoxy- 1 -methyl ethane (b) 2-methoxy-2-methyl ethane

   (c) 2-methoxypropane (d) Isopropylmethyl ether

4. The correct order of decreasing acid strength of the following compound is:



(a) i>ii>iii (b) iii>ii>i

(c) ii>i>iii (d) ii>iii>i

5. The major product obtained on reaction of phenol with NaOH followed by CO_2 and acidification is:

(a) Benzoic acid (b) Salicylaldehyde

(c) Salicyclic acid (d) Phthalic acid

6. Which of the following alcohol on dehydration with conc. H_2SO_4 gives but-2-ene?

(a) butan- 1-ol (b) butan-2-ol

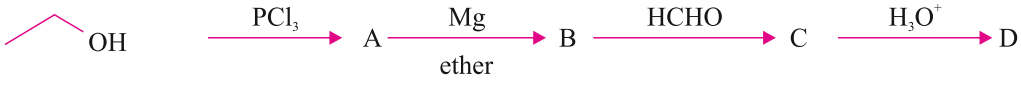
(c) 2-methylpropan-l-ol (d) both a and b

7. Which of the following alcohol give iodoform test?

(a) Butan-1-ol (b) Propan-1-ol

(c) Propan-2-ol (d) Ethanol

8. In the following sequence of reaction. The product D is



(a) n-butyl alcohol (b) n-propyl alcohol

(c) Propanal (d) Butanal

9. Correct statement in case of n-butanol and t-Butanol is:

(a) both are having equal solubility in water

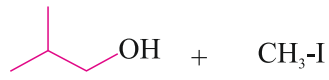
(b) 1-butanol is more soluble in water

(c) boiling point of t-butanol is lower than n-butanol

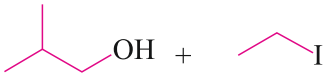
(d) boiling point of n-butanol is lower than t-butanol

10. The major products of following reaction are:



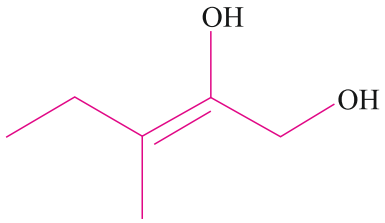
(a) 

(b) 

(c) 

(d) 

11. Write the IUPAC name of the compound given below.



(a) 3-methylpent-2-ene-1,2-diol

(b) 2-methylp ent-2-ene-1,2-diol

(c) 3-methylpent-3-ene-2,3-diol

(d) 3-methylpent-2-ene-1,2-diol

12. Which of the following are used to convert RCHO into RCH_2OH ?

(a) H_2/Pd (b) $LiA1H_4$

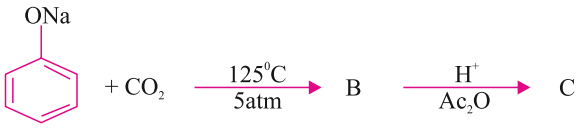
(c) $NaBH_4$ (d) All of the above

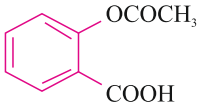
13. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields-

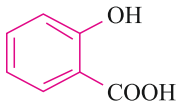
(a) *o*-cresol (b) *m*-cresol

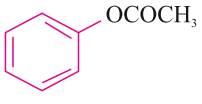
(c) 2,4-dihydroxytoluene (d) benzyl alcohol

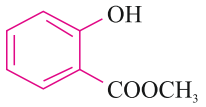
14. The product C in given reaction is-ONa

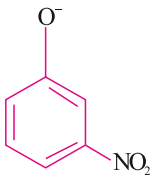


(a) 

(b) 

(c) 

(d) 

15. Which of the following species can act as the strongest base?
    (a) ^{-}OH
    (b) ^{-}OR
    (c) $^{-}OC\text{-}_6H_5$
    (d) 

16. CH_3CH_2OH can be converted into CH_3CHO by.....
    (a) catalytic hydrogenation
    (b) treatment with $LiA1H_4$
    (c) treatment with pyridinium chlorochromate (PCC)
    (d) treatment with $KMnO_4$

17. Which of the following reactions will yield phenol?
    (a) Fusion of chlorobenzene with NaOH at 300 atm.
    (b) Diazotization of aniline followed by heating with water.
    (c) Sulphonation of benzene followed by treatment with NaOH then acidification.
    (d) All of the above

II FILL IN THE BLANKS

1. Phenol on reaction with bromine water gives white precipitate of.....
2. Ethanoic acid on reaction with $LiAlH_4$ forms.....
3. Reaction of.....with Grignard reagent gives primary alcohols.
4. Phenols are commercially manufactured by oxidation followed by acidification of.....
5. Reaction of alcohols/phenols with carboxylic acids is termed as.....
6. .....test is used to distinguish primary, secondary and tertiary alcohols.
7. Dehydration of tertiary alcohols is .....than primary alcohols.
8. Dehydration of alcohols to form ether is ..... type reaction.
9. Benzyl alcohol on reaction with $KMnO_4$ followed by acidification forms.....
10. $SOCl_2$ converts propan-1 -ol to .....

III ASSERTION REASON TYPE QUESTIONS

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.

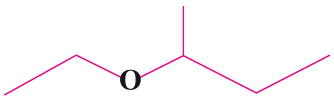
(A) Assertion and reason both are correct and reason is correct explation of assertion

(B) Both assertion and reason are correct statement but reason is not correct explation of assertion.

(C) Assertion is correct statement but reason is wrong statement.

(D) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION :** *p*-Nitrophenol is more acidic than phenol.
   REASON : Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.
2. **ASSERTION :** IUPAC name of the compound is 2-ethoxy-2-methylethane.



   REASON : 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].
3. **ASSERTION :** Bond angle in ethers is slightly less than the tetrahedral angle.
   REASON : There is a repulsion between the two bulky (-R) groups.
4. **ASSERTION :** *o*-Nitrophenol is less soluble in water than the in and *p*-isomers.
   Reason in and *p*-Nitrophenols exist as associated molecule.
5. **ASSERTION :** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid .
   REASON: Lewis acid polarises the bromine molecule.
6. **ASSERTION :** Ethanol is a weaker acid than phenol.
   REASON : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.
7. **ASSERTION :** Phenols give *o*-and *p*-nitrophcnol on nitration with dil. HNO_3.
   REASON : -OH group in phenol is o-, p- directing.

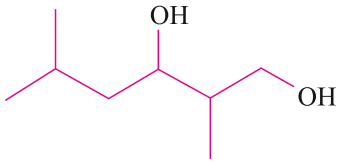
8. **ASSERTION :** Cumene is used commercially for production of phenol.
   REASON : The side product formed in this reaction is acetone which is another useful compound.
9. **ASSERTION :** Protonation of phenol is difficult than ethanol.
   REASON : Ethyl group in ethanol is electron releasing.
10. **ASSERTION :** Tertiary alcohols gives turbidity almost immediately on treatment with $ZnCl_2$ /HCl.
    REASON : Tertiary carbocation formed is very stable and undergoes substitution easily.

IV ONE WORD TYPE QUESTIONS

1. Which reagent used to convert primary alcohol to carboxylic acid?
2. Out of *ortho* and *para*- nitrophenol which is more steam volatile?
3. What is the major product of bromination of anisole?
4. Which reaction is used to convert phenol to salicylaldehyde?
5. Out of ethanol and phenol, which is more acidic?
6. Which reagent could be used to reduce aldehyde selectively in presence of ester group?
7. Which reagent(s) are best to convert propene to propan-l-ol?
8. Out of primary, secondary and tertiary alcohols which is most acidic?
9. Name the product formed, when phenol is treated with cone. HNO_3 .

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

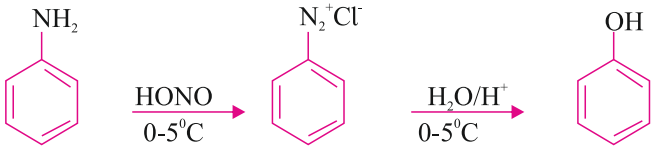
1. Write IUPAC name of the following compound:



Ans: 2,5-Dimethylhexan-1,3-diol

2. How is phenol obtained from aniline ?

Ans:



3. Why phenol is acidic in nature ?

Ans: Due to stability of phenoxide ion by resonance

4. Among HI, HBr and HCI which is most reactive towards alcohols. Why?

Ans: Due to lowest bond dissociation enthal of HI, it is most reactive.

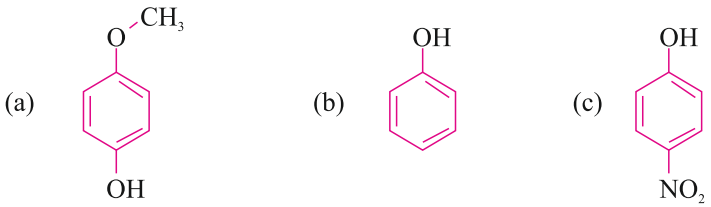
5. Name a compound which is used as antiseptic as well as disinfectant'.

Ans: Solution of phenol : 0.2% antiseptic, 2% disinfectant

6. What is nitrating mixture for monosubstitution of phenol?

Ans: Dilute HNO_3

7. Arrange the following in decreasing order of their acidic character:

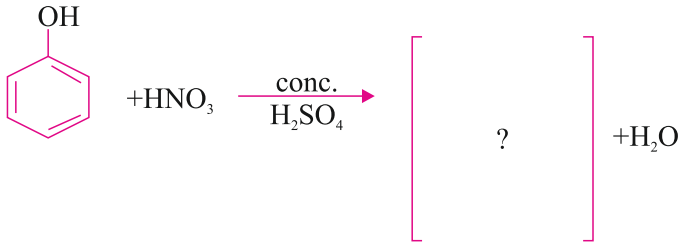


Ans: (c) > (b) > (a)

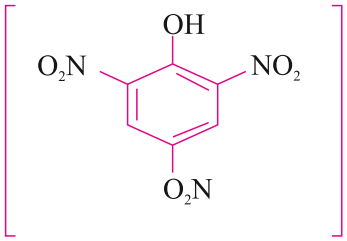
8. Why lower alcohols are soluble in water while higher alcohols are not?

Ans: Due to formation of hydrogen bonds, lower alcohols are soluble but increase in hydrophobic chain decreases solubility.

9. Complete the following reaction :



Ans:



10. What happens when CH_3CH_2OH heated with red P and HI ?

Ans:.

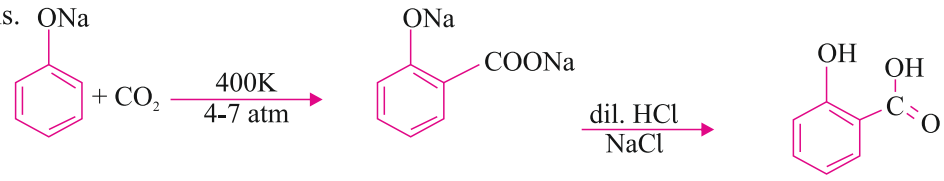


11. Ethanol has higher boiling point than methoxymethane. Give reason.

Ans : Because of H- bonding in ethanol.

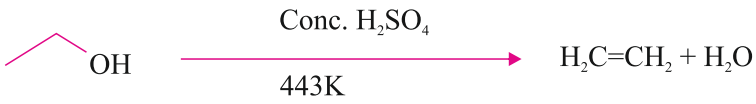
12. Explain Kolbe's reaction with example.

Ans.



13. How could you convert ethanol to ethene ?

Ans .



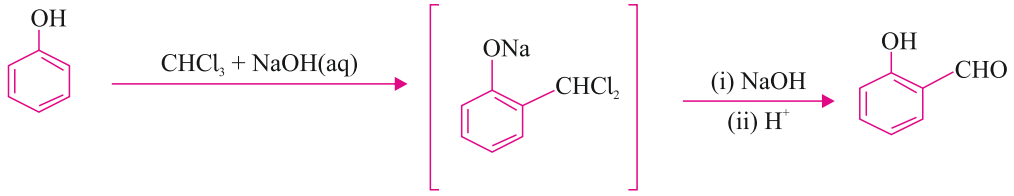
SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. Out of t-butyl alcohol and n-butanol, which one will undergo acid catalysed dehydration faster and why?

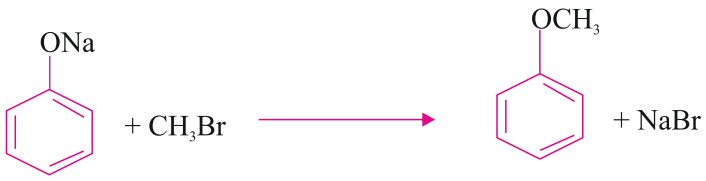
Ans: t-Butyl alcohol will undergo dehydration faster due to formation of stable tertiary carbocation intermediate.

2. Carry out the following conversions:
   (a) Phenol to salicaldehydc
   (b) t-butylchloride to t-butyl ethyl ether
   (c) Propene to propan-l-ol
3. Write the steps involved in the mechanism for the formation of ethanol from ethene.
4. Predict the reagent for carrying out the following conversions:
   (a) Phenol to benzoquinone
   (b) Anisole to *p*-bromoanisole
   (c) Phenol to 2,4,6-tribromophenol
5. Write one chemical reaction to illustrate the following:
   (a) Reimer-Tiemann reaction
   (b) Williamson synthesis

Ans: (a)

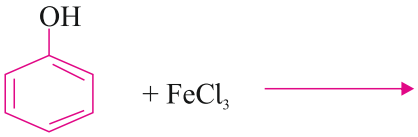


(b)

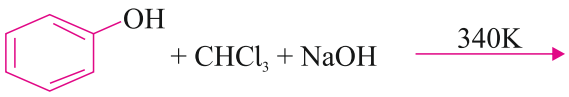


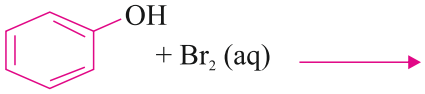
6. Complete the following the equations and name the products:

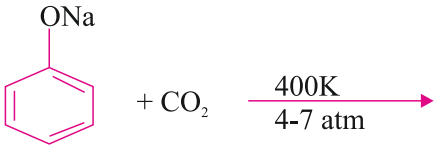
(i)



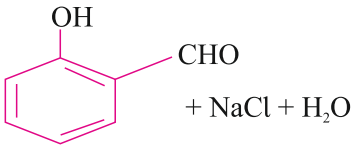
(ii)

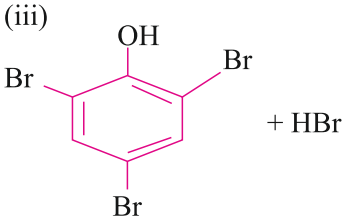


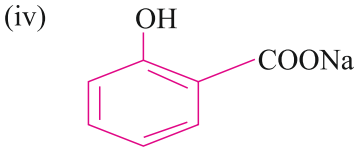
(iii) 

(iv) 

Ans: (i) $[Fe(C_6H_5O)_3]^{3-}$+HC1

(ii) 

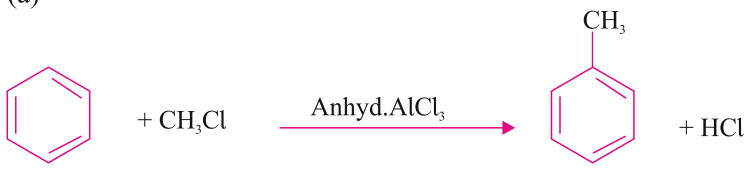
(iii) 

(iv) 

7. Write an example for the following name reactions :

(a) Friedel-Crafts reaction (b) Coupling reaction

Ans: (a)



(b)



8. Account for the following:
   (a) Phenol has a smaller dipole moment than methanol.
   (b) Phenol undergoes electrophilic substitution reactions faster than benzene.

Ans: (a) Due to delocalization of electrons of oxygen in phenol.
   (b) Due to +R effect of -OH group in phenol which activates phenyl nucleus by increasing electron density as compared to benzene.

9. Give one reaction of alcohol involving cleavage of :
   (a) C-O bond (b) O-H bond

Ans: (a)

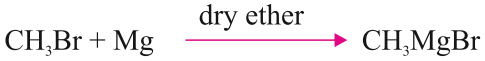


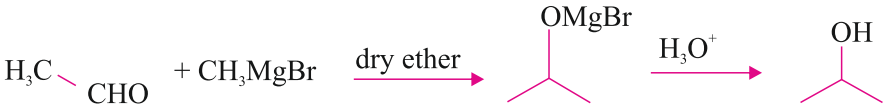
(b)



10. Ethereal solution of an organic compound 'X' when heated with Mg gave 'Y' which on treatment with CH_3CHO followed by acid hydrolysis gave 2-propanol. Identify the compound 'X'. What is 'Y' known as ?

Ans:





11. Account for the following:
   (a) Phenol has a smaller dipole moment than CH_3OH.
   (b) Phenol do not give protonation reactions readily.

Ans: (a) because phenol has electron attracting benzene ring.
   (b) due to the resonance and positive charge on oxygen, it does not have tendency to accept a proton.

12. While separating a mixture of *o*- and *p*-nitrophcnols by steam distillation, name the isomer which is steam volatile? Give reasons.

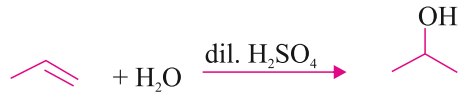
Ans: *o*-Nitrophenol is steam volatile because it has intramolecular H-bonding.

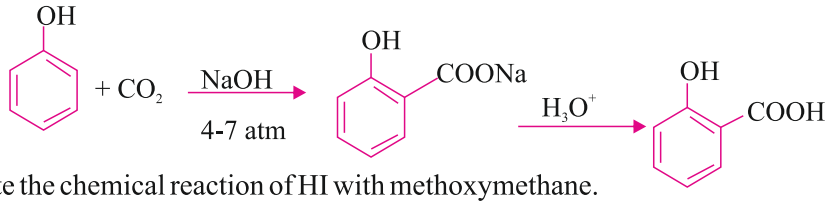
13. Write the reactions and conditions involved in the conversion of:

(a) Propene to propan-2-ol

(b) Phenol to salicylic acid

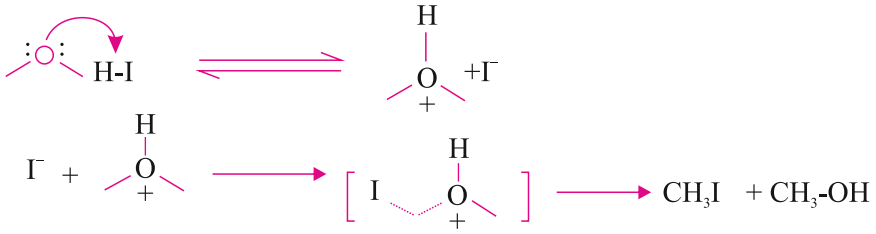
Ans:

(a) 

(b) 

14. Write the chemical reaction of HI with methoxymethane.

Ans:



15. Ethers are relatively inert. Justify

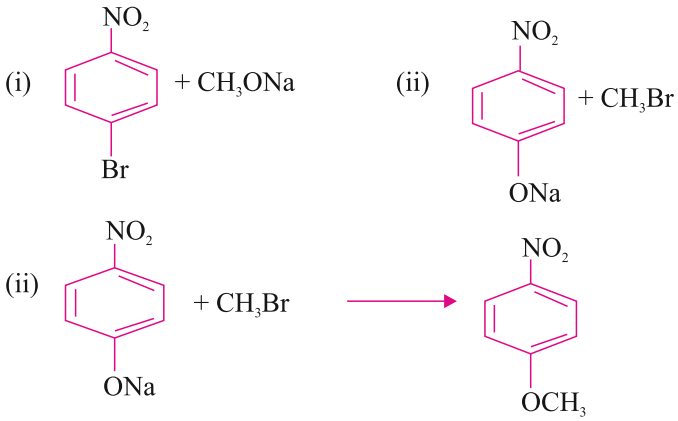
Ans: Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides (C-O-C).

16. How will you distinguish between CH_3OH and C_2H_5OH?

Ans: $C_2H_5OH + 4I_2 + 3Na_2CO_3(heat) \rightarrow CH_3I + HCOONa + 5NaI + 2H_2O + 3CO_2$

17. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4- nitrobenze and why?

Ans:



18. Arrange in order of boiling points :

(a) C_2H_5-O-C_2H_5, C_4H_9COOH, C_4H_9OH

(b) C_3H_7CHO, $CH_3COC_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

Ans: (a) $C_4H_9COOH > C_4H_9OH > C_2H_5$-O-$C_2H_5$

(b) $(CH_3CO)_2O > C_2H_5COOCH_3 > CH_3COC_2H_5 > C_3H_7CHO$

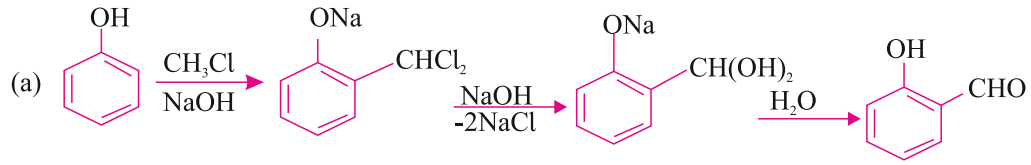
19. Describe the following reactions with examples :

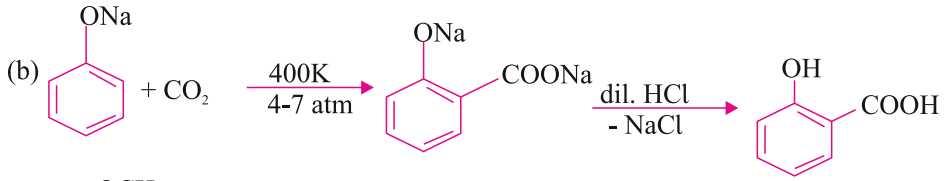
(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

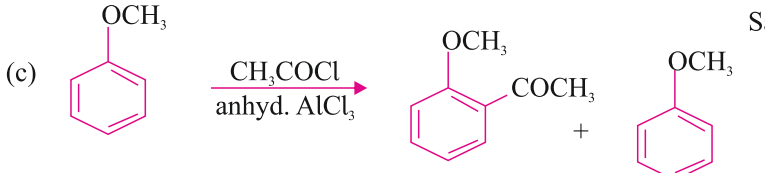
(c) Friedel Crafts acylation of anisole

Ans:





Salicylic acid

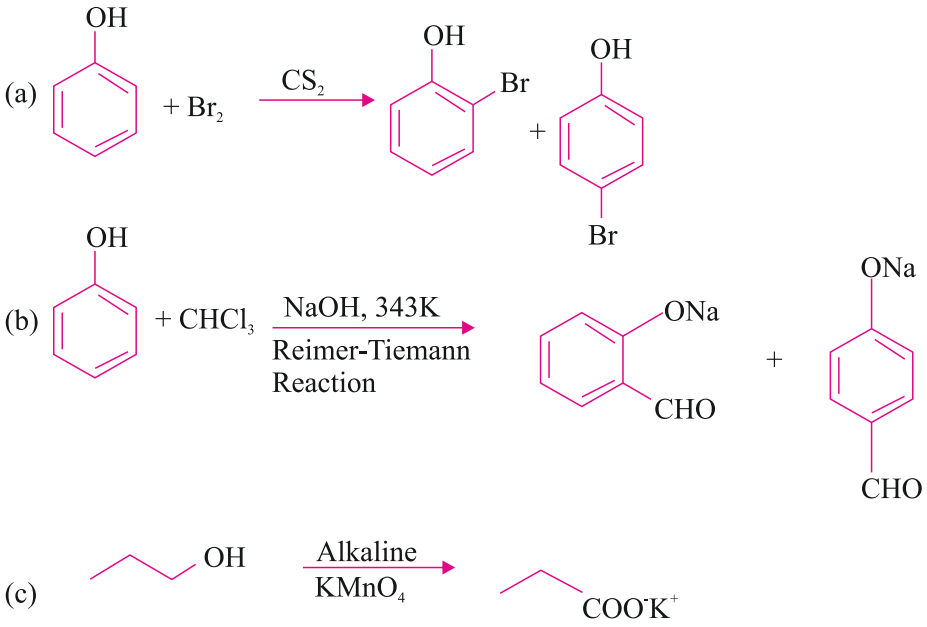


20. Give equations of the following reactions:

(a) Bromine in CS_2 with phenol

(b) Treating phenol with chloroform in presence of aqueous NaOH

(c) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.



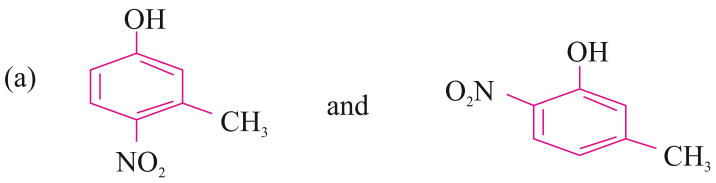
21. Write the structure of the major products of the following:

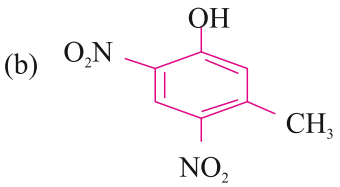
(a) Mononitration of 3-methylphenol

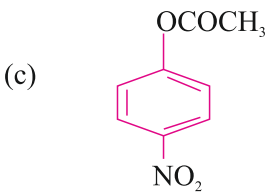
(b) Dinitration of 3-methylphenol

(c) Mononitration of phenyl ethanoate

Ans : -OH and -CH_3 are *o*-and *p*-directing groups. The products are:







22. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with cone. HCl or HNO_3. Explain.

Ans: In acidic medium alcohols protonated then loses H_2O to form a carbocation. If HCl is used which is strong nucleophile causes nucleophilic substitution and HNO_3 causes oxidation.

23. Name the reagents which arc used in the following conversions:

(a) Primary alcohol to an aldehyde

(h) Butan-2-one to butan-2-ol

(c) Phenol to 2,4,6-trinitrophenol

Ans: (i) PCC, a complex of chromium trioxide with pyridine and HCl.

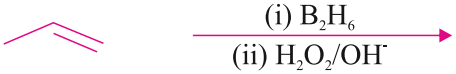
(ii) $NaBH_4$, sodium borohydride

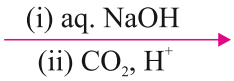
(iii) Br_2(water)

24. Write major products of following reactions:

(i) 

(ii) 

(iii) 

(iv) C_6H_5OH 

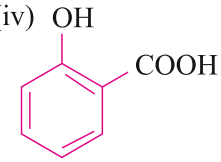
(v) $CH_2Br\text{-}CH_2Br$ 

(vi) $C_2H_5NH_2$ 

Ans: (i) $CH_3CH_2CH_2CH_2OH$

(ii) $CH_3CH{=}CHCHO$

(iii) $CH_3CH_2CH_2OH$

(iv) 

(v) $CH_2OH\text{-}CH_2OH$

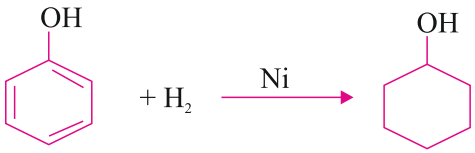
(vi) CH_3CH_2OH

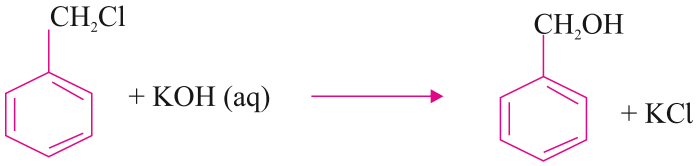
25. How will you convert :

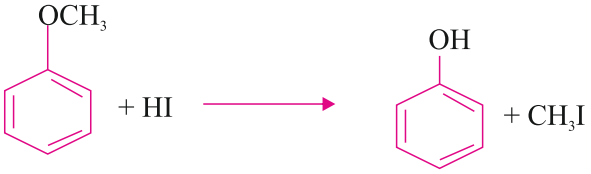
(a) Phenol to cyclohexanol

(b) Benzyl chloride to benzyl alcohol

Ans:

(i) 

(ii) 

(iii) 

LONG ANSWER TYPE QUESTIONS (5 Marks)

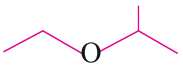
1. An alcohol A($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives carboxylic acid 'B' ($C_4H_8O_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443K gives compound 'C' with aqueous H_2SO_4. 'C' gives compound 'D' ($C_4H_{10}O$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidised. Identify A, B, C and D and write their structure.

Ans: A: $(CH_3)_2CHCH_2OH$ C: $(CH_3)_2C=CH_2$

B: $CH_3CH(CH_3)COOH$ D: $(CH_3)_3$-C-OH

2. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot conc. HI produced two alkyl halides which on hydrolysis from compound 'B' and 'C' . Oxidation of B gives an acid 'D' whereas oxidation of 'C' gave a ketone E. Deduce the structure of A, B, C, D and E.

Ans:

A. 

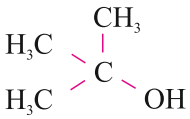
B. 

C. 

