STUDENT SUPPORT MATERIAL

Class XII
Chemistry

तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन

Session 2016-17

KENDRIYA VIDYALAYA SANGATHAN
NEW DELHI

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आयुक्त
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Commissioner

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A WORD TO MY DEAR STUDENTS

It gives me great pleasure in presenting the Students' Support Material to all KV students of class XII.

The material has been prepared keeping in mind your needs when you are preparing for final exams and wish to revise and practice questions or when you want to test your ability to complete the question paper in the time allotted or when you come across a question while studying that needs an immediate answer but going through the text book will take time or when you want to revise the complete concept or idea in just a minute or try your hand at a question from a previous CBSE Board exam paper or the Competitive exam to check your understanding of the chapter or unit you have just finished. This material will support you in any way you want to use it.

A team of dedicated and experienced teachers with expertise in their subjects has prepared this material after a lot of exercise. Care has been taken to include only those items that are relevant and are in addition to or in support of the text book. This material should not be taken as a substitute to the NCERT text book but it is designed to supplement it.

The Students' Support Material has all the important aspects required by you; a design of the question paper, syllabus, all the units/chapters or concepts in points, mind maps and information in tables for easy reference, sample test items from every chapter and question papers for practice along with previous years Board exam question papers.

I am sure that the Support Material will be used by both students and teachers and I am confident that the material will help you perform well in your exams.

Happy learning!

28/10

Santosh Kumar Mall
Commissioner, KVS

FOREWORD

The Students' Support Material is a product of an in-house academic exercise undertaken by our subject teachers under the supervision of subject expert at different levels to provide the students a comprehensive, yet concise, learning support tool for consolidation of your studies. It consists of lessons in capsule form, mind maps, concepts with flow charts, pictorial representation of chapters wherever possible, crossword puzzles, question bank of short and long answer type questions with previous years' CBSE question papers.

The material has been developed keeping in mind latest CBSE curriculum and question paper design. This material provides the students a valuable window on precise information and it covers all essential components that are required for effective revision of the subject.

In order to ensure uniformity in terms of content, design, standard and presentation of the material, it has been fine tuned at KVS Hqrs level.

I hope this material will prove to be a good tool for quick revision and will serve the purpose of enhancing students' confidence level to help them perform better. Planned study blended with hard work, good time management and sincerity will help the students reach the pinnacle of success.

Best of Luck.

U.N. Khaware
Additional Commissioner (Acad.)

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STUDENT SUPPORT MATERIAL

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CONTENTS

SOLID STATE (UNIT 1)

Key points (summary at a glance)

MATTER is everything around us. Matter can occupy space and has mass. Matter is of three types: solid , liquid & gas .

The characteristic properties of the solid state: Definite mass, volume and shape, Intermolecular distances short, Intermolecular forces strong constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions, incompressible and rigid.

CLASSIFICATION OF SOLIDS: On the basis of the nature of orderness present in the arrangement of their constituent particles, Solids are classified as **crystalline** and **amorphous** .

a) Crystalline solids: long range order of arrangement of constituent particles, sharp melting points, anisotropic ,undergo clean cleavage.

b) Amorphous solids: short range order of arrangement of constituent particles , melt over a range of temperature , isotropic , undergo an irregular cut.

Types of crystalline solids: Depending upon the nature of bonds, crystalline solids are of four types

1) Molecular solids 2) Ionic solids 3) Covalent solids 4) Metallic solid

Crystal type	Constituent particles	Major binding force	Properties	Example
1) **MOLECULAR**	Small molecules	Vander waal's forces	Soft, low MP, volatile, insulators	Solid CO_2, wax, iodine, etc
2) **IONIC**	Positive and negative ions	Electrostatic forces of attraction	Brittle, high MP, very high heat of fusion	NaCl, MgO, ZnS, LiF, etc
3) **COVALENT**	Atoms	Covalent bonds	Very hard, high MP, high heat of fusion, insulator	Quartz, diamond etc. Exception is graphite
4) **METALLIC**	Positive ions and mobile electrons	Metallic bonds	Very soft to very hard, ductile and malleable, conductors	All metals and alloys

AMORPHOUS SOLIDS :

- On heating become crystalline at some temperature therefore some glass objects from ancient civilizations are found to be milky in appearance because of some crystallization.
- Called pseudo solids or super cooled liquids because Like liquids, they have a tendency to flow therefore glass panes fixed to windows or doors of old buildings are slightly thicker at the bottom because the glass flows down very slowly

- Amorphous solids are **isotropic** (the value of any physical property electrical resistance or refractive index would be same along any direction) in nature due to irregular arrangement of constituent particles.,.

  CRYSTALLINE SOLIDS are **anisotropic** in nature, that is, some of the physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals.

  CRYSTAL LATTICE: A regular three dimensional arrangement of points in space is called a crystal lttice.

- only 14 possible three dimensional lattices called **Bravais Lattices**.

Characteristics of a crystal lattice:

(a) Each point in a lattice is called **lattice point** or **lattice site** that represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(b) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Seven crystal structures : Cubic, Tetragonal, Orthorhombic, Monoclinic, Hexagonal, Rhombohedral, Triclinic

UNIT CELL : The unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterised by six parameters edges : a, b, c angles : α, β and γ.

(i) Dimensions along the three edges, a, b and c. These edges may or may not be mutually perpendicular.

(ii) Angles between the edges, α (between b and c) , β (between a and c) and γ (between a and b).

Types of Unit Cells: Broadly divided into two categories

i) Primitive and ii) Centred unit cells.

(a) **Primitive Unit Cells :** When constituent particles are present only on the corner positions of a unit cell. No of atoms present in this unit cell = 8 x 1/8 = 1 (Each Corner atom contributes 1/8th portion to the unit cell)

  - No of lattice points: 8 coordination No: 6

(b) **Centred Unit Cells :** constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell.

Centred unit cells are of three types:

(i) **Body-Centred Unit Cells:** A unit cell contains one constituent particle (atom, molecule or ion) at its body-centre and eight particles are at its corners. No of atoms present in this unit cell = (8 x 1/8) + 1 = 2

- No of lattice points: 9 coordination No: 8

(ii) **Face-Centred Unit Cells:** A unit cell contains one constituent particle present at the centre of each face, along with eight particles at its corners. No of atoms present in this unit cell = (8 x 1/8) + (6 x ½) = 1 + 3 = 4

- No of lattice points: 14 coordination No: 12

(iii) **End-Centred Unit Cells:** Unit cell contains one constituent particle present at the centre of any two opposite faces along with eight particles at its corners. No of atoms present in this unit cell = (8 x 1/8) + (2 x ½) = 1 + 1= 2

- No of lattice points: 10

NO. ATOMS PER UNIT CELL (Z):

Type of unit cell	No. of atoms At corners	No. of atoms In faces	No. of atoms At the center	Total
Primitive cube	8 x 1 / 8 = 1	0	0	1
Body Centered Cubic (B.C.C)	8 x 1 / 8 = 1	0	1	2
Face Centered Cubic (F.C.C)	8 x 1 / 8 = 1	6 x 1 / 2 = 3	0	4

CLOSE PACKING : In solids, constituent particles are closely packed, leaving the minimum vacant space.

(a) CLOSE PACKING IN ONE DIMENSION: only one way , arrange them in a row and touching each other.

- The number of nearest neighbours of a particle is called its **coordination number**.
- In one dimensional close packed arrangement, the coordination number is 2.

(b) CLOSE PACKING IN TWO DIMENSION:

(i) Square close packing: The coordination number is 4.

(ii) Hexagonal close packing: The coordination number is 6.

- Better close packing structure than square close packing structure.
- **Voids: Triangular void** : In the hexagonal close packing 2-dimentional structure there are some voids (empty spaces),triangular in shape

(c) CLOSE PACKING IN THREE DIMENSIONS : Three dimensional close packed structure can be generated by placing hexagonal close packed layers one over the other.

(i) **Covering Tetrahedral Voids:** ABAB .... pattern. This structure is called hexagonal close packed (hcp).

(ii) **Covering Octahedral Voids**: ABCABC... (or) cubic closed packed (ccp) (or) face centred cubic (fcc) structure.

VOIDS: Unutilized or vacant spaces left after packing.

Tetrahedral void: A void between four touching spheres. Smaller in size.

Octahedral void: A void between six touching spheres. Bigger than tetrahedral voids.

- Let the number of close packed spheres be N, then:

  The number of octahedral voids generated = N

  The number of tetrahedral voids generated = 2N

PACKING EFFICIENCY:

i) In a Simple Cubic Lattice:= 52.38%

ii) In a Body- Centred Cubic Structures : 68%

iii) In a Face- Centred Cubic (HCP and CCP) Structures: 74%

- **ccp and hcp structures have maximum packing efficiency**

CALCULATION OF DENSITY OF THE UNIT CELL: $r = Z \times M / N_A \times a^3$

Where Z = No. of atoms per Unit cell, M = Atomic mass / Molecular mass in gm

N_A = Avagadro number = 6.023×10^{23}, a = Cell edge in cm

r = Density of the unit cell in g cm^{-3}

VALUES OF Z AND a :

Name of the unit cell with Example	Value of Z	Relation of 'a' with 'd'	Relation of 'a' with 'r'	Inter ionic Distance
Simple cubic	1	d = 2r = a	$a = 2r \Rightarrow r = a / 2$	
B.C.C(CsCl type)	2	$d = 2r = (\sqrt{3}\, a) / 2$	$r = (\sqrt{3}\, a) / 4$	$r^+ + r^- = (\sqrt{3}a) / 2$
F.C.C(NaCl type)	4	$d = 2r = (\sqrt{2}\, a) / 2$	$r = a / (2 \sqrt{2})$	$r^+ + r^- = a / 2$

Where

d ----- Distance between the nearest neighbor.

r ---- Radius of the atom.

r^+ -- Radius of the cation

r^- ---- Radius of the Anion.

DEFECTS OR IMPERFECTIONS: Irregularities in the arrangement of constituent particles. The defects are of two types:

a) Point defects: The irregularities from ideal arrangement around a point or an atom in a crystalline substance.

b) Line defects: The irregularities from ideal arrangement in entire rows of lattice points.

Point defects in NON- IONIC CRYSTAL can be classified as:

(i) Vacancy defect (ii) Interstitial defect

(i) Vacancy defect: some of the lattice sites are vacant . Density decreases**.**

ii) Interstitial defect: Some constituent particles occupy interstitial sites in addition to normal lattice sites. Increases density**.**

Point defects in IONIC CRYSTAL can be classified as:

(i) **Stoichiometric defects**

ii) **Non-Stoichiometric point defects**

iii) **Impurity Defects**:

(i) **STOICHIOMETRIC DEFECTS**: in which stoichiometry of the compound is not disturbed.

Two types of point defects are commonly found in the crystalline i**onic** substances.

Schottky Defects:

- cations & anions in equal number are missing from the crystal lattice giving rise to vacancies or voids.
- more common in ionic compounds with high coordination numbers .
- The positive and negative ions are of similar size. e.g., NaCl, CsCl, KCl and KBr, AgBr
- Since the solid with a Schottky defect contains lesser number of ions as compared to a prefect crystal, the density of the crystal will be less as compared to that of the perfect crystal.

Frenkel Defects:

- The ion, usually cation (smaller ion)instead of being in its expected location, is found in one of the interstitial / voids.
- There is a large difference in size between the positive and negative ions, Eg : ZnS, AgCl, AgBr and AgI.
- The density of crystals exhibiting Frenkel defect remains unchanged as the ions are present in the interstitial sites without changing the nass of the substance.

ii) **NON-STOICHIOMETRIC POINT DEFECTS:** The defects in which stoichiometry of the compound is disturbed.

There are of two types: 1) **Metal excess defect** **2) Metal deficiency defect**.

a) **Metal excess defects due to anionic vacancies**:

- Alkali halides like NaCl and KCl show this type of defect.The anionic vacancies are occupied by unpaired electrons called **F-centres** (from the German word **Farbenzenter** for colour centre/point).

  Ex : a)They impart yellow colour to the crystals of NaCl. b) Excess of lithium makes LiCl crystals pink. c) Excess of potassium makes KCl crystals violet (or lilac).

b) **Metal excess defects due to presence of interstial cations:**

- Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

  $ZnO \longrightarrow Zn^{2+} + ½\,O_2 + 2e^-$

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

c) **Metal deficiency due to absence of cations:** positive ions missing from their lattice sites.

Extra negative charge is balanced by some nearby metal ions with higher positive charge. e.g. FeO, FeS .

iii) IMPURITY DEFECTS:

- cation vacancies are produced due to impurity ion at lattice site.

  e.g. molten NaCl containing a little amount of $SrCl_2$ is crystallized, some of the sites of Na^+ ions are occupied by Sr^{2+}. The cationic vacancies produced are equal in number to that of Sr^{2+} ions.

PROPERTIES OF SOLIDS:

I. Electrical properties:

Conductors: allow maximum current to flow through them , conductivity range order is 10^4 to 10^7 ohm^{-1} m^{-1}, due to the presence of mobile electrons. Conductivity of metals decrease with increase in temperature.

Insulators : do not allow electric current to flow through them. The electrical conductivity of insulators is the order of 10^{-20} to 10^{-10} ohm^{-1} m^{-1}.

Semiconductors: Electrical conductivity of a semiconductor at normal temperatures lies between a good conductor and an insulator. The range of conductivity is 10^{-6} to 10^4 ohm^{-1} m^{-1}. Eg : Silicon and germanium . Unlike metals the conductivity of semiconductors increases with temperature because the weakly bound extra electron or positive hole become free by the increased temperature.

The conduction in the crystal without adding any external substance is called **intrinsic conduction.**

Doping is a process of mixing pure silicon or germanium with an impurity.

Doping enhances the conductivity and the products are called **extrinsic semiconductors**. They are two types :

(a) **n- type semiconductor**: **(Doping with e- rich impurity)**

obtained by doping Si or Ge with a group 15 elements (Electron – rich impurities) like P. Out of 5 valence electrons , only 4 are involved in bond formation and the fifth electron is delocalized and can be easily provided to the conduction band.

(b) **p – type semi conductor** : **(Doping with e- deficient impurity)**

obtained by doping Si or Ge with a group 13th elements (Electron – deficient impurities) like Gallium which contains only 3 valence electrons. Due to missing of 4th valence electron, electron hole or electron vacancy is created. The movement of these positively charged hole is responsible for the conduction.

13 and 15 or 12 and 16 Groups compounds

- A large variety of solid state materials have been prepared by combination of **groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si.**

- Typical compounds of **groups 13 – 15 are** InSb, AlP and GaAs. Gallium arsenide
- Typical compounds of **groups 12 – 16 are** ZnS, CdS, CdSe and HgTe .
- In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

MAGNETIC PROPERTIES:

- **Diamagnetic solids** due to paired electron (↓↑) and repelled in the external magnetic field. Ex: H_2O, NaCl.
- **Paramagnetic solids** due to unpaired electrons, weakly attracted into the applied external magnetic field. Ex : Fe^{3+}, O_2, Cu^{2+}, etc.,
- **ferromagnetic solids**, the metal ions are grouped together into small regions called **domains**. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field (↑↑↑↑). This interaction leads to an increase in magnetic moment. Ordering of domains persist even when magnetic field is removed so make permanent magnets .Ex: Iron, Cobalt and Nickel .
- A**ntiferromagnetic solids**: when in a magnetic field all the domains get oriented in equal no.in parallel & antiparallel (↓↑↓↑) direction of the magnetic field, and cancel each other's magnetic moment. Ex: MnO, MnO_2, Mn_2O_3.
- F**errimagnetic solids** when in a magnetic field all the domains get oriented randomly (↑↑↓↑↑↓) which resulting in some magnetic moment. Ex. Magnetite (Fe_3O_4), ferrite [M Fe_2O_4] where M = Mg (II), Cu (II).

FREQUENTLY ASKED QUESTIONS (VERY SHORT ANSWERS(1 MARK)

Q1) Classify the following solids as metallic, molecular, amorphous, covalent or ionic.(i) SO_2 (ii) Diamond (iii) I_2 (iv) MgO (iv) Ag (v) Quartz (vi) Ar

(**Ans1) Metallic solid** – Ag; **Covalent solid** – Quartz, diamond ; **Molecular solids** - I_2, Ar, SO_2 ; **Ionic solids** MgO

Q2**) Why LiCl / NaCl (common salt) / KClacquires pink / yellow / violet colour when heated in Li/Na / K vapours respectively?**

Ans2) The Cl^- ions diffuse to the surface and form LiCl/NaCl/KCl . An electron is released which diffuses into the crystal and occupies an anionic site called F centres. The colour is due to excitation of electrons when they absorb energy from visible light falling on the crystal.

Q3) Which point defect in the crystals does not alter the density of the relevant solid?

Ans3) Frenkel defect.

Q4) What happens to the density of KCl crystal by the addition of $CaCl_2$ crystal.

(Ans4) In KCl crystal, the Ca^{2+}ion from $CaCl_2$ will replace K^+ ions. Since one Ca^{2+}ion will replace two K^+ ion in order to make the system electrically neutral. Thus, the density of KCl crystal will decrease.

Q5) A metallic crystal crystallizes into a lattice containing a sequence of layers AB AB AB ……Any packing of spheres leaves out voids in the lattice. What % by volume of this lattice is empty space?

OR

A metallic crystal crystallizes into a lattice containing a sequence of layers ABC ABC ABC ……Any packing of spheres leaves out voids in the lattice. What % by volume of this lattice is empty space?

(Ans 5) AB-AB type of packing means hexagonal close packing & ABCABC.. type of packing means cubic close packing. In both cases. 74% space is occupied and 26% is empty.

Q6) What type of alignment in crystals make them ferromagnetic?

Ans6) Magnetic dipoles are parallel to one another.

Q7) What happens when ferrimagnetic Fe_3O_4 is heated to 850 kelvin and why? OR What happens when a ferromagnetic substance subjected to high temperature?

Ans7) It becomes paramagnetic due to randomisation of spins.

Q8) Which solid is the best material for converting sunlight into electricity?

Ans8) Amorphous silica**.**

SHORT ANSWER QUESTIONS (2MARKS)

Q9) Write two differences between isotropy and anisotropy.

Ans9:

Isotropy	**Anisotropy**
i) It is property by which substances show identical, electrical and optical properties in all directions.	It is property by which substances show different electrical and optical properties in all directions.
(ii) Amorphous solids show isotropy	Crystalline solids show anisotropy.

Q11)A compound formed by elements X and Y crystallizes in a cubic structure in which the X atoms are at the corners of a cube and the Y atoms are at the face centres. What is the formula of the compound.

(**Ans11**) For a cubic structure, No. of X atoms at the corner of the unit cell = 8 x1/8 =1

No. of Y atoms at the face centre of the unit cell =6 x1/2=3

Formula of the compound = XY_3

Q12) Gold (atomic radis =0.144 nm). Crystalises in face centred Unit cell. What is the length of a side of a cell?

Ans12) For fcc unit cell : $a = 2\sqrt{2}\, r$

$a = 2 \times 1.414 \times 0.144 = 0.407$nm

Q13) A cubic solid is made of two elements P & Q. Atoms Q are at the corners of the cube and P are at the body center. What is the formula of the compound. What are the Co-ordination numbers of P & Q.

Ans13) No of atoms of P = 1 No of atoms of Q = 8 x 1/8 =1

Formula of compound =PQ

Co-ordination no. of P =8 & Co-ordination no. of Q =8.

Q14) In terms of band theory, what is the difference between a conductor, semicoductor and an insulator

Ans14) Energy gap between filled band and conduction band is high in insulator. In conductors, there is no energy gap between filled band & conduction band. In semiconductors there is energy gap between conduction band and filled band, but is intermediate of as in

SHORT ANSWER QUESTIONS (3 MARKS)

Q15) Find the type of lattice for cube having edge length of 400 pm, atomic wt. = 60 and density = 6.25 g/cc.

(Ans19) Let the no. of atoms in a unit cell = Z

Density = $Z \times M / N_A \times a^3$ Z= $d \times N_A \times a^3 / M$

$Z = 6.25 \times 6.022 \times 10^{23} \times 64 \times 10^{-24} / 60 = 4$, The unit cell has 4 atoms, $\therefore$ It is face centered cubic lattice.

Q16) A metallic element has cubic lattice. Edge length of lattice cell is 2A^{0}. The density of metal is 2.4g cm^{-3}. How many units cell are present in 200g of metal.