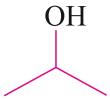
D. CH_3- COOH

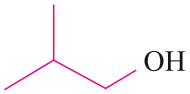
E. 

3. Which of the following compounds gives fastest reaction with HBr and why?

(i) 

(ii) 

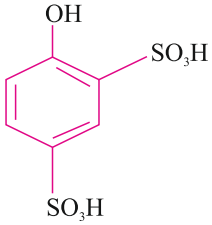
(iii) 

(iv) 

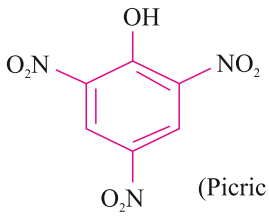
Ans: (i) $(CH_3)_3C$-OH

Due to formation more stable of carbocation

4. Phenol, C_6H_5OH when reacts with concentrated sulphuric acid, forms 'Y'. The compound, 'Y' is reacted with concentrated nitric acid to form 'Z'. Identify 'Y' and 'Z' explain why phenol is not converted commercially to Z by reacting it with cone. HNO_3

Ans: 

(Y)



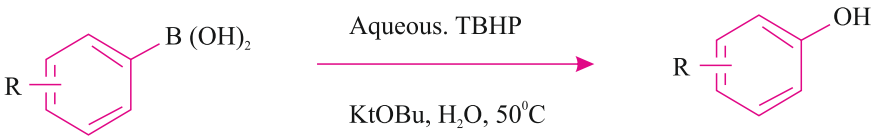
(Picric acid)

(Z)

CASE-STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

In the past few decades, phenols have received great attention in modern synthetic chemistry since ever Runge and Laurent made the first discovery in 1834 and 1841, respectively with regard to this motif, which is frequently found in natural products, flavonoids and pharmaceutically important compounds associated with certain bioactivities, such as antibacterial, antifungal, antibiotic, anti-inflammatory, antiviral, anxiolytic and antioxidant activities. Conventional methods for the large-scale synthesis of phenols include the Hock process, diazotization of aromatic amines and nucleophilic substitution reactions. Academicians have focused on the development of alternative approaches, for example, C-H activation of arenes and oxidation of C-Si bonds and C-halo bonds. Recently, the direct hydroxylation of aryl boronic acids to phenols has gained a lot of attention. In this context, a variety of oxidative methods employing metal catalysts, $Cu(OAc)_2$-H_2O_2, $CuSO_4$-phenanthroline, $CuC1_2$-miceller systems, Cu_2O-NH_3, $[Ru(bpy)_3C1_2]$-$6H_2O$, Al_2O_3-H_2O_2, and H_3BO_3-H_2O_2 has been developed. On the otherhand, the metal-free oxidative process are also competitive, Oxone, nBu_4NHSO_5, NH_2OH, H_2O_2-poly(N-vinylpyrrolidone), I_2-H_2O_2, Amberlite IR-120-H_2O_2, N-oxides, MCPBA, $NaClO_2$, photoredox catalysis, electrochemical oxidation, $(NH_4)_2S_2O_8$, PEG-400-H_2O_2, WERSA-H_2O_2, WEBPA-H_2O_2, nanoparticles of Ag, Cu_2O, and Fe_2O_3/silica gel and TBHP/$C1_3CCN$. Despite these efficient oxidative processes, developing a new methodology free from metal oxidants and organic solvents is highly desirable. As part of our research interest involving metal-free oxidation reactions herein, a new protocol for the direct hydroxylation of aryl boronic acids with TBHP in the aqueous medium is reported (Scheme 1).



Scheme 1: Hydroxylation of aryl boronic acids.

Reference : Tanveer MahmadAlli Shaikh, **Synthesis of Phenols via Metal-Free Hydroxylation of Aryl Boronic Acids with Aqueous TBHP**, *Journal of Chemistry*, vol. **2020**, Article ID 1543081, 7 pages, 2020. https://doi.org/10.1155/2020/1543081

(A) Which of the following method of preparation of phenols is least likely to take place at 298K?

(a) Nucleophilic substitution in chlorobenzene

(b) Reaction of diazonium salt with water.

(c) Oxidation followed by acidification of cumene

(d) Reaction of benzene sulphonic acid with NaOH followed by acidification

(B) In which of the following haloarene, nucleophilic substitution will be fastest to yield corresponding phenol?

(a) Chlorobenzene

(b) *p*-Chloronitrobenzene

(c) *p*-Cholrotoluene

(d) *p*-Chloroanisole

(C) Aniline on reaction with $NaNO_2$ + HCl forms (X). (X) converts to (Y) on reaction with KI. (X) and (Y) are respectively-

(a) Benzene diazonium chloride, iodobenzene

(b) Iodobenzene, Ethoxybenzene

(c) Iodobenzene, Benzene

(d) Benzene diazonium chloride, Phenol

(D) Phenols on reaction with bromine water forms-

(a) Colourless, 2-Bromophenol

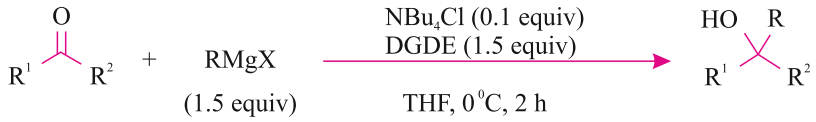
(b) Dark coloured mixture of 2-Brornophenol and 4-Bromophenol

(c) White precipitate of 2,4,6-tribromophenol

(d) Yellow colouration of 2,4-dibromophenol

2. **Read the passage and answer the following questions:**

On the basis of the investigation of the combinational effect of quaternary ammonium salts and organic bases, an added-metal-free catalytic system for nucleophilic addition reactions of a variety of Grignard reagents to diverse ketones in the solvent has been developed to produce tertiary alcohols in good to excellent yields. By using tetrabutylammonium chloride (NBu_4C1) as a catalyst and diglyme (DGDE) as an additive, this system strongly enhances the efficiency of



R^1=Aryl and alkyl
R^2=Aryl and alkyl

R=alkyl and allyl
X=Br, Cl

good to excellent yields

addition at the expense of enolization and reduction. NBu_4C1 should help to shift the Schlenk equilibrium of Grignard reagents to the side of dimeric Grignard reagents to favor the additions of Grignard reagents to ketones via a favored six-membered transition state to form the desired tertiary alcohols, and DGDE should increase the nucleophilic reactivities of Grignard reagents by coordination. This catalytic system has been applied in the efficient synthesis of Citalopram, an effective U.S. FDA-approved antidepressant, and a recyclable version of this catalytic synthesis has also been devised.

Reference : Hua Zong, Huayin Huang, Junfeng Liu, Guangling Bian, and Ling Song **Added-Metal-Free Catalytic Nucleophilic Addition of Grignard Reagents to Ketones** *J. Org. Chem.* **2012**, 77, 10, 4645-4652

(A) Which ketone and Grignard reagent can be used to form 2-methylbutan-2-ol ?

(B) Write structure and IUPAC name of product formed reaction of allyl magnesium bromide with acetophenone?

(C) Which reaction will take place at faster rate and why?

(i) Benzaldehyde + Propyl magnesium bromide

(ii) Propanal + Benzyl magnesium bromide

(D) Why Grignard reagent is stored under anhydrous conditions?

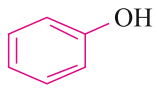
3. **Read the passage and answer the following questions:**

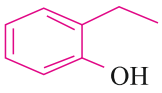
Phenols are compounds that possess a hydroxyl group directly attached to an aromatic. carbocyclic nucleus. Phenol is the trivial name for rnonohydroxybenzene. The *o*-, *m*-, and *p*-cresols are monohydroxytoluenes ($CH_3.C_6H_4OH$) and are distinct in their properties and reactions from the isomeric side-chain hydroxy compound, benzyl alcohol ($C_6H_5.CH_2OH$), which is a typical aromatic alcohol. Simple monohydric phenols are either corrosive liquids or low melting solids. The dihydric and trihydric phenols are solids. The mono-hydroxy compounds are only slightly soluble in water but are miscible with organic solvents. Water solubility increases and solubility in organic solvents

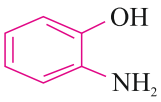
decreases with the introduction of additional hydroxyl groups. They are all characterized by, and distinguished from, the aliphatic or aromatic alcohols by their ready solubility in aqueous alkali. Phenols and the cresols are widely used as antiseptics and disinfectants; the cresols are contained in the wood preserving fluid, creosote. Many phenols have wide application in the industrial production of plastics, dyestuffs, insectides, selective weedkillers, and germicides.

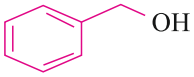
Reference : P.W.G. Smith, A.R. Tatchell, **Phenols**, *Aromatic Chemistry*, 1969

(A) Which of the following is not a phenol?

(a) 

(b) 

(c) 

(d) 

(B) Which of the following phenol has highest pK_a value?

(a) Phenol (b) p-nitrophenol

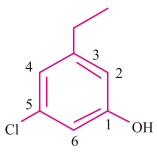
(c) o-nitrophenol (d) o-cresol

(C) Phenols may be characterized by the reaction with-

(a) $FeCl_3$ (b) Br_2 water

(c) $NaHCO_3$ (d) both $FeCl_3$ and $NaHCO_3$

(D) Write IUPAC name of following phenol.



ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. c 2. d 3. c 4. c 5. c 6. d 7. c 8. b 9. c 10. c

11. a 12. d 13. d 14. a 15. b 16. c 17. d

II FILL IN THE BLANKS

1.	2.4,6-tribrornophenol	2.	Ethanol
3.	Methanal	4.	Cumene
5.	Esterification	6.	Lucas
7.	easier	8.	S_N2
9.	Benzoic acid	10.	1 -Chloropropane

III ASSERTION REASON TYPE QUESTIONS

1. (A) 2. (D) 3. (D). 4. (C) 5. (D) 6. (C) 7. (A) 8. (A) 9. (B) 10. (A)

IV ONE WORD ANSWER

1.	PCC	2.	*ortho*-nitrophenol
3.	*para*-bromoanisole	4.	Reimer-Tiemann reaction
5.	Phenol	6.	$NaBH_4$
7.	$B_2H_6/H_2O_2, OH^-$	8.	Primary
9.	2,4,6-Trinitrophenol		

CASE STUDY QUESTIONS

PASSAGE: 1 : (A) b (B) b (C) a (D) c

PASSAGE: 2:

(A) CH_3COCH_3, C_2H_5MgCl

(B) $C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_2\text{-}CH{=}CH_2$ (C) i

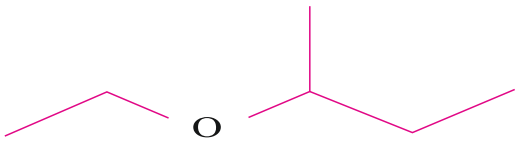
(D) It react with water to form alkane R-Mgx+H-OH→R-H+Mg-X-OH

PASSAGE: 3: (A) d (B) d (C) a (D) 3-Ethyl-5-Chloro Phenol

UNIT TEST
CHAPTER-10

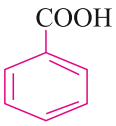
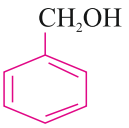
Maximum Marks : 20 **Time : 1 Hour**

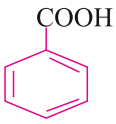
1. Write the IUPAC name of:

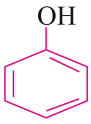


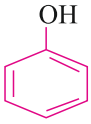
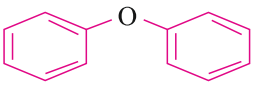
2. A and B in the following reaction are :



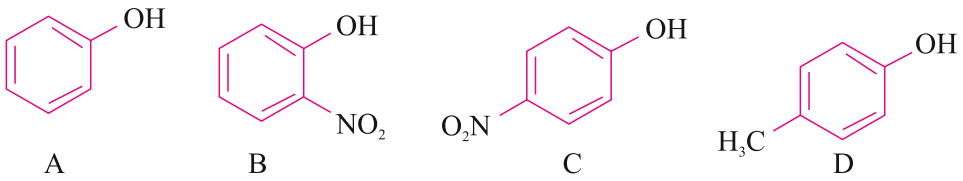
(a) A-  B- 

(b) A-  B- 

(c) A-  B- 

(d) A-  B- 

3. The correct order of acidic strength of following phenols:



A B C D

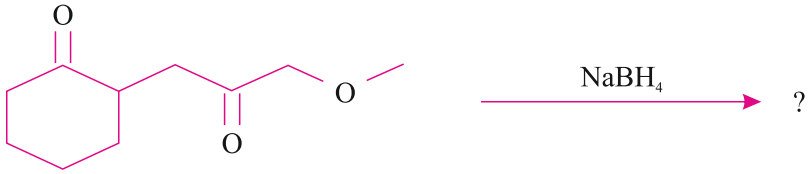
(a) A<B<C<D

(b) B<A<C<D

(c) D<A<B<C

(d) D<C<B<A

4. Identity the product: a



5. $(CH_3)_3C\text{-}OCH_3 + HI \rightarrow ?$

6. Give reactions for following name reactions

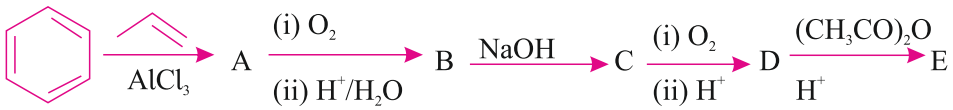
(I) Kolbe's reaction

(ii) Williamsons synthesis

7. Write the products formed by nitration of phenol . Which of the product has higher boiling point and why ?

8. Identify the product formed when ethanol is heated at 413 K. Write the mechanism of the reaction.

9. Complete the reaction sequence, A to E. Also name the reaction involved in conversion of B to D.



10. How will you convert :

(i) Ethanol to propan-2-ol

(ii) Aniline to phenol

(iii) Methanol to methoxyethane

11. Explain the following:
    (i) Alcohols are more soluble in water than ethers of comparable molar mass.
    (ii) t-butylchloride on heating with sodium methoxide gives 2- methylpropene instead of t-butylmethly ether.
    (iii) Reaction of phenol with bromine leads to formation of 2,4,6- tribromophenol .

UNIT 12
Aldehydes, Ketones and Carboxylic

Points to Remember

Nomenclature

Aldehydes and Ketones

Common names: replace -e from alkyl group by aldehyde or ketone e.g. CH_3 CHO is acetaldehyde

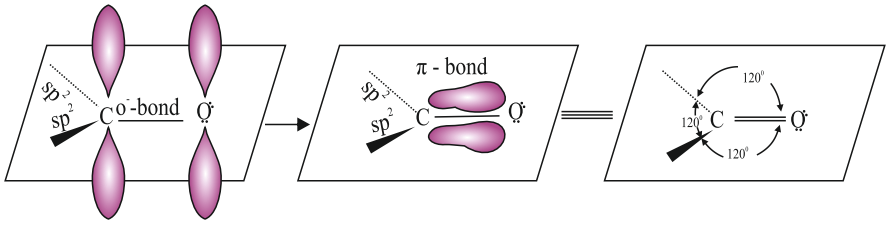
IUPAC names: replace -e by -al for aldehydes and - one for ketones e.g. CH_3 CHO is ethanal and CH_3 $COCH_3$ is propanone.

Carboxylic Acids

Common names: end with -ic acid e.g. CH_3CH_2COOH is propionic acid

IUPAC names: replace -e in corresponding alkanes by -oic acid e.g. CH_3CH_2COOH is propanoic acid.

Structure of Carbonyl group



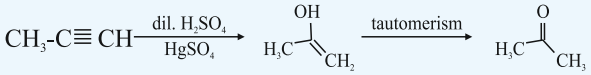
Carbonyl carbon is sp^2 Hybridised and planar in shape, with one sigma and one π bond between C=O

General Methods:

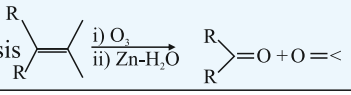
(a) **Contolled oxidation/dehydrogenation of primary and secondary aicohols**

Primary alcohol gives aldehyde, secondary gives ketones, tertiary undergoes dehydrationm

(b) **Hydration of Alkynes**



(c)Ozonolysis

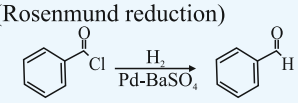


Preparation of Aldehydes, Ketones and Carboxylic Acids

Aldehydes:

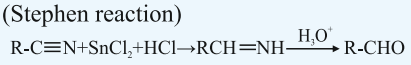
(a) From acyl chloride

(Rosenmund reduction)

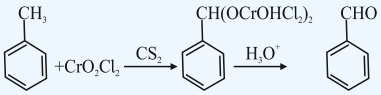


(b) From nitriles and esters

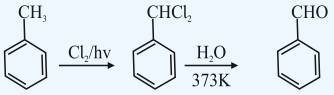
(Stephen reaction)



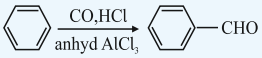
(c) From hydrocarbons (Etard Reaction)



(d) (Side chain chlorination)

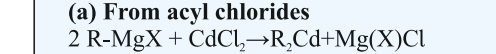


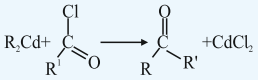
(e) (Gatterman-Koch reaction)



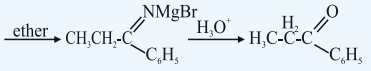
Ketones:

(a) From acyl chlorides

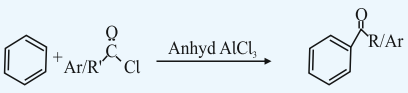




(b) from nitriles $CH_3CH_2CN + C_6H_5MgBr$

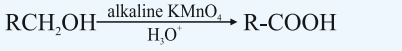


(c) From benzene

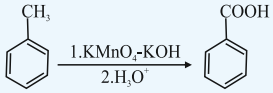


Carboxylic Acids:

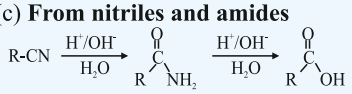
(a) **From Primary alcohois/aldehydes**



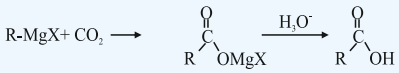
(b) **From alkylbenzene**



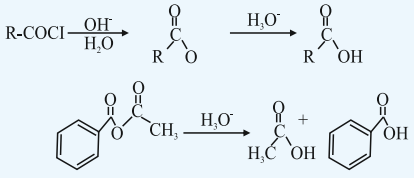
(c) **From nitriles and amides**



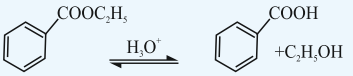
(d) **From Grignard reagent**



(e) **From acyl halides and anhydrides**

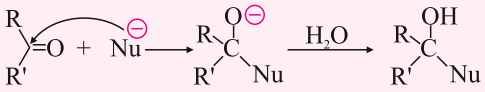


(f) **From esters**



Reactions of Aldehydes, Ketones and Carboxylic Acids

Aldehyde and Ketones
Nucleophilic Addition reaction

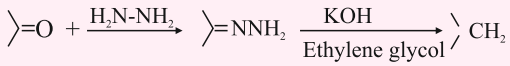


Reduction: Aldehydes and ketones converts to primary and secondary alcohols respectively in presence of $NaBH_4$ / $LiAlH_4$. $NaBH_4$ selectively reduces aldehydes and ketones only in presence of other carbonyl containing functional groups including carboxylic acids, esters etc.

Clemmensen reduction:



Wolf - Kishner Reduction:



Oxidation:

Tollens' Test.

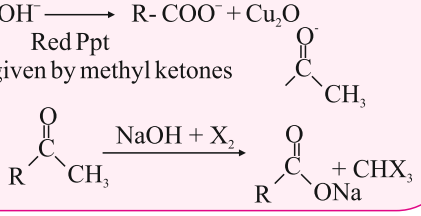
$R\text{-}CHO + 2\,[Ag(NH_3)_2]^+ + OH^- \longrightarrow RCOO^- + 2\,Ag + 2\,H_2O + 4\,NH_3$

Silver mirror

Fehling's Test

$R\text{-}CHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow R\text{-}COO^- + Cu_2O + 3\,H_2O$ (Red Ppt)

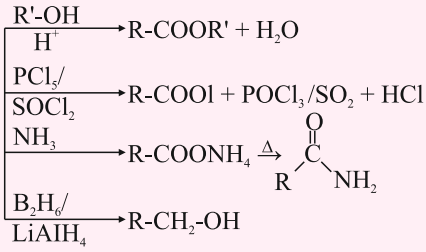
Haloform reaction: given by methyl ketones

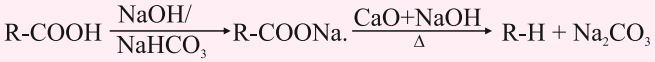


Carboxylic Acids

Acidic nature : $R\text{-}COOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2$ Brisk effervescence

Formation of carboxylic acid derivatives:





This reaction is useful in redcing the size of carbon chain

Hell-Volhard Zelinsky reaction: $R\text{-}CH_2\text{-}COOH \xrightarrow[ii)\ H_3O^+]{i)\ X_2/\ Red\ P} R\text{-}\underset{X}{\underset{|}{C}}H\text{-}COOH$

substitution takes place at alpha carbon

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Which product is formed when benzaldehyde is treated with concentrated KOH solution?

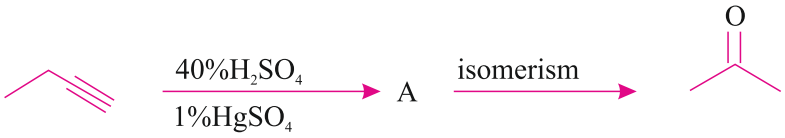
(a) 

(b) 

(c) 

(d) 

2. Structure of 'A' and type of isomerism in the above reaction are respectively-



(a) Prop-1-en-2-ol, metamerism

(b) Prop-1 -en-1-ol, tautomerism

(c) Prop-2-en-2-ol, geometrical

(d) Prop-1-en-2-ol, tautomerism

3. Compound A and C in the following reaction are:-



(a) identical (b) position isomer

(c) functional group isomer (d) optical isomer

4. Toluene  the product 'C' is:-

(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO

(c) C_6H_5COOH (d) $C_6H_5CH_3$

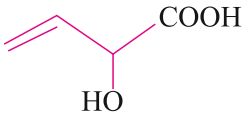
5. Among the following which has the lowest pk_a value:-

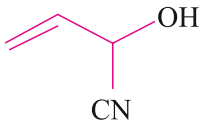
(a) CH_3COOH (b) HCOOH

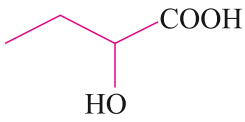
(c) $(CH_3)_2CHCOOH$ (d) CH_3CH_3OH

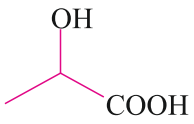
6. $CH_3CHO + HCHO \xrightarrow[\text{Heat}]{\text{dil.NaOH}} A \xrightarrow[H_3O]{HCN} B$

B the structure of 'B' is:-

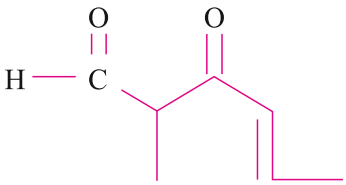
(a) 

(b) 

(c) 

(d) 

7. The IUPAC name of compound is:



(a) 2-Formylhex-2-ene-3-one

(b) 5-methyl-4-oxohex-2-en-5-al

(c) 3-keto-2-methylhex-5-enal

(d) 3-keto-2-methylhex-4-enal

8. Which of the following reactions will not result in the formation of carbon-carbon bond?

(a) Cannizzaro reaction (b) Wurtz reaction

(c) Friedel Crafts reaction (d) Reimer-Tiemann reaction

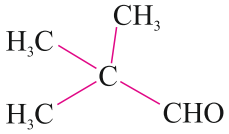
9. Reduction of aldehydes and ketones into hydrocarbon using zinc amalgam and conc. HCl is called.....

(a) Dow process (b) Cope reduction

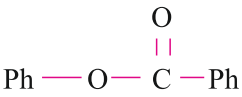
(c) Wolf-Kishner reduction (d) Clemmensons Reduction

10. Which of the following compound do not undergo aldol condensation?

(a) CH_3CH_2CHO (b) CH_3CHO

(c) CH_3COCH_3 (d) 

11. The treatment of following compound with NaOH yields.....as major product.



(i) Phenol (ii) Sodium phenoxide

(iii) Sodium benzoate (iv) Benzophenone

(a) I,II (b) III only

(c) I,III (d) IV only

12. Which of the following will undergo Cannizzaro reaction?

(a) Acetophenone (b) Propanone

(c) 2,2-Dimethylpropanal

(d) Both acetophenone and 2,2-Dimethylpropanal

13. Which of the following neither gives Fehling's test nor iodoform test?

(a) Benzaldehyde (b) Ethanal

(c) Propanone (d) Acetophenone

14. Which reagent(s) is/are best for following conversion?

CH_3-CH=CH-CN$\rightarrow CH_3$-CH=CH_3-CHO

(a) H_2, Pd-$BaSO_4$ (b) DiBAL-H

(c) H_2/Ni (d) $NaBH_4$

15. Benzophenone can be obtained by the reaction of -

(a) Benzoyl chloride + Benzene + anhy. $AlCl_3$

(b) Benzoyl chloride + Diphenyl anion

(c) Benzoyl chloride + Phenyl magnesium chloride

(d) Benzene + carbon monoxide+$ZnCl_2$

16. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?

(a) Butan-l-ol (b) Butan-2-ol

(c) Both of these (d) None of these

17. Reaction of alkene **X** with with O_3 followed by H_2O_2/ Zn forms propanone and ethanal. Alkene **X** is-

(a) Pent-3-ene (b) Pent-2-ene

(c) 2-Methylbut-2-ene (d) 2,2-Dimethylprop-1-ene

II FILL IN THE BLANKS

1. Tollens' reagent is chemically.....
2. Reaction of phthalic acid with ammonia followed by strong heating gives.....
3. Acetyl chloride may be converted into acetaldehyde by .....reduction.
4. Groups like nitro- and chloro- .....acidity of aromatic carboxylic acids.
5. Phenol and benzoic acid can be distinguished by the reaction with.....
6. On reaction of propanal with Fehling's reagent red precipitate of ..... is formed.
7. Reaction of Grignard reagent with .....results into formation of primary alcohols.
8. Lower aldehydes are soluble in water due to.....interactions with water molecules.
9. DIBAL-H is used to reduce nitriles or esters to corresponding.....
10. Reaction of ethyl magnesium bromide with carbon dioxide followed by acidification gives .....

III ASSERTION REASON TYPE QUESTIONS

The question given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

(a) Assertion and reason both are correct and reason is the correct explanation of the assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION:** Reaction of pentanoic acid with Cl_2/ Red P followed by water gives 2-chloropentanoic acid.
   REASON: The substitution takes places at α-carbon.
2. **ASSERTION:** Carboxylic acids are higher boiling than aldehydes and ketones of comparable molar masses.
   REASON: Due to strong intermolecular H-bonding in carboxylic acids.
3. **ASSERTION:** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
   REASON: Carboxyl group increases electron density on ring.
4. **ASSERTION:** Benzaldehyde undergoes Cannizzaro reaction.
   REASON: It contains one α-hydrogen.
5. **ASSERTION :** Formaldehyde is a planar molecule.
   REASON : It contains sp^2 hybridised carbon atom.
6. **ASSERTION :** Compounds containing -CHO group are easily oxidised to corresponding carboxylic acids.
   REASON : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.
7. **ASSERTION :** The α-hydrogen atom in carbonyl compounds is less acidic.
   REASON : The anion formed after the loss of α-hydrogen atom is resonance stabilised.
8. **ASSERTION :** Aromatic aldehydes and formaldehyde undergo Cannizaro reaction.
   REASON : Aromatic aldehydes are almost as reactive as formaldehyde.
9. **ASSERTION :** Aldehydes and ketones, both react with Tollens' reagent to form silvery mirror.
   REASON : Both, aldehydes and ketones contain a carbonyl group.
10. **ASSERTION:** Ketones are oxidised under drastic conditions.
    REASON: Oxidation of ketones gives carboxylic acids having carbons lesser than parent molecule.

IV ONE WORD TYPE QUESTIONS

1. Name the product formed by addition of one equivalent of monohydric alcohol to aldehydes.
2. Name the product formed by the reaction of benzene with CO, HCl in presence of anhyd. $AlCl_3$

3. Which reagent is used to convert carboxylic acid to corresponding alcohol?
4. Which reaction is carried out to reduce the number of carbons from carboxylic acids?
5. Which ester will be formed by the reaction of methanol and propanoic acid?
6. Write the major product formed by the reaction of benzaldehyde and acetophenone.
7. Which reagent will be best to convert ketone to corresponding alcohol in presence of carboxylic acid?
8. Which reagent converts carboxylic acids into corresponding anhydrides?
9. Name the carboxylic acid formed by reaction of cyclohexene with $KMnO_4$-H_2SO_4 and heating.

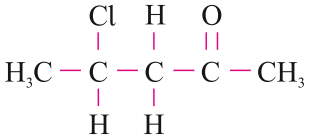
VERY SHORT ANSWER TYPE QUESTIONS (1 Marks)

1. Arrange the following compounds in increasing order of their acidic strengths:
   $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$

Ans. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.

Ans.



3. Which type of aldehyde can undergo Cannizzaro reaction?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogen.

4. Name the aldehyde which does not give Fehling's test.

Ans. Benzaldehyde.

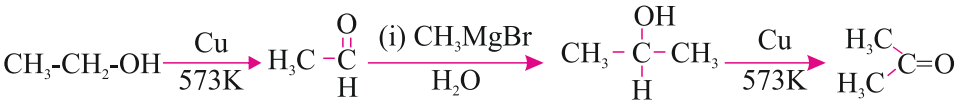
5. Arrange the following in order of their increasing reactivity towards HCN:
   CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$

Ans. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

6. Arrange the following compounds in increasing order of their boiling point:
   CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

8. How is acetone obtained from ethanol?

Ans. 

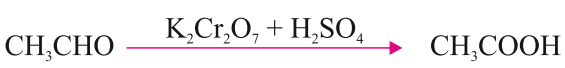
9. Why do aldehydes and ketones have lower boiling point than alcohols?

Ans. Due to presence of associated molecules with H-bonding in alcohols.

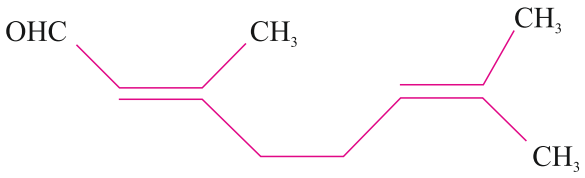
10. Write reaction between acetyl chloride and dimethyl cadmium.

Ans. 

11. What happens when CH_3CHO is treated with $K_2Cr_2O_7$ in presence of H_2SO_4?

Ans. 

12. Write IUPAC name of following compound:



Ans. 3,7-Dimethylocta-2,6-dien-1-al

13. Give balanced equation and name of products when CH_3COOH is treated with PCl_5?

Ans. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

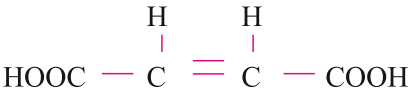
14. What product is obtained when ethyl benzene is oxidized with alkaline $KMnO_4$?

Ans. Benzoic acid (C_6H_5COOH) is obtained.

15. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Give reason.

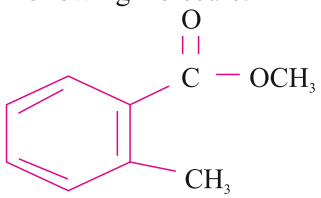
Ans. Due to $-CH_3$ group, which shows +I effect and steric hindrance caused by two $-CH_3$ groups.

16. Write IUPAC names of the following compound:



Ans. But-2-ene-1,4-dioic acid

17. Write the IUPAC name of following molecule:



Ans. Methyl-2-methylbenzoate.

18. Why does benzoic acid does not undergo Friedel-Crafts reaction?

Ans. -COOH group in C_6H_5COOH is an electron withdrawing group, which deactivates the benzene ring, hence electrophilic substitution becomes difficult.

19. Benzaldehyde gives a positive test with Tollens' reagent but not with Fehling's and Benedict solutions. Why ?

Ans. It is due to stronger oxidising nature of Tollens' reagent as compared to Fehling's and Benedict's solution and cannot oxidise benzaldehyde to benzoic acid. In general, all these three can oxidise aliphatic aldehydes.

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How will you convert:

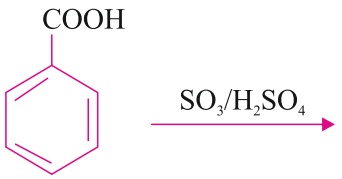
(i) $C_2H_2 \rightarrow CH_3COOH$

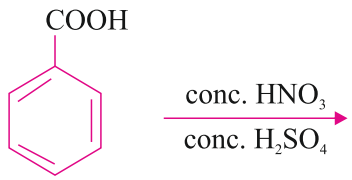
(ii) $C_6H_5CONH_2 \rightarrow C_6H_5COOH$

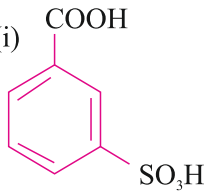
Ans. (i) $C_2H_2 \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[dil.\ H_2SO_4]{KMnO_4} CH_3COOH$

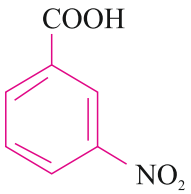
(ii) $C_6H_5CONH_2 + HNO_2 \rightarrow C_6H_5COOH + N_2 + H_2O$

2. Complete the following:

(i) 

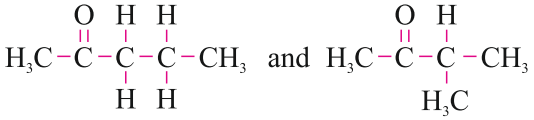
(ii) 

Ans.(i) 

(ii) 

3. An organic compound 'X' has molecular formula $C_6H_{10}O$. It does not reduce Fehling's solution but forms a bisulphite compound. It also gives positive Iodoform test. What are possible structure of 'X' ? Explain.

Ans. 'X' gives positive test with Iodoform. It is methyl ketone.



are possible structures of the compound.

4. Give the chemical test to distinguish between:

(i) CH_3CHO and $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$

(ii) CH_3CHO and C_6H_5CHO

Ans. (i) CH_3CHO gives Tollen's reagent test.

$$CH_3CHO + 2AgNO_3 + 2NH_4OH \rightarrow CH_3COOH + 2Ag + 2NH_4NO_3 + 2H_2O$$

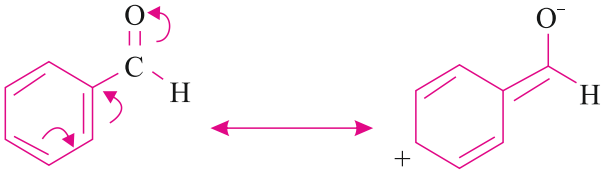
(ii) CH_3CHO gives brick red ppt. Silver mirror

$$CH_3CHO + 2CuSO_4 + 4NaOH \rightarrow CH_3COOH + Cu_2O + Na_4SO_4 + 2H_2O$$

Brick red ppt.

5. Is benzaldehyde more reactive or less reactive in nucleophilic addition reactions than propanal ? Explain your answer.

Ans. Carbon atom of carbonyl is C_6H_5CHO is less reactive than that of propanal. C_6H_5CHO is less polar due to resonance.

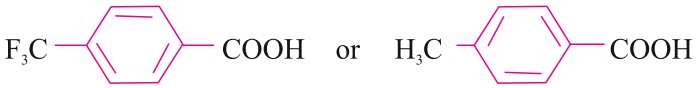


6. Which acid of each pair shown here would you expect to be stronger ?

(i) CH_3CO_2H or CH_2FCO_2H

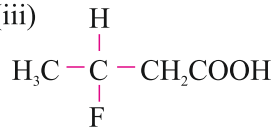
(ii) CH_2FCO_2H or CH_3ClCO_2H

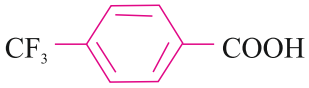
(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

(iv) 

Ans. (i) FCH_2COOH

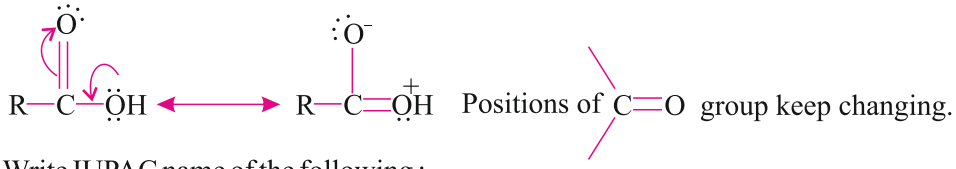
(ii) CH_2FCOOH

(iii) 

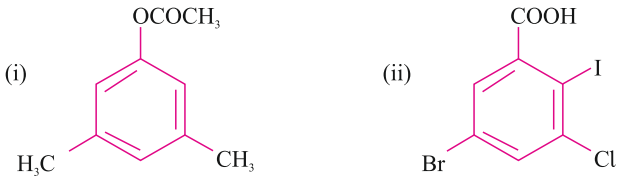
(iv) 

7. Carboxylic acids do not give reactions of aldehydes and ketones why?

Ans. It is due to resonance



8. Write IUPAC name of the following :



Ans. (i) 3,5-dimethylphenylethanoate.

(ii) 5-Bromo-3-chloro-2-iodobenzoic acid.

9. Distinguish between :

(i) C_2H_5OH and CH_3CHO

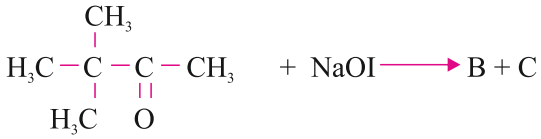
(ii) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$

Ans. (i) CH_3CHO gives silvery mirror with Tollens' reagent while C_2H_5OH does not.

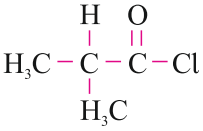
(ii) Acetophenone will give yellow ppt. of iodoform while $C_6H_5CH_2CHO$ will not.

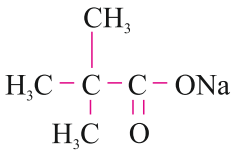
10. Complete the following reactions by identifying A, B and C :

(i) $A + Hydrogen(g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CHCHO$

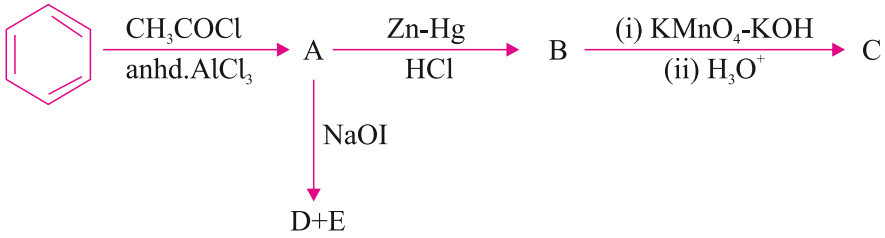
(ii) 

Ans.

(i) 'A' is 

(ii) 'B' is CHI_3 and 'C' is 

11. Write the structures of A,B,C,D and E in the following reactions:



Ans. A=CH_3COCH_3

B=$C_6H_5CH_2CH_2$

C=C_6H_5COOH

D=C_6H_5COONa

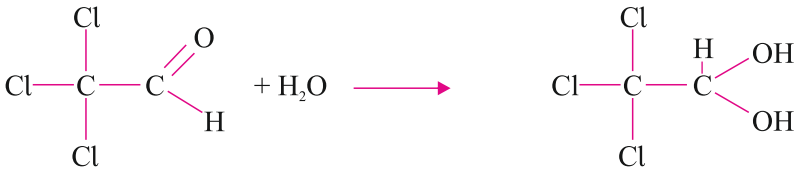
E=CHI_3

12. Aldehydes usually do not form stable hydrates but chloral normally exists as chloral hydrate. Give reason.

Ans. In case of aldehyde reaction is reversible.

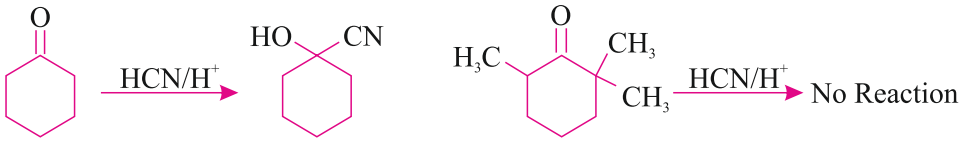


In case of $CC1_3CHO$, Cl atoms increases positive charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.

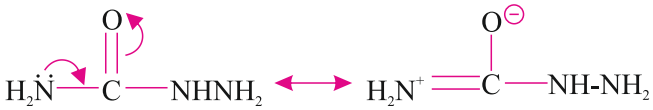


13. Give possible explanation for the following:
    (i) Cyclohexanone forms cyanohydrins in good yield but 2,2,6-trimethyl cyclohexanone does not.
    (ii) There are two - NH_2 groups in semicarbazide. However,only one is involved in formation of semicarbozone.

Ans. (i) Due to steric hindrance for CN^- at C=O due to 3-methyl groups at α-position.



(ii) Only one -NH_2 group attached to C=O is involved in resonance. As result electron density on these -NH_2 group decreases and hence does not act as nucleophile.



14. Convert the following in not more than two steps:
    (i) Benzoic acid to Benzadehyde
    (ii) Propanone to propene

Ans. (i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{Pd\text{-}BaSO_4} C_6H_5CHO$

(ii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CHCH_3 \xrightarrow{conc.\ H_2SO_4} CH_3\text{-}CH{=}CH_2$

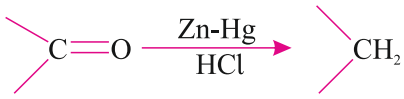


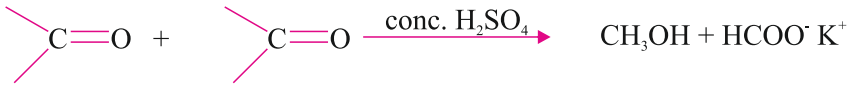
15. Write the reactions involved in the following reactions:

(i) Clemmensen reduction

(ii) Cannizzoro reaction

Ans.

(i) 

(ii) 

16. Convert the following

(i) Ethylbenzene to benzoic acid

(ii) Ethanal to but-2-enal

Ans.

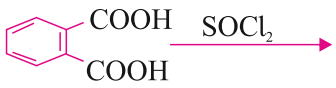
(i) $C_6H_5C_2H_5 \xrightarrow{K_2Cr_2O_7/H^+} C_6H_5COOH$

(ii) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHCH_2CHO \xrightarrow{\text{heat}} CH_3\text{-}CH{=}CH\text{-}CHO$

(OH)

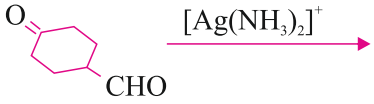
17. Predict the organic products of the following reactions:

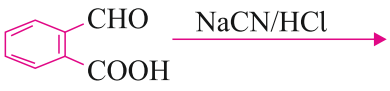
(i) 

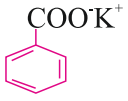
(ii) 

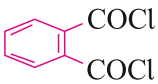
(iii) 

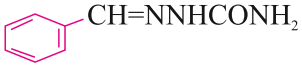
(iv) 

(v) 

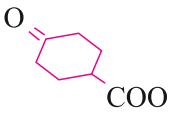
(vi) 

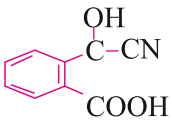
Ans. (i) 

(ii) 

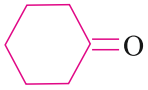
(iii) 

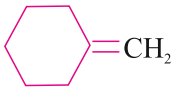
(iv) 

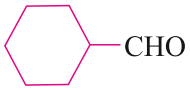
(v) 

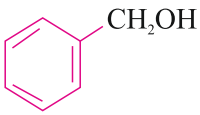
(vi) 

18. Complete the following as missing starting material, reagent or products:

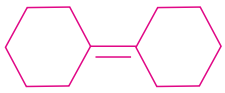
(i)..... $\xrightarrow[Zn\text{-}H_2O]{O_3}$ 2 

(ii) 

..... 

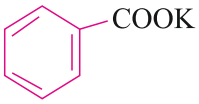
(iii) 

$\xrightarrow[KOH\ heat]{KMnO_4}$ .....

Ans.(i)  (ozonolysis)

1,2-Dicyclohexylethene

(ii) $B_2H_6/THF, H_2O_2/(Hydroboration)\ OH^-$, then PCC

(iii) 

(Oxidation)

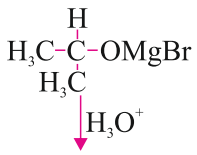
Patassium benzoate

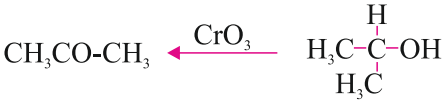
19. How can the following converted:

(I) Ethanol→Acetone

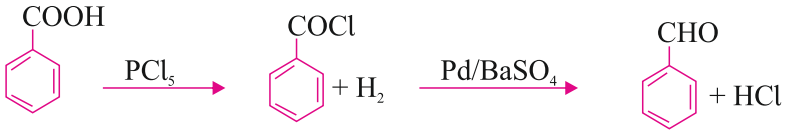
(ii) Benzene→Acetophenone

(iii) Benzoic acid → Benzaldehyde

Ans.(i) $CH_3CH_2OH \xrightarrow[CrO_3 \text{ or PCC}]{[O]} CH_3CHO \xrightarrow[dry\ ether]{CH_3MgBr}$ 





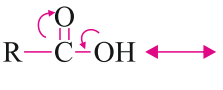


20. Give reason for the following:

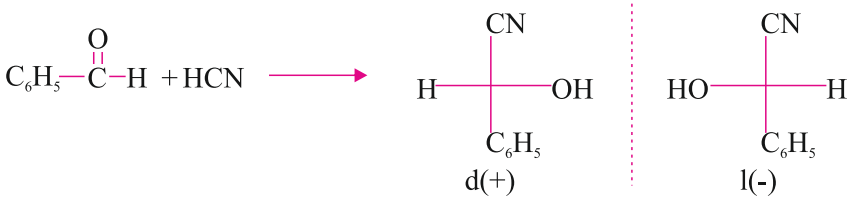
(i) Carboxylic acids do not give characterstic reactions of carbonyl groups.

(ii) Treatment of C_6H_5CHO with HCN gives a mixture of two isomers which cannot be separated even by fractional distillation.

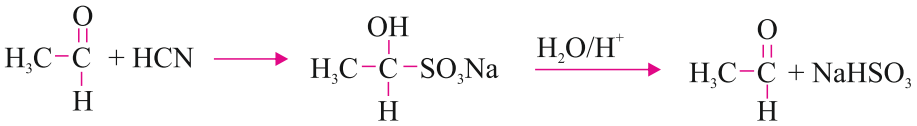
(iii) Sodium bisulphite is used for purification of ketones and aldehydes.

Ans.   Because of resonance, the position of C=O group is changing.

(ii) Due to two optical isomers fractional distillation is not possible.



(iii) Due to formation of addition compound of aldehydes and ketones with $NaHSO_3$ whereas impurities do not.



21. Write tests to distinguish between:

(i) CH_3CHO and C_6H_5CHO

(ii) C_6H_5-OH and CH_3COOH

(iii) Pentanal and pentan-2-one

Ans. (i) CH_3CHO gives brick red ppt. with Fehling while C_6H_5CHO not.

(ii) Phenol does not give brisk effervescence but CH_3COOH gives this test with $NaHCO_3$.

(iii) Pentanal forms silver mirror but pentan-2-one does not.

22. Convert:

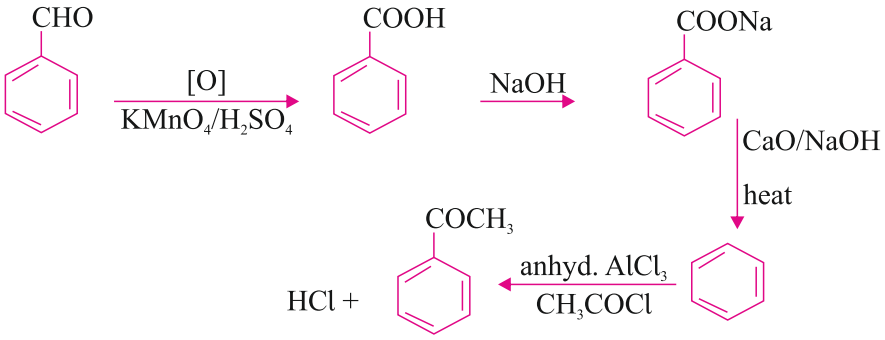
(i) Benzaldehyde to acetophenone

(ii) Malonic acid to acetic acid

(iii) Acetaldehyde to Butan-2-ol

Ans.

(i)



(ii) $H_2C(COOH)_2 \xrightarrow{heat} CH_3COOH + CO_2$

(iii) $2CH_3CHO \xrightarrow{OH^-} CH_3-CH(OH)-CH_2-CHO \xrightarrow[H_2SO_4/\Delta]{conc.} H_3C-C(H)=C(H)-CHO \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

Butanol-2-ol

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Write chemical reaction to affect the following transformations:

(i) Butan-1-ol→ Butanoic acid

(ii) Benzyl alcohol to phenylethanoic acid

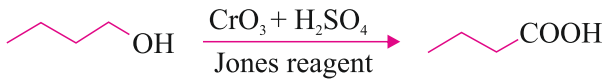
(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid

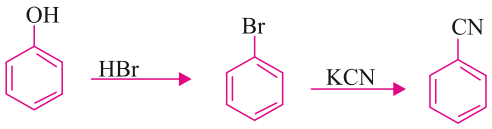
(iv) 4-methylacetophenone to terephthalic acid

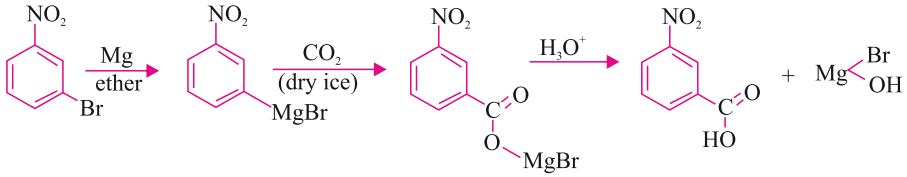
(v) Cyclohexane→ Hexane-1,6 dioic acid

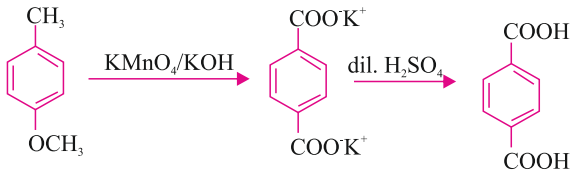
(vi) Butanal→Butanoic acid

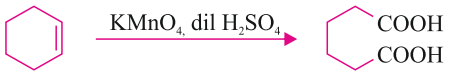
Ans.

(i) 

(ii) 

(iii) 

(iv) 

(v) 

2. Draw the structure of the following derivatives:

(i) 2,4-dinitrophenylhydrazone of C_6H_5CHO

(ii) Cyclopropanone oxime

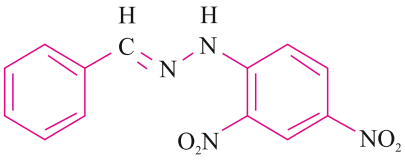
(iii) Acetaldehyde dimethylacetal

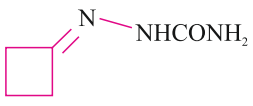
(iv) Semicarbazone to cyclobutanone

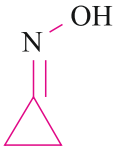
(v) Ethylene ketal of hexan-3-one

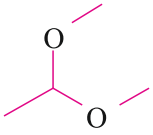
(vi) Methylhemiacetal of formaldehyde

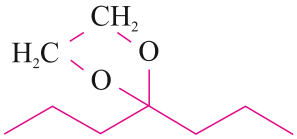
Ans.

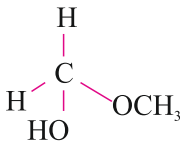
(i) 

(iv) 

(ii) 

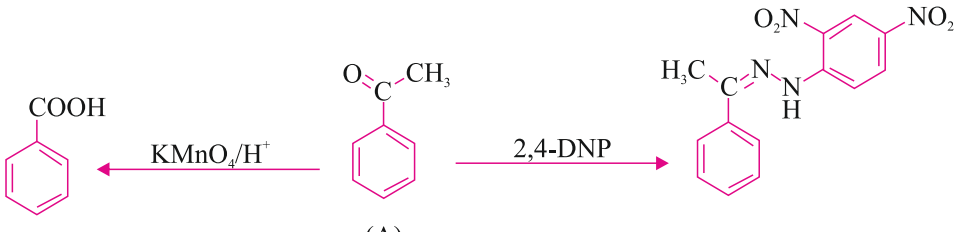
(iii) 

(v) 

(vi) 

3. An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollens' or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

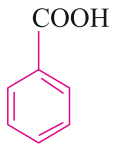
Ans:



(A)

(i) I_2/NaOH
(ii) H^+

CHI_3 + Yellow ppt.
(B)



(C)

4. Give reason for the following:

(i) C_6H_5COOH is weaker than formic acid.

(ii) HCOOH and CH_3COOH differentiated by Tollens' reagent.

(iii) R-COOH do not give characteristic reaction with >C=O.

(iv) Carboxylic acids are stronger acids than phenols.

(v) Acid amides are weakly basic in nature.

Ans. (i) In C_6H_5COOH, C_6H_5-destablize carboxylate ion due to its +R effect.

(ii) Presence of -CHO group.

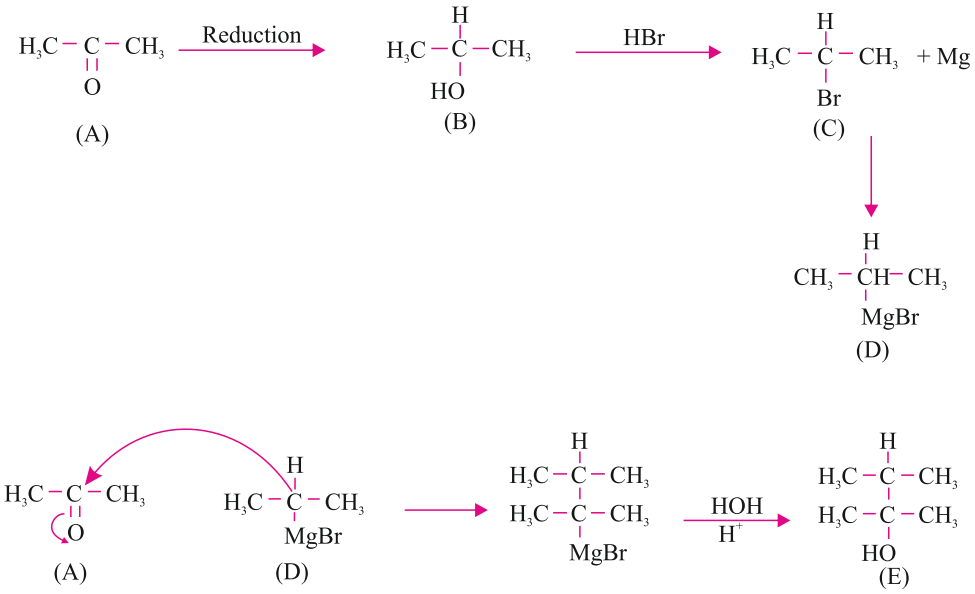
(iii) >C=O group is sterically hindered in carboxylic acid.

(iv) Dispersal of negative charge on carboxylate ions than phenoxide ion.

(v) Acid amides are basic due to lone pair of electrons on nitrogen atom.

5. An organic compound 'A' (C_3H_6O) is resistant to oxidation but forms compound 'B' (C_3H_8O) on reduction. 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D'which reacts with 'A' to form a product which on hydrolysis gives 'E'. Identify 'A'to 'E'.

Ans. 'A' must be ketone.



CASE-STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

Carboxylic acids are compounds with excellent chemical and physical properties, the most particular characteristics of this type of organic compounds, is their high solubility in polar solvents, as water, or alcohols, methanol, ethanol, etc. Chemical structure contains a carbonyl function (-C=O) and an hydroxyl group (OH), these groups interact easily with polar compounds, forming bridges of H, obtaining high boiling points. The carbonyl group (C=O) is considered a one of the most functional groups involved in many important reactions. The carboxylic acids are the most important functional group that present C=O.

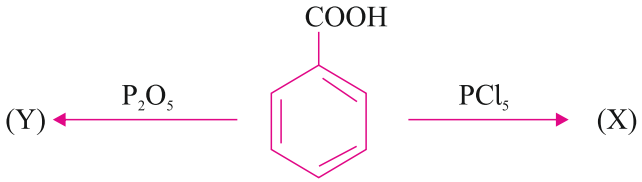
This type of organic compounds can be obtained by different routes, some carboxylic acids, such as citric acid, lactic acid or fumaric acid are produced from by fermentation, most of these type of carboxylic acids are applied in the food industry. Historically, some carboxylic acids were produced by sugar fermentation. Synthetics route, there are different synthesis reactions such as reactions of oxidation from alcohols in the presence of strong oxidants such as $KMnO_4$, oxidation of aromatic compounds among other routes.

For example, citric acid is a carboxylic acid, can be obtained by different routes, synthetic, enzymatic and naturally occurring, is considered harmless and cheap, used in the food industry, because is non-toxic, has a thermal stability to the 175°C. Bian et al., in 2017, reported the use of citric acid impregnated in porous material for the synthesis of Ni particles. They showed, that the presence of citric acid, is important in the dispersion of the Ni particles when are incorporate in porous materials, thus inhibiting the agglomeration.