(Ans21) Edge length = 2A° = 2×10^{-8}cm

Volume of cell = $(a)^3$ =$(2x\,10^{-8})^3$ = $8x\,10^{-24}$ cm^{-}

volume of metal = 200gm / 2.4g cm^{-3} =83.3 cm^{3}

No of unit cells = volume of metal / volume of unit cell

No of unit cells= 83.3 / $8x\,10^{-24}$ = 10^{25}

Q17) Silver crystallizes in FCC lattice. If edge length of unit cell is 4.077 x 10^{-8} cm and density is 10.5 g/cm^{3} , calculate atomic mass of silver.

Ans17) $\rho = (Z\,m) / (a^3 \times N_A)$

$10.5 = (4 \times M)/(4.077 \times 10^{-8})^3 \times 6.023\times10^{23}$

M=107.09 g/mol.

Q18) Niobium crystallizes in body centred cubic structure. If density is 8.55 g/cm^{3}. If Density is 8.55 g/cm^{3}. Calculate atomic radius of niobium (At. Mass of Niobium=93).

Ans18) $\rho = (Zm)/(a^3N_A)$

$8.55 = (2 \times 93)/a^3 \times 6.023 \times 10^{23}$, a^3=$2\times93/(8.55\times6.023\times10^{23})$,

$a=[3.6\times10^{-23}]^{1/3}$ = **<u>3.302 x 10^{-8} cm</u>**

Q 19 a (i) Why Frenkel defect is not found in pure alkali metal halides?

(ii) Name point defect a crystal which lowers the density of Crystal?

b) Ferric oxide Crystallises in a hexagonal close packed array of oxides with two out of every three octahedral holes occupied by ferric ions. Derive the formula of ferric oxide.

Ans19) (i Frenkel defect is not found in pure alkali metal halides because the size of ions (cation) is large and they do not fit into interstitial spaces.

(ii) Schottky defect

b) No. of Ferric ions for each oxide ion = 2/3

Chemical formula= $Fe_{2/3}\ O \cong Fe_2O_3$

Q20) In a face centered cubic lattice atoms of A occupy corner of cell and that of B occupy face centers. One of the A atoms is missing from one corner of a unit cell. Find the simplest formula of compound.

(Ans20) Number of atoms of A at the corner of unit cell = 7 x (1/8) = 7/8

Number of atoms of B at faces of unit cell = 6 x 1/2=3

A : B = (7/8) : 3

Formula of compound = A_7B_{24}

Q21) Thallium chloride, TlCl crystallizes in either a simple cubic lattice or a face centred cubic lattice or a face centred cubic lattice of Cl^- ion with Tl^+ ion in the holes. If the density of the solid is 9 gcm^{-3} and edge of the solid is 3.85×10^{-8} cm, what is the unit cell geometry?

Ans21) $\rho = Z.m/a^3N_A$,

$9 = Z \times 240/(3.85\times10^{-8})^3 \times 6.023\times10^{23}$

$Z = 9 \times 3.85 \times 3.85 \times 3.85 \times 10^{-24} \times 6.023\times10^{23}/240$

$Z = 1.289 \approx 1$, So, TlCl is simple cubic.

Q22) A mineral contains Ca, O and Ti. Oxygen atoms are present at face centres, calcium atoms are present at corners and titanium atoms at centre of cube. Find the oxidation number of titanium in the mineral.

Ans22) No. of Ca atoms = $8 \times 1/8 = 1$ No. of O atoms = $6 \times 1/2 = 3$

No. of Ti atoms =

Formula of mineral is $CaTiO_3$

Let oxidation number of Ti is x

So, In $CaTiO_3$ $+2 + x + (-2 \times 3) = 0$

$x = +4$ Oxidation state of titanium is + 4 in this mineral.

VALUE BASED QUESTION

Q1. Earth receives enormous amount of energy from sunlight. The problem of shortage of power can be solved if we could convert solar energy into electricity. A device which generates electrical power from sunlight is called solar cell or photovoltaic cell. Solar cells are made up of silicon doped with arsenic and silicon doped with boron. Answer the following questions:

i) when silicon is doped with arsenic, what type of semiconductor is obtained ? Explain

ii) what type of semiconductor is obtained by doping silicon with boron ?

iii) Give any two applications (other than solar cells) of semiconductors.

iv) what values are associated with the phenomenon ?

A) (i) Silicon belongs to 14th group and arsenic belongs to 15th group . Adding As is an e^- rich impurity therefore n type of semiconductor due to an extra electron.

(ii) Boron belongs to 13th group- an e^- deficient impurity is added therefore p type semiconductor due to holes.

(iii) As diode and amplifier

(iv) a) using alternate sources of energy like solar energy

b) keeping environment clean and saving fossil fuels

ASSIGNMENT FOR PRACTICE

Q1. Define: (i) Crystal lattice (ii) Co-ordination number

Q2. (a) Name the type of point defect that occurs in a crystal of zinc sulphide.Q2 (b) Examine the illustrate of a portion of the defective crystal given below and answer the following questions:

i) What are these type of vacancy defects called?

ii) How is the density of a crystal affected by these defects?

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?

Q3. What is the percentage efficiency of packing in the case of simple cubic lattice?

Q4. What are F centres?

Q5. Name an element with which silicon should be doped to give n-type of semiconductor.

Q6. What is the total number of atoms and lattice points per unit cell in i) fcc cell ii) bcc cell?

Q7. Name the non stoichiometric point defect responsible for colour in alkali halides?

Q8. What is the nature of crystal defect produced when sodium chloride is doped with $MgCl_2$?

Q9. Copper is conducting as such while copper sulphate is conducting only in molten state or in aqueous solution?

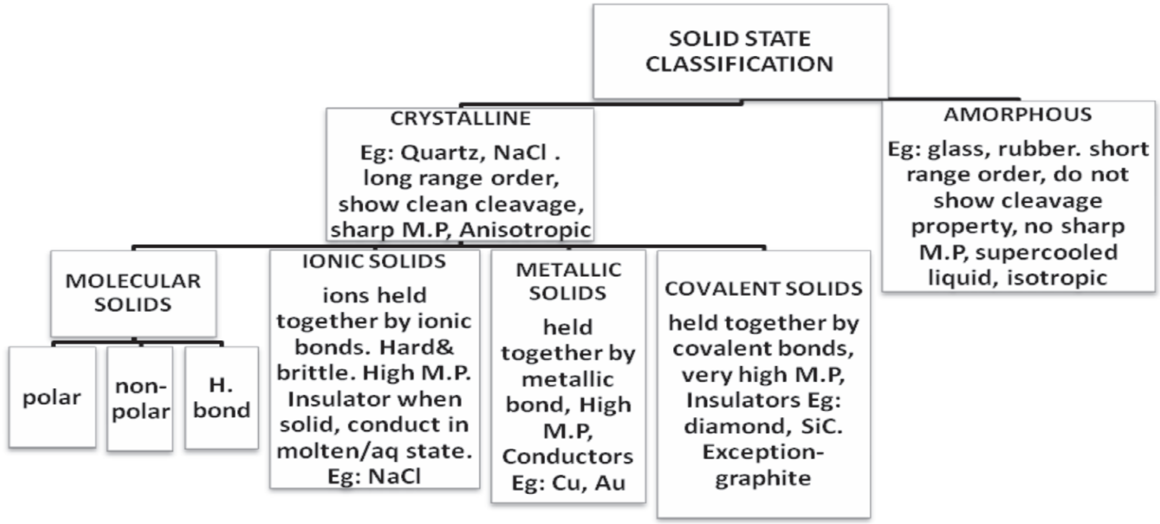
Q11. Why does frenkel defect does not change the density of AgCl crystal?

Q12. In an ionic compound the anion(N^-) form cubic close type of packing. While the cation (M^+) ions occupy one third of the tetrahedral voids. Deduce the empirical formula of the compound and the coordination number of (M^+) ions.

Q13. An element X with an atomic mass of 60g/mol has density of 6.23g cm^{-3}. If the edge length of its cubic unit cell is 400 pm, identify the type of cubic unit cell. Calculate the radius of an atom of this element.

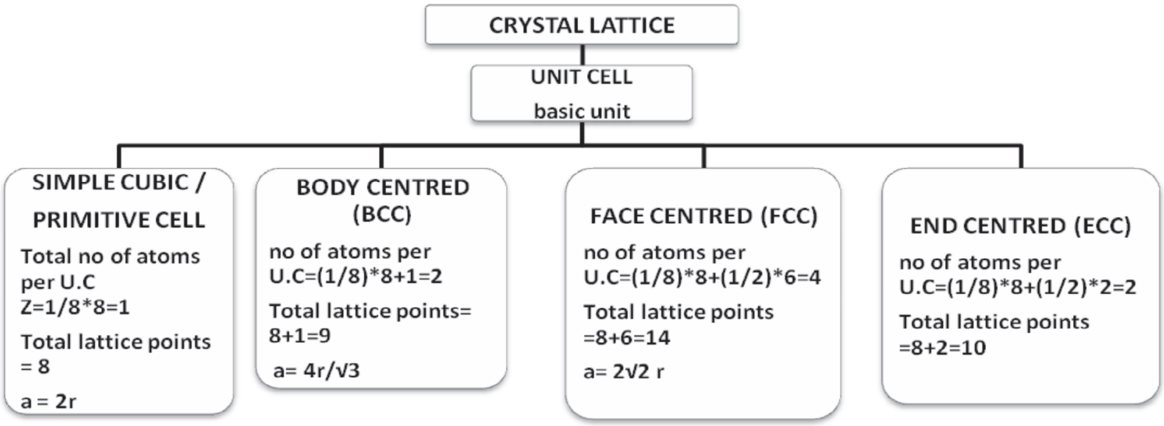
Q14. How many octahedral voids are there in l mole of a compound having cubic close packed structure?

Q15. With the help of suitable diagrams, on the basis of band theory, explain the difference between i) A conductor and an insulator. ii) A conductor and a semi conductor.



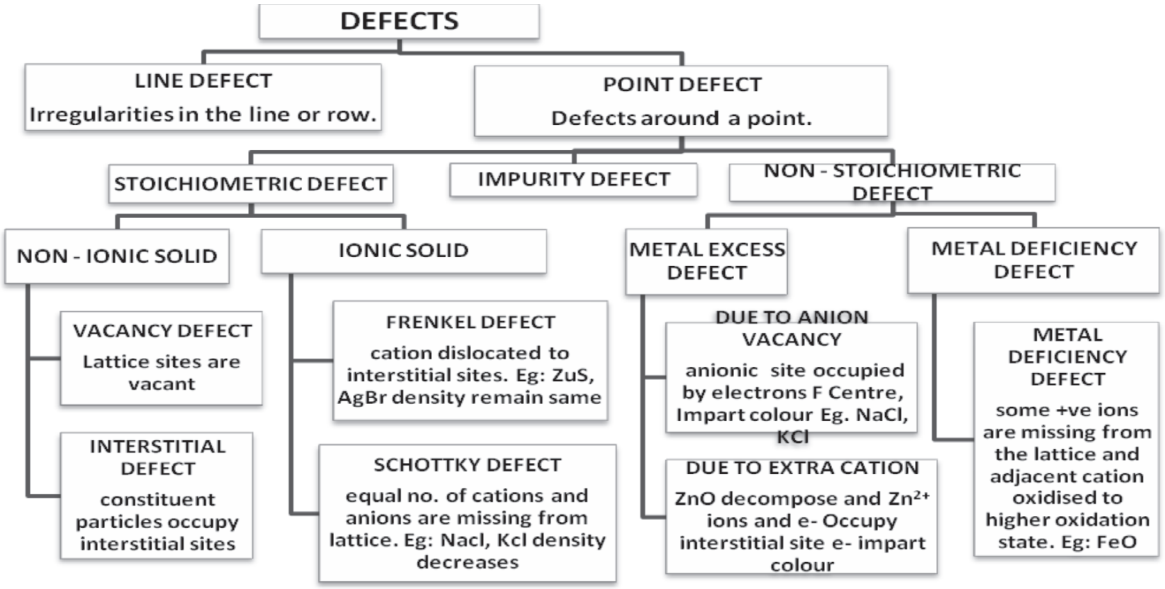
SOLID STATE CLASSIFICATION

- **CRYSTALLINE** Eg: Quartz, NaCl . long range order, show clean cleavage, sharp M.P, Anisotropic
  - **MOLECULAR SOLIDS**
    - polar
    - non-polar
    - H. bond
  - **IONIC SOLIDS** ions held together by ionic bonds. Hard& brittle. High M.P. Insulator when solid, conduct in molten/aq state. Eg: NaCl
  - **METALLIC SOLIDS** held together by metallic bond, High M.P, Conductors Eg: Cu, Au
  - **COVALENT SOLIDS** held together by covalent bonds, very high M.P, Insulators Eg: diamond, SiC. Exception-graphite
- **AMORPHOUS** Eg: glass, rubber. short range order, do not show cleavage property, no sharp M.P, supercooled liquid, isotropic



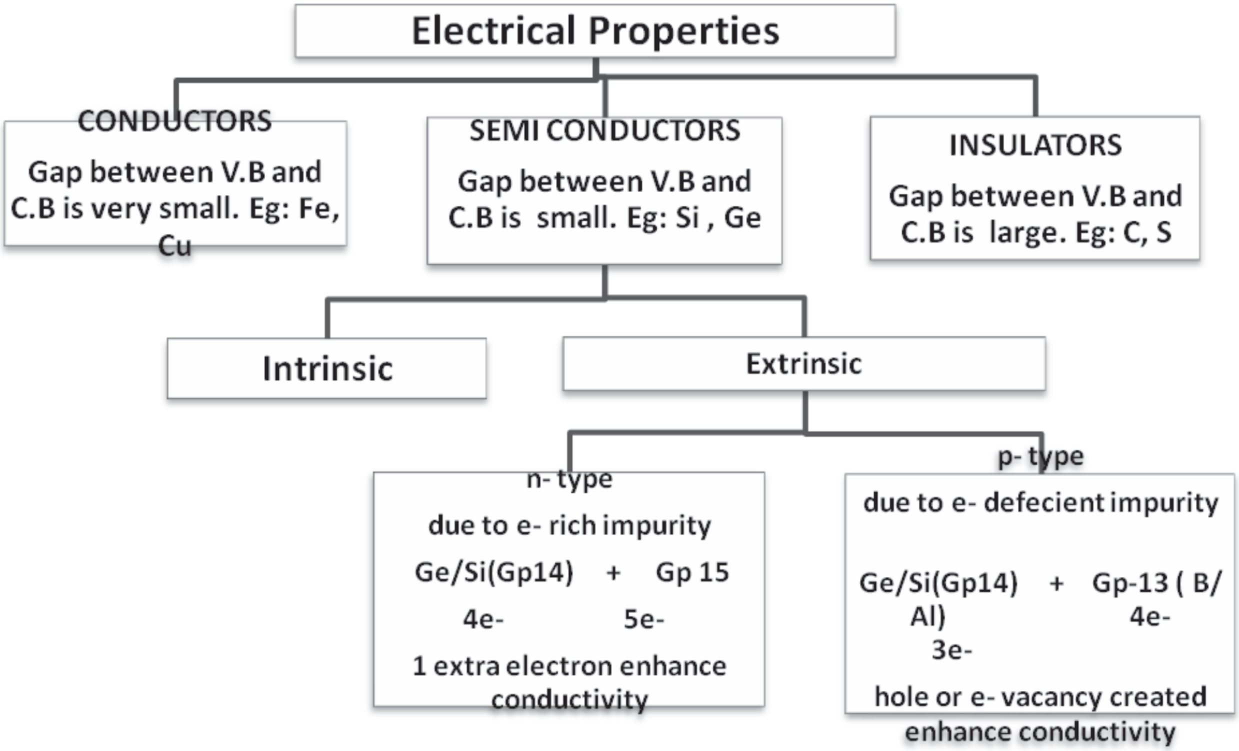
CRYSTAL LATTICE

- **UNIT CELL** basic unit
  - **SIMPLE CUBIC / PRIMITIVE CELL**
    Total no of atoms per U.C Z=1/8*8=1
    Total lattice points = 8
    a = 2r
  - **BODY CENTRED (BCC)**
    no of atoms per U.C=(1/8)*8+1=2
    Total lattice points= 8+1=9
    a= 4r/√3
  - **FACE CENTRED (FCC)**
    no of atoms per U.C=(1/8)*8+(1/2)*6=4
    Total lattice points =8+6=14
    a= 2√2 r
  - **END CENTRED (ECC)**
    no of atoms per U.C=(1/8)*8+(1/2)*2=2
    Total lattice points =8+2=10



DEFECTS

- **LINE DEFECT** Irregularities in the line or row.
- **POINT DEFECT** Defects around a point.
  - **STOICHIOMETRIC DEFECT**
    - **NON - IONIC SOLID**
      - **VACANCY DEFECT** Lattice sites are vacant
      - **INTERSTITIAL DEFECT** constituent particles occupy interstitial sites
    - **IONIC SOLID**
      - **FRENKEL DEFECT** cation dislocated to interstitial sites. Eg: ZuS, AgBr density remain same
      - **SCHOTTKY DEFECT** equal no. of cations and anions are missing from lattice. Eg: Nacl, Kcl density decreases
  - **IMPURITY DEFECT**
  - **NON - STOICHIOMETRIC DEFECT**
    - **METAL EXCESS DEFECT**
      - **DUE TO ANION VACANCY** anionic site occupied by electrons F Centre, Impart colour Eg. NaCl, Kcl
      - **DUE TO EXTRA CATION** ZnO decompose and Zn^{2+} ions and e- Occupy interstitial site e- impart colour
    - **METAL DEFICIENCY DEFECT**
      - **METAL DEFICIENCY DEFECT** some +ve ions are missing from the lattice and adjacent cation oxidised to higher oxidation state. Eg: FeO



Electrical Properties

CONDUCTORS

Gap between V.B and C.B is very small. Eg: Fe, Cu

SEMI CONDUCTORS

Gap between V.B and C.B is small. Eg: Si , Ge

INSULATORS

Gap between V.B and C.B is large. Eg: C, S

Intrinsic

Extrinsic

n- type

due to e- rich impurity

Ge/Si(Gp14) + Gp 15
4e- 5e-

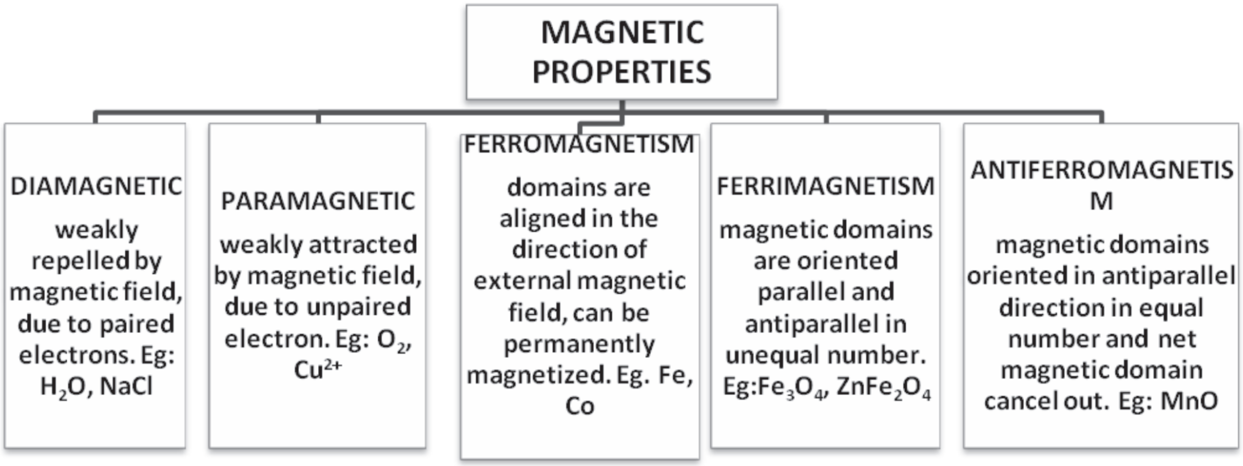
1 extra electron enhance conductivity

p- type

due to e- defecient impurity

Ge/Si(Gp14) + Gp-13 (B/ Al)
4e- 3e-

hole or e- vacancy created enhance conductivity



MAGNETIC PROPERTIES

DIAMAGNETIC

weakly repelled by magnetic field, due to paired electrons. Eg: H_2O, NaCl

PARAMAGNETIC

weakly attracted by magnetic field, due to unpaired electron. Eg: O_2, Cu^{2+}

FERROMAGNETISM

domains are aligned in the direction of external magnetic field, can be permanently magnetized. Eg. Fe, Co

FERRIMAGNETISM

magnetic domains are oriented parallel and antiparallel in unequal number. Eg:Fe_3O_4, $ZnFe_2O_4$

ANTIFERROMAGNETISM

magnetic domains oriented in antiparallel direction in equal number and net magnetic domain cancel out. Eg: MnO

SOLUTION (UNIT 2)

KEY CONCEPTS

SOLUTION is the homogeneous mixture of two or more than two components. Most of the solutions are binary i.e. consists of two components out of which that is present in the largest quantity called solvent & one which is present in smaller quantity called solute.