Derivatives of carboxylic acid, as alkyl halides, esters, and amides, present different and important application in diverse areas. In the case of esters, these are obtained from the reaction between carboxylic acids and alcohols in presence of an acid catalyst usually H_2SO_4 with heat, this type of reaction is known as esterification. In the case of the amides, it is obtained in the presence of an amine, may be primary and secondary, with a carboxylic acid, in this reaction also can be used a catalyst and heat to accelerate the reaction.

Reference : Aide Sienz-Galindo, Lluvia I. Lopez-Lopez, Fabiola N. de la Cruz- Duran, Adali O.Castafieda-Facio, Leticia A. Ramirez-Mendoza, Karla C. Cordova-Cisneros and Denisse de Loera-Carrera (March 15th 2018). **Applications of Carboxylic Acids in Organic Synthesis, Nanotechnology and Polymers, Carboxylic Acid-Key Role in Life Sciences**, Georgiana Ileana Badea and Gabriel Lucian Radu, *IntechOpen*, DOI: 1 0.5772/intechopen.74654.

(A) Identify A and B in following reaction:



(B) Assertion: Carboxylic acids are highly acidic.
Reason: Carboxylate ion is resonance stabilised.

(a) Assertion and reason both are correct and reason is the correct explanation of the assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

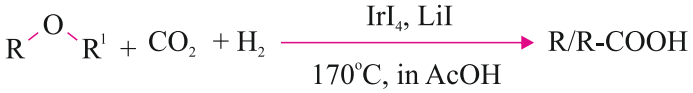
(C) What happens when phthalic acid reacts with ammonia followed by strong heating?

(D) How acetyl chloride may be converted to ethanoic acid?

2. **Read the passage and answer the following questions:**

'Tetrahydrofuran (THF) is a bulk chemical, which can be obtained from various feedstocks including biomass. In addition, the C5 carboxylic acids are much more expensive than THF. Therefore, we adopted THF as model ether to study the catalytic system (Table 1). The reaction could be efficiently accelerated by IrI_4 catalyst and LiI promoter in AcOH solvent at 170 °C, and the yield of C5 carboxylic acids reached 70% after 16 h (entry1). The products contained two isomers, i.e., pentanoic acid and 2-methylbutanoic acid, and their molar ratio was 58:42. A little C6 carboxylic acids were also formed in the reaction. The rest of the THF substrate was converted to butane.

In addition, trace of methane was also detected. We also tried different Ir catalyst precursors, such as $Ir(CO)(PPh_3)_2C1$, $Ir(CO)_2(acac)$, and $IrCl_3$, the results indicated that they were not as efficient as IrI_4 . We set the reaction time at 8 h and tested other catalytic systems. The IrI_4 catalyst was essential to the reaction because no target product was observed without it. The Rh catalyst was effective for synthesis of carboxylic acids via olefin and/or alcohol hydrocarboxylation with CO_2 and H_2. Whereas in this work no product was obtained when RhI_3

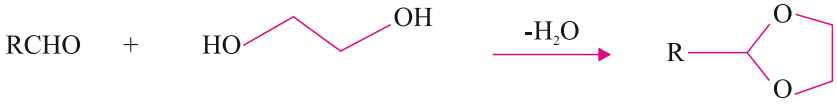


(A) How ethers can be distinguished from carboxylic acid?

(B) Propanol reaction with.....and.....respectively gives.

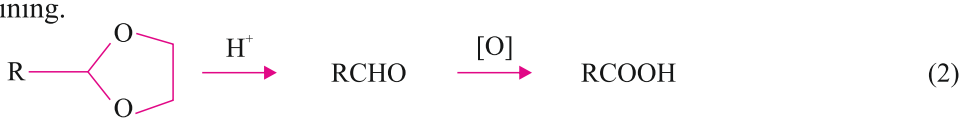
3. **Read the passage and answer the following questions:**

The acetal is the most common protecting group for aldehydes and 1,3-dioxolanes are the most commonly encountered type of acetal, usually prepared by reaction of the aldehyde with ethylene glycol with azeotropic removal of water (eq1). Regeneration of the carbonyl is normally out with aqueous acid.



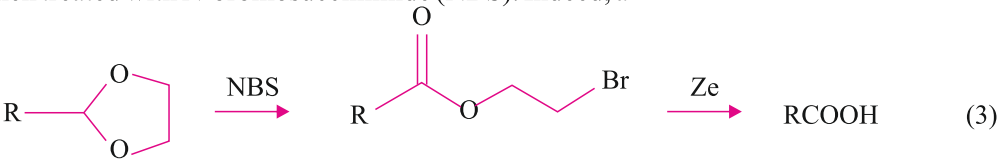
(1)

We have been concerned with the general problem of converting dioxolanes into Carboxylic acids without employing acid to first remove the protective group (eq 2). The non-acidic alternative to eq 2 would allow the introduction of acid groups into a molecule containing.



(2)

various acid-sensitive functionalities. Our solution to this problem is outlined in eq 3. Prugh and McCarthy in 1966 showed that cyclic acetals are converted into bromo esters when treated with N-bromosuccinimide (NBS). Indeed, a



(3)

variety of dioxolanes give good yields of the corresponding 2-bromoethyl esters when refluxed with NBS in CCl_4. For example, 3-phenyl-1,3-dioxolane gives a 98% yield Of 2-bromocthyl benzoate (88% after distillation).

The transformation of eq 3 is completed by a zinc-induced elimination which yields the acid upon workup. Despite the precedent for this second step, a variety of reaction conditions failed to give any acid from 2-bromoethyl benzoate.

Zinc in refluxing THF gave no reaction. Even zinc which had activated with copper sulfate was ineffective and ultraactive zinc from the potassium metal or sodium naphthalenide reduction of zinc chloride also failed to promote elimination. Zinc in refluxing methanol or ethanol gives 42-46% benzoic acid plus 47-52% of transesterification product. Ester interchange can be avoided by using zinc in refluxing THF to give a 44% yield of benzoic acid and a recovery of starting material. Addition of catalytic sodium iodide improves the yield of benzoic acid from this reaction to with only of starting material recovered.

Reference : Lawrence C. Anderson, Harold W. Pinnick, **Preparation of carboxylic acids from protected aldehydes** *J. Org. Chem.* **1978**, 43, 17, 3417-3418 **https://doi.org/10.1021/io00411a044**

(A) The formation of acetal from aldehyde is an example of ..... reaction.

(B) Which of the following reagent(s) can be used to convert butan-1-ol to butanoic acid?

(a) 1. KMnO4 — KOH 2. H^+

(b) CrO_3 — H_2SO_4

(c) Both i) and ii)

(d) None of these

(C) Write the structure of the product formed when propanal reacts with methanol.

(D) What happens when propanal reacts with ethyl magnesium iodide followed by reaction with dilute acid?

4. **Read the passage and answer the following questions:**

Nucleophilic additions to a carbonyl group leading to tetrahedral species which are products or intermediates in a mechanistic sequence occupy a central place in biochemistry as well as in organic chemistry. It has been shown recently that the structural pathway for the nucleophilic addition of an amino group to carbonyl can be mapped on the basis of crystal structure data. However, from structural data alone no direct information about the energy variation along the reaction pathway can Obtained. Furthermore, it was not entirely clear to what extent steric requirements of substituents on the nucleophile and the carbonyl group. as well as crystal packing effects, influence the arrangement of the reactive centers. An an attempt to till these gaps we have carried out calculations on the reaction path of the simple model system.

$CH_2=O+H^- \rightarrow CH_3O^-$

corresponding to nucleophilic addition of hydride anion to formaldehyde to produce methanolate anion. A calculation has also been made for the system consisting of an ammonia and a formaldehyde molecule at a of 20 nm.

Reference : H. B. Buergi, J. M. Lehn, G. Wipft, **Ab initio study of nucleophilic addition to a carbonyl group**, *J. Am. Chem. Soc.* 1974, 96, 6, 1956-1957, Publication Date: March 1, 1974 https://doi.org/10.1021/ja00813a062

(A) Which of the following nucleophilic reaction generates chiral carbon?

(a) Benzaldehyde + KOH

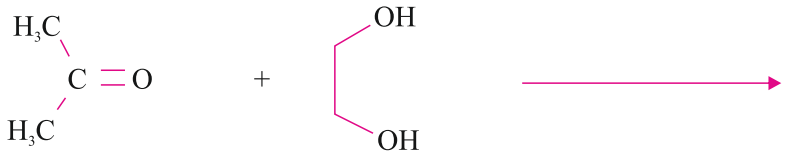
(b) Benzaldehyde + ammonia

(c) Propanone + KOH

(d) Propanone + ammonia

(B) Write the major product on reaction of acetophenone with CH_3-NH_2?

(C) Complete the reaction:



(D) Which will undergo reaction with 2,4-dinitrophenylhydrazine at fastest rate?

(a) Acetophenone (b) Propanone

(c) Benzaldehyde (d) Propanal

ANSWERS

I MULTIPLE CHOICE QUESTIONS

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

II FILL IN THE BLANKS

1.	Ammoniacal silver nitrate	2.	Phthalimide	3.	Rosenmund
4.	Increases	5.	$NaHCO_3$	6.	Cu_2O
7.	Methanal	8.	H-bonding.	9.	Aldehydes
10.	Propanoic acid				

III ASSERTION REASON TYPE QUESTIONS

III. 1. (a) 2. (a) 3. (c) 4. (c) 5. (a) 6. (b) 7. (d) 8. (c) 9. (d) 10. (b)

IV ONE WORD ANSWER QUESTIONS

1.	Hemiacetal	2.	Benzaldehyde	3.	$LiA1H_4$ or B_2H_6
4.	Decarboxylation	5.	Methyl propanoate		

6. 1,3-diphenylprop-2-en-l-one or benzalacetophenone

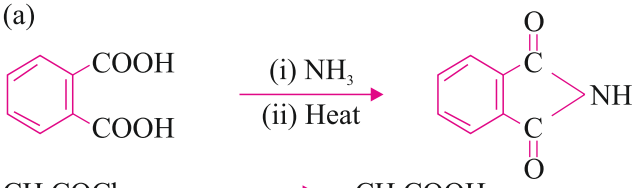
7.	$NaBH_4$	8.	P_2O_5 or H^+/Δ	9.	Hexane-1,6-dioic acid

CASE STUDY TYPE QUESTIONS

PASSAGE : 1

(A) $X=C_6H_5COCl$ $Y=(C_6H_5CO)_2O$

(B) (a)

(C) 

(D) $CH_3COCl \xrightarrow[H_2O/H^+]{} CH_3COOH$

PASSAGE : 2

(A) With $NaHCO_3$ carboxylic acids give brisk effervescence, whereas ethers cannot.

(B) PCC/PdC

PASSAGE :3

(A) Nucleophilic addition reaction

(B) (c)

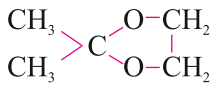
(C) $CH_3CH_2CH(OCH_3)_2$

(D) $(C_2H_5)_2CHOH$

PASSAGE :4

(A) (c)

(B) $C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=N\text{-}CH_3$

(C) 

(D) (d)

UNIT TEST
CHAPTER-11

Maximum Marks : 20 **Time : 1 Hrs.**

1. Identify the correct product in following reaction:



(a) 

(b) 

(c) 

(d) 

2. Which of the following reagent(s) is most suitable for following conversion?

   Propanone → Propane

   (a) PCC (b) $LiAlH_4$

   (c) 1. $KMnO_4$-KOH 2. H^+ (d) Zn(Hg) /HCl

3. The highest pK_a value is observed in-

   (a) Phenol (b) Benzoic acid

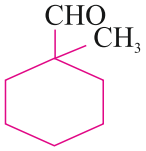
   (c) 4-nitrobenzoic acid (d) Ethanoic acid

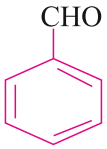
4. Which of the following undergoes nucleophilic addition reaction at fastest rate?

   (a) Benzaldehyde (b) Acetophenone

   (c) Methanal (d) Ethanal

5. Cannizzaro reaction is not given by-

   (a) 

   (b) 

   (c) HCHO (b) CH_3CHO

6. How will you distinguish between:

   (a) Benzaldehyde and acetophenone

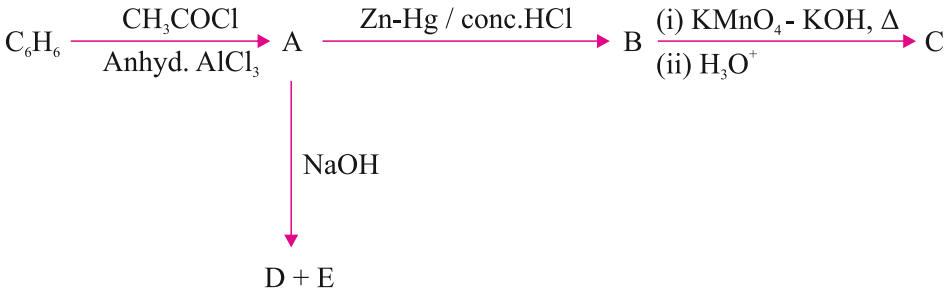
   (b) Benzoic acid and benzophenone

7. How butanoic acid can be synthesised using appropriate:

   (a) Grignard reagent

   (b) Amide

8. Arrange following in ascending order of given properties:
   (a) Ethanal, ethanol, methoxymethane, propane (boiling point)
   (b) Propanal, benzaldehyde, acetophenone (reactivity towards nucleophilic addition reaction)
9. Complete the reaction sequence by writing structures of A-E. Also name the reaction involved in the conversion of A to B.



10. Explain following:
   (a) α hydrogens in aldehydes and ketones are acidic in nature.
   (b) There are two $-NH_2$ groups in semicarbazide. However only one involves in the formation of semicarbazone.
   (c) Propanone is less reactive than propanal towards nucleophilic addition reactions.
11. How will you carry out following conversions?
   (a) Bromobenzene to 1-phenylethanol
   (b) Benzoic acid to *m*- nitrobenzyl alcohol
   (c) Propanone to propene

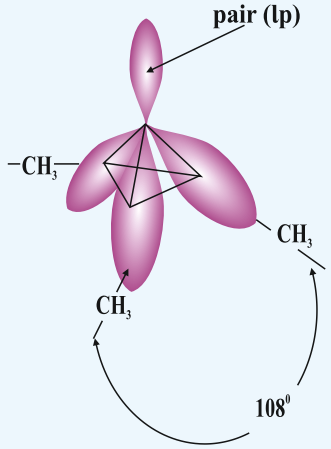
UNIT 13

AMINES

Points to Remember

Geometry

Pyramidal shape



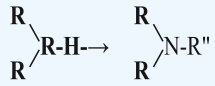
Nomenclature

Common Names:- Amine is used as suffix after alkyl group e.g. $CH_3CH_2NH_2$ is ethylamine

IUPAC names:- e is replaced by - amine e.g. $CH_3CH_2NH_2$ is ethanamine.

Classification and Nomenclature of Amines

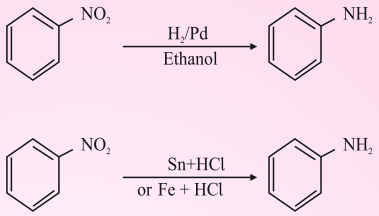
Classification

$NH_3 \rightarrow RNH_2 \rightarrow$ 

Primary(1^0) Primary(2^0) Primary(3^0)

Method of Preparation

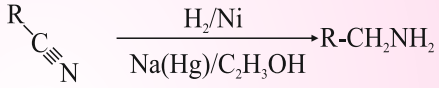
1. Reduction of Nitro compounds



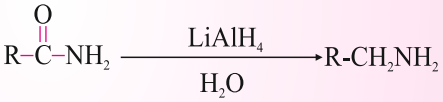
2. Ammonolysis Alkyl Halides



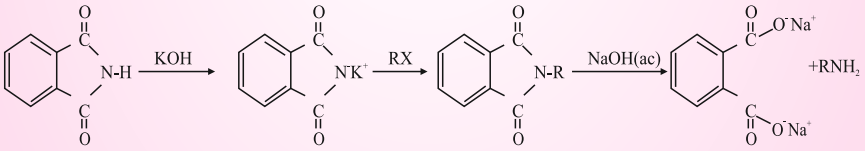
3. Reduction of nitriles



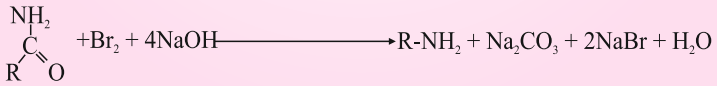
4. Reduction of amide



5. Gabriel phthalimide sythesis



6. Hoffmann bromamide degeneration reaction.



Reactions

(i) Basic character amines

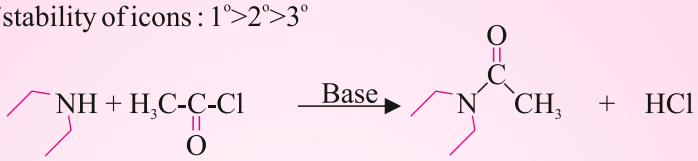
.React with acid to form salts $R\text{-}NH_2 + HX \rightleftharpoons R\text{-}\overset{+}{N}H_3\overset{-}{X}$ (salt)

.React with base to regenerate parent amines

$RNH_3X^- + OH \longrightarrow RNH_2 + H_2O + X$

.Order of stability of icons : $1^o > 2^o > 3^o$

(ii)



(iii)**Carbylamine reaction:**

$R\text{-}CH_2 + CHCl_3 + 3KOH \xrightarrow{\triangle} R\text{-}NC + 3KCl + 3H_2O$

(iv)**With nitrous acid**

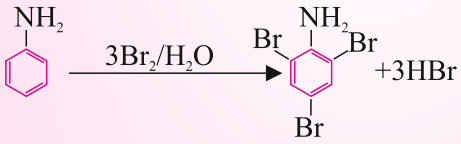
$RNH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R\text{-}N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

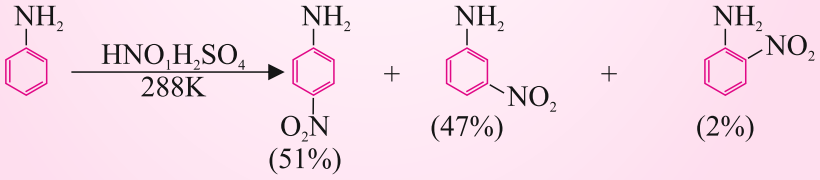
$C_6H_5NH_2 \xrightarrow[273\text{-}27BK]{NaNO_2 + HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

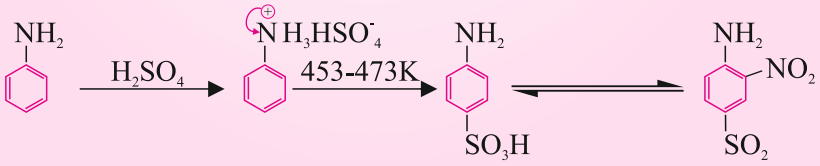
(v) **With Benzene sulfonyl chloride**



(vi)**Electrophilic Substitution**







OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. In the nitration of benzene using conc. H_2SO_4 and conc. HNO_3 the species which initiates the reaction is:

   (a) NO^+ (b) NO_2^+

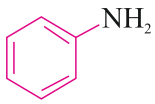
   (c) NO_2^- (d) NO_3^-

2. The correct IUPAC name of CH_2=CH-CH_2NHCH_3

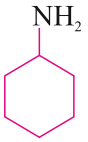
   (a) Allylmethyl amine (b) 2-Aminopent-4-ene

   (c) 4-Aminopent-l-ene (d) N-Methylprop-2-enamine

3. Which is the weakest base?

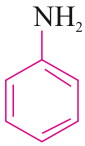
   (a) 

   (b) 

   (c) 

   (d) 

4. The correct order of basic strength for the following compound is:

   (i) 

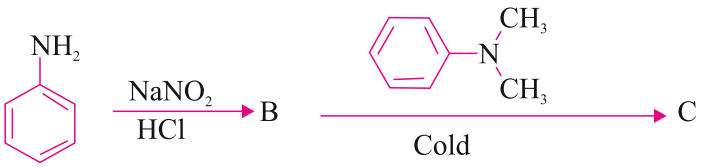
   (ii) 

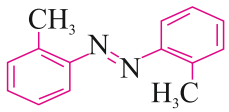
   (iii) 

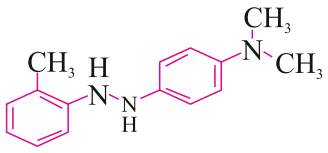
   (a) ii < iii < i (b) iii < i < ii

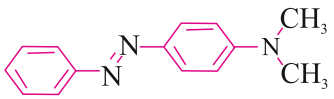
   (c) iii < ii < i (d) ii < i < iii

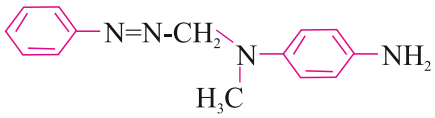
5. The structure of 'C' in following reaction sequence would be -



(a) 

(b) 

(c) 

(d) 

6. Which of the following statement about primary amine is false?

   (a) Aryl amines react with nitrous acid to produce phenol

   (b) Alkyl amines are stronger base than ammonia

   (c) Alkyl amines are stronger base than aryl amines

   (d) Alkyl amines react with nitrous acid to produce alcohol

7. Which of the following is most stable diazonium salt?

   (a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$

   (c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$

8. Method by which aniline can not be prepared is:

   (a) Reduction of nitrobenzene with H_2/Pd in ethanol.

   (b) Potassium salt of phthalimide treated with chlorobenzene

   (c) Hydrolysis of phenyl isocyanide with acidic solution

   (d) Degradation of benzamide with bromine in alkaline medium solution.

9. In the chemical reaction:

   $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$ 'A' + 'B' + $3H_2O$

   The compound 'A' and 'B' are respectively:

   (a) $CH_3CH_2CONH_2$ and 3KCl

   (b) CH_3CH_2NC and K_2CO_3

   (c) CH_3CH_2NC and 3KCl

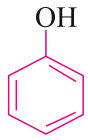
   (d) CH_3CH_2CN and 3KCl

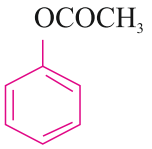
10. An amide (A) reacts with bromine in aqueous NaOH and forms amine containing 3 carbons. Identify (A):

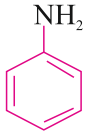
(a) 2- Methylpropanamide (b) Propanamine

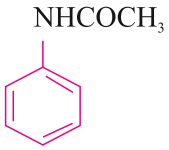
(c) Butanamide (d) None of these

11. Which of the following compound will give significant amount of *meta* product during mononitration reaction?

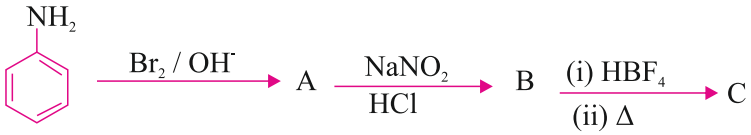
(a) 

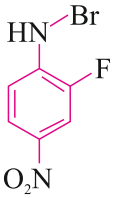
(b) 

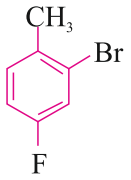
(c) 

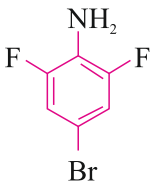
(d) 

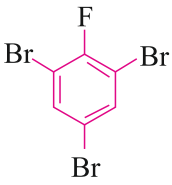
12. The final product C in the following sequence of reaction is:



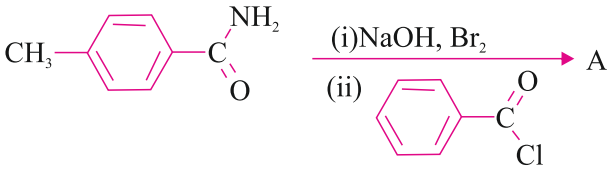
(a) 

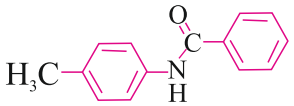
(b) 

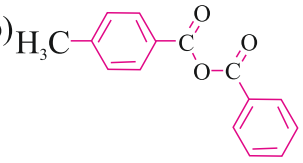
(c) 

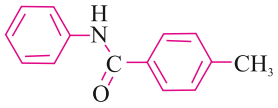
(d) 

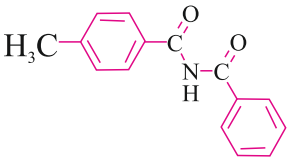
13. In the reaction, the structure of product A is:



(a) 

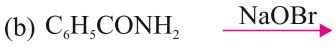
(b) 

(c) 

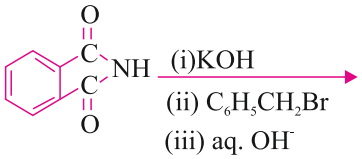
(d) 

14. Which of the following reactions from benzylamine:

(a) 

(b) 

(c) 

(d) 

15. Bromobenzene can be prepared from benzene diazonium chloride by its treatment with-

(a) Cu/HBr

(b) Br_2, HBr

(c) CuBr/HBr

(d) Br_2/CCl_4

II FILL IN THE BLANKS

1. Reaction of nitrobenzene with Fe + HC1 results into the formation of.....
2. Aromatic amines are.....bases while aliphatic amines are.....bases than ammonia.
3. Gabriel phthalimide synthesis is used for synthesis of .....amines.
4. Benzenesulphonyl chloride is also known as.....reagent.
5. Butanamide on reaction with $LiAlH_4$ forms.....
6. To reduce activation of aniline it is deactivated by.....reaction.
7. Nitration of aniline forms *para* and ..... isomers of nitroaniline as major products.
8. Benzene diazonium chloride may be converted into phenol by reaction with .....at 283 K.
9. Primary amines are soluble in water due to.....

III ASSERTION REASON TYPE QUESTIONS

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.

(a) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION** : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

   REASON : Acyl group sterically hinders the approach of further acyl groups.

2. **ASSERTION :** Hoffmann's bromamide reaction results into formation of primary amines.

   REASON : Primary amines are more basic than secondary amines.

3. **ASSERTION :** N-Ethylbenzene sulphonamide is soluble in alkali.

   REASON : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

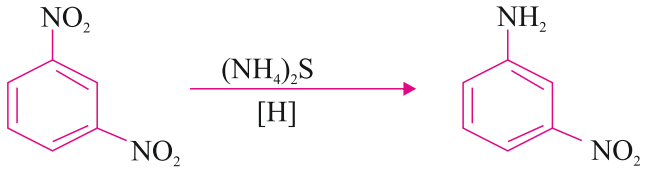
4. **ASSERTION :** N, N-Diethylbenzene sulphonamide is insoluble in alkali.
   REASON : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.
5. **ASSERTION :** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HC1 in the presence of steam.
   REASON : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.
6. **ASSERTION :** Aromatic 1° amines can not be prepared by Gabriel phthalimide synthesis.
   REASON : Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.
7. **ASSERTION :** Acetanilide is less basic than aniline.
   REASON : Acetylation of aniline results in decrease of electron density on nitrogen.
8. **ASSERTION:** n-Propylamine has higher boiling point than trimethylamine.
   REASON: Among n-Propylamine molecules, there is hydrogen bonding but there is not hydrogen bonding in trimethylamine.
9. **ASSERTION:** Aniline does not undergo Friedel Crafts reaction.
   REASON: Friedel Crafts reaction is an electrophilic substitution reaction.
10. **ASSERTION:** Ethylamine is more basic than aniline.
    REASON: Due to +I effect of ethyl group electron density on nitrogen increases.

IV ONE WORD TYPE QUESTIONS

1. Name the reaction in which primary amines reacts with $CHCl_3$ and KOH forming foul smelling substance.
2. Write the IUPAC name of white precipitate formed by reaction of aniline with bromine water.
3. Write the product formed by the Hoffmann bromamide degradation of of benzamide.
4. Is CH_3CONH_2 weaker/stronger base than $CH_3CH_2NH_2$?
5. Which type of electrophilic substitution reaction is not possible with aniline?
6. Name the product formed when benzene diazonium chloride reacts with H_3PO_2.
7. Name the reaction which is used to convert diazonium salt into corresponding halide by reacting with Cu(I) halides.
8. Which type of reaction involves in the cleavage of C-X bond in ammonolysis ?

VERY SHORT ANSWER TYPE QUESTIONS (1 Marks)

1. Convert *m*-dinitrobenzene to m-nitroaniline.



2. Write IUPAC name of $CH_3\text{-}N(CH_3)\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH_3$

Ans. 3-Methyl-N,N-dimethylpentanamine

3. Give one use of quantemary ammonium salts.

Ans. It is used as detergents, e.g., $[CH_3(CH_2)_{15}N(CH_3)_2]^+Cl^-$

4. What is Hinsberg's reagent?

Ans. Benzene sulphonyl chloride, $C_6H_5\text{-}SO_2Cl$

5. Why aniline dissolves in HCl?

Ans. $C_6H_5NH_2 + HCl \rightarrow [C_6H_5NH_3]^+Cl^-$

It dissolves due to its basic nature.

6. How will you test the presence of primary amine?

Ans. By carbylaminc test.

$RNH_2 + CHCl_3 + 3KOH \rightarrow R\text{-}NC + 3H_2O$

7. What is vapour phase nitration?

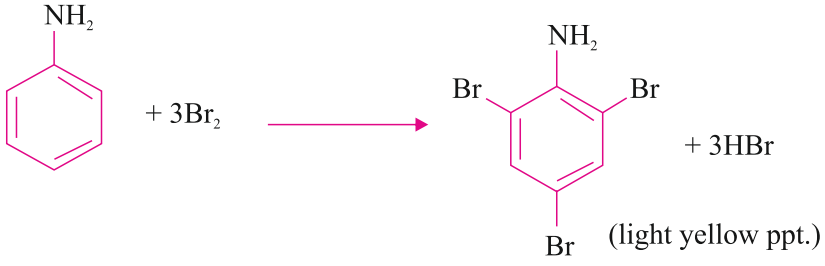
Ans. $CH_4 + HNO_3 \rightarrow CH_3NO_2$

(High temperature and nitration in vapour phase only)

8. Direct nitration of aniline is not carried out. Explain.

Ans. (H_2SO_4 + HNO_3) easily oxidizes aniline into tarry complex product due to high electron- density on the benzene ring of aniline.

9. What happens when aniline is treated with bromine?



10. Write a chemical equation to illustrate the ammonolysis.

Ans. For alcohols:

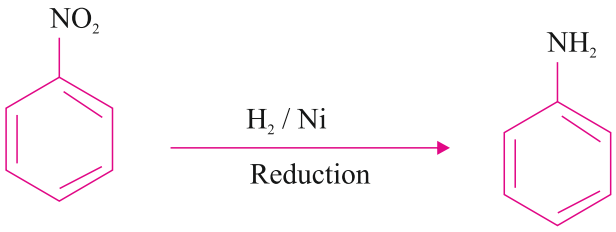
$$C_2H_5OH \xrightarrow[Al_2O_3 / 620K]{NH_3} C_2H_5NH_2 \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_2NH \xrightarrow{C_2H_5OH} (C_2H_5)_3N$$

For alkyl halides:

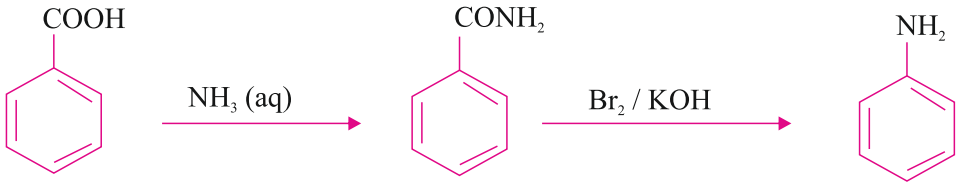
$$C_2H_5I \xrightarrow[-HI]{NH_3 / 373K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow[-HI]{C_2H_5I} [(C_2H_5)_4N]^+I^-$$

11. Prepare/convert nitrobenzene into aniline.

Ans.



12. Convert C_6H_5COOH to $C_6H_5NH_2$



13. Write isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

14. Arrange the following compounds in increasing order of solubility in water:

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

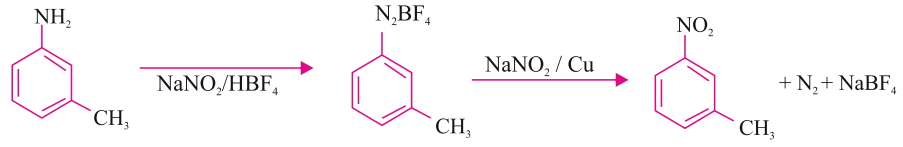
SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

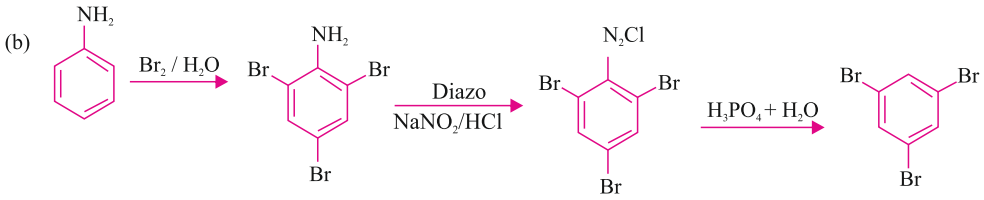
1. How will you convert following :

(a) 3-Methlylaniline to 3-nitrotoluence

(b) Aniline to 1,3,5-tribromobenzene

(a)



(b) 

2. A compound 'A' having molecular formula C_3H_7ON reacts with Br_2 in presence of NaOH to give compound. 'B' This compound 'B' reacts with HNO_2 to form alcohol and N_2 gas. Identify compound 'A' and 'B' and write the reactions involved.

$$\underset{(A)}{CH_3CH_2CONH_2} \xrightarrow[NaOH]{Br_2} CH_3CH_2NH_2 \xrightarrow{HNO_2} \underset{(B)}{C_2H_5OH} + N_2 + H_2$$

3. Account for following:

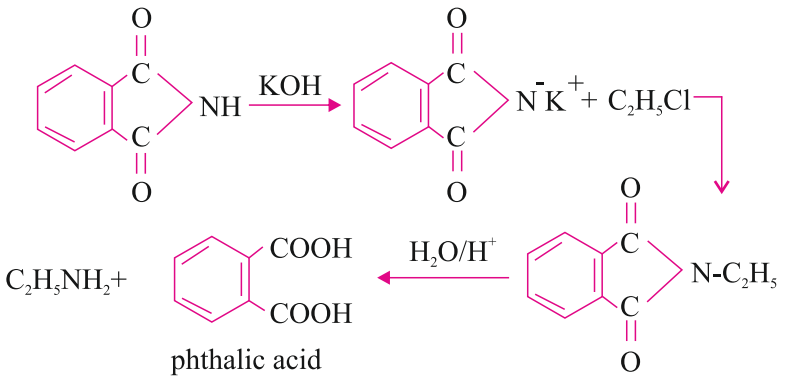
(i) Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions but aniline on nitration gives a substantial amount of *m*-nitroaniline.

(ii) Aniline does not undergoes Friedel Crafts reaction.

Ans. (i) It is because aniline is protonated to form anilinium cation, in which $-NH_2$ group is *meta*-directing.

(ii) It is because aniline is basic, can form adduct with $AlCl_3$ which deactivates the ring.

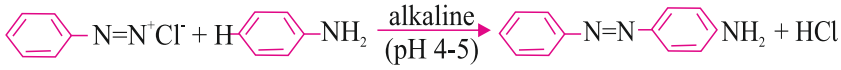
4. How will you synthesise ethanamine by Gabriel phthalimide synthesis?



5. Write short notes on following:

(a) Coupling reaction

(b) Ammonolysis

Ans : (a) 

(b) Ammonolysis :

$$R - X + NH_3 \rightarrow R - NH_2 + HX$$

$$RNH_2 + R\text{-}X \rightarrow (R)_2NH + HX$$

$$(R)_2NH + R - X \rightarrow (R)_3N + HX$$

$$(R)_3N + R - X \rightarrow [R_4N^+]X^-$$

6. Account for the following :

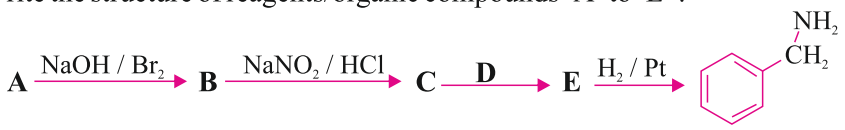
(a) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(b) Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

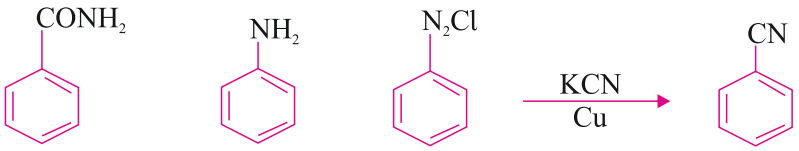
Ans. (a) - NH_2 is electron releasing group so electrophilic substitution takes place faster.

(b) Nitro compounds are more polar than hydrocarbons therefore have more van der Waals forces of attraction.

7. Write the structure of reagents/organic compounds 'A' to 'E' :



Ans :



A B C D E

8. What happens when :

(a) An alkyl halide reacts with $AgNO_2$ and product is reduced.

(b) An alkyl halide is treated with AgCN and product is hydrolysed.

(c) Methyl magnesium is treated with cyanogen chloride.

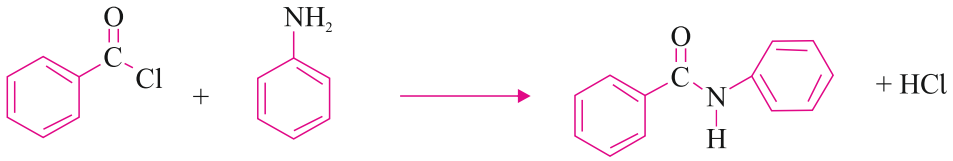
Ans. (a) $R - X + AgNO_2 \xrightarrow[-AgX]{} R - NO_2 \xrightarrow[[H]]{Sn/HCl} R - NH_2$

(b) $R - X + AgCN \xrightarrow[-AgX]{} RNC \xrightarrow{H_2O/H^+} RNH_2 + HCOOH$

(c) $CH_3MgBr + CN - Cl \rightarrow CH_3CN + Mg\begin{matrix}Cl\\Br\end{matrix}$

9. Write reaction for benzoylation of aniline.

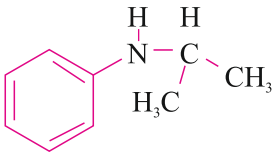
Ans :



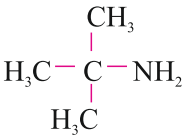
N-phenyl benzamide

10. Draw structure of the following compounds:
    (a) N-isopropylaniline
    (b) t-butylamine

Ans : (a)



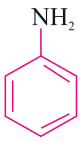
(b)



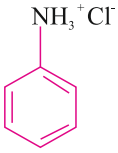
11. Give reasons:
    (a) Electrophilic substitution in aromatic amines takes place more readily than benzene
    (b) CH_3CONH_2 is weaker base than $CH_3CH_2NH_2$.

Ans: (a) $-NH_2$ group in aromatic amines shows +R effect and increases electron density on ring and facilitating the attack of electrophile.
    (b) In ethanamide the electron pair on nitrogen is in resonance with carbonyl group so electrons are less readily available than ethanamide.

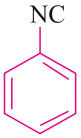
12. An organic aromatic compound 'A' with the molecular formula C_6H_7N is sparingly soluble in water. 'A' on treatment with dil. HCl gives a water soluble compound 'B'. 'A' also reacts with chloroform in presence of alcoholic KOH to form an obnoxious smelling compound 'C'. 'A' reacts with benzene sulphonyl chloride to form and alkali soluble compound 'D'. 'A' reacts with $NaNO_2$ and HCl to form a compound `E' which on reaction with phenol forms an orange dye Elucidate the structures of the organic compounds from 'A' to 'F'.



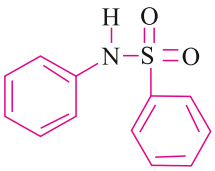
A



B

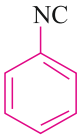


C

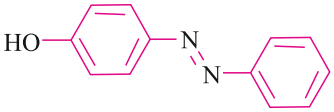


D

E



F



LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Arrange the following :

(a) In decreasing order of pK_b value

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(b) In increasing order of basic strength:

(i) Aniline , *p*-nitroaniline and *p*- toluidine

(ii) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(c) In decreasing order of basic strength :

$C_6H_5NH_2$, $(CH_3)_2NH$, CH_3NH_2

(d) Decreasing order of basic strength in gas phase :

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, NH_3

(e) Increasing order of boiling point :

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Ans : (a) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(b) (i) *p*- nitro aniline < aniline < *p* -toluidine

(ii) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(c) $(CH_5)_2NH_2 > CH_3NH_2 > CH_6N(CH_3)_2 > C_6H_5NH_2$

(d) $(C_2H_5)_3N > (C_2H_5)NH > C_2H_5NH_2 > NH_3$

(e) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

2. How will you convert :

(i) Ethanoic acid into methanamine

(ii) Hexane nitrile into 1- aminopentane

(iii) Methanol into ethanoic acid

(iv) Ethanamine into methanamine

Ans:

(ii) $\underset{\text{Hexane nitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{partial hydrolysis}]{\text{Conc. HCl}} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{1-Aminopentane}}{CH_3(CH_2)_4NH_2}$

(iii) $\underset{\text{Methanol}}{CH_3OH} \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{KCN\ (alc.)} CH_3CN \xrightarrow{H^+/H_2O} \underset{\text{Ethanoic acid}}{CH_3COOH}$

(iv) $\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[(NaNO_2 + HCl)]{HNO_2} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3COOH \xrightarrow{\text{aq. } NH_3} CH_3COONH_4 \xrightarrow{\text{heat}} CH_3CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

3. Write short note on the following :-

(a) Carbylamine reaction

(b) Diazotization

(c) Hoffmann bromide reaction

(d) Coupling reaction

(e) Ammonolysis

(i) **Carbylamine reaction** : When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identity the presence of primary amine or chloroform.

$$RCH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow RCH_2NC + 3KCl + 3H_2O$$



$+ CHCl + 3KOH\ (alc) \longrightarrow$



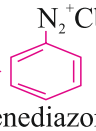
$+ 3KCl + 3H_2O$

Aniline — Phenyl isocyanate

(b) **Diazotization** : When primary aromatic amine is treated with $NaNO_2$ and HCl at 273-278K, diazonium salt is obtained. This reaction is known as diazotization.



$+ NaNO_2 + HCl \xrightarrow{273 - 278K}$



$+ 2H_2O$

Aniline — Benzenediazonium chloride

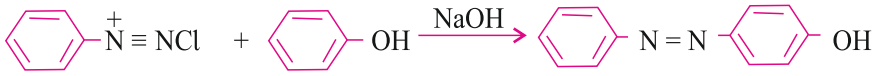
Benzenediazonium chloride is a very important synthetic compound, which can be changed into haloarenes, phenol, cyanobenzene, benzene etc.

(c) **Hoffmann's bromide reaction** : When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.



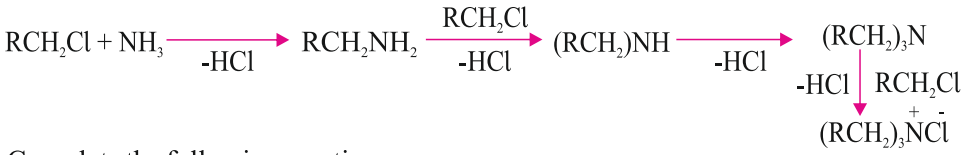
This reaction is used to reduce one carbon atom form a compound.

(d) **Coupling reaction** : When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes arc produced in which diazo (- N = N -) group is retained. Coupling reactions generally take place at *p*-position of phenol or aromatic amines.



Benzendiazonium chloride | Phenol | *p*-Hydroxyazobeneze (Azo dye)

(e) **Ammonolysis** : Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.



4. Complete the following reaction :-

(i) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

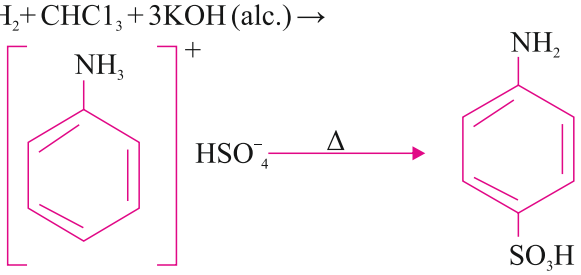
(ii) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(iii) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(iv) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(v) $C_6H_5NH_2 + CHCl_3 + 3KOH\ (alc.) \rightarrow$

Ans: (i)



(ii) $C_6H_6+N_2+HC1+CH_3CHO$

(iii) $C_6H_5NHCOCH_3+.CH_3COOH$

(iv) $C_6H_6+H_3PO_3+HCl+N_2$

(v) $C_6H_5NC+3KCl+3H_2O$

5. Accomplish the following conversion :-

(I) $C_6H_5NO_2 \rightarrow C_6H_5COOH$

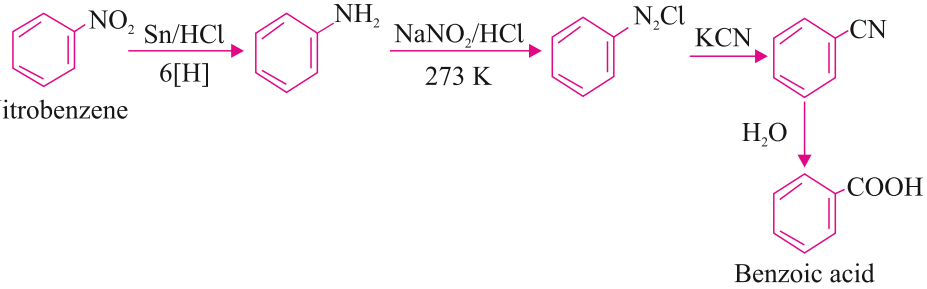
(ii) Benzene $\rightarrow$ *m*-bromophenol

(iii) $C_6H_6COOH \rightarrow C_6H_5NH_2$

(iv) Aniline $\rightarrow$ 2,4,6 -Tribromoaniline

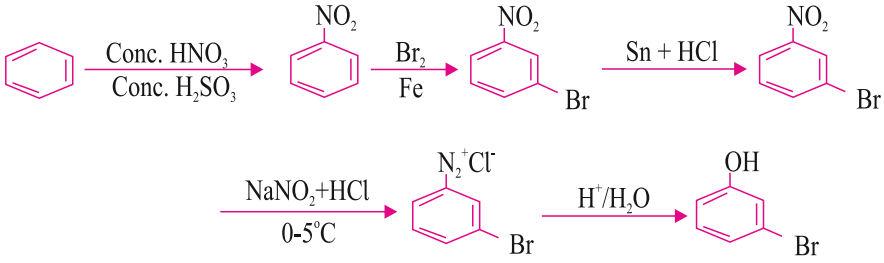
(v) Benzylchloride $\rightarrow$ 2-phenylethanamine

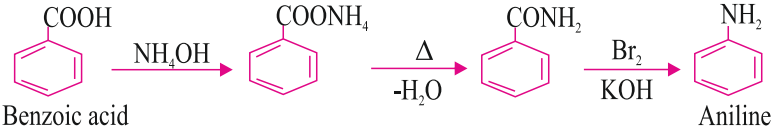
Ans:-

(i) 

Nitrobenzene

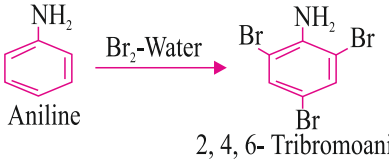
Benzoic acid

(ii) 

(iii) 

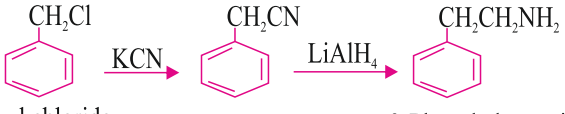
Benzoic acid

Aniline

(iv) 

Aniline

2, 4, 6- Tribromoaniline

(v) 

Benzyl chloride

2-Phenylethanamine

7. Write A,B and C in the given reaction sequences;

(i) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

(iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow[\Delta]{H_2O/H_+} C$

(iv) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(v) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{partial hydrolysis}]{OH^-} B \xrightarrow{NaOH/Br_2} C$

Ans. (i) $C_6H_5CN, C_6H_5COOH, C_6H_5CONH_2$

(ii) $CH_3CH_2CN, CH_3CH_2NH_2, CH_3CH_2OH$

(iii) $C_6H_5NH_2, C_6H_5N_2Cl, C_6H_5OH$

(iv) $CH_3CONH_2, CH_3NH_2, CH_3OH$

(v) $CH_3CH_2CN, CH_3CH_2CONH_2, CH_3CH_2NH_2$

CASE-STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

Friedel-Crafts (FC) reaction is an important method to incorporate carbon skeletons into aromatic system. Great successes have been achieved for the hydroarylation of neutral arenes (such as toluene, anisole, and their homologues). Because the FC reactions typically require Lewis acid catalysts, for arenes containing nitrogen atom, the substrate scope of FC reactions are quite limited due to the coordination between amine and Lewis acid catalyst, except indole and pyrrole. Being profited from the extremely weak basic properties, acid-catalyzed additions of indole and pyrrole to alkenes have obtained great achievements. However, the hydroarylation of alkaline arenes to alkenes still remains many challenges. Some researches have shown the possibility of hydroarylation between the parent anilines $C_6H_5NH_2$ and alkenes. However, the reaction of arenes with stronger basicity (such as N,N-dimethylaniline and N,N-diethylaniline) still is a big problem, due to their ability to coordinate with Lewis acid catalyst which can lead to deactivation of the aromatic ring. Furthermore, alkaline arenes can trap the proton in the C-H activation process and the reaction will be terminated as result.

Recently, Bertrand et al. reported an anti-Bredt cyclic diaminocarbene which showed increased λ-accepting character without diminishing its cs-donor property. We found that Gold(I) compound derived from this new carbene can be used as effective catalyst for the FC reaction between alkenes and N,N-dialkylanilines. Now, these new FC reactions are receiving more and more research interests. As we known, most of the electrophilic substitution reactions followed the Markovnikov rule. For the FC reaction of alkenes, the reactions following the Markovnikov rule should form branched product. Only several examples were reported on the formation of linear product by anti-Markovnikov rule. For the FC reactions between alkenes and N, N-dialkylanilines catalyzed by carbene Gold(I), both Markovnikov and anti-Markovnikov hydroarylations were observed and all these reactions gave high para-selectivity products. The selectivity to the branched or linear product was highly depended on the structure of alkenes.

Reference : Wu, H., Zhao, T. & Hu, X. **Friedel-Crafts Reaction of N,N-Dimethylaniline with Alkenes** *Catalyzed by Cyclic Diaminocarbene-Gold(I) Complex*. *Sci Rep* 8, 11449 (2018). https://doi.org/10.1038/s41598-018-29854-0

(A) Why aniline does not undergoes Friedel-Crafts reaction?

(B) Write reaction to convert aniline into N,N-dimethylaniline.

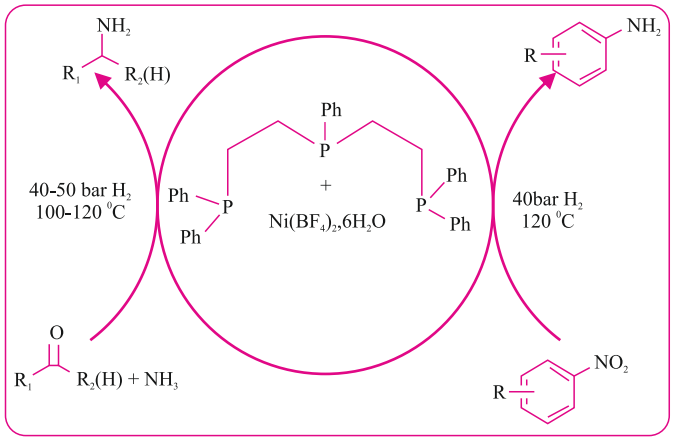
(C) How *p*- nitroaniline can be synthesised from aniline?

(D) Why -NH_2 group in aniline is *ortho-* , *para*- directing?

2. **Read the passage and answer the following questions:**

The development of base metal catalysts for industrially relevant amination and hydrogenation reactions by applying abundant and atom economical reagents continues to be important for the cost-effective and sustainable synthesis of amines which represent highly essential chemicals. In particular, the synthesis of primary amines is of central importance because these compounds serve as key precursors and central intermediates to produce value-added fine and bulk chemicals as well as pharmaceuticals, agrochemicals and materials. Here we report a Ni-triphos complex as the first Ni-based homogeneous catalyst for both reductive amination of carbonyl compounds with ammonia and hydrogenation of nitroarenes to prepare all kinds of primary amines. Remarkably, this Ni-complex enabled the synthesis of functionalized and structurally diverse benzylic, heterocyclic and aliphatic linear and branched primary amines as well as aromatic primary amines starting from inexpensive and easily accessible carbonyl compounds

(aldehydes and ketones) and nitroarenes using ammonia and molecular hydrogen. This Ni-catalyzed reductive amination methodology has been applied for the amination of more complex pharmaceuticals and steroid derivatives. Detailed DFT computations have been performed for the Ni-triphos based reductive amination reaction, and they revealed that the overall reaction has an inner-sphere mechanism with H_2 metathesis as the rate-determining step.



Reference : Kathiravan Murugesan, Zhihong Wei, Vishwas G. Chandrashekhar, Haijun Jiao, Matthias

Beller, Rajenahally V. Jagadeesh **General and selective synthesis of primary amines using Ni-based homogeneous catalysts**_*Chem. Sci.*, 2020,11, 4332-4339

(A) Convert nitrobenzene to chlorobenzene.

(B) What happens when butanone reacts with ammonia according to scheme given above.

(C) Mention one method, other than mentioned here for conversion of nitrobenzene to aniline.

3. **Read the passage and answer the following questions:**

For a group of nitro-substituted anilines and diphenylamines, a plot of PICHA (ordinate) against pK_{BH}^{+} gave a straight line of slope 0.6. That is, the acidities of the amines seemed to be affected to a smaller extent by ring substitution than were their basicities.

$$ArNH_3^+ \xleftarrow{H^+} ArNH_2 \xrightarrow{-H^+} ArNH^-$$

This result was somewhat surprising because, although resonance with the nitro group occurs in both the neutral amine and the anion, and hence affects both equilibria, it involves a very important charge dclocalization in the amide anion.



. It has been suggested that the nitro substituent has an anomalous effect in acid mixtures (2), where some of the pK_{BH}^{+} values had been determined. In the course of extending the H— scale to very basic values, we had the opportunity to use amines containing substituents other than nitro (3) and to determine if the unusual effect of substituents on acidity vis-a-vis basicity was due to the presence of nitro groups. In accompanying papers the pK_{BH}^{+} values (4) and the pK_{HA} values of these aromatic amines are reported. (The basicities of amines are described, as is customary, in terms of the acidity of their conjugate acids.)

Reference : Ross Stewart and Douglas Dolman. **A comparison of the acidity and basicity of aromatic amines**. *Canadian Journal of Chemistry.* 45(9): 925-928. https://doi.org/10.1139/v67-156

(A) Which of the following has highest $_pK_a$ value?

(a) Aniline

(b) *p*-nitoaniline

(c) *m*-nitroaniline

(d) *o*-nitroaniline

(B) Why basic strength of aliphatic amines are higher than ammonia?

(C) What will be the correct order of basic strength of following: Et NH_2, $(Et)_2$ NH, $(Et)_3N$

(D) What happens when aniline reacts with sulphuric acid?

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. b 2. d 3. a 4. d 5. c
6. a 7. b 8. c 9. c 10. c
11. c 12. d 13. a 14. a 15. c

II FILL IN THE BLANKS

1. Aniline
2. weaker, stronger
3. Primary aliphatic
4. Hinsberg
5. Butanamine
6. Acetylation
7. *meta*
8. Water.
9. H-bonding

III ASSERTION REASON TYPE QUESTIONS

1. c 2. c 3. a 4. b 5. a 6. c 7. a 8. a 9. b 10. a

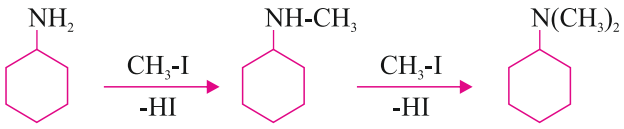
IV ONE WORD TYPE QUESTIONS

1. Carbylamine reaction
2. 2,4,6-tribromoaniline
3. Aniline
4. weaker
5. Friedel-Crafts reaction
6. Benzene
7. Sandmeyer
8. S_N2

CASE STUDY BASED QUESTIONS

PASSAGE : 1

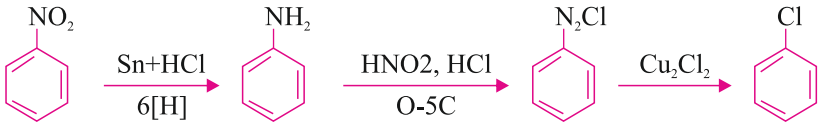
(A) Aniline forms salt with anhydrous $AlCl_3$.

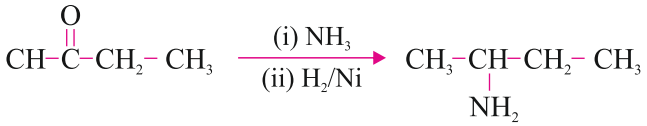
(B) 

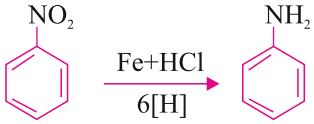
(C) Refer NCERT Page - 403

(D) Due to +R effect of $-NH_2$ Sp.