EXPRESSING CONCENTRATIONS OF SOLUTIONS

- Mass percentage: Mass of solute per 100g of solution.

  Mass% = (mass of solute/total mass of solution) X 100

- Volume percentage: volume of solute per 100ml of solutions .

  Volume % = (volume of solute/ total volume of solution) X 100

- Parts per million: parts of a component per million (10^6) parts of the solution.

  ppm = no. of parts of the component/ total no. of parts of all components of the sol^n X 10^6

- Mole fraction(x): It is the ratio of no. of moles of one component to the total no. of moles of all the components present in the solution .

  For binary solution :- the no. of moles of A and B are n_A and n_B respectively so,
  $x_A = n_A/n_A+n_B$; $x_B = n_B/ n_A+n_B$
  In binary solution $x_A + x_B = 1$

- Molarity: No. of moles of solute dissolved in one litre of solution .

  Molarity(M) = moles of solute/ vol. of solution in litre

- Molality(m) : No. of moles of solute per kg of the solvent.

  Molality(m) = moles of solute/mass of solvent in kg

  Molality is independent of temp. whereas molarity is a function of temp. because vol. depends on temp. and mass does not.

HENRY'S LAW

It states that at a constant temp. the solubility of the gas in liquid is directly proportional to the pressure of the gas above the surface of the liquid .

It also states that the partial pressure (p) of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution.

$$P = K_H X$$

K_H is Henry's law constant .

APPLICATION OF HENRY'S LAW

- To increase the solubility of CO_2 in soda water and soft drinks the bottle is sealed under high pressure.

- To avoid bends , toxic effects of high concentration of nitrogen in the blood the tanks used by scuba divers are filled with air diluted with He.

RAOULT'S LAW :- it states that :

1) For a solution of volatile liquid , the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

$P_A = P^0_A X_A$; $P_B = P^0_B X_B$

The total pressure is equal to sum of partial pressure.

$P_{total} = P_A + P_B$

2) For a solution containing non-volatile solute the vapour pressure of the solution is directly proportional to the mole fraction of the solvent.

$P_A \alpha X_A$ $P_A = P^0_A X_A$

IDEAL SOLUTION

The solution which obeys Raoult's law over the entire range of concentration when enthalpy of mixing and vol. of mixing of pure component to form solution is zero.

CONDITIONS

I. $P_A = P^0_A X_A$ $P_B = P^0_B X_B$

II. $\Delta H_{mix} = 0$

III. $\Delta V_{mix} = 0$

This is only possible if A-B interaction is nearly equal to those between A-A and B-B interactions. Ex:- solution of n-hexane and n-heptane.

NON IDEAL SOLUTION

The solution which do not obey Raoult's law over the entire range of concentrations.

CONDITIONS

I. $P_A \neq P^0_A X_A$ $P_B \neq P^0_B X_B$

II. $\Delta H_{mix} \neq 0$

III $\Delta V_{mix} \neq 0$

The vapour pressure of such solutions is either higher or lower than that predicted for Raoult's law .

I. If vapour pressure is higher, the solutions shows positive deviation (A-B interaction are weaker than those between A-A and B-B).

Ex: mixture of ethanol and acetone .

$P_A > P^0_A X_A$; $P_B > P^0_B X_B$

ΔH_{mix} = Positive ΔV_{mix} = Positive

II. If vapour pressure is lower, the solution shows negative deviation (A-B interaction are stronger than those between A-A and B-B).

Ex: mixture of chloroform and acetone .

$P_A < P^0_A X_A$; $P_B < P^0_B X_B$

ΔH_{mix} = negative ΔV_{mix} = negative

AZEOTROPE

Mixture of liquid having the same composition in liquid and vapour phase and boil at constant temp. Azeotrope are of two types :-

a) Minimum boiling azeotrope :- The solution which shows a large positive deviation from Raoult's law . ex- ethanol –water mixture.

b) Maximum boiling azeotrope :- the solution which shows large negative deviation from Raoult's law. Ex- nitric acid – water mixture.

COLLIGATIVE PROPERTIES Properties of ideal solution which depends upon no. of particles of solute but independent of the nature of the particles are called colligative properties.

1. **RELATIVE LOWERING OF VAPOUR PRESSURE**

$P^0_A - P_A / P^0_A = X_B$

$X_B = n_B / n_A + n_B$

For dilute solution, $n_B << n_A$, hence n_B is neglected in the denominator.

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

$P^0_A - P_A / P^0_A = W_B \times M_A / M_B \times W_A$

2. **ELEVATION OF BOILING POINT**

$\Delta T_b = k_b m$Where , $\Delta T_b = T_b - T^0_b$

K_b = molal elevation constant / Ebullioscopic constant

m = molality

$M = k_b \times 1000 \times W_B / \Delta T_b \times W_A$

3. **DEPRESSION IN FREEZING POINT**

$\Delta T_f = K_f m$Where , $\Delta T_f = T^0_f - T_f$

K_f = molal depression constant / Cryoscopic constant

m = molality

$M = k_f \times 1000 \times W_B / \Delta T_f \times W_A$

4. **OSMOTIC PRESSURE**

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.

$\Pi = CRT$

$\Pi = n/VRT$ (n = no. of moles; V= volume of solution(L)

R= 0.0821 Latm mol^{-1} ; T= temperature in kelvin

ISOTONIC SOLUTION

Two solutions having same osmotic pressure and same concentration.

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 blood cell.

VAN'T HOFF FACTOR (i)

Ratio of normal molecular mass to the observed molecular mass of the solute.

i = normal molecular mass/ observed molecular mass

= observed colligative properties/ calculated value of colligative properties

$i<1$ (for association) $i>1$ (for dissociation)

MODIFIED FORMS OF COLLIGATIVE PROPERTIES

1) $P^0_A - P_A / P^0_A = i \times n_B/n_A$

2) $\Delta T_b = i \times K_b\, m$

3) $\Delta T_f = i \times K_f\, m$

4) $\Pi = i \times CRT$

FREQUENTLY ASKED QUESTIONS (1 MARK QUESTIONS)

Q1. How does the molarity of a solution change with temperature?

Ans. Molarity decreases with increase in temperature as volume of solution increase with increase in temperature.

Q2. Under what condition do non-ideal solutions show negative deviations?

Ans. When the new forces of interaction between the components are stronger than those in the pure components, then non-ideal solutions show negative deviation.

Q3. What are minimum boiling azeotrops? Give one example.

Ans. Minimum boiling azeotrops are those which boil at lower temperature than boiling point of each component in pure state, e.g., 95.5% ethyl alcohol and 4.5% water by mass.

Q4. What do you understand by the term that K_f for water is 1.86 K kg/mol ?

Ans. It means that the freezing point of water is lowered by 1.86 K when 1 mol of non- volatile solute is dissolved in 1 kg of water.

Q5. Why is osmotic pressure of 1 M KCl higher than 1 M urea solutions?

Ans. This is because KCl dissociates to give K^+ and Cl^- ions while urea being a molecular solid does not dissociates into ions in the solution.

2 MARKS QUESTIONS

Q1. State Henry's Law. What is the significance of K_H ?

Ans. Henry's Law: It state that “the partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution” , and is expressed as : $p=K_HX$ where,K_H is the Henry's Law constant Significance of K_H : Higher the value of Henry's law constant K_H ,the lower is the solubility of the gas in the liquid .

Q2. How is that measurement of osmotic pressure is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions?

Ans. The osmotic pressure method has the advantage over elevation in boiling point or depression in freezing point for the determining molar masses of macromolecules because

1. Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.
2. Compared to other colligative properties, its magnitude is large even for very dilute solutions.

Q3. Suggest the most important type of intermolecular interaction in the following pairs :

i) n-hexane and n-octane

ii) methanol and acetone

Ans. i) Dispersion or London forces as both are non-polar.

ii) Dipole-dipole interactions as both are polar molecules.

Q4. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN .

Ans. Mass of solution = 6.5g + 450g = 456.5g

$$\text{Mass \% of aspirin} = \frac{\text{Mass of aspirin}}{\text{Mass of solution}} \text{ x } 100$$

=6.5/456.5 X 100 = 1.424%

Q5. The partial pressure of ethane over a saturated solution containing $6.56 \text{ x } 10^{-2}$ g of ethane is 1 bar. If the solution contains $5.00 \text{ x } 10^{-2}$ g of ethane, then what shall be the partial pressure of the gas?

Ans. According to Henry's law , $m = K_H \text{ x } p$

Case 1- $6.56 \text{ x } 10^{-2} g = K_H \text{ x } 1 \text{ bar}$

or $K_H = 6.56 \text{ x } 10^{-2} \text{ g bar}^{-1}$

Case 2- $5.00 \text{ x } 10^{-2} \text{ g} = (6.56 \text{ x } 10^{-2} \text{ g bar}^{-1}) \text{ x } p$

$$\frac{5.00\text{x}10^{-2}\text{ g}}{6.56 \text{ x } 10^{-2}\text{ gbar}^{-1}} \quad \text{or} \quad p = 0.762 \text{ bar.}$$

3 MARK QUESTIONS

Q1. Non-ideal solution exhibit either positive or negative deviations from Raoult's law. What are these deviation and why are they caused? Explain with one example for each type.

Ans. When the vapour pressure of a solution is either higher or lower than that predicted by Raoult's law, then the solution exhibits deviation from Raoult's law. These deviation are caused when solute - solvent molecular interactions A – B are either weak or stronger than solvent – solvent A – B or solute – solute B – B molecular interactions. Positive deviations : When A – B molecular interactions are weaker than A – A and B – B molecular interaction . For example, a mixture of ethanol and acetone.

Negative deviations: When A – B molecular interaction are stronger than A – A and B – B molecular interaction. For example, a mixture of chloroform and acetone.

Q2 . a) Why is an increase in temperature observed on mixing chloroform and acetone?

b) Why does sodium chloride solution freeze at a lower temperature than water?

Ans: a) The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules, they start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

b) When a non- volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.

Q3. A solution of glycerol($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500g of water. This solution has a boiling point of 100.42C while pure water boils at 100C. what mass of glycerol was dissolved to make the solution?(K_b of water = 0.512 K kg/mol)

Ans. $\Delta T_b = 100.42°C - 100°C = 0.42°C$ or 0.42K; $W_A = 500g$; $K_b = 0.512$ K kg / mol ;

$M_B = 92$ g /mol Substituting these values in the expressions,

$$W_B = \frac{\Delta T_b \times M_B \times W_A}{K_b \times 1000}$$

$$W_B = \frac{0.42 \times 92 \times 500}{0.512 \times 1000} = 37.73g$$

Q4. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27C.

Ans. $$\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$$

Molar mass of $CaCl_2$,M_B =40+2 X 35.5 = 111 g mol^{-1}

Therefore, Molar mass of $CaCl_2$,$W_B = \frac{0.75 \text{ atm} \times 111 g/mol \times 2.5 L}{2.47 \times 0.0821 \times 300 K} = 3.42g$

Q5. The molar freezing point depression constant for benzene is 4.90K $kgmol^{-1}$. Selenium exists as polymer Se_X. When 3.26 gm of Se is dissolved in 226gm of benzene, the observed freezing point is 0.112^0C lower than for pure benzene. Decide the molecular formula of Selenium.(At.wt. of selenium is 78.8 g mol^{-1})

Ans $\Delta T_f = \frac{1000 \text{ x } K_f \text{ x } W_B}{W_A \text{ x } M_B}$

$0.112 \text{ K} = \frac{1000 \text{ x } 4.90 \text{ x } 3.26}{226 \text{ x } M_B}$

$M_B = \frac{1000 \text{ x } 4.90 \text{ x } 3.26}{226 \text{ x } 0.1112} = 631 \text{ g/mol}$

Number of Se atoms in a molecule = $\frac{631 \text{ x g/mol}}{78.8 \text{ g/mol}} = 8$

Therefore, molecular formula of Selenium = Se_8

5 MARKS QUESTION

Q1. a) State Raoult's Law for a solution containing volatile components.

How does Raoult's law become a special case of Henry's Law?

b) 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of a benzene by 0.40 K. Find the molar mass of the solute. (K_f for benzene = 5.12 K kg mol^{-1})

Ans. a) For a solution of volatile liquids , Raoult's law states that the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution, i.e., $p_A \propto x_A$

OR

$p_A = p^o_A x_A$ According's to Henry's Law , the partial pressure of a gas in vapour phase (p) is directly proportional to mole fraction (x) of the gas in the solution.

i.e., p = $K_H x$ on comparing it with Raoult's Law it can be seen that partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution

i.e; $p \propto x$

only the proportionality constant K_H differs from p^0_A . Thus, it become a special case of Henry's law in which $K_H = p^o_A$.

b) Substituting the values of various terms involved in equation $M_B = \frac{K_f \text{ x } W_B \text{ x } 1000}{\Delta T_f \text{ x } W_A}$

$M_B = \frac{5.12 \text{ x } 1.00 \text{ x } 1000}{0.40 \text{ x } 50} = 256 \text{g mol}^{-1}$

Q2. a) Calculate the molarity of a sulphuric acid solution in which the mole fraction of water is 0.85.

b) The graphical representation of vapour pressure of two component system as a function of composition is give alongside.

i) Are the A – B interaction weaker , stronger or of the same magnitude as A – A and B – B

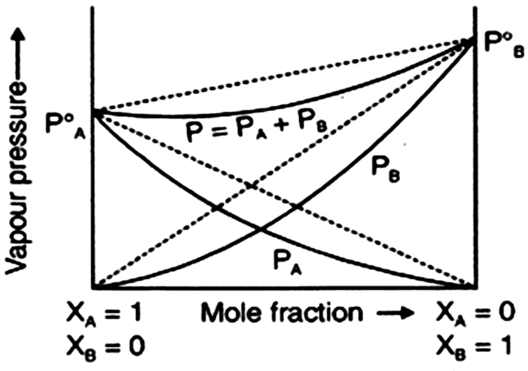
ii) Name the type of deviation shown by this system from Raoult's law.

iii) Predict the sign of $\Delta_{mix}H$ for this system.

iv) Predict the sign of $\Delta_{mix}V$ for this system.

v) Give an example of such a system.

vi) What type of Azeotrope will this system form, if possible ?



P-X graph for non-ideal solution showing –ve deviation

Ans. a) $\frac{n_A}{n_A + n_B} = 0.85$ .... i)

$\frac{n_B}{n_B + n_A} = 1\text{-}0.85 = 0.15$ ii

Dividing (ii) by (i), we get

$$\frac{n_B}{n_A} = \frac{0.15}{0.85} \text{ or } \frac{n_B}{1000/18} = \frac{0.15}{0.85} \text{ or } n_B = \frac{0.15 \times 1000}{0.85 \times 18}$$

hence molality = 9.8m

b) i) Stronger ii) Negative deviation iii)Negative iv) Negative iv) Negative

v) A liquid mixture consisting of 20% acetone and 80% chloroform by mass.

vi) Maximum boiling azeotrope.

VALUE BASED QUESTIONS

Q1 A doctor advised a patient suffering from high blood pressure to take less quantity of salt .

(1) What is the role of salt in increasing blood pressure ?

(2) How does low intake of salt helps in reducing the blood pressure ?

(3) What is the value associated with this ?

Ans. (1) High intake of salt further increases the sodium chloride concentration as well as osmotic pressure . therefore the blood pressure also increases . as a result inflow of water in cell causes water retention, which leads to swelling in the body.

(2) Low intake of salt reduces osmotic pressure as well as blood pressure.

(3) Proper awareness is needed and a person should be cautious and careful about his diet .

ASSIGNMENT

Q1. Define mole fraction.

Q2. What type of intermolecular attractive interaction exists in the pair of methanol and acetone?

Q3. What do you understand by “colligative properties” ?

Q4. Why is the vapour pressure of a solution of glucose in water lower than that of water?

Q5. State any two characteristics of ideal solutions.

Q6. Some liquids on mixing form “azeotrpoes”. What are azeotropes ?

Q7. Define molal elevation constant or ebullioscopic constant .

Q8. What is “reverse osmosis “ ?

Q9. Derive an equation to express that relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute in it when the solvent alone is volatile.

Q10. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law ?

Q11. Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500g of water such that it boils at 100°C ?

Q12. 18 g of glucose , $C_6H_{12}O_6$ (Molar Mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil ? (K_b for water = 0.52 K kg mol^{-1} ,boiling point of pure water = 373.15 K)

Q13. After removing the outer shell of the two eggs in dil. HCl, one is placed in distilled water and the other in a saturated solution of NaCl . What will you observe and why ?

Q14. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 26.0g of heptane and 35.0 g of octane ?

FLOW CHART

Expressing Conc of Solution

Mass Percentage

$w/w = \frac{W_B \times 100}{W_A+W_B}$

Mass by Vol %

$(W/V) = \frac{W_B \times 100}{V(\text{in ml})}$

Mole Fraction

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

Molality

$m = \frac{n_B}{W_A\ (\text{in Kg})}$

Volume % (v/ v)

$= \frac{V_B \times 100}{V_A+V_B}$

Parts per million

$(ppm) = \frac{W_B \times 10^6}{W_A+W_B}$

Molarity

$M = \frac{n_B}{V\ (\text{in L})}$

Mole Fraction

$X_B=n_B/\ n_A+n_B$

Colligative Properties

Relative lowering of Vapour Pressure

$\frac{P^\circ_A - P_A}{P^\circ_A} = X_b$

Elevation in B.P

$\Delta T_b = K_b \times m$

$\Delta T_b = T_b - T^\circ_b$

Depression in F. P

$X_b \Delta T_f = K_f \times m$

$P^\circ A \Delta T_f = T_f{}^\circ - T_f$

Osmotic Pressure

$\pi = CRT$

$\pi = \frac{n_B}{V} RT$

SOLUTIONS

Ideal Solution

i) $P_A=P^\circ_A X_A$

$P_B=P^\circ_B X_B$

ii) $\Delta H=0$

iii) $\Delta V=0$

Non Ideal Solution

Positive Deviations

i) $P_A> P^\circ_A X_A$

$P_B> P^\circ_B X_B$

ii) $\Delta H > O$ (+ve)

iii) $\Delta V> O$ (+ve)

Negative Deviations

i) $P_A< P^\circ_A X_A$

$P_B< P^\circ_B X_B$

ii) $\Delta H< O$ (-ve)

iii) $\Delta V < O$ (-ve

ELECTROCHEMISTRY (UNIT-3)

KEY POINTS

Resistance – obstacle in the flow of electricity.

Resistivity – resistance offered by the conductor with unit volume.

Conductivity – conductance of the ions present in 1 cubic centimeter solution. It is the reciprocal of resistivity.

1. Effect of dilution of conductivity – conductivity decrease with dilution because number of ions in per ml of solution decrease.
2. Effect of dilution of molar conductivity – molar conductivity of strong electrolytes, increase with dilution because ionic mobility, increase, whereas molar conductivity of weak electrolyte increase because degree of dissociation of it increases so number of ions increase .
3. Kohlrausch law – conductivity of an electrolyte at infinite dilution is the sum of individual contribution of anion and cation of the electrolyte .
4. Faraday's law of electrolysis - First law – amount of substance deposited at the electrode during electrolysis is directly proportional to the quantity of electricity passed through electrolyte .

   Second law – when same amount electricity is passed through different electrolytic solution, amount of substances deposited is proportional to their chemical equivalent weights .
5. Fuel cell – it converts combustion energy of fuel into electricity . H_2 and CH_4 can be used as fuel in it .
6. Corrosion – Molar corrosion of metal is an electro chemical phenomenon .

   Anode :- $2\,Fe \rightarrow 2Fe^{2+} + 4\,e^-$ (oxidation)

   Cathode :- $O_2 + 4\,H^+ + 4e^- \rightarrow 2H_2O$ (reduction)

   Atmospheric Oxidation :- $2Fe^{2+}(aq) + 2H_2O\,(l) + \frac{1}{2}\,O_2 \rightarrow Fe_2O_3\,(g) + 4H^+\,(aq)$

   Rate of corrosion increase in acidic medium . also increase in the presence of salt and oxygen but rate decreases in basic medium .