PASSAGE : 2

(A) 

(B) 

(C) 

PASSAGE : 3

(A) (d)

(B) Due to +I effect of -R gps present in aliphatic amines

(C) $(Et)_2NH$, $(Et)_3N$, $EtNH_2$

UNIT TEST
CHAPTER-13

Maximum Marks : 20 **Time Allowed : 1 Hour**

1. Benzamide reacts with Br_2 and NaOH forming..... 1

2. The correct order of basicity of amines is: 1
   (a) Ammonia > Ethanamine > Aniline
   (b) Ethanaminc > Ammonia > Aniline
   (c) Ammonia > Aniline > Ethanamine
   (d) Ethanamine > Aniline > Ammonia

3. When aniline reacts with $NaNO_2$/HCl then reaction with CuCN followed by acidic hydrolysis. What will be the final product of the reaction? 1
   (a) Nitrobenzene (b) Benzaldehyde
   (c) Benzoic acid (d) Phenol

4. Assertion: Aniline forms 2,4,6-tribromoaniline on reaction with bromine water.
   Reason: $-NH_2$ is *ortho*, *para*- directing. 1
   (a) Both assertion and reason are correct statements and reason is correct explanation of assertion.
   (b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

5. Assertion: Primary amines cannot be synthesised by Gabriel phthalimide synthesis.
Reason: Due to steric hindrance caused by bulky group substitution is not possible.

(a) Both assertion and reason are correct statements and reason is correct explanation of assertion. 1

(b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

6. How will you synthesise butanamine by Gabriel phthalimide synthesis? 2

7. Distinguish between following pair of compounds: 2

(a) Aniline and Benzylamine

(b) Methylamine and Dimethylamine

8. How will you convert? 2

(a) Ethanoic acid to methanamine

(b) Aniline to *p*-bromoaniline

9. 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 $C_6H_{13}N$. Write the structures and IUPAC names of compounds A, B and C. 3

10. Write short notes on following: 3

(a) Benzoylation reaction

(b) Hoffmann bromamide degradation reaction

(c) Carbylamine reaction

I1. Explain: 3

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than CH_3CONH_2.

(c) Nitration of aniline gives significant amount of *meta*-nitroaniline in addition to *o*- and *p*-nitroaniline.

UNIT 14

BIOMOLECULES

Points to Remember

Biomolecules

These are the macromolecules essential for survival of life, e.g. carbohydrotes, proteins, etc.

Carbohydrates

These are polyhydrory aldehydes or ketones or their derivatives, e.g. glucose.

Sugars

These are the carbothydrates having sweet taste.
They may be reducing or non-reducing.

Glucose

•It is obtained by hydrolysing starch or cane sugar.
•its reactions are as:

Glucose $\xrightarrow[\Delta]{HI}$ n-hexane:

NH_2OH (3 mol) → Oxime
Br_2 Water → Gluconic acid
Acelylation (CH_3COCl) → Pentaacetate
HNO_3 → Saccharic Acid

Sucrose

•It contains D-(+)glucose and D(-) fructose joined together by β -1,2-glycosidic linkage.
•It is also called invert sugar.

Proteins

These are polymers of *a*-amino acids.

Amino Acids

These contain amino as well as carboxyl functional group.
They may be essential or non-essential,

Zwitter Ion

Ion containing positive as well as negative charge is called zwitter ion.

e.g. $R-\underset{\overset{+}{N}H_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$

Denaturation

• It is the process of destroying 2^0 or 3^0 structure of protein by heating and by changing pH.
•Due to this, protein losts its biological activity.
•e.g. coagulation of egg white on boiling.

Structure of Proteins

Primary structure: It shows the sequence of amino acids in a

Vitamins, Nucleic Acids and Hormones

Vitamins

These are essential but in very small amounts.
Vitarrins A, D, E and K are fat soluble while rest are water soluble.

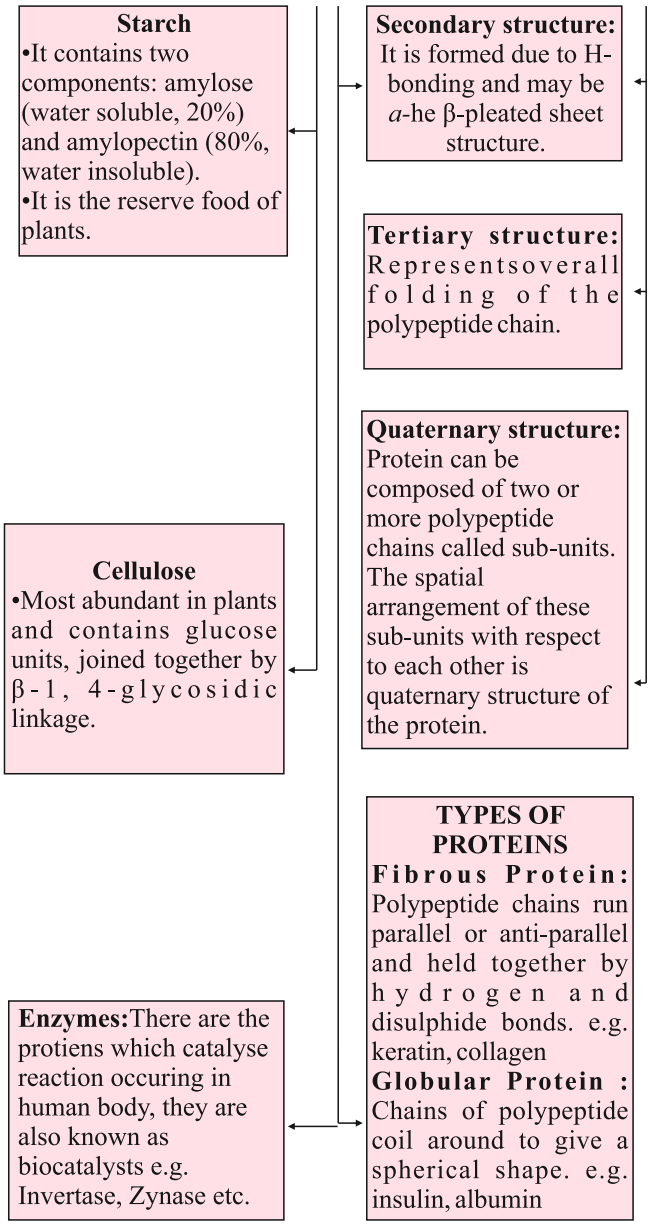
Deficiency Diseases

Vitamin	Deficiency Disease
A	Xerophithalmia
B_1	Beri-beri
B_{12}	Pernicious anaemia
C	Scurvy
D	Rickets
E	Infertility
K	Icreased blood clotting time
H	Loss of hair

Nucleic acid: These are the polymer of nucleotides(Sugar + base+ Phosphoric acid)

DNA	RNA
i) Double helical.	i) Single stranded.
ii) Sugar is 2-deoxyribose.	ii) Sugar is ribose.
iii)Bases : A, T, G, C.	iii)Bases : A,U,G,C
iv)Property of replication.	iv)Do not replicate.
v) It is responsible for transmission of heredity Caracter	v) Helps in protein biosynthesis.

Hormones: These are the chemicals secreted by Endocrine glands.


Starch
•It contains two components: amylose (water soluble, 20%) and amylopectin (80%, water insoluble).
•It is the reserve food of plants.
Cellulose
•Most abundant in plants and contains glucose units, joined together by β-1, 4-glycosidic linkage.
Enzymes: There are the protiens which catalyse reaction occuring in human body, they are also known as biocatalysts e.g. Invertase, Zynase etc.
Secondary structure: It is formed due to H-bonding and may be a-he β-pleated sheet structure.
Tertiary structure: Represents overall folding of the polypeptide chain.
Quaternary structure: Protein can be composed of two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units with respect to each other is quaternary structure of the protein.
TYPES OF PROTEINS
Fibrous Protein: Polypeptide chains run parallel or anti-parallel and held together by hydrogen and disulphide bonds. e.g. keratin, collagen
Globular Protein : Chains of polypeptide coil around to give a spherical shape. e.g. insulin, albumin

1. **Carbohydrates :** These are optically active polyhydroxy aldehydes or ketones or the compounds which produce these on hydrolysis.

2. **Classification :**

   (i) Monosaccharides : Those carbohydrates which cannot be hydrolysed into further simpler carbohydrates. *E.g.,* glucose, fructose, galactose etc.

   (ii) Disaccharides : Those carbohydrates which produces two monosaccharides on hydrolysis. *E.g.,* sucrose, maltose and lactose.

   (iii) Oligosaccharides : Those carbohydrates which give two to ten monosaccharides on hydrolysis.

   (iv) Polysaccharides : Those carbohydrates which on hydrolysis give large number of monosaccharides hydrolysis. *E.g.,* starch, cellulose, glycogen.

3. **Sugar :** Carbohydrates which are sweet in taste.

   (i) Reducing sugars : Those which reduce Fehling's or Tollen's reagent due to availability of free aldehydic groups. *E.g.,* glucose, fructose, galactose.

   (ii) Non-reducing sugars : Those which do not reduce Fehling's or Tollen's reagent. They do not have free aldehydic group. *E.g.,* sucrose.

4. **Glucose :** It is a monosaccharide with molecular formula $C_6H_{12}O_6$.

5. **Preparation :**

   (i) From sucrose :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad \text{(only from sucrose)}$$

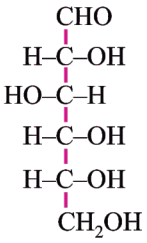
   (ii) From starch :

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

6. **Structure :**

Fischer structure :

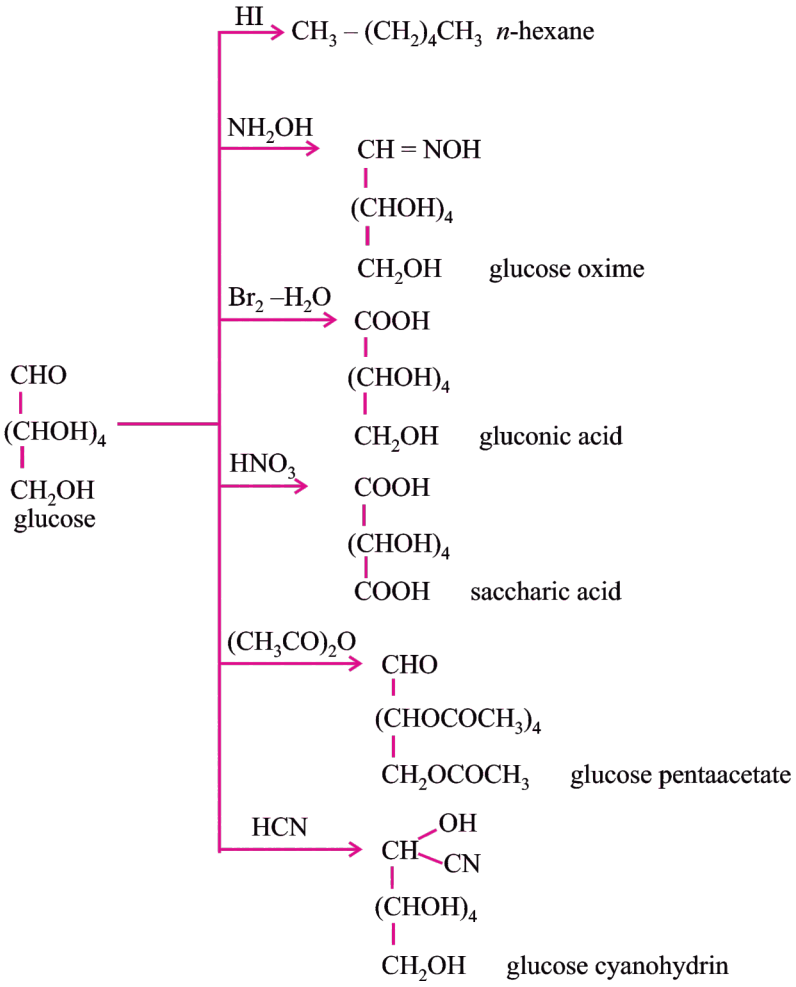
(+) glucose has 'D' configuration as shown :



D-(+)-glucose

'D'- means – OH group on first chiral 'C' from the bottom is on right hand and (+) means it is dextrorotatory *i.e.,* it rotates plane polarized light towards right.

Reactions of glucose :



Objections against open chain structure of glucose

The open chain structure was unable to explain the following reactions :

(a) It does not give the 2, 4-DNP test, Schiff's test and does not form the hydrogensulphite product with $NaHSO_3$.

(b) The pentacetate of glucose does not react with NH_2OH, indicating the absence of free aldehydic group.

(c) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

After which a close chain (cyclic) structure of glucose was proposed by Haworth.

* Anomers are isomers which have a different configuration at C-1 functional group c-atom

7. **Glycosidic linkage :** The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

8. **Proteins :** These are macro molecules made up of amino acids joined by amide linkage [– (– CONH –) –] is here called as peptide linkage. These are required for growth and development of the body.

9. **Amino acids :** These contain an amino (- NH_2) and an acidic (- COOH) group and are therefore amphoteric in nature. In solution they exist in the form of zwitter ion (a dipolar ion).

10. **Native state of protein :** The parental state or the natural state in which the protein is found.

11. **Denaturation of protein :** Destruction of the native state of protein is denaturation. It can be brought by physical and chemical methods. The 2° and 3° structures are destroyed, only 1° structure is retained.

Enzymes : These are biocatalyst and generally globular proteins *e.g.,* invertase, zymase, phenylalanine hydroxylase, urease etc.

Main characteristics of enzymes :

(i) It speed up the biological reaction upto million times.

(ii) It is highly specific and work on lock and key theory.

(iii) It is highly sensitive to pH and temperature.

12. **Nucleic acids :** These are biomolecules which are long chain polymers of nucleotides. They are of two types :

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

13. Nuceloside = Base + Sugar

Nucleotide = Base + Sugar + Phosphoric acid

I MULTIPLE CHOICE QUESTIONS

1. Which of the following acids is a vitamin?

(a) aspartic acid (b) ascorbic acid

(c) aoiphic acid (d) saccharic acid

Which one given below is non-reducing sugar?

(a) glucose (b) sucrose

(c) maltose (d) lactose

3. In a protein molecule amino acids are linked together by:

(a) peptide bond (b) dative bond

(c) glycosidic bond (d) phospodiester bond

4. One strand of DNA has the sequence. ATGCTT, the sequence of complementary strand would be:

(a) TCCGAA (b) TACGTA

(c) TACGAA (d) TAGCTA

5. Which of the following vitamin given below is water soluble?

(a) vitamin C (b) vitamin D

(c) vitamin K (d) vitamin E

6. In both DNA and RNA, base and phosphate ester linkage are at

(a) C'_5 and C'_2 respectively of sugar molecule

(b) C'_2 and C'_5 respectively of sugar molecule

(c) C'_3 and C'_5 respectively of sugar molecule

(d) C'_5 and C'_1 respectively of sugar molecule

7. The two functional groups present in a typical carbohydrates are:
   (a) -OH and -COOH (b) -CHO and -COOH
   (c) >C=0 and -OH (d) -CHO and -COCI
8. The presence or absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA.
   (a) 1st (b) 2nd
   (c) 3rd (d) 4th
9. Which of the following is called invert sugar
   (a) lactose (b) sucrose
   (c) maltose (d) glucose
10. Which of the following carbohydrates is a disaccharides?
   (a) maltose (b) cellulose
   (c) maltase (d) starch
11. Which one of the following is not an aldose?
   (a) Glucose (b) Ribose
   (c) Fructose (d) Galactose
12. Which of the following contain transition metal?
   (a) Vitamin C (b) Chlorophyll
   (c) Haemoglobin (d) RNA
13. Which of the following does not have glycosidic linkage?
   (a) Maltose (b) Amylose
   (c) Galactose (d) Sucrose
14. Fibrous proteins are present in:
   (a) Haemoglobin (b) Albumin
   (c) Collagen (d) Insulin

15. Hydrolysis of lactose with dilute acid yields
    (a) equimolar mixture of D-glucose and D-fructose
    (b) equimolar mixture of D-glucose and D-galactose
    (c) equimolar mixture of D-galactose and D-fructose
    (d) equimolar mixture of D-galactose and D-sucrose

Matching Column Type

16. Match the carbohydrate in Column I with its characteristic given in Column II

Column-I	Column-II
(A) Lactose	(p) Ketohexose
(B) Starch	(q) Disaccharide
(C) Sucrose	(r) Polysaccharide
(D) Fructose	(s) on hydrolysis gives β-D-glucose and β-D-galactose

    (a) A—s, B—r, C—p, D—q
    (b) A—p, B—q, C—r, D—s
    (c) A—r, B—s, C—p, D—q
    (d) A—s, B—r, C—q, D—p

17. Match the carbohydrate in Column I with its characteristic given in Column II

Column-I	Column-II
(A) Keratin	(p) protein
(B) Haemoglobin	(q) β-pleated protein
(C) Riboflavin	(r) α-amino acid
(D) Glycine	(s) Water soluble vitamin

    (a) A-p. B-q. C-s, D-r
    (b) A-q, B-p, C-s, D-r
    (c) A-q, B-p. C-r, D-s
    (d) A-s, B-r, C-q, D-p

18. The no. of chiral carbon present in (β-D-(+)-glucose is:
    (a) 2 (b) 4 (c) 5 (d) 1

II FILL IN THE BLANKS

1. The disease beri-beri is caused due to lack of .....
2. Scurvy is caused due to deficiency of .....

3. .....(carbohydrate) is not digested by human beings.
4. .....on hydrolysis gives D-glucose and D-galactose.
5. Amylose and amylopectin are the two components of.....
6. Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called .....
7. Carbohydrates which reduce Tollen's reagent are called .....
8. Deficiency of ..... leads to xerophthalmia and night blindness.
9. .....contains pentose sugar, and base whereas.....contains pentose sugar, base as well as phosphate group.
10. The pair of stereoisomers which differ only in the configuration of the hydroxyl group at C-1 are called .....

III ASSERTION-REASON TYPE QUESTIONS

In each of the following questions, a statement of Assertion (A) is given followed by a corresponding statement of Reason (R) just below it. Of the statements, mark the correct answer as

(a) Both assertion and reason are correct, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is incorrect.

(d) Assertion is incorrect but reason is correct.

1. **ASSERTION :** A solution of sucrose in water is dextro rotatory but on hydrolysis in presence of little HCl it becomes laevorotatory.
   REASON : Sucrose on hydrolysis gives unequal amount of glucose and fructose as a result sign of rotation changes.
2. **ASSERTION** : Fructose does not contain aldehyde group but still reduce Tollen's reagent.
   REASON : In the presence of base, fructose undergoes rearrangement to form glucose and mannose.

3. **ASSERTION :** D-(+)-Glucose is dextrorotatory in nature.
   REASON : 'D' represents its dextrorotatory nature.
4. **ASSERTION :** Vitamin D can be stored in our body.
   REASON : Vitamin D is fat soluble vitamin.
5. **ASSERTION :** All naturally occurring α-amino acids except glycine are optically active.
   REASON : Most naturally occurring amino acids have D-configuration.
6. **ASSERTION :** In presence of enzyme, substrate molecule can be attacked by the reagent effectively.
   REASON : Active sites of enzymes hold the substrate, molecule in a suitable position.
7. **ASSERTION:** Sucrose is a non-reducing sugar.
   REASON : It has glycosidic linkage.
8. **ASSERTION:** Vitamin C has to be continuously supplied through diet.
   REASON: Vitamin C is a water soluble vitamin.
9. **ASSERTION :** Cellulose is not digested by human beings.
   REASON : Cellulose is a polymer of β-D-glucose.
10. **ASSERTION:** Non-essential amino acids are not necessary for protein synthesis.
    REASON: Non-essential amino acids are produced in the human body.

IV ONE WORD ANSWER TYPE QUESTIONS

1. Which of the two components of starch is water soluble?
2. Write the product formed when glucose is treated with HI.
3. What are the products of hydrolysis of maltose?
4. Name the purines present in DNA.
5. Write the name of linkage joining two amino acids.
6. The deficiency of which vitamin causes the disease pernicious anaemia.
7. Name the base that is found in nucleotide of RNA only.
8. Name the vitamin whose deficiency is responsible for poor coagulation of blood.
9. Write the product formed on reaction of D-glucose with Br_2 water.
10. Name the polysaccharide which is stored in the liver of animals.

VERY SHORT ANSWER TYPE QUESTION (1Marks)

Q. 1. What structural feature is required for a carbohydrate to behave as reducing sugar ?

Ans. The carbonyl group of any one monosaccharide present in carbohydrate should be free.

Q. 2. Give the significance of (+) sign in the name D-(+)-glucose.

Ans. (+) sign indicates dextro-rotatory nature of glucose.

Q. 3. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give reason.

Ans. The – CHO group reacts with – OH group at C-5 to form a cyclic hemiacetal.

Q. 4. Why is sucrose called invert sugar ?

Ans. When sucrose is hydrolysed by water, the optical rotation of solution changes from positive to negative.

Q. 5. Name the amino acid which is not optically active.

Ans. Glycine.

Q. 6. Give reason : Amylase present in the saliva becomes inactive in the stomach.

Ans. HCl present in stomach decreases the pH.

Q. 7. Which forces are responsible for the stability of α-helical structure of proteins ?

Ans. Hydrogen bonding.

Q. 8. Which nucleic acid is responsible for carrying out protein synthesis in the cell ?

Ans. RNA (Ribonucleic acid)

Q. 9. When RNA is hydrolysed, there is no relationship among quantities of different bases obtained. What does this fact suggest about structures of RNA ?

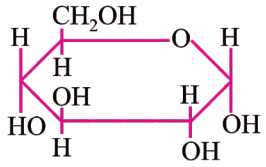
Ans. RNA is single stranded.

Q. 10. What type of linkage holds together the monomers of DNA and RNA ?

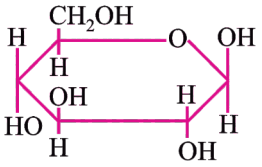
Ans. Phosphodiester linkage.

Q. 11. Give the Howarth projection of D-glucopyranose.

Ans.



α-D(+) Glucopyranose



β-D(+) Glucopyranose

Q. 12. Where does the water present in the egg go after boiling the egg ?

Ans. On boiling, during denaturation process water gets absorbed in denaturated proteins.

Q. 13. Name a protein which is insoluble in water.

Ans. Keratin.

Q. 14. Mention two important functions of carbohydrates in plants.

Ans. Major energy source, storage molecules like starch in plants.

Q. 15. Name two of the different types of RNA molecules found in cells of organisms.

Ans. tRNA, mRNA, rRNA.

Q. 16. Why are carbohydrates generally optically active ?

Ans. Because they contain one or more chiral atom.

Q. 17. During curdling of milk, what happens to sugar present in it ?

Ans. Lactose changes to lactic acid.

Q. 18. The two strands in DNA are not identical but complementary. Explain.

Ans. Base pairing rule is followed; A = T and G ≡ C.

Q. 19. If one strand of DNA has the sequence 5'-G-G-A-C-T-A-C-T-3', what is the sequence of bases in the complementary strand ?

Ans. 3'-C-C-T-G-A-T-G-A-5'

Q. 20. What are monosaccharides ?

Ans. Sugars which cannot be hydrolysed to give simpler units or compounds.

Q. 21. What is the difference between native protein and denatured protein ?

Ans. Proteins found in a biological system with unique 3D-structure and biological activity is called native protein. When native protein is subjected to physical and chemical change, protein loses its biological activity and is called denatured protein.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Define the following terms in relation to proteins :

(i) Peptide linkage (ii) Denaturation

Ans. (i) Peptide linkage : A link between two amino acids with loss of water – CO – NH – peptide linkage.

(ii) A process that changes the three dimensional structure of native protein is called denaturation of protein. It results into breaking of hydrogen bonds and disulphide linkages. Thus, a completely denatured protein has a shape of random coil.

Q. 2. List the reactions of glucose which cannot be explained by its open chain structure.

Ans. (i) Despite having the aldehyde group, glucose does not give 2, 4 DNP test or Schiff's test.

(ii) It does not form hydrogensulphite addition product with $NaHSO_3$.

(iii) The penta acetate of glucose does not react with hydroxylamine indicating the absence of free – CHO group.

Q. 3. Explain what is meant by :

(i) Biocatalyst (ii) Glycosidic linkage

Ans. (i) Biocatalysts are the catalysts which increases the rate of metabolism biochemical reactions.

(ii) The linkage between the monosaccharide units through oxygen is called glycosidic likage.

Q. 4. Explain the following terms :

(i) Invert sugar **(ii) Polypeptides**

Ans. (i) An equimolar mixture of glucose and fructose produced on hydrolysis of sucrose is called invert sugar. It is called so because sucrose is dextro rotatory whereas its hydrolysis product is laevo rotatory.

(ii) Polypeptides are polymers of amino acids containing less than 100 amino acids. For example, oxytocin, vasopressin, etc.

Q. 5. Name the product of hydrolysis of sucrose. Why is sucrose not a reducing sugar ?

Ans. On hydrolysis, sucrose gives equimolar mixture of D-(+)-glucose and D-(−)-fructose. Sucrose is not a reducing sugar as glucose and fructose are linked through their reducing centres in structure of sucrose.

Q. 6. State clearly what are known as nucleotides and nucleosides.

Ans. A nucleoside contain only two basic components of nucleic acids *i.e.,* pentose sugar and nitrogenous base.

A nucleotide contains all the three basic components of nucleic acids *i.e.,* a phosphoric acid group, pentose sugar and nitrogenous base.

Q. 7. Describe what do you understand by primary structure and secondary structure of proteins.

Ans. Primary structure of proteins : The protein in which amino acids linked with each other in a specific sequence is said to be the primary structure of that protein.

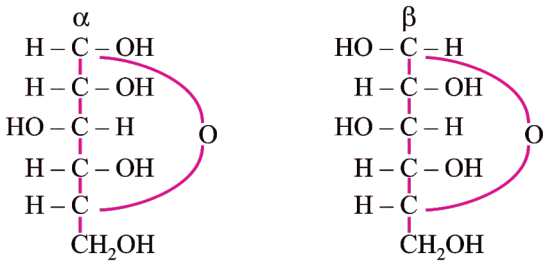
Secondary structure of proteins : It refers to the shape in which a long polypeptide chain can exist *i.e.,* α-helix and β-pleated structure.

Q. 8. What is essentially the difference between α-form of glucose and β-form of glucose ? Explain.

Ans. α-form of glucose and β-form of glucose differ only in the configuration of the hydroxyl group at C_1 in cyclic structure of glucose/hemiacetal form of glucose.

Q. 9. What are anomers ? Give the structures of two anomers of glucose.

Ans. Monosaccharides which differs in configuration at functional *gp-c*-atom (C_1 and C_2), *e.g.,* α-glucose and β-glucose.



α-Glucose β-Glucose

Q. 10. Write the hydrolysed product of :

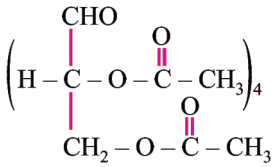
(i) Maltose **(ii) Cellulose**

Ans. (i) α-D-glucose (ii) β-D-glucose

Q. 11. (i) Acetylation of glucose with acetic anhydride gives glucose penta-acetate. Write the structure of penta acetate.

(ii) Explain why glucose penta acetate does not react with hydroxylamine ?

Ans. (i)



Glucose pentaacetate

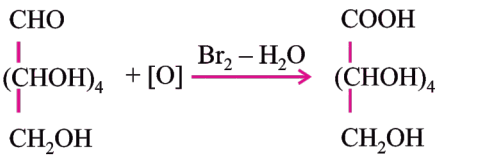
(ii) The molecule of glucose penta acetate has a cyclic structure in which – CHO is involved in ring formation.

Q. 12. Write the products of oxidation of glucose with :

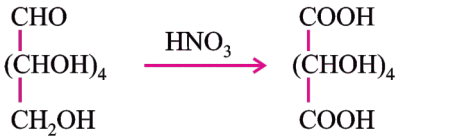
(i) Bromine water

(ii) Nitric acid

Ans. (i)



Glucose Gluconic acid

(ii) 

Glucose Saccharic acid

Q. 13. State two main differences between globular and fibrous proteins.

Ans.

	Globular protein		**Fibrous protein**
(i)	They form a α-helix structure.	(i)	They have β-pleated structure.
(ii)	They are water soluble.	(ii)	They are water insoluble.

Q. 14. What are essential and non-essential amino acid ? Give two examples of each type.

Ans. Essential amino acids are those which are not produced in our body and required to be supplied from outside, *e.g.,* valine, leucine.

Non-essential amino acids are those which are produced by our body, *e.g.,* glycine, alanine.

Q. 15.Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

Ans. Protein albumin present in egg white gets denatured *i.e.,* 2° & 3° structures are destroyed and 1° structure is retained.

Q. 16. Describe two important functions of nucleic acids.

Ans. (i) DNA is responsible for transfer of heredity information from one generation to another.

(ii) RNA is responsible for protein synthesis.

(i) What type of linkage is responsible for the formation of proteins ?

(ii) Write the product formed when glucose is treated with HI.

Ans. (i) Vitamin C.

(i) Peptide linkage.

(ii) n-hexane.

Q.17.Differentiate between the following :

(i) Secondary and tertiary structure of protein

(ii) α-helix and β-pleated sheet structure of protein

(iii) Fibrous and globular protein

Ans. (i) **Secondary structure** is responsible for the shape of protein α-helix and β-pleated sheets in which polypeptide chains have peptide bonds.