   Prevention of corrosion

   1. By Galvanization: - coating of Zn. on iron
   2. By Cathodic protection :- Mg is joined with iron which behaves like anode and iron like cathode .
   3. By painting and oiling

IMPORTANT FORMULAE

S.No	***Formula***	***What to calculate***	***Another form of the formula***
1	$E^\circ \text{cell} = E^\circ_{cathode} - E^\circ_{anode}$	*Cell potential of a cell can be calculated by this equation*	$E^\circ \text{cell} = E^\circ_R - E^\circ_L$
2	$E \text{ cell} = E^\circ \text{cell} - \frac{0.0591}{n} \log \frac{1}{M^{n+}}$	*Half Cell potential of a half cell can be calculated by this expression*	
3	$E \text{ cell} = E^\circ \text{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$	*Cell potential of a cell can be calculated by this expression*	
4	$E^\circ \text{cell} = \frac{0.0591}{n} \log Kc$	*To calculate cell potential from Kc and vice versa*	$\log Kc = \frac{n \times E^\circ \text{cell}}{0.0591}$
5	$\Delta G^\circ = nF E^\circ \text{cell}$	*To calculate cell potential from free energy change and vice versa*	$E^\circ \text{cell} = -\frac{\Delta G^\circ}{nF}$
6	$R = \rho \frac{l}{A}$	To calculate resistance	$\rho = \frac{RA}{l}$
7	$G^* = R \acute{K}$	To calculate cell constant	$\acute{K} = G/R$
8	$\wedge_m = \frac{K \times 1000}{M}$	To calculate the molar conductivity	
9	$W = Z \times I \times t \quad Z = E/96500$	*Amount of a substance produced at any electrode*	
10	$\frac{W1}{E1} = \frac{W2}{E2}$	*Amount of a substance produced at an electrode of different cells connected in a series*	

Frequently asked question

1 mark

1.) Give the relationship between molar conductivity and specific conductivity ?

Ans. $\wedge_m = k\,(1000\backslash M)$

2.) What is meant by limiting molar conductivity ?

Ans. The molar conductivity of a solution at infinity dilution is called limiting molar conductivity

3.) What is the unit of molar conductivity?

Ans . $ohm^{-1}cm^{2}mol^{-1}$

4.) What is the effect of dilution or concentration of specific conductance ?

Ans. Specific conductance decrease with dilution because it is the conduction power of ion present in unit volume of solution and number of ion in unit volume decrease . Specific conductance increase with concentration

2 marks

1.) What is fuel cell. Write two chemicals which can be used as fuel

Ans . The cell which converts combustion energy of fuel into electricity .

Methane and hydrogen can be used as fuel

$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

$O_2 + 2H_2O\,(l) + 4e^- \rightarrow 4OH^-(aq)$

2.) What type of battery is the lead storage battery? write the anode and the cathode reaction and the overall reaction occurring when current is drawn from it (reaction during discharge of it)

Ans. Lead storage battery is the secondary cell. So it can be recharged by passing direct current through it .

Discharge reaction –

At anode $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4\,(s) + 2e^-$

At cathode $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow 2PbSO_4\,(aq) + 2H_2O(l)$

Overall solution

$Pb + PbO_2 + 4H^+ + SO_4^{2-}(aq) \rightarrow 2PbSO_4 + 2H_2O$

3.) How many moles of mercury will be produced by electrolyzing 1.0 M $Hg\,(NO_3)_2$

Solution with a current of 2.00 A for three hours ?

$[Hg(NO_3)_2 = 200.6$ g.]

Ans . Current = 2A
Time = 3h = 3(60)(60)s
w = ZIt
Z for Hg in compound = E \96500 = 200.6/2(96500)
w= 200.6 (3)(60)(60)\2(96500)
w= 22.45g
number of moles = 22.45\200.6 = 0.112 mol

4.) Represent the galvanic cell in which the following reactions take place
$Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
i.) Which one of its electrode is negative charged
ii.) The reaction taking place at each of its electrode
iii.) The carrier of current with this cell.

Ans . The cell represents as

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Ag^{+}(aq) \mid Ag(s) \mid$

i.) Zn electrode is negatively charged

ii.) At anode

iii.) $Zn(s) \rightarrow Zn^{2+} + 2e^{-}$

iv.) At cathode
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

iv.) Ions are the carrier of current within the cell

5.) State faraday's law. how much change is required for the reduction of 1 mole of Cu^{2+} to Cu?

Ans. Statement
$Cu^{2+} + 2e \rightarrow Cu$
Change required for the required for the reduction of 1 mole Cu^{2+} = 2F
2F=2(96500 C) = 193000C

3 marks

1.) Determine the value of equilibrium constant and ΔG^{0} for the following reaction
$Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2 Ag(S)$
(E^{0} = 1.05V)

Ans. n=2 $\Delta G^{0} = -nF E^{0}$
$\Delta G^{0} = -2\ (96500)\ C\ (1.05)\ V$
$\Delta G^{0} = -202650 J\ mol^{-1} = -202.65\ KJ\ mol^{-1}$
$-nFE^{0} = -2.303\ RT\ 100\ Kc$
1ogKc = nFE^{0}\2.303RT
=nE^{0}\0.0591
=2(1.05\0.0591) = 35.532 g

Kc = antilog 354.532g
Kc = 3.411×10^{35}

2). Calculate the standard electrode potential of Ni $^{2+}$ // Ni electrode if emf of the Ni $^{2+}$/Ni(0.01) // Cu $^{2+}$(0.1) / Cu (s) is 0.059V. Given E^0_{cell} = 0.34 V

Ans. Ecell = 0.059V
E^0 Cu = 0.34 V (Cu^{+2}) = 0.1 M
Ecell = E^0_{cell}- 0.0591/n log [Ni $^{2+}$ (aq)] / [Cu^{2+}(aq)]
0.059 = E^0cell – 0.059/2 log 0.01/0.1
0.059 = E^0cell – 0.0295 log $\frac{1}{10}$
0.059 = E^0cell -0.0295 (log 1 – log 10)
= E^0cell – 0.0295(-1)
0.059 = E^0cell + 0.0295
E^0 cell = 0.05g – 0.0295 = 0.0295v
E^0 cell = E^0c- E^0a
0.0295 = 0.34 - E^0 anode
E^0 anode = 0.34 – 0.0295 = 0.3105V

3) The resistance conductivity cell filled with 0.1 M KCl solution is 100 Ohm. if the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02 M KCl solution . Conductivity of 0.1 M KCl solution is 1,29 m^{-1}

Ans. i) Cell constant G = conductivity (resistance)
= 1.29 S m^{-1} (100Ω)
1.29 m^{-1} or 1.29 cm^{-1}

ii) conductivity of 0.02 M KCl solution
(k) = cell constant \resistance = 1.29 cm^{-1}\520Ω
2.48 x 10^{-3} S cm^{-1}

iii) molar conductivity
$\wedge_m$ = k x 1000\M = 2.48 x 10^{-3} x 1000/0.02
= 124S cm^2 mol^{-1}

4) Give an example of a fuel cell and write the cathode and anode reaction for it .

Ans. Galavanic cell that are designed to convert the energy of combustion of fuel like hydrogen , methane, methanol directly into electrical energy are called fuel cell

Cathode reaction $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode reaction $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Overall reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

5 marks questions

Q.1) i) Define the molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and strong electrolyte

ii.) The resistance of a conductivity cell containing 0.001M KCl solution at 298K is 1500Ω. What is the cell constant if the conductivity of 0.01M KCl solution at 298 K is 0.146 (10^{-3}) S cm^{-1}

Ans.) i) Molar conductivity – it is defined as the conductance of the solution which contain one mole of electrolyte such that entire solution is in between two electrodes kept one centimeter apart sharing unit area of cross section

(ii) Given conductivity K = 0.146 (10^{-3}) S cm^{-1}

Cell constant G = k(R)

= $0.146 \times 10^{-3} \times 1500 = 0.219\ cm^{-1}$

Q. 2 (i) Write the formulation for galavanic cell in which the reaction

$Cu(s) + 2Ag^+ (aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

Takes place , Identify the cathode and the anode reaction in it

ii) Write Nernst equation calculate the emf of the following cell

$Sn(s)\ /\ Sn^{2+}(0.04M)\ //\ H^+\ (0.02M)\ /\ H_2(g)\ \ Pt(s)$ (given $E^0\ Sn^{2+}/Sn = -0.14V$)

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

$2Ag^+(aq)\ + 2e^- \rightarrow 2Ag\ (s)$

$Cu(s) + 2Ag^+\ (aq)\ \rightarrow Cu^{2+}(aq) + 2Ag(S)$

$Cu_{(s)}/Cu^{++}_{(aq)}\ ||\ Ag^+_{(aq)}\ |\ Ag_{(s)}$

Cu is acting as anode whereas Ag is acting as cathode

i.) $Sn\ (s) \rightarrow Sn^{2+}(Aq) + 2e^-$

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

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

$E_{cell} = E^0_{cell} - 0.0591\backslash 2 \log [Sn^{2+}/(H^+)^2]$

$= (\ E^0H^+/H_2 - E^0Sn^{2+}/\ Sn) - 0.0591/2 \log 0.04/(0.02)^2$

$= +0.14V - 0.0591\ V = 0.0809\ V$

VALUE BASED QUESTION

Manu and his father went to shop to purchase a battery for their inverter. Shopkeeper showed them two types of batteries, one with lead plates and the other with cadmium plate. The battery with cadmium plate was more expensive than the lead battery. Manu's father wanted to buy lead battery as it was cheaper.

(i) As a student of chemistry, why would you suggest Manu's father to buy expensive cadmium battery? Give two reasons.

(ii) What are the values associated with the above decision?

Answer)

(i) Harmful effects of lead on human being and on the environment: lead is a cumulative poison. Lead keeps on accumulating in the tissues of the human body and in the leaf tissues of the plants. Lead is very poisonous metal.

- (a) It damages organs like liver, kidney and intestine.
- (b) It induces abnormalities in fertility and pregnancy.
- (c) It causes coagulation of proteins.
- (d) It interferes with the development and maturation of red blood corpuscles (RBCs) in the human body. Due to prolonged effect of lead, the red blood cells get stippled. The malformation of red blood cells leads to a disease called anaemia.

(ii) It is wise to choose sustained long-term benefit than short-time gain with regard to health/ money. Less usage of lead battery keeps ourselves and the environment healthy.

Assignment

1. Calculate the e.m.f. of the cell:

   $Mg|Mg^{2+}(0.001\ M)||Cu^{2+}(0.0001\ M)|Cu$

   Given: $E^0_{Cu2+/Cu} = 0.34V$; $E^0_{Mg2+/Mg} = -2.375V$ [**Hints:**2.651V]

2. (a) Explain Kohlrausch's law of independent migration of ions. Mention two applications of this law.

   (b) Define molar conductivity. How does it vary with temperature?

3. Resistance of a solution(A) is 50 ohm and that of solution (B) is 100 ohm, both the solution being take in the same conductivity cell, if equal volumes of solution(A) and (B) are mixed, what will be the resistance of the mixture ,using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing. [**Hints:** 66.66 Ω]

4. The conductivity of 0.001M CH_3COOH is $4.95X10^{-5}Scm^{-1}$.Calculate its dissociation constant. Given limiting molar conductivity is 390.5S $cm^2\ mol^{-1}$. [**Hints**:α=0.126]

5. Calculate the potential of the following cell reaction at 298 K.

   $Sn^{4+}(1.50M) + Zn(s) \longrightarrow Sn^{2+}(0.5M) + Zn^{2+}(2.0M)$

   ($E^o_{cell} = 0.89V$.) [**Hints**: 3.17V]

6. How many moles of electrons are required to

   (i) Reduce 1 mol of MnO_4^- to Mn^{2+}

   (ii) Produce 10.0g of Al from molten Al_2O_3.

   [**Hints:** (i) 5 mol of electron (ii) 1.11 mol Al]

7. Why does a dry cell becomes dead after a long time, even if it has not been used?

   [Hints; Acidic NH_4Cl corrde the Zinc container]

8. What type of a battery is lead storage battery? Write the anode, the cathode reactions & overall reaction occouring in a lead storage battery.

9. How can you increase the reduction potential of an electrode.?

   [**Hints**: For the reaction It can be increased by

   a. increase in concentration of M^{n+} ions in solution

   b. by increasing the temperature].

10. Calculate emf of the following cell at 298K

    $Zn/Zn^{2+}(10\text{-}4M)||\ Cu^{2+}(10^{-2}M)/Cu$

    Given: $E°_{Zn2+/Zn} = -0.76V$ $E°_{Cu2+/Cu} = +0.34V$ [**Hints**: emf = 1.1591V]

11. Electrolysis of KBr (aq) gives Br_2 at anode but KF (aq) does not give F_2. Give reason.

12. Explain the meaning of the terms:

    (a) Ionic mobility

    (b) Over Voltage

13. What is Electrochemical series? List its two characteristics.

14. Account for the following observations:

    (a) In a dry cell, the build up of ammonia gas around the carbon cathode should disrupt the electric current, but in the practice this does not happen.

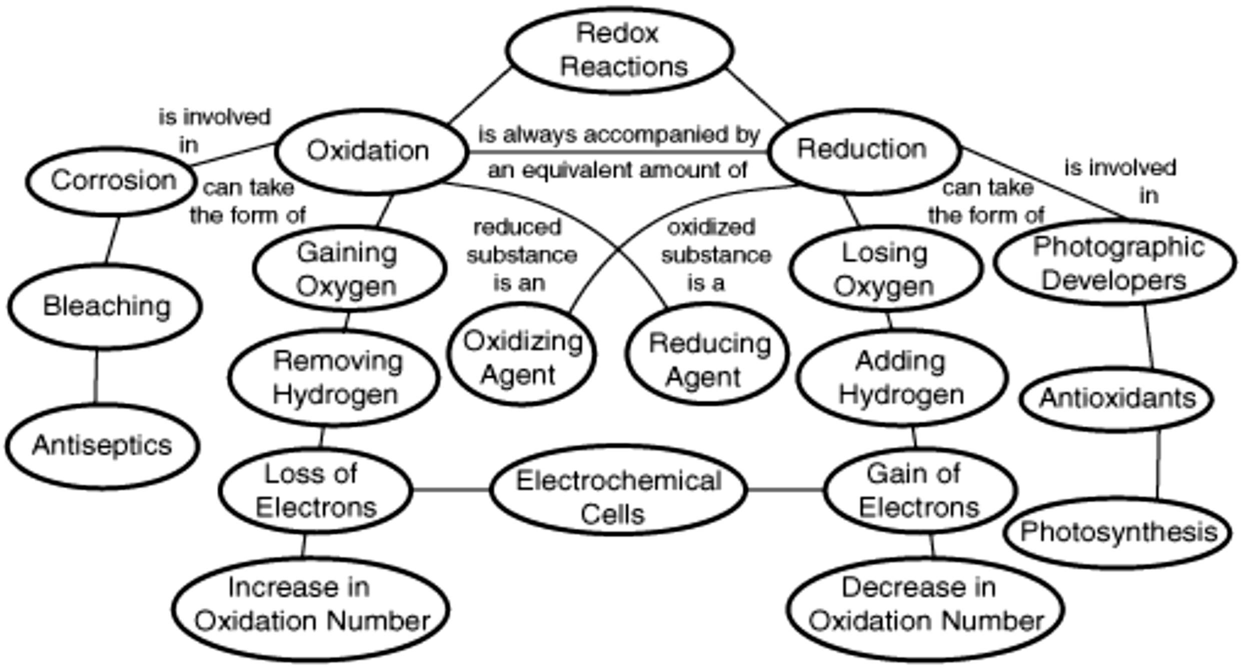
    (b) Ordinary dry cells are not rechargeable.

15. Explain the following observations:

    (a) The product of electrolysis of molten NaCl are sodium metal and chroline gas.

    (b) The product of electrolysis of aqueous sodium chloride solution are NaOH, Cl_2 and H_2.

ELECTROCHEMISTRY MIND MAP



CHEMICAL KINETICS (UNIT 4)

KEY CONCEPTS

1. **Rate of reaction**:- For a reaction R $\rightarrow$ P,

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

$$= \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

Unit of rate of reaction:- 1. $molL^{-1}s^{-1}$ 2. atm s^{-1}

2. **Unifying rate of reaction**

For the reaction $2HI \rightarrow H_2 + I_2$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Similarly, for the reaction

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

3. **Differential rate law (Rate law)**

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} \propto [A]^x\,[B]^y$$

$$\text{Rate} = k\,[A]^x\,[B]^y$$

$$-\frac{d[R]}{dt} = k[A]^x[B]^y$$

This is Differential rate equation.

4. **Order of reaction:-** For the reaction $aA + bB \rightarrow cC + dD$

Rate = $K[A]^x\,[B]^y$

x + y = order of reaction.(where x & y may or may not equal to stoichiometric coffecient)

Note:-

i. if x + y = 1, reaction is called **I order reaction**.

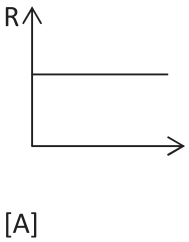
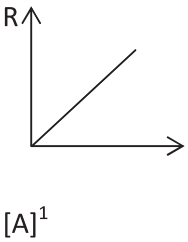
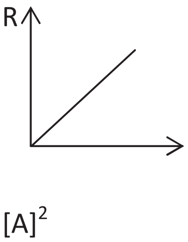
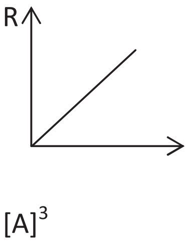
ii. if x + y = 2, reaction is called **II order reaction**.

iii. if x + y = 3, reaction is called **III order reaction**.

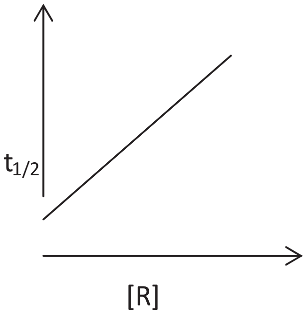
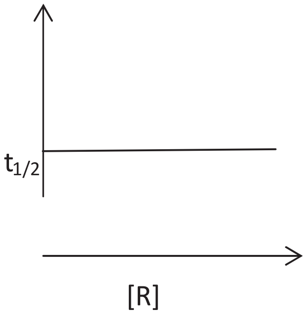
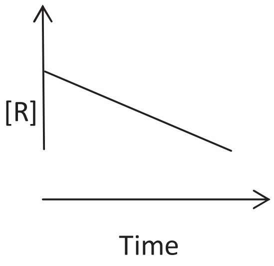
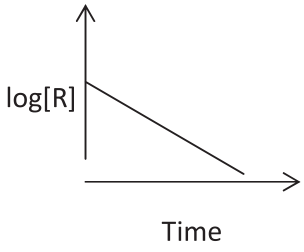
iv. if x + y = 0, reaction is called **zero order reaction**.

v. if x + y = fraction , reaction is called **fractional order reaction**.

5. Units of rate constants and graph between rate and conc. of reactant

Order of reaction	zero	first	second	third
Unit of rate constt.	$MolL^{-1}s^{-1}$	s^{-1}	$Mol^{-1}L^{+1}s^{-1}$	$Mol^{-2}L^{+2}s^{-1}$
Relation b/w rate & conc of Reactant	$R \alpha [A]^0$	$R \alpha [A]^1$	$R \alpha [A]^2$	$R \alpha [A]^3$
Graph b/w rate & conc of Reactant				

6. Integrated rate equation for zero order and first order reaction

	for zero order reaction	for first order reaction
Integrated rate equation	$k = \frac{[R]_0 - [R]}{t}$	$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$
Half life	$t_{1/2} = [R]_0/2K$	$t_{1/2} = 0.693/K$
Graph b/w half-life & conc of Reactant		
Graph b/w conc .of reactant & time		

Note:- 1. For zero order reaction $t_{1/2} \alpha$ conc. of reactant.

2. For I order reaction $t_{1/2}$ is independent of conc of reactant.
3. $t_{1/2} \alpha [conc]^{1-n}$ where n = order of reaction.

7. **Arrhenius equation**

   $\log K = \log A - E_a/2.303RT$

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

IMPORTANT DEFINITIONS

1 **Pseudo first order reaction:-** reaction which is appeared to be of higher order. But, actually these are of first order reaction. Such reaction is called pseudo first order reaction.

Eg. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ molecularity of reaction is two and Order of reaction is one.