Tertiary structure represents overall folding of polypeptide chain and give rise to the fibrous or globular molecular shape.

(ii) **α-helix structure :** The peptide chains coiled up to form right handed helix involving H-bonding (Intramolecular).

β-pleated sheets : The peptide chains lie side by side together by intermolecular hydrogen bonding.

(iii) Same as Q. 16 (Two marks questions)

Q.18.(i) Name the four bases present in DNA.

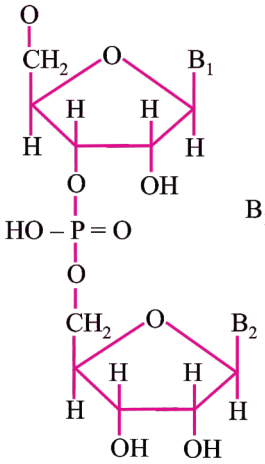
(ii) Which of them is not present in RNA ?

(iii) Give the structure of a nucleotide of DNA.

Ans. (i) Adenine, Guanine, Thymine, Cytosine.

(ii) Thymine.

(iii)



B_1 & B_2 = Nitrogeneous bone (Adenine, guanine, Cytosine or thymine)

Q.19. Glucose or sucrose are soluble in water but cyclohexane and benzene are insoluble in water. Explain.

Ans. Glucose contain 5 – OH groups and sucrose contain eight – OH groups, because of this they form intermolecular hydrogen bonding, so they are soluble in water. But benzene and cyclohexane doesn't contain – OH groups hence doesn't form intermolecular hydrogen bonding, so they are not soluble in water.

Q.20.(i) Fructose contains a keto group but still it reduces Tollen's reagent. Explain.

CBSE STUDY BASED QUESTIONS

PARAGRAPH 1

Read the passage given below and answer the following questions:

Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. Carbohydrates are the main source of energy that is ingested by the human body . Brain mainly utilizes the glucose. Red blood cells also use glucose only. Fiber in the diet is not digested by human body due to lack of cellulase enzyme. Glucose is the major enegy source in the body. Glycogen is the storage form of glucose and glycogen is stored in skeletal muscles and liver. If glucose intake exceeds than it is utilized in the body it is converted into fat. Riboses are utilized in formation of deoxyribonucleic acid . Carbohydrates are polyhydroxy alcohol with potentially active carbonyl group which may be aldehyde or keto group. Carbohydrates can be classified on the basis of carbon atom present in the carbohydrates. Carbohydrates are classified into four types monosaccharides, disaccharides, oligosaccharides, polysaccharides. Monosaccharides cannot be hydrolyzed further into simpler form. They may contain 3-7 carbon atoms but monosaccharides containing 5-6 carbon atoms are more abundant in nature. All monosaccharides reduce Tollen's reagent as well as Fehling's solution and hence are called reducing sugars. Pentoses and hexoses have cyclic structures, Furanose and pyranose. Disaccharides give two monosaccharides on hydrolysis. Polysaccharides may be homopolysaccharides and heteropolysaccharides. Plants produce carbohydrates by photosynthesis. In most animals, carbohydrates are the quickly accessible reservoir of

energy. The main function of carbohydrates is to provide energy, but they also play an important ro:e in the structure and function of the body organs and nerve cells.

The following questions are multiple choice questions. Choose the most appropriate answer:

Q1. Which of the following statements is **not** true about glucose?

(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.

Q2. The α-and β-forms of glucose are

(a) isomers of D(+) glucose and L(–) glucose respectively

(b) anomers of glucose

(c) isomers which differ in the configuration of C-2

(d) isomers which differ in the configuration of C-5

Q3. The monosaccharide constituents of lactose are:

(a) α-D-glucose and b-D-fructose

(b) α-D-glucose only

(c) β-D-glucose only

(d) β-D-glucose and β-D-galactose

Q4. Glycogen is a branched chain polymer of a-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_____.

(a) Amylose (b) Amylopectin

(c) Cellulose (d) Glucose

PARAGRAPH 2

Proteins are very important biomolecules of living systems. α-Amino acids are the building blocks of proteins. About 20 α-amino acids have been isolated by the hydrolysis of proteins. Ten amino acids which the body cannot synthesize are called essential amino acids. The remaining ten are called non-essential amino acids. Proteins are complex nitrogeneous polymers of amino acids connected through peptide bonds. Protein is very important in sports performance as it can boost glycogen storage , reduce muscle soreness and promote muscle repair. For those who are active regularly , there may be benefit from consuming a portion of protein at each mealtime and spreading protein intake throughout the day. Protein intake that exceeds the recommended daily allowance is widely accepted

for both endurance and power athletes. The various techniques utilized to rate protein will be discussed. Traditionally, sources of dietary protein are seen as either being of animal or vegetable origin. Animal sources provide a complete source of protein (i.e. containing all essential amino acids), whereas vegetable sources generally lack one or more of the essential amino acids. Animal sources of dietary protein, despite providing a complete protein and numerous vitamins and minerals, have some health professionals concerned about the amount of saturated fat common in these foods compared to vegetable sources. The advent of processing techniques has shifted some of this attention and ignited the sports supplement marketplace with derivative products such as whey, casein and soy. Individually, these products vary in quality and applicability to certain populations.

The following questions are multiple choice questions. Choose the most appropriate answer:

Q1. Which one of the following statements is correct ?
- (a) All amino acids are optically active
- (b) All amino acids except glycine are optically active.
- (c) All amino acids except glutamic acid are optically active.
- (d) All amino acids except lysine are optically active.

Q2. Proteins are found to have two different types of secondary structures viz. α-helix and β-pleated sheet structure. a-helix structure of protein is stabilised by:
- (a) Peptide bonds
- (b) van der Waals forces
- (c) Hydrogen bonds
- (d) Dipole-dipole interactions

Q3. Which of the following is an example of Globular proteins ?
- (a) Myosin
- (b) Albumin
- (c) Collagen
- (d) Fibroin

Q4. Which of the statements about "denaturation" given below are correct?
- (1) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
- (2) Denaturation leads to the conversion of double strand of DNA into single strand.
- (3) Denaturation affects primary structure which gets distorted.

(a) (2) and (3) (b) (1) and (3)
(c) (1) and (2) (d) (1), (2) and (3)

Paragraph 3

The particles in the nucleus of cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids. Nucleic acids are long chain polymers of nucleotides. Nucleotides are low molecular weight intracellular compounds that play major roles in physiological and biological functions, They act as precursors for nucleic acid synthesis and are also fundamental for intermediary metabolism. The two types of nucleic acids found in the chromosomes of cells of mammals are called 'deoxyribonucleic acid' and 'ribonucleic acid'. They are usually abbreviated as DNA and RNA respectively. As they are found in the nuclus of cells , they are called nucleic acids.Nucleotides and nucleic acids turn over rapidly, especially in growing tissues or those undergoing constant cell renewal. Tissues that grow have a net formation of new DNA and a rapid turnover of RNA . Nucleotides cosist of a nitrogenous base (purine or pyrimidine), a pentose (ribose or deoxyribose), and one or more phosphate groups. The nitrogenous bases are derived from two parent heterocyclic molecules. The major purines found in living organisms are adenine and guanine, while cytosine, thymine, and uracil are the major pyrimidine bases. Nitrogenous bases can be formed from amino acid precursors or reutilized after their release from nucleic acid breakdown via the salvage pathway. The purine ring carbon atoms formed from the dispensable amino acids glycine, glutamic acid, and aspartame. The carbon atoms pyrimidines are derived from carbamoyl phosphate and aspartame. It has been concluded that there are about six billion base pairs in the DNA of a single human cell.

The following questions are multiple choice questions. Choose the most appropriate answer:

Q1. Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?

(a) 5' and 3' (b) 1' and 5'

(c) 5' and 5' (d) 3' and 3'

Q2. In DNA, the complementary bases are:

(a) Uracil and adenine: cytosine and guanine

(b) Adenine and thymine: guanine and cytosine.

(c) Adenine and thymine: guanine and uracil

(d) Adenine and guanine: thymine and cytosine.

Q3. The correct statement regarding RNA and DNA is:

(a) The sugar component RNA is arabinose and sugar in DNA is ribose

(b) The sugar component in RNA is 2rdeoxyribose and the sugar component in DNA is arabinose.

(c) The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose.

(d) The sugar component in RNA is ribose and sugar component in DNA is 2' deoxyribose

Q4. Which one of the following is not present in RNA ?

(a) Uracil (b) Ribose

(c) Thymine (d) Phosphate

ANSWERS

I 1. (b) 2. (b) 3. (a) 4. (c) 5. (a) 6. (c) 7. (c) 8. (b) 9. (b) 10. (a) 11. (c) 12. (c) 13. (c) 14. (c) 15. (b) 16. (a)-(q, s), (b) -(r) (c)-(q), (d)-(p) 17. (a)-(p, q), (b)-(p), (c)-(s), (d)-(r) 18. b

II 1. Amylose 2. n-Hexane 3. α-D-glucose 4. Adenine and guanine 5. Peptide linkage. 6. Vitamin B_{12} 7. Uracil 8. Vitamin K. 9. Gluconic acid 10. Glycogen.

III 1. Vitamin B 2. Vitamin C 3. Cellulose 4. Lactose 5. Starch 6. Polysaccharides 7. Reducing sugars 8. vitamin A 9. Nucleoside, nucleotide 10. Anomers

IV 1. (c) 2. (a) 3. (c) 4. (a) 5. (c) 6. (a) 7. (b) 8. (a) 9. (b) 10. (d)

CASE STUDY BASED QUESTIONS

PARAGRAPH 1 : 1. (c) 2. (b) 3. (d) 4. (b)

PARAGRAPH 2 : 1. (b) 2. (c) 3. (b) 4. (c)

PARAGRAPH 3: 1. (b) 2. (b) 3. (d) 4. (c)

UNIT TEST
CHAPTER - 14

M.M. : 20 **Time Allowed : 1 Hours**

1. Name polysaccharide which is stored in the liver of animals. (1)
2. Name the enantiomer of D-glucose. (1)
3. Why is sucrose called invert sugar? (1)
4. Name the building blocks of proteins. (1)
5. Give the structure of simplest optically active amino acid. (1)
6. What are anomers? Give the structures of two anomers of glucose. (2)
7. Write the hydrolysed products of (2)
   (i) maltose (ii) cellulose
8. What are vitamins? How are they classified? (2)
9. What do you understand by (3)
   (a) denaturation of protein?
   (b) specificity of an enzyme?
10. Differentiate between the following: (3)
    (1) secondary and tertiary structure of protein.
    (ii) a-Helix and b-pleated sheet structure of protein.
    (iii) fibrous and globular proteins.
11. (i) Name four bases present in DNA. (3)
    (ii) Which of them is not present in RNA.
    (iii) Give the structure of a nucleotide of DNA.

CBSE Sample Question Paper 2021-22

Term 1

Subject: Chemistry (043)

Time: 90 Minutes **Max. Marks: 35**

General Instructions:

1. The Question Paper contains three sections.
2. Section A has 25 questions. Attempt any 20 questions.
3. Section B has 24 questions. Attempt any 20 questions.
4. Section C has 6 questions. Attempt any 5 questions.
5. All questions carry equal marks.
6. There is no negative marking.

SECTION A

This section consists of 25 multiple choice questions with overall choice to attempt **any 20** questions. In case more than desirable number of questions are attempted, ONLY first 20 will be considered for evaluation.

1. Which of the following statements is true:

(a) melting point of phosphorous is less than that of nitrogen

(b) N_2 is highly reactive while P_4 is inert

(c) nitrogen shows higher tendency of catenation than P

(d) N-N is weaker than P-P

2. Which of the following is a non-stoichiometric defect?

(a) Frenkel defect

(b) Schottky defect

(c) metal deficiency defect

(d) interstitial defect

3. Identify the law which is stated as:

"For any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction."

(a) Henry's law

(b) Raoult's law

(c) Dalton's law

(d) Gay-Lussac's Law

4. Pink colour of LiCl crystals is due to:

(a) Schottky defect

(b) Frenkel defect

(c) metal excess defect

(d) Metal deficiency defect

5. Which of the following isomer has the highest melting point:
(a) 1,2-dicholorbenzene
(b) 1,3 -dichlorobenzene
(c) 1,4-dicholorbenzene
(d) all isomers have same melting points
6. Which one of the following reactions is not explained by the open chain Structure of glucose:
(a) formation of pentaacetate of glucose with acetic anhydride.
(b) formation of addition product with 2,4-DNP reagent
(c) silver mirror formation with Tollen's reagent
(d) existence of alpha and beta forms of glucose.
7. Williamson's synthesis of preparing dimethyl ether is an:
(a) S_N^1 reaction
(b) elimination reaction
(c) S_N^2 reaction
(d) nucleophilic addition reaction
8. Chlorine water loses its yellow colour on standing because:
(a) HCl gas is produced, due to the action of sunlight.
(b) a mixture of HOCl and HCl is produced in the presence of light
(c) HOCl and hydrogen gas is produced
(d) a mixture of HCl and ClO_3 is produced, due to the action of sunlight
9. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is:
(a) protonation of alcohol molecule
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester
10. Amorphous solids are:
(a) isotropic
(b) anisotropic
(c) isotopic
(d) isomeric
11. Which of the following reactions is used to prepare salicylaldehyde?
(a) Kolbe's reaction
(b) Etard reaction

(c) Reimer- Tiemann reaction
(d) Stephen's reduction.
12. Which of the following is an example of a solid solution?
(a) sea water
(b) sugar solution
(c) smoke
(d) 22 carat gold
13. The boiling points of alcohols are higher than those of hydrocarbons of comparable masses due to:
(a) hydrogen bonding
(b) ion – dipole interaction
(c) dipole- dipole interaction
(d) van der Waal's forces.
14. Which of the following has the lowest boiling point:
(a) H_2O
(b) H_2S
(c) H_2Se
(d) H_2Te
15. Which of the following statement is correct:
(a) Fibrous proteins are generally soluble in water
(b) Albumin is an example of fibrous proteins
(c) In fibrous proteins, the structure is stabilised by hydrogen bonds and disulphide bonds
(d) pH does not affect the primary structure of protein.
16. Major product obtained on reaction of 3-Phenyl propene with HBr in presence of organic peroxide
(a) 3- Phenyl-1- bromopropane
(b) 1 –Phenyl -3- bromopropane
(c) 1-Phenyl -2-bromopropane
(d) 3-Phenyl -2- bromopropane
17. Which of the following is a correct statement for C_2H_5Br?
(a) it reacts with metallic Na to give ethane.
(b) it gives nitroethane on heating with aqueous solution of $AgNO_2$
(c) it gives C_2H_5OH on boiling with alcoholic potash.
(d) it forms diethylthioether on heating with alcoholic KSH.

18. Covalency of nitrogen is restricted to:

(a) 2 (b) 3

(c) 4 (d) 5

19. Solubility of gases in liquids decreases with rise in temperature because dissolution is an:

(a) endothermic and reversible process

(b) exothermic and reversible process

(c) endothermic and irreversible process

(d) exothermic and irreversible process

20. All elements of Group 15 show allotropy except:

(a) nitrogen

(b) arsenic

(c) antimony

(d) bismuth

21. Which of the following is a polysaccharide?

(a) glucose

(b) maltose

(c) glycogen

(d) lactose

22. Substance having the lowest boiling point:

(a) Hydrogen

(b) Oxygen

(c) Nitrogen

(d) Helium

23. Lower molecular mass alcohols are:

(a) miscible in limited amount of water

(b) miscible in excess of water

(c) miscible in water in all proportions

(d) immiscible in water

24. Maximum oxidation state exhibited by chlorine is:

(a) +1 (b) +3

(c) +5 (d) +7

25. In which of the following cases blood cells will shrink:

(a) when placed in water containing more than 0.9% (mass/ volume) NaCl solution.

(b) when placed in water containing less than 0.9% (mass /volume) NaCl solution.

(c) when placed in water containing 0.9% (mass/volume) NaCl solution.

(d) when placed in distilled water.

SECTION B

This section consists of 24 multiple choice questions with overall choice to attempt any 20 questions. In case more than desirable number of questions are attempted, only first 20 will be considered for evaluation.

26. How much ethyl alcohol must be added to 1 litre of water so that the solution will freeze at– 14°C ? (K_f for water = 1.86°C/mol)

(a) 7.5 mol

(b) 8.5 mol

(c) 9.5 mol

(d) 10.5 mol

27. Which reagents are required for one step conversion of chlorobenzene to toluene?

(a) $CH_3Cl / AlCl_3$

(b) CH_3Cl, Na, Dry ether

(c) CH_3Cl/Fe dark

(d) $NaNO_2$/ HCl /0-5^{0}C

28. On partial hydrolysis, XeF_6 gives:

(a) XeO_3 +4HF

(b) XeO_2F + HF

(c) $XeOF_4$ + H_2

(d) XeO_2F_2 + 4HF

29. Which one of the following statement is correct about sucrose :

(a) It can reduce tollen's reagent however cannot reduce fehling's reagent

(b) It undergoes mutarotation like glucose and fructose

(c) It undergoes inversion in the configuration on hydrolysis

(d) It is laevorotatory in nature.

30. Phenol does not undergo nucleophilic substitution reaction easily due to:

(a) acidic nature of phenol

(b) partial double bond character of C-OH bond

(c) partial double bond character of C-C bond

(d) instability of phenoxide ion

31. Which of the following has highest ionisation enthalpy?

(a) Nitrogen

(b) Phosphorus

(c) Oxygen

(d) Sulphur

32. Metal M ions form accp structure. Oxide ions occupy ½ octahedral and ½ tetrahedral voids. What is the formula of the oxide?

(a) MO (b) MO_2

(c) MO_3 (d) M_2O_3

33. The reaction of toluene with Cl_2 in presence of FeCl3 gives 'X' while theof toluene with Cl_2in presence of light gives 'Y'. Thus 'X' and 'Y' are:

(a) X = benzyl chloride Y = o and p – chlorotoluene

(b) X = m – chlorotoluene Y = p – chlorotoluene

(c) X = o and p–chlorotoluene Y = trichloromethylbenzene

(d) X= benzyl chloride, Y = m-chlorotoluene

34. Ozone is a/ an_____molecule and the two O-O bond lengths in ozone_____are (i)_____and (ii)_____

(a) linear, 110pm ; 148pm

(b) angular, 110pm ; 148pm

(c) linear, 128pm ; 128pm

(d) angular, 128pm ; 128pm

35. Water retention or puffiness due to high salt intake occurs due to:

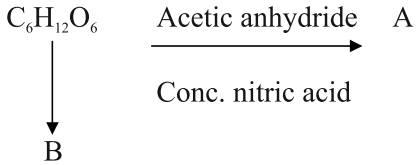
(a) diffusion

(b) vapour pressure difference

(c) osmosis

(d) reverse osmosis

36. In the following reaction,identify A and B:



(a) A= $COOH-(CH_2)_4-COOH$, B= $OHC-(CHOCOCH_3)_4-CH_2OCOCH_3$

(b) A= $COOH-(CH_2)_4-CHO$, B= $OHC-(CHOCOCH_3)_4-CH_2OCOCH_3$

(c) A= $OHC-(CHOCOCH_3)_3-CH_2OCOCH_3$ B= $COOH-(CH_2)_4-CHO$,

(d) A= $OHC-(CHOCOCH_3)_4-CH_2OCOCH_3$ B= $COOH-(CH_2)_4-COOH$

37. In lake test for Al^{3+} ions, there is the formation of coloured 'floating lake'. It is due to:

(a) Absorption of litmus by $[Al(OH)_4]^-$

(b) Absorption of litmus by $Al(OH)_3$

(c) Adsorption of litmus by $[Al(OH)_4]^-$

(d) Adsorption of litmus by $Al(OH)_3$

38. A unit cell of NaCl has 4 formula units. Its edge length is 0.50 nm. Calculate the density if molar mass of NaCl = 58.5 g/mol.

(a) 1 g/cm^3 (b) 2 g/cm^3

(c) 3 g/cm^3 (d) 4 g/cm^3

39. Which one of the following are correctly arranged on the basis of the property indicated:

(a) $I_2 < Br_2 < F_2 < Cl_2$ [increasing bond dissociation enthalpy]

(b) $H_2O > H_2S < H_2Te < H_2Se$ [increasing acidic strength]

(c) $NH_3 < N_2O < NH_2OH < N_2O_5$ [increasing oxidation state]

(d) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$ [increasing bondangle]

40. What would be the reactant and reagent used to obtain 2, 4-dimethylpentan-3-ol?

(a) propanal and propyl magnesium bromide

(b) 3-methylbutanal and 2-methyl magnesium iodide

(c) 2-dimethylpropanone and methyl magnesium iodide

(d) 2- methylpropanal and isopropyl magnesium iodide

41. o-hydroxy benzyl alcohol when reacted with PCl_3 gives the product as (IUPAC name)

(a) o- hydroxy benzyl chloride

(b) 2- chloromethylphenol

(c) o-chloromethylchlorobenzene

(d) 4-hydroxymethylphenol

42. Which of the following statements is true:

(a) Ammonia is the weakest reducing agent and the strongest base among Group 15 hydrides.

(b) Ammonia is the strongest reducing agent as well as the strongest base among Group 15 hydrides.

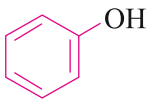
(c) Ammonia is the weakest reducing agent as well as the weakest base among Group 15 hydrides.

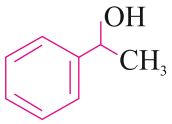
(d) Ammonia is the strongest reducing agent and the weakest base among Group 15 hydrides.

43. Identify the secondary alcohols from the following set:

(i) $CH_3CH_2CH(OH)CH_3$

(ii) $(C_2H_5)_3COH$

(iii) 

(iv) 

(a) (i) and (iv)

(b) (i) and (iii)

(c) (i) and (ii)

(d) (i), (iii) and (iv)

44. Alkenes decolourise bromine water in presence of CCl_4 due to formation of:

(a) allyl bromide

(b) vinyl bromide

(c) bromoform

(d) vicinal dibromide

45. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Electron gain enthalpy of oxygen is less than that of Flourine but greater than Nitrogen.

Reason (R): Ionisation enthalpies of the elements follow the order Nitrogen >Oxygen > Fluorine

Select the most appropriate answer from the options given below:

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A.

(c) A is true but R is false.

(d) A is false but R is true.

46. Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion (A): Alkyl halides are insoluble in water.
Reason (R): Alkyl halides have halogen attached to sp3 hybrid carbon. Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

47. Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion(A): Molarity of a solution changes with temperature.
Reason (R): Molarity is a colligative property.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

48. Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion(A): SO_2 is reducing while TeO_2 is an oxidising agent.
Reason(R): Reducing property of dioxide decreases from SO_2 to TeO_2.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

49. Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion (A):Cryoscopic constant depends on nature of solvent.
Reason(R):Cryoscopic constant is a universal constant.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

SECTION C

This section consists of 6 multiple choice questions with an overall choice to attempt any5. In case more than desirable number of questions are attempted, ONLY first 5 will be considered for evaluation.

50. Match the following:

I	II
(i) Amino acids	(A) Protein
(ii) Thymine	(B) Nucleic acid
(iii) Insulin	(C) DNA
(iv) Phosphodiester linkage	(D) Zwitter ion
(v) Uracil	

Which of the following is the best matched options?

(a) i-A, v- D, iii- C, iv-B

(b) i-D, ii-C, iii- A, iv-B

(c) i-D, v- D, iii- A, iv-B

(d) i-A, ii- C, iii- D, iv-B

51. Which of the following analogies is correct:

(a) Nitrogen: $1s^2 2s^2 2p^3$ :: Argon: $1s^2 2s^2 2p^6$

(b) Carbon: maximum compounds :: Xenon: no compounds

(c) XeF_2: Linear :: ClF_3: Trigonal planar

(d) Helium: meteorological observations:: Argon: metallurgical processes

52. Complete the following analogy:

Same molecular formula but different structures: A:: Non superimposable mirror images: B

(a) A:Isomers B: Enantiomer

(b) A: Enantiomers B: Racemic mixture

(c) A: Sterioisomers B: Retention

(d) A: Isomers B: Sterioisomers

CASE1: Read the passage given below and answer the following questions 53-55

Early crystallographers had trouble solving the structures of inorganic solids using X-ray diffraction because some of the mathematical tools for analyzing the data had not yet been developed. Once a trial structure was proposed, it was relatively easy to calculate the

diffraction pattern, but it was difficult to go the other way (from the diffraction pattern to the structure) if nothing was known a priori about the arrangement of atoms in the unit cell. It was important to develop some guidelines for guessing the coordination numbers and bonding geometries of atoms in crystals. The first such rules were proposed by Linus Pauling, who considered how one might pack together oppositely charged spheres of different radii.

Pauling proposed from geometric considerations that the quality of the "fit" depended on the radius ratio of the anion and the cation.

If the anion is considered as the packing atom in the crystal, then the smaller cation fills interstitial sites ("holes"). Cations will find arrangements in which they can contact the largest number of anions. If the cation can touch all of its nearest neighbour anions then the fit is good. If the cation is too small for a given site, that coordination number will be unstable and it will prefer a lower coordination structure. The table below gives the ranges of cation/anion radius ratios that give the best fit for a given coordination geometry.

Coordination number	Geometry	$\rho = r_{cation}/R_{anion}$
2	linear	0 - 0.155
3	triangular	0.155 - 0.225
4	tetrahedral	0.225 - 0.414
4	square planar	0.414 - 0.732
6	octahedral	0.414 - 0.732
8	cubic	0.732 - 1.0
12	cuboctahedral	1.0

(Source: Ionic Radii and Radius Ratios. (2021, June 8). Retrieved June 29, 2021, from https://chem.libretexts.org/@go/page/183346)

Q53. The radius of Ag^+ ion is 126pm and of I^- ion is 216pm. The coordination number of Ag^+ ion is:

(a) 2

(b) 3

(c) 6

(d) 8

Q54. A solid AB has square planar structure. If the radius of cation A^+ is 120pm, calculate the maximum possible value of anion B^-

(a) 240 pm

(b) 270 pm

(c) 280 pm

(d) 290 pm

Q55. A "good fit" is considered to be one where the cation can touch:

(a) all of its nearest neighbour anions.

(b) most of its nearest neighbour anions.

(c) some of its nearest neighbour anions.

(d) none of its nearest neighbour anions.