2. **Molecularity of reaction:-**The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

Types of reaction based on molecularity

Unimolecular reactions	Bimolecular reactions	Trimolecular or termolecular reactions
molecularity of reaction = 1	molecularity of reaction = 2	molecularity of reaction = 3
$NH_4NO_2 \rightarrow N_2 + 2H_2O$	$2HI \rightarrow H_2 + I_2$	$2NO + O_2 \rightarrow 2NO_2$

NOTE:-

i. It is theoretical value.

ii. It cannot be zero or a non integer.

iii. molecularity greater than three is not observed.

iv. molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

3. **Order of reaction:-** the power to which conc. term of a reactant is raised in rate law expression is called order of w.r.t. that reactant. The sum of powers of conc. of all reactants in rate law expression is called order of reaction.

for the reaction $aA + bB \rightarrow cC + dD$

$$\text{Rate} = K[A]^x [B]^y$$

$$x + y = \text{order of reaction.}$$

NOTE:-

i. Order of a reaction is an experimental quantity ii. It can be zero and even a fraction

iii. Order is applicable to elementary as well as complex reactions

4. **Elementary step:-** Many reactions complete in a number of steps. Each individual step of a reaction is called elementary step.

Eg. The reaction $2O_3 \rightarrow 3O_2$ completes in two steps.

$O_3 \rightarrow O_2 + O$ step 1 fast reaction

$O + O_3 \rightarrow 2O_2$ step 2 slow reaction

Thus the reaction has two elementary steps.

NOTE:-

i. In elementary step stoichiometric coefficient of balanced equation is order w.r.t. that reactant.

ii. The slowest step in a reaction is called the **rate determining step.**

5. **Activation energy:-** The additional energy which is required by the molecules of reactants to cause effective collision is called Activation energy. It is denoted by E_a and is given as-

   Activation energy = threshold energy – average energy of molecules of reactants

6. **Threshold energy:-**The minimum energy which must be required by the molecules of reactants to cause effective collision is called threshold energy.

7. **Collision frequency:-** The number of collision of reactant moleules per unit volume of reaction mixture per second is called collision frequency.

IMPORTANT QUESTIONS

1 MARKS QUESTIONS

Q1. Calculate the overall order of a reaction which has the rate expression. Rate = $k\,[A]^{1/2}\,[B]^{3/2}$

Ans Order of reaction = 1/2 + 3/2 = 2 i.e. second order reaction.

Q2. Define the term : activation energy

Ans The additional energy which is required by the molecules of reactants to cause effective collision is called Activation energy.

Q3. What is the unit of rate constant for a Pseudo first order reaction?

Ans s^{-1}

Q4. Give an example of Pseudo first order reaction.

Ans $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Q5. The rate constant of a reaction is 0.005 $molL^{-1}s^{-1}$. What is the order of this reaction?

Ans Zero order reaction

2 MARKS QUESTIONS

Q1. In a reaction, 2A $\rightarrow$ Products, the concentration of A decreases from 0.5mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

Ans Rate = – change in conc. of A/2 x time interval

= – [0.4-0.5]/2X10 = 0.005 mol $litre^{-1}min^{-1}$

Q2. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

Ans Given K= 60 s^{-1}, $[R]_o$=1, [R]=1/16, t = ?

t = 2.303/K log $[R]_o$ /[R]

= 2.303/60 log 16 = 3.84X10^{-2} s

Q3. Define the following terms : i) elementary reaction ii) half-life period of a reaction

Ans i) Many reactions complete in a number of steps. Each individual step of a reaction is called elementary step.

ii) Time during which amount of reactant remains half of its initial amount is called half-life period of a reaction.

Q4. Give three important difference between rate of reaction and rate constant of reaction.

Ans

S.No.	rate of reaction	rate constant of reaction
1	It is the change in concentration of reactant or product in a unit interval of time.	It os the rate of reaction when molar conc. of each of the reactants is unity.
2	Its unit is $molL^{-1}s^{-1}$.	Its unit depends upon the order of reaction.
3	The rate of reaction at any instant of time depends upon the molar conc. of the reactants at that time	The rate constant does not depend upon the molar conc. of the reactants.

Q5. Give four important difference between order of reaction molecularity of reaction.

Ans

S.No.	order of reaction	molecularity of reaction
1	It is sum of the powers of the concentration of the reactants in the rate law expression	The number of reacting species taking part in an elementary reaction, which must collide to give products is called molecularity of a reaction.
2	Order of a reaction is an experimental quantity.	It is theoretical value.
3	It can be zero and even a fraction.	It cannot be zero or a non integer.
4	Order is applicable to elementary as well as complex reactions.	molecularity is applicable only for elementary reactions.

3 MARKS QUESTIONS

Q1. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction

Ans When reaction is completed 99.9%, $[R]n = [R]_0 – 0.999[R]_0$

$k = 2.303/t \log R_0/R$

$= 2.303/t \log R_0 /[R]_0 – 0.999 R_0$

$= 2.303/t \log 10^3$

$t = 6.909/k$

For half-life of the reaction

$t_{1/2} = 0.693/k$

$t/t_{1/2} = 6.909/0.693 = 10$

Q2. The rate constants of a reaction at 500K and 700K are $0.02s^{-1}$ and$0.07s^{-1}$ respectively. Calculate the values of Ea and A.

Ans $\text{Log}k_2/k_1 = E_a/2.303R \log[T_2 – T_1/T_2 \times T_1]$

$\text{Log } 0.07/0.02 = E_a/2.303X8.314X \log[700\text{-}500/700X500]$

$E_a = 18230.8J$

$\log k = \log A – E_a/2.303RT$

$\log 0.02 = \log A – 18230.8/20303X8.314X500$,

$A= 1.61$

Q3. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans Given t=40min, $[R]_o = 100$, $[R]=100\text{-}30=70$

$k = 2.303/t \log R_0/R$

$= 2.303/40 \log 100/70$

$= 0.0575(\log 100\text{-}\log 70) = 0.0575(2\text{-}1.8451) = 0.00890 min^{-1}$

$t_{1/2} = 0.693/k = 0.693/0.00890 = 77.86 min.$

Q4. The decomposition of hydrocarbon follows the equationk = (4.5 × $10^{11}s^{-1}$) $e^{-28000K/T,}$ Calculate Ea.

Experiment	[A]/mol L–1	[B]/mol L–1	Initial rate of formation/
			$molL^{-1}s^{-1}$
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}
Determine i) the rate law ii) order of reaction and iii) the rate constant for the reaction.			

Ans Let the rate law is Rate = $K[A]^x [B]^y$

Hence, $6.0 \times 10^{-3} = K[0.1]^x [0.1]^y$ ————i

$7.2 \times 10^{-2} = K[0.3]^x [0.2]^y$ ———————ii

$2.88 \times 10^{-1} = K[0.3]^x [0.4]^y$ ——iii

$2.40 \times 10^{-2} = K[0.4]^x [0.1]^y$ —————— iv

On dividing eq. (i) by eq. (iv), $1/4 = [1/4]^x$, X = 1 on dividing eq. (ii) by eq. (iii) $1/4 = [1/2]^y$, $[1/2]^2 = [1/2]^y$, y = 2 Therefore,

i) the rate law is Rate = $K[A]^1 [B]^2$

ii) order of reaction = X + Y =1+2 = 3

iii) rate constant for the reaction K = Rate/$[A]^1 [B]^2$
$= 6.0 \times 10^{-3} / /[0.1]^1 [0.1]^2 = 6.0\ mol^{-2}L^2s^{-1}$.

5 MARKS QUESTIONS

Q1. (a) The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

(b) A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

Ans (a) Given$t_{1/2}$= 5730 years, $[R]_o$=100, [R]=80
$K = 0.693/ t_{1/2} = 0.693/5730 = 1.21X\ 10^{-4}\ year^{-1}$.
$t = 2.303/K \log [R]_o /[R] = 2.303/1.21X\ 10^{-4} \log 100/80 = 1.9033X\ 10^{-4} (\log 100 - \log 80)$
$= 1.9033X\ 10^{-4} (2-1.9031) = 1.9033X\ 10^{-4} (0.0969) = 1845$ year

(b) (i) Rate = $K[A]^1 [B]^2$

(ii) Rate = $K[A]^1 [3B]^2 = 9K[A]^1 [B]^2$ hence, it becomes 9 times.

(iii) Rate = $K[2A]^1 2[B]^2 = 8K[A]^1 [B]^2$ hence, it becomes 8 times.

ASSIGNMENTS

Q1. Which is the rate determing step in the elementary steps? 1

Q2. Define collision frequency. 1

Q3. Identify the order of reaction if $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} 1

Q4. Define the terms:- i) Threshold energy ii) Elementary reaction 2

Q5. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half ? 2

Q6. Explain effect of i) temperature ii) presence of catalyst on the rate of reaction 3

Q7. Give the relation between half-life and concentration of reactants for n^{th} order of reaction. Also draw graph for zero and first order reaction showing relation between $t_{1/2}$ & concentration of reactant. 3

Q8. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction. 3

Q9. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature. 3

Q10. For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data are obtained. 5

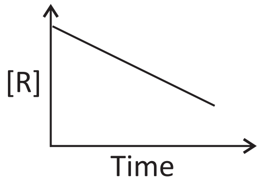
t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

HOTS QUESTIONS

1 The activation energy for the reaction $2HI(g) \rightarrow H_2 + I_2\ (g)$ is 209.5 kJ mol^{-1} at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy? 3

2 Consider the reaction $R \rightarrow P$. the change in concentration of R with time is shown in the following plot:



I. Predict the order of reaction

ii. Derive the expression for the time required for the completion of reaction

iii. What does the slope of the above line indicate

VALUE BASED QUESTION

Q. It is observed that the smaller particles react more rapidly than the larger particles of same mass. For example coal dust burns rapidly than that of the larger lumps of coal. Smaller chips of wood burns more rapidly than that of a log of wood of the same mass.

(i) A lump of coal burns at moderate in air while coal dust burns explosively. Explain.

(ii) Powdered sugar dissolves in water faster than crystalline sugar. Why?

(iii) Why liquid bromine reacts slowly as compared to vapours of bromine.

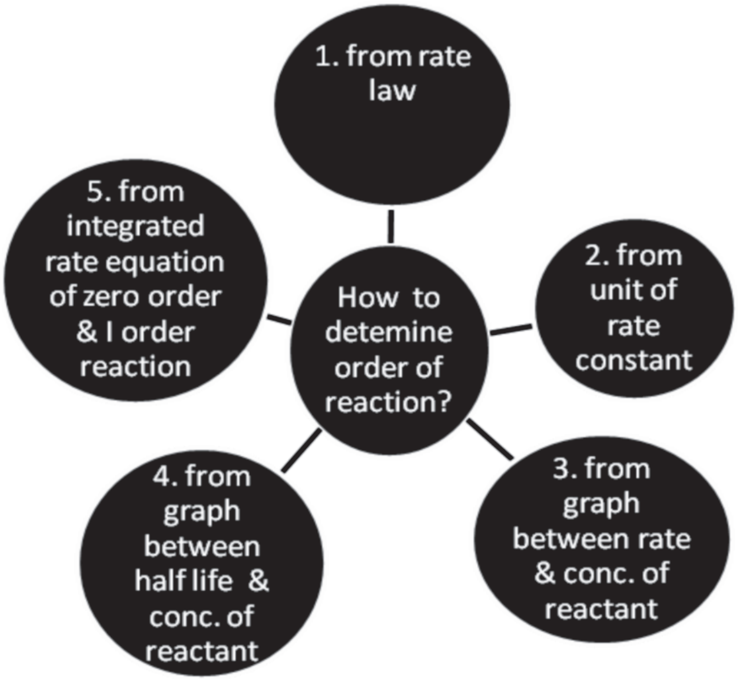
Answer.

(i) In case coal dust, greater area is available as compared to the solid coal. This means that the coal dust will react faster than the lump of coal. Since combustion is an exothermic reaction, greater amount of heat evolved in the combustion of coal dust leaves to explosion also.

(ii) Sugar in the powdered state has more surface area as compared to the crystalline sugar. As a result, the powdered sugar is expected to dissolve in water at a faster rate than crystalline sugar.

(i) In the vapour state, the molecules of bromine have more kinetic energy than in liquid state. Therefore, collision with the molecules of other results in the vapour state will be faster than in the liquid state. Moreover, in the liquid state, the surface area available for the chemical reaction is more as compared to the liquid state. Hence, bromine in the vapour state reacts at a faster rate compared with the liquid state.

MIND MAP



SURFACE CHEMISTRY (UNIT 5)

KEY POINTS

- **The branch of chemistry which deals with the study of surface phenomena .**
- **Adsorption:**The phenomenon of attracting and retaining the molecules of a substance at the surface of a solid or a liquid resulting into higher concentration of the molecules on the surface than in the bulk.
- **Adsorbent:** The substance where adsorption occurs.
- **Adsorbate:** The substance that get adsorbed.
- **Absorption:** The phenomenon in which the particles of gas and liquid get uniformly distributed throughout the body of the solid.
- **Desorption:** The process of removal of an adsorbed substance from the surface on which it is adsorbed .
- **Sorption:** Whenboth absorption and adsorption occur together and are not distinguishable.
- **Mechanism of adsorption :** arises due to unbalanced force of attraction on the surface of solids that are responsible for attracting the adsorbate particles on the surface.
- The extent of adsorption increases with increase in surface area.

Gibbs energy change during adsorption : During adsorption, there is always decrease in residual force i.e., there is decrease in surface energy, which appears as heat. Therefore adsorption is an exothermic process i.e. $\Delta H = -$ ve .

Also movement of the particles are restricted in this process. Therefore $\Delta S = -$ ve

According to Gibbs Helmholtz equation : $\Delta G = \Delta H - T\Delta S$, or $\Delta G = (-\Delta H) - T(-\Delta S)$

for adsorption to occur. ΔG must be negative which is possible only when $\Delta H > T\Delta S$

- **Types of Adsorption: physical and chemical adsorption**

1. **Physical adsorption** : When the particles of adsorbate are held to the surface of adsorbent by weak Vander Waals forces,

   Characteristics of physical adsorption: Lack of specificity, Low enthalpy of adsorption, Reversible in nature , no activation energy required ,Decrease with increase in temperature .

2. **Chemical adsoption :** When the molecules of adsorbate are held to the surface of adsorbent by strong chemical forces.

   Characteristics of chemical adsorption: Highly specific in nature, High enthalpy of adsorption, Irreversible in nature, initially it Increases with increase in temperature as it needs activation energy, very slow .

   Adsorption Isotherm: The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm. (It's a plot / curve between extent of adsorption x/m and pressure P at constant T)

Freundlich adsorption Isotherm

$x/m = K.P^{1/n} (n>1)$

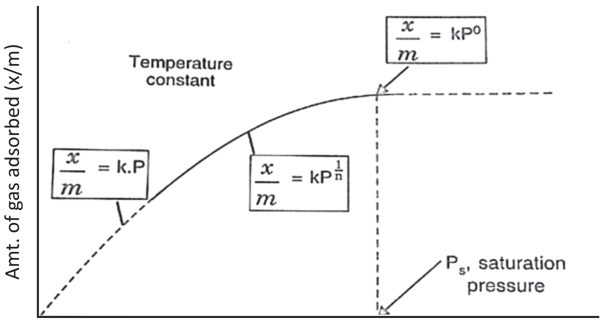
$\text{Log } x/m = \log k + 1/n \log P$

The factor 1/n can have values between 0 & 1.

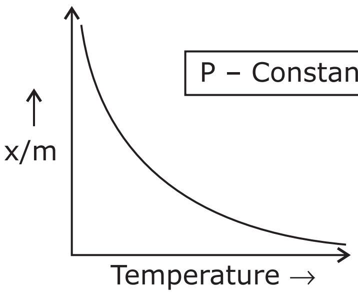
When 1/n=0, x/m= constant which shows that adsorption is independent of pressure.

When 1/n=1, x/m=kP, the adsorption varies directly with pressure

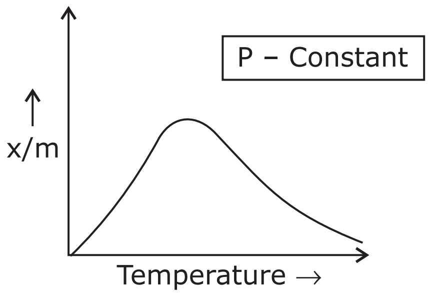
- The variation in the amount of gas adsorbed by the adsorbent with temperature at constant pressure can be expressed by means of a curve termed as adsorption isobar.



Adsorption isotherm in term of Freundlich.



Physical adsorption



Chemical adsorption

Factors Affecting adsorption

- **Nature of adsorbent :** Transition metals act as good adsorbents for gases due to vacant or half filled d orbitals and high charge-size ratio**.**
- **Surface area of adsorbent :** surface area α adsorption.
- **Nature of adsorbate :** Easily liquefiable gases like ammonia HCl carbon dioxide etc. are adsorbed to a much greater extent than permanent gases like nitrogen,Hydrogen,etc.
- **Pressure :** At constant temperature , Adsorption α pressure
- **Temperature :** adsorption α 1/T.
- **Activation of solid absorbent :** It is done by subdividing the solid into smaller particles or by passing super-heated steam to increase its adsorbing power**.**

Adsorption from solutions : In case of adsorption from *solution* phase.

Extent of adsorption (x/m) α 1/T.

Extent of adsorption (x/m) α surface area of the adsorption.

Extent of adsorptoin (x/m) α concentration of the solute.

The extent of adsorption depends on the nature of adsorbent and the adsorbate.

APPLICATIONS OF ADSORPTION:

(a) Gas masks

(b) Production of high vaccum

(c) Humidity control

(d) Removal of colouring matter from solutions

(e) Hetrogeneous catalysis

(f) Separation of inert gases

(g) Softening of hard water

(h) De-ionization of water

CATALYSIS : Substances which alter the rate of reaction, themselves remaining chemically and quantitatively unchanged after the reaction and the phenomenon is called catalysis.

HOMOGENEOUS CATALYSIS- When the reactants and the catalysts are in the same phase

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{NO(g)} 2SO_3$$

HETEROGENEOUS CATALYSIS- The catalytic process in which the reactants and the catalysts are in different phases.

$$N_2\,(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_2$$

AUTO CATALYSIS –when one of the products increases the rate of reaction by acting as a catalysts.

FEATURES OF SOLID CATALYSTS-

1. **ACTIVITY –**The activity of a catalysts depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active.

   eg- $2H_2O + O_2 \rightarrow 2H_2O$

2. **SELECTIVITY-** The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.

   $CO + 3H_2 \rightarrow CH_4 + H_2O$
   $CO + 2H_2 \rightarrow CH_3OH$
   $CO + H_2 \rightarrow HCHO$

ZEOLITESare shape- selective catalysts because of their honey-comb like structures. Chemically **microporus aluminosilicates**.

The reaction taking place in zeolites depend upon :The size and shape of reactant and product molecules and Pores and cavities of the zeolites.

- Zeolites widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation.
- zeolite catalysts used in petroleum industries. **ZSM-5**, converts alcohols directly into gasoline(petrol)

COLLOIDAL STATE

- The substances whose solutions could pass through filter paper and animal membrane, having higher rate of diffusion are called CRYSTALLOIDS.
- Substances whose solution can pass through filter paper and not animal membrane, having slower rate of diffusion are called COLLOIDS. particle size 1nm to 1000nm

Classification is based on following criteria

- Physical state of dispersed phase and dispersion medium.
- Nature of interaction between dispersed phase and dispersion medium.
- Types of particles of the dispersed phase

Dispersion phase {DP} and Dispersion medium {DM}

- The phase which is dispersed in the other (medium) is called DP or internal phase, or discontinuous phase.
- The phase or medium in which the dispersion is made is called dispersion medium (DM) or external phase or continuous phase.

Classification on the basis of affinity of DP for DM : lyophobic and lyophilic colloids

- **Lyophobic colloids (solvent hating colloids) :** These colloids cannot be prepared by simply mixing dispersed phase with dispersion medium, they need stabilizing agent to preserve them , irreversible. Ex: colloidal solutions of gold , silver, $Fe(OH)_3$, As_2S_3, etc.
- **Lyophilic colloids (solvent loving):** Directly formed by mixing DP with a suitable liquid(the dispersion medium), self-stabilizing , reversible sols. sol of starch, gum, gelatin, rubber.