CHEMISTRY (043)

Marking Scheme

SECTION A

1. (d) N-N is weaker than P-P

other statements as incorrect as Phosphorus has a higher melting point due to bigger size than Nitrogen. Nitrogen is inert due to formation of triple bonds and has a lower covalence due to non - availability of d–orbitals

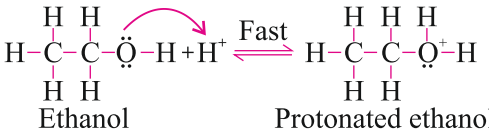
2. (c) metal deficiency defect (anion is missing from lattice site)

In Frenkel defect the smaller ion occupies the interstitial sites and Schottky defect equal number of cations and anions are missing. Interstitial defect an atom or molecule occupies intestinal sites so in these three defects the ratio of positive and negative ions (Stoichiometric) of a solid is not disturbed in these three

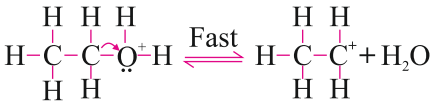
3. (b) Raoult's law
4. (c) Metal excess defect (formation of F centres)
5. (c) 1,4-dicholorbenzene (para isomers are more symmetric and ortho and meta)
6. (d) existence of alpha and beta forms of glucose .
7. (c) S_N^2 reaction (alkoxide ion reacts with primary alkyl halide in a single step to form ether)
8. (b) a mixture of HOCl and HCl is produced in the presence of sunlight

   $Cl_2(g) + H_2O(l) \rightarrow HCl(g) + HOCl(aq)$
9. (a) protonation of alcohol molecule

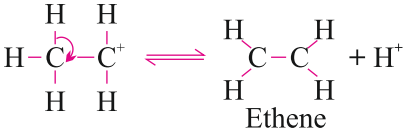
Step 1 : Formation of protonation alcohol



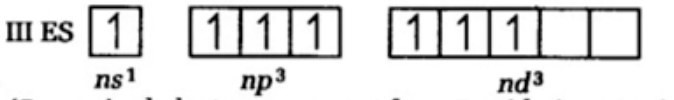
Step 2 : Formation of carbocation it is the slowest step and hence the determining step of the reaction



Step 3 : Formation of ethene by of a proton



12. (d) 22 carat gold (it is an alloy so solid in solid solution)
13. (a) Hydrogen bonding (alcohols form intermolecular hydrogen bonds)
14. (b) H_2S (boiling point increases down the group but water forms strong hydrogen bonds so has higher boiling point than H_2S)
15. (d) pH does not affect the primary structure of protein (pH effects the tertiary structure)
16. (b) 1 –Phenyl -3- bromopropane
    $(C_6H_5)CH_2CH=CH_2$ + HBr (organic peroxide) → $(C_6H_5)CH_2CH_2CH_2Br$ (anti-Markovnikov addition)
17. (b) It gives nitroethane on heating with aqueous solution of $AgNO_2$
    (C_2H_5Br reacts with metallic Na to give butane, gives ethene on boiling with alcoholic potash. and forms C_2H_5SH (thiol) on heating with alcoholic KSH)
18. (c) 4 (Covalency of nitrogen is restricted to 4 due to non availability of d orbitals)
19. (b) Exothermic and reversible process (according to Le -Chatlier principle Solubility of gases in liquids decreases with rise in temperature)
20. (a) Nitrogen (due to small size and high electronegativity N-N is weak)
21. (c) Glycogen (It is a polymer of glucose)
22. (d) Helium (He is monoatomic and has low atomic mass)
23. (c) Miscible in water in all proportions Lower molecular mass alcohols are able to form hydrogen bonds with water
24. (d) +7 (Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$)



(7 unpaired electrons account for +7 oxidation state)

25. (a) When placed in water containing more than 0.9% (mass/ volume) NaCl solution because fluid inside blood cells is isotonic with 0.9% NaCl solution

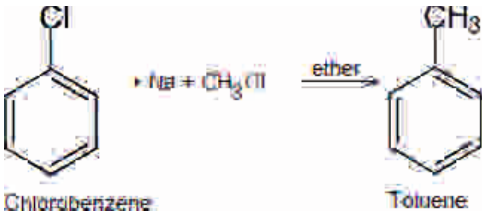
SECTION B

26. (a) 7.5 mol
    $\Delta T_f = K_f m$
    $\Delta T_f = \frac{K_f n2 \times 1000}{W1}$

$14 = \frac{1.86 \times n2 \times 1000}{1000}$

n2 = 7.5 mol

27. (b) CH_3Cl, Na, Dry ether



28. (d) $XeO_2F_2 + 4HF$

$XeF_4 + H_2O \rightarrow XeO_2F_2 + 4HF$

29. (c) It undergoes inversion in the configuration on hydrolysis

30. (b) Partial double bond character of C-OH bond

31. (a)Nitrogen (High IE of N is because of smallest size in the group and completely half - filled p subshell)

32. (d) M2O3

Metal M ions form ccp structure. Let number of ions of M be : X No. of tetrahedral voids = 2x

No. of octahedral voids = x

Number of oxide ions will be 1/2 x + ½ (2x) = 3/2 x

Formula of oxide = MxO3/2 x = M_2O_3

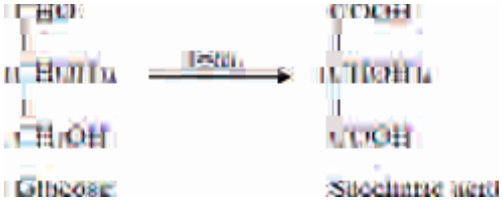
33. (c) X = o and p–chlorotoluene Y = trichloromethylbenzene

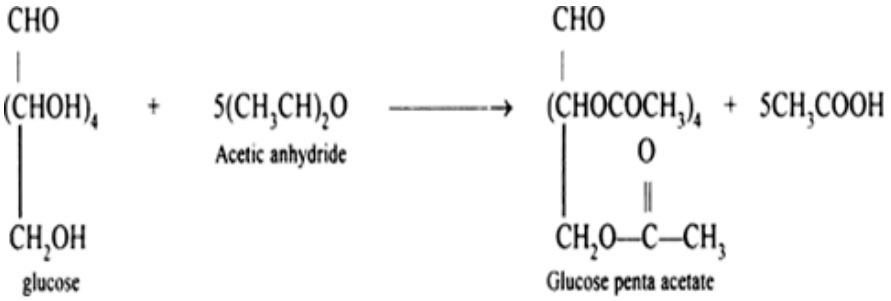
The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' due to electrophilic substitution reaction taking place at ortho and para positions and reaction in the presence of light gives 'Y', due to substitution reaction occurring via free radical mechanism. Thus 'X' and 'Y' are X = o and p–chlorotoluene Y = trichloromethylbenzene

34. (d) angular, 128pm ; 128pm (Ozone is a resonance hybrid of two equivalent structures)

35. (c) Osmosis

36. (d) A= $OHC\text{-}(CHOCOCH_3)_4\text{-}CH_2OCOCH_3$ B= $COOH\text{-}(CH_2)_4\text{-}COOH$





37. (d) Adsorption of litmus by $Al(OH)_3$

In lake test for Al^{3+} ions, there is the formation of coloured 'floating lake' In lake test for Al^{3+} ions, there is the formation of coloured 'floating lake' due to adsorption

38. (c) 3 g/cm^3

Using formula

$$\text{Density} = \frac{(Z \times m)}{(a^3 \times Na)}$$

$$d = \frac{4 \times 58.5}{(0.5 \times 10^{-7})^3 \times 6.023 \times 10^{23}} = 3.1 \text{ g/cm3}$$

39. (d) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$ [increasing bond angle] correct order

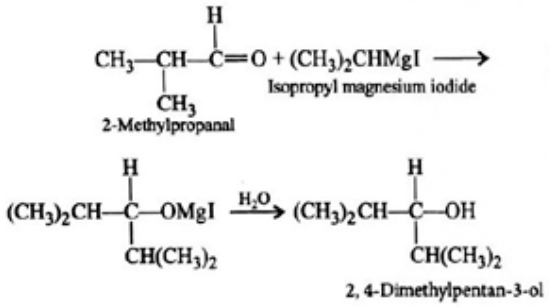
(a) $I_2 < Br_2 < F_2 < Cl_2$ [increasing bond dissociation enthalpy]: incorrect order , correct order is $Cl_2 > Br_2 > F_2 > I_2$.

(b) $H_2O > H_2S < H_2Te < H_2Se$ [increasing acidic strength]: incorrect order , correct order is

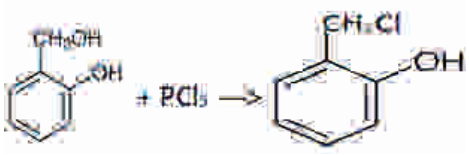
$H_2O < H_2S < H_2Se < H_2Te$

(c) $NH_3 < N_2O < NH_2OH < N_2O_5$ [increasing oxidation state] : incorrect order NH_3 (Oxidation state -3) N_2O (Oxidation state +1) NH_2OH(Oxidation state -1) N_2O_5 (Oxidation state +5)

40. (d) 2- methylpropanal and isopropyl magnesium iodide



41. (b) 2- Chloromethylphenol

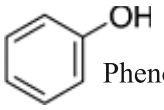


42. (a)Ammonia is the weakest reducing agent and the strongest base among Group 15 hydrides. The reducing character of hydrides increases down the group due to decrease in bond dissociation enthalpy.

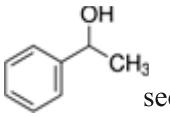
43 (a) (i) and (iv)

(i) $CH_3CH_2CH(OH)CH_3$ (secondary)

(ii) $(C_2H_5)_3COH$ (tertiary)

(iii) 

Phenol not an alcohol

(iv) 

secondary

44. (d)Vicinal dibromide

$CH_2=CH_2 + Br_2 \rightarrow BrCH_2 - CH_2Br$

45. **(c)**

Assertion: Electron gain enthalpy of oxygen is less than that of Flourine but greater than Nitrogen. (correct)

Reason: Ionisation enthalpies of the elements follow the order Nitrogen > Oxygen > Fluorine (incorrect)

Ionisation enthalpies of the elements follow the order Fluorine >Nitrogen > Oxygen

46. (b) Assertion: Alkyl halides are insoluble in water. (correct)

Reason: Alkyl halides have halogen attached to sp^3 hybrid carbon. (correct)

Alkyl halides are insoluble in water because they are unable to form hydrogen bonds with water or break pre-existing hydrogen bonds.

47. (c) Assertion: Molarity of a solution changes with temperature. (correct)
Reason: Molarity is a colligative property. (incorrect)
Molarity is a means to express concentration. It is not a physical property.

48. (a) Assertion: SO_2 is reducing while TeO_2 is an oxidising agent. (correct)
Reason: Reducing property of dioxide decreases from SO_2 to TeO_2 (correct and reason for Assertion)

49. (c) Assertion: Cryoscopic constant depends on nature of solvent. (correct)
Reason: Cryoscopic constant is a universal constant (incorrect) Cryoscopic constant various with type of solvent

SECTION C

50. (b) i-D, ii-C, iii- A, iv-B

Amino acids form proteins and exist as zwitter ion , Thymine is a nitrogenous base in DNA, Insulin is a protein , phosphodiester linkage is found in nucleic acids so also in DNA and Uracil is nitrogenous base found in RNA which is a nucleic acid.

51. (d) Helium: meteorological observations :: Argon: metallurgical processes Nitrogen: $1s^2 2s^2 2p^3$ :: Argon: $1s^2 2s^2 2p^6$ is configuration of Neon not Argon Carbon: maximum compounds :: Xenon: no compounds , Xenon forms compounds XeF_2: Linear :: ClF_3: Trigonal planar , ClF_3 is T shaped not trigonal planar

52. (a) A : Isomers B: Enantiomer

Isomers have Same molecular formula but different structure Enantiomers are Non superimposable mirror images

53. (c) 6

The radius of Ag^+ ion is 126pm and of I^- ion is 216pm. The coordination number of Ag^+ ion is:
$\rho = r_{cation}/r_{anion} = 126/216 = 0.58$

Radius ratio lies in the range 0.414 – 0.732, so has coordination number 6 or 4 according to the table.

Since none of the options is 4, so the answer is 6

54. (d) 290 pm

Square planar means ratio ratio is between 0.414 – 0.732

If radius of cation is 120 pm then anion should be in the range ρ = rcation/ranion 0.414 = 120/ x so x = 289.8 = 290 pm 0.732 = 120/ x so x = 163.9 = 164 pm

55. (a) all of its nearest neighbour anions.

PRACTICE PAPER (TERM-1)

Subject : Chemistry

Maximum Marks : 35 **Time : 90 minutes**

General Instructions:

- The Question Paper contains three sections.
- Section A has 25 questions. Attempt any 20 questions.
- Section B has 24 questions. Attempt any 20 questions.
- Section C has 6 questions. Attempt any 5 questions.
- All questions carry equal marks.
- There is no negative marking.

[SECTION A]

This section consists of 25 multiple choice questions with overall choice to attempt any 20 questions. In case more than desirable number of questions are attempted, only first 20 will be considered for evaluation.

1. Dissolution of potassium dichromate in water is exothermic. On increasing the temperature, solubility of potassium dichromate in water will-

a) increases b) decreases

c) no change d) unpredictable

2. The Henry's law constants (in kbar) for three gases P, Q, R and S for water as solvent are 144, 46, 40 and 0.413 respectively. The gas with highest solubility in water is-

a) P b) Q

c) R d) S

3. Consider two solids A and B:

Solid A is hard and malleable, conductor of electricity in solid as well as in molten state. Solid B is hard and brittle and conducts electricity in molten state but not in solid. A and B are …….. and.....respectively.

a) NaCl, Iron b) Graphite, diamond

c) Copper, $MgCl_2$ d) ZnS, graphite

4. Colligative properties depend on -

a) the nature of the solute particles dissolved in solution.

b) the number of solute particles in solution.

c) the physical properties of the solute particles dissolved in solution.

d) the nature of solvent particles.

5. Which of the the following is incorrect regarding ideal solutions ?

a) $\Delta H_{mix} = 0$ b) $\Delta G_{mix} = 0$

c) $\Delta V_{mix} = 0$ d) Follows Raoult's Law over entire range of concentration

6. Which of the following is not a constituent base of DNA?

a) Adenine b) Guanine

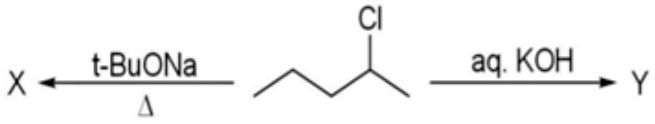
c) Cytosine d) Uracil

7. The haloalkane which undergoes nucleophilic substitution reaction with inversion of the configuration:

a) 1-Chloropropane b) Chlorobenzene

c) 2-Chloropropane d) 2-Chlorobutane

8. In given reactions, X and Y are respectively-



a) Pent-1-ene, Pent-2-ene b) Pent-2-ene, Pentan-2-ol

c) Pentan-2-ol, Pent-2-ene d) Pent-1-ene, Pentan-2-ol

9. Phenol on reaction with bromine water forms-

a) Colourless, 2-bromophenol

b) Dark coloured mixture of 2-bromophenol and 4-bromophenol

c) White precipitate of 2,4,6-tribromophenol

d) Yellow colouration of 2,4-dibromophenol

10. The α and β forms of D (+)-glucose are known as -

a) Enantiomers b) Anomers

c) Epimers d) Diastereomers

11. α-amino acid which is optically inactive is-

a) Lysine b) Phenylalanine

c) Valine d) Glycine

12. The correct order of acidic strength is-

a) HF > HCl > HBr > HI b) HI > HBr > HCl > HF

c) HCl > HF > HBr > HI d) HF > HBr > HCl > HI

13. Compound with the square pyramidal geometry and sp^3d^2 hybridisation is:

a) $XeOF_2$ b) $XeOF_4$

c) XeO_4 d) XeO_2F_2

14. Number of S=O bonds and S-O bonds in sulphuric acid are …. and …. respectively.

a) 1, 3 b) 2, 1

c) 2, 2 d) 3, 1

15. Which of the following is incorrect about noble gases?

a) Highly unreactive b) low boiling point

c) Large positive electron gain enthalpy d) Very low ionization enthalpy

16. Which of the following element has lowest ionization enthalpy?

a) N b) O

c) F d) Ne

17. Cu(II) on reaction with aqueous NH_3 forms-

a) colourless complex b) deep blue complex

c) white precipitate d) yellow precipitate

18. Covalence of nitrogen in dinitrogen pentoxide is-

a) 2 b) 3

c) 4 d) 5

19. Which of the following combination will give 2-methylpropan-1-ol ?

a) $HCHO + (CH_3)_2$-CHMgBr b) $HCHO + CH_3CH_2CH_2MgBr$

c) $CH_3CHO + CH_3CH_2MgBr$ c) 2-methylprop-1-ene + dilute H_2SO_4

20. Stereoisomers related by non-superimposable mirror images are termed as-

a) Enantiomers b) Anomers

c) Epimers d) Diastereomers

21. A racemic mixture has optical rotation.

a) positive b) negative

c) zero d) fixed

22. Sugar present in DNA is-

a) Ribose b) Deoxyribose

c) Glucose d) Sucrose

23. The reaction through which phenol is converted into salicylic acid is-

a) Kolbe's b) Reimer-Tiemann

c) Williamson d) Sandmeyer

24. Which of the following is not a characteristic of a crystalline solid?

a) Definite and characteristic heat of fusion.

b) Isotropic nature.

c) A regular arrangement of constituent particles.

d) A true solid

25. A solid structure is made up of two elements Q and R. Q occupies all the corners, R occupies half of the face centres of the lattice structure. What will be formula of solid?

a) QR b) QR_2

c) Q_2R_3 d) Q_3R_2

[SECTION B]

This section consists of 24 multiple choice questions with overall choice to attempt any 20 questions. In case more than desirable number of questions are attempted, only first 20 will be considered for evaluation.

26. Which of the following solution will exhibit negative deviation from Raoult's law?

a) Chloroform+Water b) Acetic acid+Toluene

c) Aniline+Phenol d) Methanol+Chloroform

27. Which of the following is non-reducing sugar?

a) Sucrose b) maltose

c) glucose d) fructose

28. Keratin present in hair is an example of -

a) Fibrous protein b) Globular protein

c) Conjugated protein d) Derived Protein

29. Which of the following statement is incorrect about D-Fructose?

a) It is a reducing sugar.

b) It reacts with hydroxylamne and HCN but not with 2,4-dinitrophenylhydrazine.

c) It has a furanose structure.

d) It is an aldohexose.

30. The shape of BrF_3 is-

a) Trigonal Planar b) Bent-T

c) Pyramidal d) Tetrahedral

31. Halide with maximum covalent character is-

a) HI b) $SnCl_4$

c) $SnCl_2$ d) SnI_2

32. Which of the following is not an appropriate reason for anomalous behaviour of fluorine?

a) very small size b) high F-F bond enthalpy

c) non-availability of d orbitals d) highest electronegativity

33. The stoichiometric defect which does not alters the density of solid is-

a) Frenkel b) Schottky

c) Vacancy d) Metal excess

34. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to -

a) low temperature

b) low atmospheric pressure

c) high atmospheric pressure

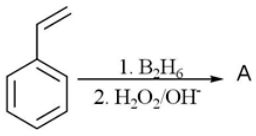
d) both low temperature and high atmospheric pressure

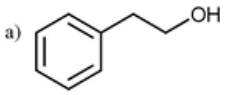
35. Dissolving 120 g of urea (molar mass 60 g/mol) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is-

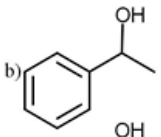
a) 1.78 M b) 2.00 M

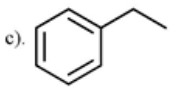
c) 2.05 M d) 2.22 M

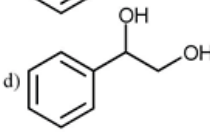
36. Product A in following reaction will be-



a) 

b) 

c). 

d) 

37. Phenol may be distinguished from ethanol by reaction with-

a) $FeCl_3$ b) Bromine water

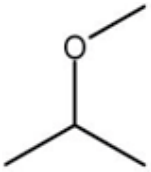
c) both of these d) None of these

38. Best reagent(s) to convert but-2-en-1-ol into but-2-enal is-

a) CrO_3 b) PCC

c) Pd/C d) $K_2Cr_2O_7/H^+$

39. IUPAC name of following compound is-



a) 1-methoxy-1-methyl ethane b) 2-methoxy-2-methyl ethane

c) 2-methoxypropane d) Isopropylmethyl ether

40. Which is the correct increasing order of boiling points of the following compounds?

a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane

b) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane

c) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene

d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

41. Which of the following has highest pK_a value?

a) Phenol b) p-nitrophenol

c) o-nitrophenol d) o-cresol

42. In the preparation of compounds of Xe, Bartlett had taken $O_2^+ PtF_6^-$ as a base compound because:

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 ionization enthalpy

d) both Xe and O_2 are gases.

For questions (43 to 49), a statement of assertion followed by a reason is given. Choose the correct answer out of the following choices:

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.

43. **ASSERTION :** Soda bottles are sealed under high pressure.

REASON : Solubility of gas in liquid is directly proportional to the pressure.

44. **ASSERTION:** Glucose on reaction with acetic anhydride forms pentaacetate.
REASON: Glucose contains five -OH groups.

45. **ASSERTION :** SF_6 cannot be hydrolysed but SF_4 can be.
REASON : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6.

46. **ASSERTION :** When NaCl is added to water a elevation in freezing point is observed.
REASON : The lowering of vapour pressure of a solution causes depression in the freezing point.

47. **ASSERTION :** *p*-nitrophenol is less acidic than phenol.
REASON : Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

48. **ASSERTION :** Treatment of chloroethane with saturated solution of AgCN give ethyl isocyanide as major product .
REASON : Cyanide ion (CN^-) is an ambidentate nucleophile .

49. **ASSERTION :** The packing efficiency is maximum for the fcc structure.
REASON : The coordination number is 6 in *fcc* structures.

[SECTION C]

This section consists of 6 multiple choice questions with overall choice to attempt any 5 questions. In case more than desirable number of questions are attempted, only first 5 will be considered for evaluation.

50. Complete the following analogy:
Primary structure of protein : A:: Secondary structure of protein : B

a) A: Hydrogen bonding, B: Glycosidic linkage
b) A: Peptide linkage, B: Hydrogen bonding
c) A: Peptide linkage, B: Disulphide bridge
d) A: Glycosidic linkage, B: Disulphide bridge

51. Complete the following analogy:
N_2O_5: A:: Bi_2O_3 : B

a) A: Acidic, B: Amphoteric
b) A: Amphoteric, B: Basic
c) A: Acidic, B: Amphoteric
d) A: Acidic, B: Basic

52. Complete the following analogy:
Butan-1-ol + Butanoic acid : A:: B : Acetylation

a) A: Esterification, B: Salicylic acid + acetic anhydride
b) A: Dehydration, B: Phenol + Methanoic acid
c) A: Esterification, B: Phenol + Ethanoic acid
d) A: Oxidation, B: Salicylic acid + acetic anhydride

Read the following passage carefully and answer the questions (Question 53 to 55):

Osmosis is the movement of solvent across a membrane induced by a solute-concentration gradient. It is very important for cell biology. Recently, it has started finding technological applications in the emerging processes of Forward Osmosis and Pressure-Retarded Osmosis. They use ultrathin and dense membranes supported mechanically by much thicker porous layers. Until now, these processes have been modelled by assuming the membrane to be ideally-semipermeable. We show theoretically that allowing for even minor deviations from ideal semipermeability to solvent can give rise to a previously overlooked mode of "breakthrough" osmosis. Here the rate of osmosis is very large (compared to the conventional mode) and practically unaffected by the so- called Internal Concentration Polarization. In Pressure-Retarded Osmosis, the power densities can easily exceed the conventional mode by one order of magnitude. Much more robust support layers can be used, which is an important technical advantage (reduced membrane damage) in Pressure- Retarded Osmosis.

Reference: Yaroshchuk, A. **Breakthrough osmosis and unusually high power densities in Pressure-Retarded Osmosis in non-ideally semi-permeable supported membranes**. *Sci Rep* 7, 45168 (2017).

53. .....is commonly used synthetic semipermeable membrane used in reverse osmosis.

a) Parchment b) Cellulose acetate
c) Polyester d) None of these

54. Solution A is hypertonic to solution B. Osmostic pressure of solution A is …….solution B.

a) more than b) less than
c) equal to d) either more or less

55. If 2.0 M aqueous solution of X at 300 K has atmospheric pressure 100 mm of Hg. What will be the atmospheric pressure of of 3.0 M aqueous solution of X?

a) 200 mm Hg b) 300 mm Hg
c) 100 mm Hg d) 150 mm Hg

SAMPLE PAPER (TERM-1)

Marking Scheme

[Section A]

Question Number **Answer and Explanation**

1 b) decreases, according to Le Chatelier's principle increase in T leads to decrease in solubility

2 d) S,Henry's law constant KH is inversely proportional to the solubility, so lower the KH higher the solubility.

3 c) Copper, $MgCl_2$ A is metallic solid and B is ionic solid

4 b) the number of solute particles Colligative properties does not depends on nature of solute or solvent

5 b) $\Delta Gmix = 0$

6 d) Uracil

7 a) 1-Chloropropane Primary alkyl halides undergoes S_N2 reaction with inversion of configuration

8 b) Pent-2-ene, Pentan-2-ol t-BuONa leads to elimination according to Saytzeff rule, aq. KOH leads to substitution.

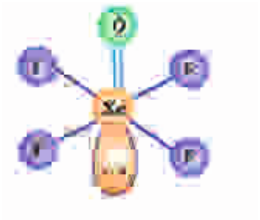
9 c) White precipitate of 2,4,6-tribromophenol

10 b) Anomers Monosachharides differ at C-1 are known as anomers

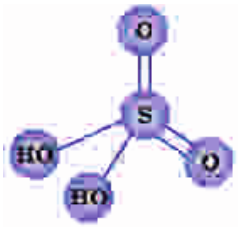
11 d) Glycine NH_2-CH_2-COOH lacks chiral carbon and optically inactive

12 b) HI > HBr >HCl >HF Greater the H-X bond length leads to easier cleavage and release of proton

13 b) $XeOF_4$



14 c) 2, 2



15 d) Very low ionization enthalpy Noble gases has completely filled valence shell, so removal of electron is very difficult and ionization enthalpy is very high

16 b) Ionization enthalpy increases in a period but due to stable p^3 configuration of N it is more stable and shows exceptionally high ionization enthalpy

17 b) Deep blue complex $Cu^{2+} + 4\,NH3 \rightarrow [Cu(NH_3)_4]^{2+}$

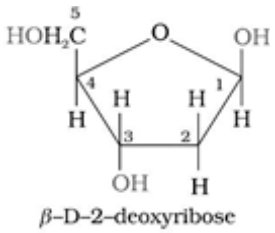
18 d) 5

19 a) HCHO + $(CH_3)_2$-CHMgBr Formaldehyde with appropriate Grignard reagent gives primary alcohol.

20 a) Enantiomers

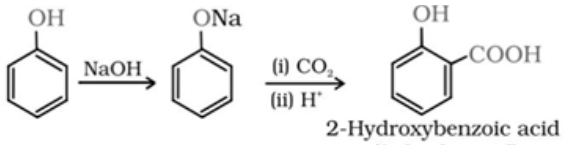
21 c) Zero Due to presence of two enantiomers in equal amount, net optical rotation is zero

22 b) Deoxyribose



β–D–2–deoxyribose

23 a) Kolbe's Reaction



2-Hydroxybenzoic acid
(Salicylic acid)

24 b) Isotopic nature Crystalline solids are anisotropic in nature.

25 c) Q2R3 Q present at corners, so Q = n R at half of the face centres, so
R = ½ × 3n = 3n/2 Q : R = n : 3n/2 = 2 : 3

[Section B]

Question Number **Answer and Explanation**

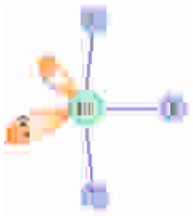
26 c) Aniline + Phenol Due to strong electrostatic attraction between anilinium cation and phenoxide ion formed by transfer of proton from phenol, vapour pressure of resulting solution decreases.

27 a) Sucrose Due to glycosidic linkage between reducing groups of glucose and fructose.

28 a) Fibrous protein

29 d) It is aldohexose D-Fructose is a ketohexose instead.

30 b) Bent-T



31 b) $SnCl_4$ Higher oxidation state of Sn favours covalent character.

32 b) High F-F bond enthalpy enthalpy of dissociation of F-F is 158.8 kJ/mol which is low as compared to other X-X bonds of halogens.

33 a) Frenkel Frenkel defect is a dislocation defect an ion leaves vacant its original site and occupies an interstitial site, so no change in density.

34 d) Both low temperature and high atmospheric pressure

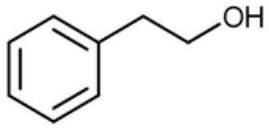
35 d) 2.22 M

n = 120/60 = 2 mol d = m/V = 1.15 g/ml

1000g / V = 1.15 g/mL V = 869.56 mL

Molarity = n/V = 2/0.0.869

36 a)



Hydroboration-oxidation reaction results into formation of alcohol contrary to the Markonikov rule.

37 c) Both of these FeCl3 gives violet complex, bromine water gives white precipitate on reaction with phenol.

38 b) PCC Pyridinium chlorochromate exclusively converts alcohols into aldehydes in presence of other groups.

39 c) 2-Methoxypropane

40 d) 1-Bromoethane < 1-Brompropane < 1-Bromobutane < Bromobenzene Increase in molecular mass leads to increase in boiling point

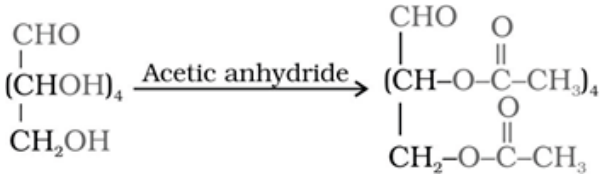
41 d) o- Cresol Higher the pKa, lower the acidic strength Methyl group being electron releasing, destabilises conjugate base and results into decrease in acidic strength. So highest pKa

42 c) Both O2 and Xe have almost same ionization enthalpy

43 a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Reason is supported by Henry's law, according to which solubility of gas in liquid increases with rise in temperature.

44 a) Assertion and reason both are correct statements and reason is correct explanation for assertion.



45 a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

46 d) Assertion is wrong statement but reason is correct statement. Addition of a non-volatile solute results into depression in freezing point.

47 d) Assertion is wrong statement but reason is correct statement. p-nitrophenol is more acidic than phenol.

48 b) Assertion and reason both are correct statements but reason is not correct explanation for assertion. AgCN is covalent compound so attack takes place from N side and isocyanide is formed.

49 c) Assertion is correct statement but reason is wrong statement. The coordination number is 12 in fcc structure.

[Section C]

Question Number **Answer and Explanation**

50 b) A: Peptide linkage, B: Hydrogen bonding Primary structure of protein is formed by peptide linkages between different amino acids; polypeptide chains are stabilised by H-bonding in secondary structure of proteins.

51 d) A: Acidic, B: Basic Oxides of higher oxidation are more acidic, trioxides of heavier members are predominantly basic

52 a) A: Esterification, B: Salicylic acid + acetic anhydride Reaction of alcohol with carboxylic acids is known as esterification. Reaction between salicylic acid and acetic anhydride is an example of acetylation.

53 b) Cellulose acetate

54 b) less than

55 d) 150 mm

Hg $\Pi = C R T$

$\Pi_1 / \Pi_2 = C_1 / C_2$

$100 / \Pi_2 = 2.0 / 3.0$ $\Pi_2 = 150$ mm Hg