Classification based on type of particles of the dispersed phase

- **Multimolecular colloids :** Consists of aggregates of a large number of atoms or smaller molecules whose diameter is less than 1 nm. Ex Au sol
- **Macromolecular colloids:** In these colloids the molecules have sizes and dimensions comparable to colloidal particles. Ex: proteins, starch, cellulose**.**
- **Associated colloids:** At low concentrations, behave as normal, strong electrolytes and at higher concentrations exhibit colloidal state properties due to the formation of aggregated particles (micelles). E.g Soaps and detergents

- The temperature only above which the formation of micelles takes place is called **Kraft temperature (T_K) .**
- **Critical Micelle Concentration:** The concentration above which micelle formation takes place.

Preparation of Lyophobic sols

- **Condensation methods :** Particles of atomic or molecular size are induced to form aggregates
- **Oxidation method :** Sulphur colloids are prepared by oxidation of H_2S by O_2.

  $SO_2 + 2H_2S \rightarrow 3S\,(sol) + 2H_2O$
- **Reduction :**Silver colloids are prepared by passing H_2 through a saturated aqueous solution of silver oxide at 65° C.
- **Hydrolysis :** Dark brown $Fe(OH)_3$ colloidal solution is prepared by adding $FeCl_3$ into boiling water.$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$
- **Double decomposition :** Arsenious sulphide colloidal solution is prepared by passing of H_2S gas into a solution of As_2O_3.
- **Exchange of solvent :** Colloidal solution of phosphorus is prepared by addition of alcohol into a solution of phosphorous in excess water.
- **Dispersion methods & Mechanical disintegration**
- **Peptisation :** Process of converting of a fresh precipitate into colloidal particles by adding suitable electrolyte is known as peptisation.

  e.g. $Fe(OH)_3$ solution is formed from $FeCl_3$.
- **Electro-disintegration (Bredig's arc method)**

Purification of colloids:

- **Dialysis :** Purification of colloidal solutions from the impurities (mainly electrolytes) by diffusion through a porous membrane such as parchment, collodion, etc.
- **Electro dialysis :** When dialysis process is accelerated by the application of a potential difference across the membrane, So ions migrate faster than the colloids **.**
- **Ultra filtration :** purification of colloidal solution using special filter paper called ultra filters(filter paper which is impregnated with gelatin or collodion followed by hardening in formaldehyde)

  Collodion: it is 4%nitrocellulose soln in alcohol and ether.

Properties of colloids:

- **Optical properties: Tyndall effect :** Due to scattering of light by colloidal particles by which the path of beam becomes visible.
- **Brownian movement:** Zig- zag movement of colloidal particles due to collision between particles of DP & DM, responsible for stability of colloids.
- **Electrophoresis :** Movement of colloidal particles under influence of electric field **.**

- **Electro-osmosis:** molecules of dispersion medium allowed to move under influence of electric field
- **Coagulation or flocculation:** Process of settling of colloidal particles into precipitate or float on surface by addition of electrolytes.

Hardy schulze law : Coagulating power of an electrolyte increases rapidly with the increase in the valency of cation or anion.

For negatively charged sol, the coagulating power of electrolytes are

$\mathbf{AlCl_3 > BaCl_2 > NaCl \text{ or } Al^{3+} > Ba^{2+} > Na^+}$

For positively charged, then the coagulating power of electrolytes follow the following order: $\mathbf{K_4[Fe(CN)_6] > PO_4^{3-} > SO_4^{2-} > Cl^-}$

Emulsion: liquid – liquid colloidal system..e.g. milk, Na-soaps, vanishing cream, etc.

Types of emulsions:

Oil in water: when oil is the dispersed phase and water is the dispersion medium, e.g. milk.

Water in oil: when water is the dispersed phase and oil is the dispersed medium, e.g. butter,

Applications of colloids:

(a) Rubber plating
(b) Sewage disposal
(c) Smoke screen
(d) Purification of water
(e) Cleaning action of soap
(f) In medicine
(h) Photography
(i) Artificial rain
(g) Formation of delta

FREQUENTLY ASKED QUESTIONS

Very short answer type questions (1 mark each)

Q1. Why are substances like platinum and palladium often used for carrying out electrolysis of aqueous solutions?

A1. Platinum and palladium are inert materials & are not attacked by the ions of the electrolyte or the products of electrolysis therefore used as electrodes for carrying out the electrolysis.

Q2. Why does physisorption decreases with the increase of temperature?

A2. Physisorption is an exothermic process i.e, heat is produced in the process.

Solid(adsorbent) + gas(adsorbate) $\rightleftharpoons$ gas/solid(gas adsorbed on solid) + heat

According to Le-Chatelier's principle, if we increase the temperature, equilibrium will shift in the backward direction, i.e, gas is released from the adsorbed surface.

Q3). Why is it necessary to remove CO when ammonia is obtained by Haber's process?

A3). CO acts as a poison for the catalyst in the manufacture of ammonia by Haber's process**.**

Q4) What is the physical states of dispersed phase and dispersion medium of froth?

A4. Dispersed phase is gas, dispersion medium is liquid.

Q5) **What is the cause of Brownian movement among colloidal particles?**

A5. Due to unequal collision between particles.

Q6) **Write the main reason for the stability of colloidal sols.**

A6. Brownian movement / charge on colloidal particles.

Q7) **Give an example of micelle system?**

A7. Sodium stearate ($C_{17}H_{35}COO^{-}Na^{+}$).

Q8) **Write down the example of Positive sol?**

A8. Ferric hydroxide sol.

SHORT ANSWER QUESTIONS (2 marks each)

Q9). **Explain what is observed**

(i) When a beam of light is passed through a colloidal soln.

(ii) Electric current is passed through a colloidal soln.

A9). (i) scattering of light by the colloidal particles takes place and the path of light becomes visible. This is known as tyndal effect.

(ii) On passing an electric current , colloidal particles move towards the oppositely charged electrodes where they loose their charge and get coagulated. This process is called electrophoresis.

Q10). **Explain: (i) Electrophoresis (ii) Coagulation**

A10). (i) The phenomenon involving the migration(movement) of colloidal particles under the influence of electric field towards the oppositely charged electrode

(ii) The process of conversion of sol into precipitate ,usually done by addition of suitable electrolytes.If the coagulated particles float on the surface of dispersion medium , the coagulation is known as flocculation.

Q11). **What are micelles?Give an example of a miceller system.**

A11. Micelles are produced by the aggregation of a large number of ions in concentrated sol . Aggregated particles are known as micelles also known as associated colloids.eg: soap , synthetic detergents..

Q12). **(i) Why is ferric chloride preffered over potassium chloride in the case of a cut leading to bleeding?**

(ii) Why is desorption important for a substance to act as a good catalyst ?

A12. (i) Blood is +vely charged colloid.One molecule of ferric chloride produces 3 –ve chloride ions while one molecule of potassium chloride produces one –ve chloride ion. Greater the –ve charge, faster the coagulation.

(ii) After the reaction is over between the adsorbed reactants, the process of desorption must take place to remove the product molecules and create space for other reactant molecules to adsorb on the catalyst surface

Q13) Differentiate between lyophilic colloids and lyophobic colloids?

Lyophilic colloids	Lyophobic colloids
a) These are easily formed by direct mixing	a) These are easily formed by special methods.
b) Particles of colloids are not easily visible even under ultra microscope.	b) Particles of colloids are easily visible under ultra microscope.
c) These are very stable.	c) These are unstable.

SHORT ANSWER QUESTIONS

(3 MARKS EACH)

Q14) Account for the following:

(i) What is collodion?

(ii) Why do we add alum to purify water?

(iii) Of physisorption and chemisorptions, which type of adsorption has a higher enthalpy of adsorption?

A14. (i) It is a 4% sol. of nitrocellulose in a mixture of alcohol and ether.

(ii) Alum coagulates colloidal impurities present in water.

(iii) Chemisorption has higher enthalpy of adsorption on account of formation of chemical bond.

Q15) (i) How can colloidal sol. of sulphur in water be prepared?

(ii) What is electrophoresis due to ?

(iii) Why is $Fe(OH)_3$ colloid +vely charged when prepared by adding $FeCl_3$ to hot water?

A15. (i) It is prepared by oxidation of H_2S by dil.HNO_3. $H_2S + [O] \longrightarrow H_2O + S$ {catalyst dil. HNO_3}

(ii) Colloidal particles carry a charge, either +ve or –ve. On passing electricity, they migrate towards the oppositely charged electrode.

(iii) The colloidal sol. of hydrated ferric oxide adsorbs +vely charged Fe^{3+} ion and therefore the colloidal sol. becomes +vely charged.

Q16) How are the following colloids different from each other in respect of dispersion medium and dispersed phase? Give an example each.

(i) An aerosol (ii) A hydrosol (iii) An emulsion

A16. (i) An aerosol is a colloidal dispersion of liquid in a gas, eg, fog

(ii) A hydrosol is a colloidal sol. of a solid in water as the dispersion medium, eg, starch sol.

(iii) An emulsion is a colloidal system with dispersed phase as well as dispersion medium as liquids, eg, oil in water.

Q17) Account for the following:

(i) On the basis of Hardy Schulze rule , explain why the coagulating power of phosphate is higher than chloride?

(ii) How does a delta form at the meeting place of sea and river water ?

(iii) Why is chemisorptions referred to as activated adsorption?

A17. (i) Minimum quantity of an electrolyte required to cause precipitation of a sol is called its coagulating value. Greater the charge and smaller the amount of electrolyte required for precipitation higher is the coagulating power of electrolyte.

(ii) River water is a colloidal sol. of clay and Sea water contains a lot of electrolytes . Coagulation takes place at the meeting place of sea and river water the coagulated clay forms delta.

(iii) Chemisorption involves formation of bonds for which activation energy is required**.**

LONG ANSWER QUESTIONS

Q18). What is adsorption ? How adsorption is classified? How does adsorption of a gas on a solid surface vary with (i) temperature (ii) pressure.

A18. Adsorption is a phenomenon in which concentration of solute is more at the surface and less in the bulk. Adsorption is classified as physisorption & chemisorptions.

Physical adsorption of a gas on solid decreases with increase in temperature and increases with increases in pressure.

Chemical adsorption first increases and then decreases with increase in temperature.

Chemical adsorption first increases and then becomes independent of pressure with increase in pressure.

Q19) a. Define : (i) Kraft temperature (ii) Zeta potential (iii) Brownian movement

b. Arrange the following ions in increasing order of flocculating power to precipitate As_2S_3 sol : $[Fe(CN)_6]^{4-}$, PO_4^{3-}, SO_4^{2-}, Cl^-

c. Give an example of oil in water & water in oil type emulsion.

A19. (i) Kraft temperature- a particular temperature only above which formation of micelles takes place.

(ii) Zeta potential- it is the potential difference between the fixed and diffused layer of opposite charges around the colloidal particles.

(iii) Brownian movement- It is a continuous zigzag motion of colloidal particles. It is due the unbalanced bombardment/collisions of the particles by the molecules of dispersion medium. It depends upon the size of the particles and viscosity of the solution.

b. $[Fe(CN)6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

c. Oil in water- milk and vanishing cream, Water in oil- butter and cold cream.

VALUE BASED QUESTION

Q. On visit to your native village, you find that a lot of smoke , dust , and some other gases are coming out of chimney of a recently setup factory.

Answer the following questions:

1. as a chemistry student what method you will suggest the factory owner to manage dust and smoke?
2. What is the basic principle involved in your suggestion?
3. What values are associated with your advice?

Ans1. Using Cottrell smoke precipitator because smoke particles are charged. when they pass through the precipitator the charged particles get attracted to opposite charged electrodes and get discharged and settle at the bottom.

Ans2. Colloidal particles are charged

Ans3. Sharing and applying scientific knowledge and concern for environment and health.

ASSIGNMENT

1. Why adsorbate particles are attracted and retained on the surface of adsorbent?
2. Write down the example of negative sol?
3. What is the difference between multimolecular and macromolecular colloids ? give one example each.
4. What do you mean by activity and selectivity of catalysts?
5. Adsorption is always exothermic?
6. Define each of the following terms

   (i) micelles (ii) peptization (iii) desorption

   b Explain what is observed when,

   (i) an electric current is passed through a sol / As_2S_3 sol

   (ii) a beam of light is passed through a sol.
7. “Chemisorption is highly specific.” Illustrate with an example.
8. “Adsorbents in finely divided form are more effective.” Why?

9. Name two compounds used as adsorbent for controlling humidity.

10. Name the catalyst used in the following process :

    (a) Haber process for the manufacture of NH_3 gas.

    (b). Ostwald process for the manufacture of nitric acid.

11. What happens :

    (a) When animal charcoal is added to a solution of methylene blue dye.

    (b) When aqueous solution of raw sugar is passed over beds of animal charcoal.

12. Suggest a mechanism of enzyme catalysed reaction along with the diagram.

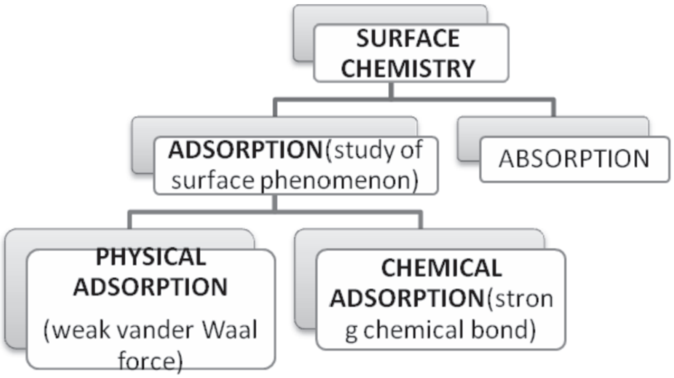
13. Diffrentiate between(a) catalysts and enzymes

    (b) promoters and poisons (with the help of an example).

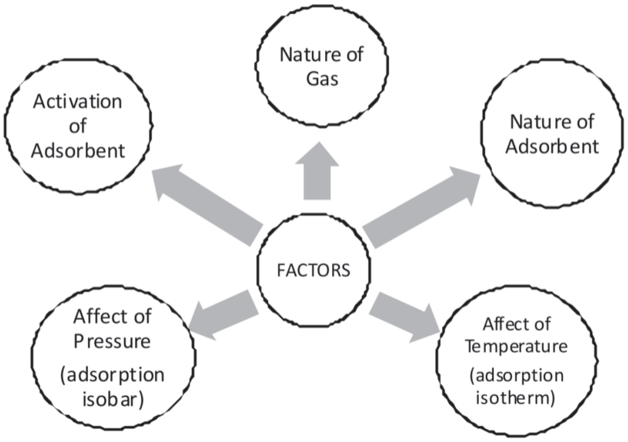
14. (a) Which property of colloids is responsible for the sun to look red at the time of setting?

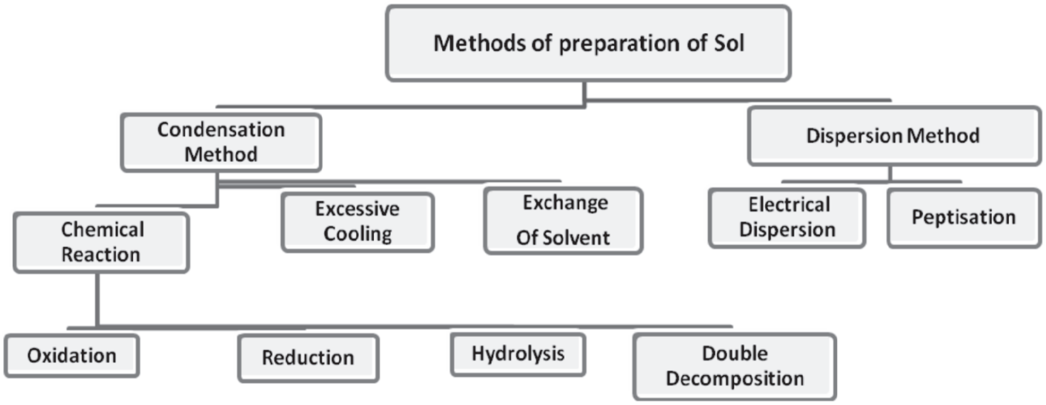
    (b) Explain the process of electrical precipitation of smoke, with diagram

    (c) Arrange the gases CO, $N_2$and CH_4 in increasing order of adsorption on the surface of charcoal in a closed vessel. Give reason.

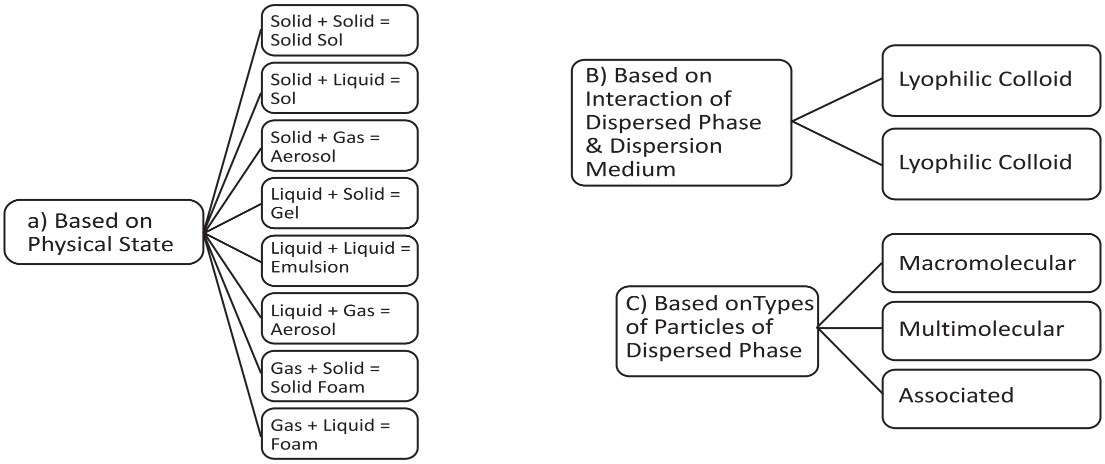


FACTORS AFFECTING ADSORPTION OF GASES ON SOLIDS



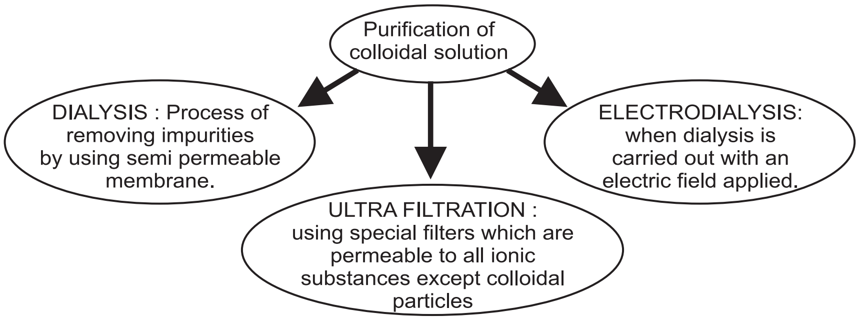


Classification of Colloids

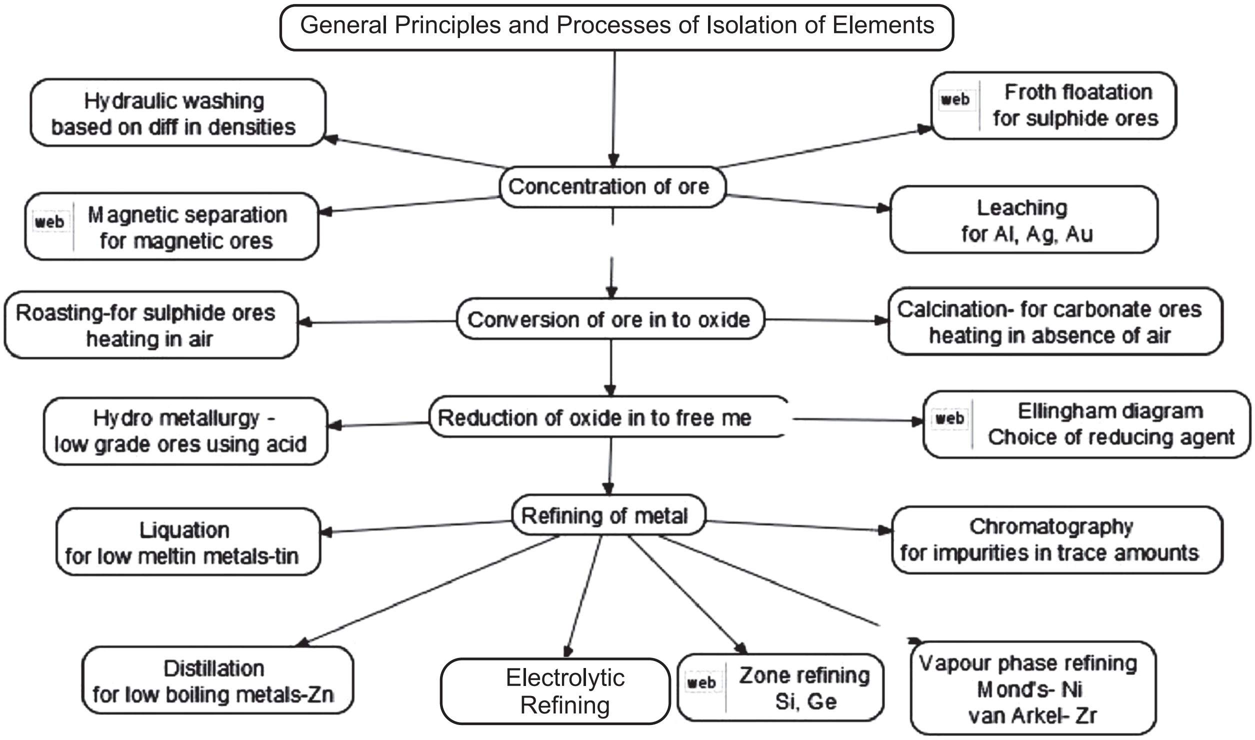


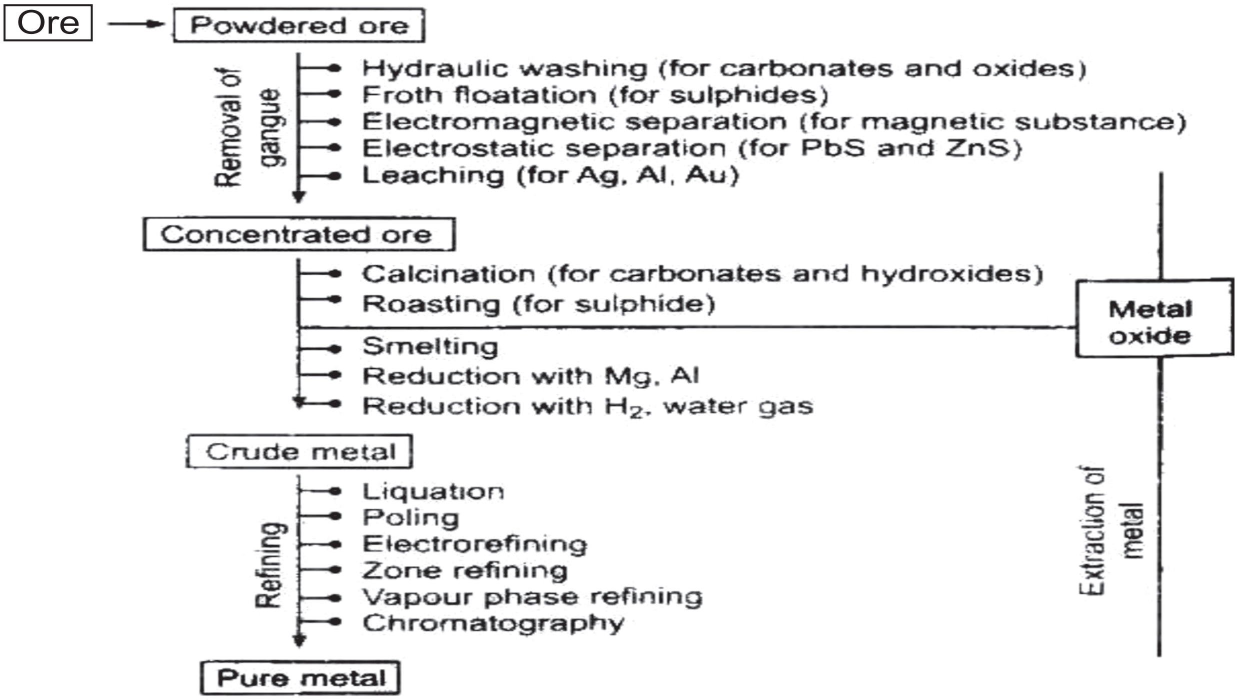
Properties of Colloids

- Tyndall 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



GENERAL PRINCIPLES AND PROCESS OF ISOLATION OF ELEMENTS (UNIT 6)





FLOW SHEET FOR EXTRACTION OF IRON:-

Iron ore(Magnetite Fe_3O_4)(Haematite Fe_2O_3)

↓

Concentration is done by Gravity separation followed by magnetic separation

↓

Calcination &Roasting i.e. Ore + Air +Heat → Moisture,CO_2,SO_2, As_2O_3 removed
And FeO oxidized to Fe_2O_3

↓

Smelting of charge i.e. mixture of ore, coke & $CaCO_3$ takes place in long BLAST FURNACE. Following reaction take place at different zones:-

↓

Pig iron is obtained, which is remelted and cooled then cast iron is obtained

FLOW SHEET FOR EXTRACTION OF COPPER:-

Copper Pyrites $CuFeS_2$

↓

Concentration is done by Froth floatation process
Powdered ore + water +pine oil +air → Sulphide ore in the froth

↓

Roasting is presence of air. following reactions take place:-
$S + O_2 \rightarrow SO_2$, $4As + 3O_2 \rightarrow 2As_2O_3$, $2CuFeS_2 + O_2$

↓

Smelting in small blast furnace of a mixture of Roasted ore, coke, and silica.
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$(slag)

↓

A mixture of Cu_2S, FeS & silica is obtained from blast furnace
known as Copper matte

↓

Bessemerisation of copper matte is done in Bessemer converter in presence of air.
Following reactions take place:-
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),
$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

↓

Melted copper is cooled, and then SO_2 is evolved. such copper is known as
BLISTER COPPER (98% Cu+2% impurities)

FLOW SHEET FOR EXTRACTION OF ALUMINIUM:-

Bauxite, $Al_2O_3.2H_2O$

↓

Concentration of ore is done by leaching. Bauxite is treated with NaOH. Following reaction takes place:-

$Al_2O_3 + 2NaOH + 3\ H_2O \longrightarrow 2\ Na\ [Al\ (OH)_4]$ and impurities of Fe_2O_3, TiO_2 & SiO_2 are removed.

↓

Na [Al $(OH)_4$], then reacts with CO_2 then pure Alumina is obtained.

$Na\ [Al(OH)_4] + 2CO_2 \longrightarrow Al_2O_3.xH_2O + 2NaHCO_3$

↓

Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2. Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e^- \longrightarrow Al$, At Anode:- $2O^{2-} \longrightarrow O_2 + 4e^-$

↓

By this process 98.8% pure Aluminum is obtained.

VERY SHORT ANSWER TYPE QUESTION
(1 marks)

Q.1. What is slag?

A.1. It is easily fusible material, which is formed when gangue still present in roasted ore combines with the flux.

e.g. CaO (flux) + SiO_2 (gangue) $\longrightarrow$ $CaSiO_3$ (slag)

Q.2. Which is better reducing agent at 983K, carbon or CO?

A.2. CO, (above 983K CO being more stable & does not act as a good reducing agent but carbon does.)

Q.3. At which temperature carbon can be used as a reducing agent for FeO?

A.3. Above 1123K, carbon can reduce FeO to Fe.

Q.4. What is the role of graphite rods in electrometallurgy of aluminium?

A.4. Graphite rods act as anode, are attacked by oxygen to form CO_2 and so to be replace time to time.

Q.5. What is the role of cryolite in electrometallurgy of aluminium?

A.5. alumina cannot be fused easily because of high melting point. Dissolving of alumina in cryolite furnishes Al^{3+} ions, which can be electrolyzed easily.

Q.6. What are depressants?

A.6. It is possible to separate two sulphide ore by adjusting proportion of oil to water in froth flotation process by using a substance known as depressant.

e.g. NaCN is used to separate ZnS and PbS.

Q.7. Copper can be extracted by hydrometallurgy but not Zn. Why?

A.7. The $E^0$of Zn is lower than that of Cu thus Zn can displace Cu^{2+}ion from its solution. On other hand side to displace Zn from Zn^{2+}ion, we need a more reactive metal than it.

Q.8. Give name and formula of important ore of iron .

A.8. Haematite – Fe_2O_3, Magnetite –Fe_3O_4, Iron pyrites FeS_2.

Q.9. Give name and formula of important ore of Copper .

A.9. Copper pyrites $CuFeS_2$, Malachite $CuCO_3 . Cu(OH)_2$, Cuprite Cu_2O.

Q.10. Give name and formula of important ore of Zinc .

A.10. Zinc blende - ZnS, Calamine- $ZnCO_3$, Zincite – ZnO .

SHORT ANSWER TYPE QUESTION

(2 makrs)

Q.1 Describe the method of refining of nickel.

A.1 to the Mond Process, Ni is heated in a stream of CO forming a volatile complex, which then decompose at higher temperature to give Ni.

At 330 – 35OK :- $Ni + 4CO \rightarrow Ni(CO)_4$

At 450 – 4 70K $Ni(CO)_4 \rightarrow Ni + 4CO$

Q.2 What is Zone Refining? Explain with example.

A.2 Zone refining is a method of obtaining a mewl in very pure state. If is based on the principal that impurities are more soluble in molten state of metal than solidified state.

In this method, a rod of impure metal is moved slowly over circular heater. The portion of the metal being heated melts & forms the molten zone. As this portion of the rod moves our of heater, it solidified while the impurities pass into molten zone. The process is repeated to obtain ultrapure metal and end of rod containing impure metal cutoff. Q.3 Write the principal of electro-refining.

A.3 In this method of purification impure metal iv made Anode and pure metal is made the cathode. On passing electricity, pure metal is deposited at the cathode while the impurities dissolve in solution as anode mud E.g. electro- refining of copper: -

At Calthode :- $Cu^{2+} + 2e^- \rightarrow Cu$

At Anode :- $Cu \rightarrow Cu^{+2} + 2e^-$

Q. 4 Write difference between calcinations and roasting.

Q.5 Describe the method of refining of Zirconium and Titanium.

A.5 Van Arkel process is used for obtaining ultrapure metal The impure metal is converted into volatile compound, which then decomposes electrically to get pure metal.

At 850K :- Zr impure) + $2I_2 \rightarrow ZrI_4$

At 2075K :- $ZrI_4 \rightarrow$ Zr (pure) + 2 I_2

Q.6 Out of C & CO. which is better reducing agent for ZnO?

A.6 Since free energy of CO from C is lower at temperature above 1120K while that of CO_2 from carbon is lower above 1323K than free energy of formation of ZnO. However, the free energy of formation of CO_2 from CO is always higher than that of ZnO. Hence. C is better reducing agent of ZnO.

Q.7 The value of $\Delta_f G°$ for Cr_2O_3 is – 540kJ/mole & that of Al_2O_3 is – 827kj/mole. Is the reducing of Cr_2O_3 possible with aluminium?

A.7 The desired conversion is

$4Al + 2Cr_2O_3 \rightarrow 2Al_2O_3 + 4Cr$

it is obtained by addition of following two reactions :-

$4Al + 3O_2 \rightarrow 2Al_2O_3$ $\Delta_f G°$ = + 540 kj/mole

$2Cr_2O_3 \rightarrow 4Cr + 3O_2$ $\Delta_f G°$ = + 540 kj/mole

Therefore, G° for desired reaction is – 827 + 540 = – 287, as a result reduction is possible.

Q.8 Copper matte consists of Cu2S and FeS. When blast of air is passed through molten matte in silicalined converter, FeS present in matte is oxidized to FeO, which combines with silica to form slag.

i) $2FeS + 3O_2 \rightarrow 2FeO + 2\,SO_2$. ii) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag).

iii) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$. iv) $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

SHORT ANSWER TYPE QUESTION

(3 makrs)

Q.1 Explain the following :-

i) Zinc but not copper is used for recovery of Ag from the complex $[Ag(CN)_2]$.

ii) Partial roasting of sulphide ore is done in the metallurgy of copper.

iii) Extraction of Cu from pyrites is difficult than that from its oxide ore through reduction.

A.1 i) Zn is more powerful reducing agent in comparison to copper. Zn is also cheaper than Cu.

ii) Partial roasting of sulphide ore forms some oxide. This oxide then reacts with remaining sulphide ore to give copper i.e. self-reduction occurs.

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

$2Cu_2O+2Cu_2S \rightarrow 6Cu + SO_2$

iii) Through carbon is good reducing agent for oxide but it is poor reducing agent for sulphides. The reduction of metal sulphide does not have large negative value.

Q.2 Explain the method for obtaining pig iron from magnetite.

A.2 Extraction of iron from Magnetite takes place in following steps :-

i) Concentration of ore :- It is done by Gravity separation followed by magnetic separation process.

ii) Calcination:- It involve heating when the volatile matter escapes leaving behind metal oxide.

$Fe_2O_3 \text{ x } H_2O \rightarrow Fe_2O_3 + xH_2O$.

iii) Roasting:- It involves heating of ore in presence of air, thus moisture, CO_2, SO_2, As_2O_3 removed and FeO oxidized to Fe_2O_3.

iv) Smelting of roasted ore:- A mixture of ore, coke & CaCO3 is smelted in long BLAST FURNACE.

Following reaction takes place at different temperature zones :-

i) Zone of reduction:- Temperature range 250°C – 700°C

$3Fe_2O_3+CO \rightarrow 2Fe_3O_4+CO_2$

$Fe_3O_4+CO \rightarrow 3FeO+CO_2$

$FeO+CO \rightarrow Fe+CO_2$

ii) Zone of slag formation:- Temperature range 800°C – 1000°C

$CaCO_3 \rightarrow CaO+CO_2$

$CaO+SiO_2 \rightarrow CaSiO_3$. $P_4O_{10}+10C \rightarrow 4P+10CO$.

$SiO2+2C \rightarrow Si+2CO$. $MnO_2+2C \rightarrow Mn+2CO$.

iii) Zone of fusion:- Temperature range 1150°C – 1350°C

$CO_2+C \rightarrow 2CO$

iv) Zone of fusion:- Temperature range 1450°C – 1950°C

$C+O_2 \rightarrow CO_2$

Thus, Pig iron is obtained from Blast Furnace.

Q.3 Describe the principles of extraction of copper from its ore.

Q.4 Name the principal ore of aluminium and describe how Al is extracted from its ore.

A.4 Important ores (i) Bauxite Al_2O_3 x H_2O (ii) Corrundum Al_2O_3. Bauxite is commercially important ore of Al.

Extraction from Bauxite ore involves the following two stages :-

i) Purification of bauxite to get pure alumina (Al_2O_3)

ii) Electrolysis of pure alumina in molten cryolite

Step: 1 - Bauxite is treated with NaOH. Following reaction takes place :-

$Al1O_3+2NaOH+3H_2O \rightarrow 2Na\,[Al(OH)_4]$ and impurities of Fe_2O_3. TiO_2 & SiO_2 are removed $Na\,[Al(OH)_4]$, then reacts with CO_2 then pure Alumina is obtained.

$Na\,[Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3\ x\ H_2O + 2NaHCO_3$

Step:2 - Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2. Graphide rods act as anode. Following reactions take place :-

At cathode: $Al^{3+} + 3e^- \rightarrow Al$, At Anode : $2O^{2-} \rightarrow O_2 + 4e^-$

By this process 98.8% pure Aluminum is obtained.

Q.5 Described the principles of extraction of Zinc from zinc blende.

A.5 Important ores of Zn:- Zinc blende – ZnS. Calamine – $ZnCO_3$, and Zincite – ZnO, ZnS is commercially important ore of Zn. Various stages involved in the extraction of Zn from ZnS are as following :–

i) Concentraction of ore:- It is concentracted by Froth flotation process followed by gravity separation process.

ASSIGNMENT

Q1 Explain: (i) Zone refining (ii) Column chromatography.

Q2 What is the role of depressant in froth floatation process?

Q3 Copper can be extracted by hydrometallurgy but not zinc. Explain.

Q4 Why copper *matte* is put in silica lined converter?

Q5 What is the role of cryolite in the metallurgy of aluminium?

Q6 Out of C and CO, which is a better reducing agent for ZnO ?

VALUE BASED QUESTION

Q. The iron pillar near Qutab Minar in Delhi is made up of wrought iron. This iron pillar was made around 400 BC by the Indian iron workers. Though wrought iron rust slowely with time but the Indian iron workers have developed a process which prevented the wrought iron pillar from rusting even after thousands of years. The rusting has been prevented because of the formation of a thin film of magnetic oxide of iron on the surface as a result of finishing treatment given to the pillar, painting it with a mixture of different salts, then heating and quenching(rapid cooling). The iron pillar is 8m high and 600kg in weight. This iron pillar stands in good condition more than 200 years after it was made. The iron pillar at Delhi is a wonder of ancient Indian metallurgy. It tell us that ancient Indians had good knowledge of metals and their alloys

(i) What is an alloy?

(ii) Name two alloys of iron.

(iii) How is an alloy made?

(iv) What are the constituents of stainless steel?

(v) Name any 2 properties of alloys which are different from the properties of the constituent metals.

Answer)

(i) An alloy is a homogeneous mixture of two or more metals (or a metal and small amount of non-metals)

(ii) Steel and stainless steel.

(iii) An alloy is prepared by mixing the various metals in molten state in required proportions, and then cooling their mixture to the room temperature.

(iv) Stainless steel is an alloy of iron, chromium and nickel.

(V) a. Alloys are harder and stronger than the metals from which they are made.

b. Alloys are more resistant to corrosion.

P-Block Elements (UNIT-7)

Key points

The general valence shell electronic configuration of p-block elements - $ns^2 np^{1-6}$

GROUP 15th ELEMENTS

Group 15 elements; N, P, As, Sb and Bi

General Electronic Configuration: ns^2np^3

Chemical properties

- Common oxidation states: -3, +3 and +5.
- Due to inert effect, the stability of +5 state decreases down the group and stability of +3 state increases.
- In the case of Nitrogen all Oxidation states from +1 to +4 tend to disproportionate in acid solution, example: $3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$

  Anomalous Behaviour of Nitrogen: - due to its small size, high electronegativity, high ionisation enthalpy and absence of d-orbital.
- N_2 has unique ability to form pπ-pπ multiple bonds whereas the heavier members of this group do not form pπ-pπ bond because their atomic orbitals are so large and diffused that they cannot have effective overlapping.
- Nitrogen exists as diatomic molecule with triple bond between the two atoms whereas other elements form single bonds in elemental state.
- N-N bond is weaker than P-P because of high inter-electronic repulsion of the non-bonding electrons due to smallbond length. Thus catenation tendency is weaker in Nitrogen.
- N cannot form dπ-pπ bond whereas other elements can.
- N cannot expand its covalency beyond four due to absence of d orbitals.

  Trends in properties

  Stability- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

  Bond dissociation enthalpy- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

  Reducing character- $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

  Basic character- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

  Bond angle - $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Dinitrogen

Preparation

1. **Laboratory preparation** – by treating an aqueous solution of NH_4Cl with sodium nitrite.

1. $4NH_4Cl + NaNO_2 \rightarrow N_2 + 2H_2O + NaCl$
2. Thermal decomposition of ammonium dichromate also gives N_2

   $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$
3. Thermal decomposition of Barium or Sodium azide gives very pure N_2.

   $Ba(N_3)_2 \rightarrow Ba + 3N_2$

Ammonia (Preparation)

1. In laboratory it is prepared by heating ammonium salt with NaOH or lime.

   $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$
2. In large scale it is manufactured by Haber process

   $N_2 + 3H_2 \rightarrow 2NH_3$

   According to Le Chatelier's principle the favourable condition for the manufacture of NH_3 are:- Optimum temperature: 700k, High pressure: About 200 atm, Catalyst: Iron oxide Promoter: K_2O & Al_2O_3

Properties

Ammonia can form coordinate bonds by donating its lone pair of electrons present on nitrogen, ammonia forms complexes.

$$\underset{\text{blue}}{Cu^{2+}} + 4NH_3 \rightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}}$$

NITRIC ACID

PREPARATION- Ostwald's process – it is based upon catalytic oxidation of ammonia by atmospheric oxygen. The main steps are-

1. $4NH_3 + 5O_2 \xrightarrow[\text{500 K, 9 Bar}]{\text{Pt/Rh}} 4NO + 6H_2$
2. $2NO + O_2 \rightarrow 2NO_2$
3. $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

PROPERTIES-

i. Concentrated HNO_3 is a strong oxidising agent and attacks most metals except noble metals like gold and Pt.

   $3Cu + 8HNO_3(dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

   $Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

ii. Cr and Al do not dissolve in HNO_3 because of the formation of a passive film of oxide on the surface.

iii. Conc. HNO_3 oxidises non-metals and their compounds-

It oxidises non-metals like I_2 to HIO_3,C to CO_2, S to H_2SO_4,P to H_3PO_4.

iv. Brown ring test is used to detect NO_3^-.

PHOSPHORUS

ALLOTROPIC FORMS:- white, red, α-black, β-black.

White phosphorus is more reactive than red phosphorus because of angular strain in P_4 molecules, in red P several P_4 molecules are linked to form polymeric chain.

PHOSPHINE

PREPARATION: $P_4+3NaOH+3H_2O \longrightarrow PH_3+3NaH_2PO_2$

PHOSPHORUS HALIDES

Phosphorus forms two types of halides PX_3 and PX_5 .

Trihalides have pyramidal shape and pentahalides have trigonal bipyramidal structure.

OXOACIDS OF PHOSPHORUS

- The acids in +3 oxidation state disproportionate to higher and lower oxidation state.

  $4H_3PO_4 \longrightarrow 3H_3PO_4+PH_3$

- Acids which contain P-H bond have strong reducing properties. Ex; H_3PO_2 it contain two P-H bond is a good reducing agent.
- Hydrogen atom are attached with oxygen in P-OH form are ionisable and causes the basicity. Ex: H_3PO_3 – dibasic and H_3PO_4 – tribasic as the structure has two P-OH and three P-OH bonds respectively.

FREQUENTLY ASKED QUESTIONS

1 mark questions :

Q1 Nitrogen does not form pentahalides Give reason .

Ans. Nitrogen does not form pentahalides because it does not possess d-orbitals hence it cannot expand its octate .

Q2 Give reason for the difference in the Reactivity of nitrogen and phosphorus

Ans. There is a triple bond in nitrogen which has high bond dissociation energy. In phosphorus thereis a single bond in the molecule of P_4 . It has lower bond dissociation energy .

Q3 Why is that nitrogen exist as gas whereas phosphorus exist as a solid ?

Ans. Due to strong $p\pi - p\pi$ bonding, nitrogen forms a triple bond giving N_2 molecules. phophorus does not form $p\pi - p\pi$ bonding , it rather forms P-P bonding giving P_4 molecule and exists as a solid.

2 marks questions :

Q1 Assign a reason for each of the following:

(i) Ammonia is a strong base than phosphine .

(ii) In group 15,the bond angle H--M--H decreases in the following order NH_3 (107.8°) , PH_3(93.6°) , AsH_3(91.8°) .

Ans (i) Both Ammonia and phosphine have pyramidal structure and both have lone pair of electrons but nitrogen being smaller than phosphorus , electron density of the lone pair on N in NH_3 is more. Therefore Ammonia is a strong base than phosphine .

Ans (ii) With the increase in size of group 15 elements as bond length increases the bond pair - bond pair repulsion decreases .Therefore the angle H--M--H decreases from NH_3 to $AsH_{3.}$

Q2 (a) What is the covalency of Nitrogen in N_2O_5 ?

(b) Ammonia is a good complexing agent .Give reason .

Ans (a) The covalency of Nitrogen in N_2O_5 is 4 .

Ans (b) Ammonia has a lone pair of electrons therefore it is a good complexing agent .

3 marks questions :

Q1 (i) NH_3 form H-bond but PH_3 does not ?

(ii) Explain NH_3 is basic while BiH_3 is feebly basic .

(iii) Why is BiH_3 the strongest reducing agent amongest all the hydrides of Group 15 elements ?

Ans (i) Due to small size & high electronegativity of nitrogen, strong H-bonding exists in NH_3 molecules . while no H-bonding is present in PH_3 .

Ans (ii) Since atomic size of N is much smaller than Bi, so electron density on the N atom is much hiigher than Bi. Therefore tendency of N to donate pair of electron is much higher is NH_3 than that of Bi in BiH_3 .

Ans (iii) As we move dowm the Group 15 , the size of the element increases and, therefore the length of the bond with hydrogen increases and its strength decreases. Thus, Bi -H bond is the weakest amongest the hydrides of elements of Group 15, and hence , BiH_3 is the strongest reducing agent .

Q2 (i) Write the order of thermal stability of the hydrides of group 15 elements . Give reason

(ii) Why does Nitrogen show catenation properties less than P?

(iii) Though Nitrogen exhibits +5 oxidation state it does not form pentahalide . Give reason .

Ans (i) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ Since the size increases down the group the E-H bond dissociation energy decreases , Therefore thermalstability decreases down the group .

Ans (ii) Property of catenation depends upon the strength of the element . Since the N-N bond strength is much weaker than P-P bond strength .Therefore N show less catenation .

Ans (iii) Nitrogen n=2 has s and p orbital only. It does not expand its covalence beyond four due to non-availabi;ity of d-orbital . Hence it does not form pentahalide .

ASSIGNMENT QUESTIONS

Q1 Why are pentahalides more covalent than trihalides ?

Q2 Bond angle in PH_4^+ is higher than that in PH_3 ?

Q3 Bismuth oxide is not acidic in any of its reactions .

Q4 All the bonds in a molecule of PCl_5 are not equal . Explain .

Q5 The +5 oxidation state of Bismuth is less stable than its +3 state . Give reason.

Q6 (a) What happens when

(i) White phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2 ?

(ii) PCl_5 is heated ?

(iii) H_3PO_3 is heated?

(b) H_3PO_2 behaves as monoprotic acid. Explain

(c) Ammonia has greater affinity for protons than phosphine. Explain

Group-16th ELEMENTS

KEY POINTS :-

1. O, S, Se, Te and Po are present in G-16th . Their general electronic conf. of last shell is ns^2,np^4.
2. Atomic and ionic radii increases down the group while ionization enthalpy and electronegativity decreases with increase in atomic number.
3. Because of compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative up to polonium..
4. Members of group 16 show oxidation number -2, +2, +4 and +6. But oxygen shows +1 state in O_2F_2.
5. They make MO_2 and MO_3 type oxides. SO_2 is reducing agent whereas TeO_2 is oxidizing agent.
6. O_2 is gas other are solid.
7. O_2 and S_2 in vapour state are paramagnetic.
8. **CONTACT PROCESS OF MANUFACTURE OFSULPHURIC ACID:-**

$S + O_2 \rightarrow SO_2\,(g)$

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (Catalyst-V_2O_5) $\Delta H = -196.6$ KJ/ mol.

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

1 MARK QUESTIONS

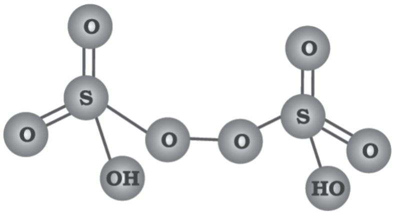
1) Sulphur has more tendency to show catenation than oxygen

Ans.) Due to stronger S-S bond and due to small size and greater interelectronic repulsion O-O bond is weaken so it can't show catenation

2) Oxygen is a gas but sulphur is a solid .

Ans.) Due to small size oxygen makes pΠ-pΠ band and exsist as 0=0. That is why oxygen is gas but sulphur is bigger in size and can't make Pπ-Pπ band so exsist as polymeric fluid form

3) Draw structure of $H_2S_2O_8$



Peroxodisulphuric acid
($H_2S_2O_8$)

4.) H_2S is more acidic than H_2O

Ans.) bond dissociation enthalpy of S-H bond is lesser than O-H bond due to bigger size of sulphur.

5.) OF_6 compound is not known why?

Ans.) due to the absence of d-orbital in oxygen it can't make OF_6.

2 MARKS QUESTIONS

1 a) SF_6 is kinetically an inert substance OR SF_6 does not hydrolyse easily. Why?

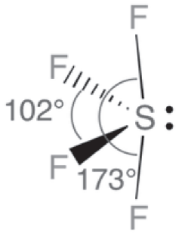
Ans.) SF_6 is less reactive because S atom is sterically protected by 6 Fluorine.

b) H_2O is liquid while H_2S is a gas.

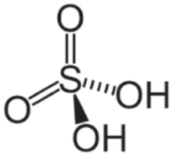
Ans.) H_2O is liquid due to intermolecular H- bonding.

2. Draw the structure of SF_4

Ans.) SF_4See-Saw geometry



3. Draw structure of H_2SO_4



4. (a) In which form sulphur shows para-magnetism?

Ans.) In vapour state.

(b) Sulphur in vapour state exhibits paramagnetic behavior. Why?

Ans.) In vapour state S_2 molecule has two unpaired electrons in antibonding π orbital

3 MARKS QUESTIONS

Q.1 Complete the following chemical equation

i.) $SO_3 + H_2SO_4 \rightarrow$

ii.) $Fe^{3+} + SO_2 + H_2O \rightarrow$

iii) $SO_2 + MnO_4^- + H_2O \rightarrow$

Ans.) i.) $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

ii.) $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

iii). $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

Q 2. (a) H_2S is less acidic than H_2Te . Why ?

Ans. Bond dissociation enthalpy of H-S bond is less

(b) Boiling point of H_2O is more than H_2S. Why?

Ans. Water has inter-molecular H-bonding due to more electro-negativity and small size of oxygen atom.

Group 17th elements

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17th.

A) Important reactions

1. $2F_2 + 2H_2O \rightarrow 4HF + O_2$
2. $Cl_2 + H_2O \rightarrow HCl + HOCl$
3. $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$
4. $H_2S + Cl_2 \rightarrow 2HCl + S$
5. IN EXCESS OF NH_3:- $8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$
6. IN EXCESS OF Cl_2 :- $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

7. IN COLD AND DILUTE NaOH :- $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$
8. IN HOT AND CONC. NaOH:- $6 NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$
9. $SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$
10. $I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$
11. $Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured substance + O → Colourless substance

B) Reasoning questions

1 Halogens have maximum negative electron gain enthalpy(ΔegH)

Ans Because they have smallest size in their respective periods

2 F has less electron gain enthalpy than that of Cl but fluorine is stronger oxidizing agent than chlorine

Ans F is stronger oxidizing agent due to its low bond dissociation energy and high hydration energy

3 F exhibits only -1 oxidation state , other halogen shows +1, +3, +5, +7 oxidation states or F does not exhibit any positive oxidation state.

Ans F is most electronegative element and due to absence of d-orbitals it can not expand its octet so it does not exhibit positive oxidation state.

4 Iron reacts with HCl gives Fe(II)chloride and not Fe(III)chloride

Ans $Fe + 2 HCl \rightarrow FeCl_2 + H_2$ H_2 liberated prevents the oxidation of $FeCl_2$ to $FeCl_3$

5 Bond dissociation energy of F_2 is less than Cl_2

Ans Due to very small size of F there is lone pair repulsion in F_2 so it has low bond dissociation energy

6 Fluorine does not undergo disproportionation

Ans Disproportionation means simultaneous oxidation-reduction. F being the most electronegative element undergoes only reduction but not oxidation.

7 NO dimerises but Cl_2O does not

Ans NO is odd electron species so it complete its octet by dimerisation

8 Bleaching by Cl_2 is permanent but by SO_2 is temporary

Ans Cl_2 bleaches by oxidation while SO_2 does it by reduction. The reduced product gets oxidized again in air and the colour returns

9 HF has lower acid strength than HI

Ans Due to larger size of I , the H-I bond is weaker than H-F bond so HI is stronger

10 I_2 is more soluble in KI than in water

Ans I_2 forms complex with KI i.e $KI + I_2 \rightarrow KI_3$

11 HClO is stronger acid than HIO

Ans ClO^- is more stable than IO^- because Cl is more electronegative, so HClO is strongeracid than HIO.

12 $HClO_4$ is stronger acid than $HClO_3$

Ans ClO_4^- is more stable than ClO_3^- due to more no. of resonating structures.

13 OF_2 should be called fluoride of oxygen and not oxide of fluorine

Ans Because F is more electronegative than O

14 Interhalogens are more reactive than halogens or ICl is more reactive than I2?

Ans They are polar and have weaker X-X' bond.

15 HF is stored in wax coated glass bottle

Ans Because HF reacts with alkali present in glass.

16 MF is more ionic than MCl (M is alkali metal)

Ans Because F^- is smaller than Cl^- and hence it is less polarisable.

17 $Cl_2 + KI \longrightarrow$ brown colour, but excess Cl_2 turns it colourless

Ans Cl_2 is stronger oxidizing agent than I_2. It first oxidizes KI into I_2 which imparts brown colour. $Cl_2 + KI \longrightarrow I_2 + 2KCl$ In excess of Cl_2, I_2 is further oxidized to HIO_3 which is colourless.

$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$

18 $HClO_4$ is stronger acidic than H_2SO_4

Ans Oxidation state of Cl in $HClO_4$ is +7. Oxidation state of S in H_2SO_4 is +6. Greater is the oxidation state of central atom, more is the acidic strength.

19 Give the reason for bleaching action of Cl_2.

Ans bleaching action is due to oxidation. $Cl_2 + H_2O \longrightarrow 2HCl + O$

Coloured substance + O $\longrightarrow$ Colourless substance

20 Name two poisonous gases which can be prepared from chlorine gas.

Ans phosgene ($COCl_2$), tear gas (CCl_3NO_2)

21 Write two uses of ClO_2.

Ans ClO_2 is used

i) as a bleachingagent for paper pulp and textiles

ii) in water treatment.

22 Why are halogens coloured?

Ans due to absorption of radiations in visibleregion which results in the excitation of outer electrons to higher energylevel. By absorbing different quanta of radiation, they display different colours.

23 How can you prepare (i) Cl_2 from HCl and (ii) HCl from Cl_2? Write reactions only

Ans (i) $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$ (ii) $H_2 + Cl_2 \rightarrow 2HCl$

24 With what neutral molecule is ClO^- isoelectronic?

Ans OF_2 (other example is ClF. It is a Lewis base)

25 Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO_2.

(ii) Chlorine gas is passed into a solution of NaI in water.

Ans (i) $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$
(ii) $I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$

26 Write the reactions of F_2 and Cl_2 with water.

Ans 1. $2F_2 + 2H_2O \rightarrow 4HF + O_2$
2. $Cl_2 + H_2O \rightarrow HCl + HOCl$

27 Why are halogens strong oxidising agents?

Ans i) ready acceptance of an electron

ii) small atomic sizes

iii) highly electronegative nature

iv) highly negative value of E^0_{red} are the reasons for the strongoxidising nature of halogens.

28 Explain why fluorine forms only one oxoacid, HOF.

Ans Due to high electro negativity and small size, fluorine forms only one Oxoacid, HOF.

29 Explain why in spite of nearly the same electro negativity, oxygen forms hydrogen bonding while chlorine does not.

Ans Because electron density on oxygen atom is much higher than that of Cl atom.

30 ClF_3 exists but FCl_3 does not. Or F never acts as central atom in the inter halogen compounds.

Ans Because F is more electronegative than Cl

31 F_2 is the most reactive of all the four common halogens.

Ans Because of low F-F bond dissociation enthalpy

32 HOI is a weaker acid than HOCl

Ans Because Cl is more electronegative than I.

C. Arrange the following as the property indicated against them.

1 F_2, Cl_2, Br_2, I_2 (increasing order of Boiling Point)

Ans $F_2 < Cl_2 < Br_2 < I_2$

2 F_2, Cl_2, Br_2, I_2 (increasing order of bond dissociation enthalpy.)

Ans $I_2 < F_2 < Br_2 < Cl_2$

3 F, Cl, Br, I (increasing order of electron gain enthalpy)

Ans I< Br< F< Cl

4 HF , HCl, HBr, HI (increasing order of acidic strength)

Ans HF < HCl <HBr< HI

5 MF,MCl, MBr, MI (decreasing order of ionic character)

Ans MF >MCl> MBr >MI

6 $HClO, HClO_2, HClO_3, HClO_4$ (increasing order of acidic strength)

Ans $HClO < HClO_2 < HClO_3 < HClO_4$

7 HF , HCl, HBr, HI (decreasing order of B.P.)

Ans HF>HI> HBr >HI>HCl

GROUP 18th ELEMENTS

KEY POINTS

GROUP 18 ELEMENTS **: He, Ne, Ar, Kr, Xe & Rn**

General electronic configuration: ns^2np^6

- **Atomic radii**- large as compared to other elements in the period since it correspond to vander waal radii.
- **Inert-** due to complete octet of outermost shell, very high ionization enthalpy and more positive electron gain enthalpies.

  The first noble compound prepared by Neil Barlett was $Xe^+PtF_6^-$.

  $O_2^+PtF_6^-$ led to the discovery of $XePtF_6$ since first ionization enthalpy of molecular oxygen ($1175kJmol^{-1}$) was almost identical with that of xenon ($1170kJmol^{-1}$).

PROPERTIES

1) $Xe(g) + F_2(g) \xrightarrow{673k,1bar} XeF_2(g)$
2) $Xe(g) + 2F_2(g) \xrightarrow{873k,7bar} XeF_2(s)$
3) $Xe(g) + 3F_2(g) \xrightarrow{573k,60-70bar} XeF_2(s)$
4) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$
5) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$
6) $XeF_6 + MF \rightarrow M^+[XeF_7]^-$
7) $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$
8) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
9) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$
10) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$(partial hydrolysis)

1 mark questions :

Q1 Why among the noble gases only Xenon is well known to form chemical compounds ?

Ans. Xenon has the largest atomic size and the smallest I.E. of all the noble gases

Q2 Name the geometries of $XeOF_4$ and XeO_3.

Ans. $XeOF_4$ is square pyramidal while XeO_3 is pyramidal .

2 marks questions :

Q1 Account for the following

(i) Noble gases are mostly chemically inert .

(ii) Deep sea divers use a mixture of He (80%) and O_2 (20%) instead of air for breathing .

Ans. (i) It is due to stable electronic configuration and high ionization enthalpies of noble gases.

Ans. (ii) Unlike N_2 of air , He is least soluble in blood even under high pressure . Therefore it does not create any problem .

Q2 (a) What prompted Bartlett to the discovery of noble gas compound ?

(b) State two importance of noble gases .

Ans. (a) The ionization enthalpy of Xe is similar to that of O_2. He first prepared compond $O_2^+PtF_6^-$. It prompted bartlett to prepare compond in which O_2 of $O_2^+PtF_6^-$ could be replaced by Xe. This is how $Xe^+PtF_6^-$ was prepared .

Ans. (b) (i) Ar is used in electric bulbs . (ii) Xe is used in head lights of cars these days .

Q3 Apply VESPR theory to deduce the structure of XeF_4 and XeF_6 .

Ans. XeF_4 has square planar structure due to presence of 4 bonded pairs of electrons and 2 lone pairs of electrons. XeF_6 has distorted octahedral structure due to presence of one lone pair of electrons and six bonded pairs of electrons .

3 marks Question

Q1 Write down the equations for the hydrolysis of XeF_4 and XeF_6 . Which of these two reaction is a redox reaction .

Ans (i) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(ii) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

Reaction :

(i) is redox reaction . Reaction

(ii) is not a redox reaction because the oxidation states of all the elements before and after the same .

Q2 (i) Why do noble gases have comparatively large atomic sizes?

(ii) Noble gases are mostly chemically inert .

(iii) XeF_2 has a straight linear structure and not a bent angular structure .

Ans (i) Due to completely filled valence shell electronic configuration ,repulsive intraction start taking place in theatom , due to which , the atomic size increases in noble gases .

(ii) It is due to stable electronic configuration and high ionization enthalpy of noble gases .

(iii) Due to sp^3d hybridisation of Xe , it has trigonal bipyramid geometry. Three equatorial positions are occupied by lone pairs of electrons to minimize repulsion , giving a linear shape to the molecule .

ASSIGNMENT

Q1 Noble gases have comparatively large atomic size.Why?

Q2 Helium is used in diving apparatus. Why?

Q3 Draw the structure of i) XeF_4 ii) XeO_3

Q4 Give 2 uses of Argon.

Q5 Complete the following reactions

i. $6XeF_4 + 12H_2O \rightarrow$

ii. $XeF_6 + 3H_2O \rightarrow$

iii. $XeF_6 + 2H_2O \rightarrow$

(partial hydrolysis)

VALUE BASED QUESTION

Q. Nitrogen combines with hydrogen to form ammonia. $N_2 + 3H_2 \rightarrow 2NH_3$.

Ammonia is the basic raw material for preparing fertilizers. Always associated with a refinery/ petrochemical industry

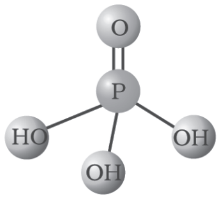
a. we have a fertilizer industry. Why? (2)

b. What is the value you derive from this. (1)

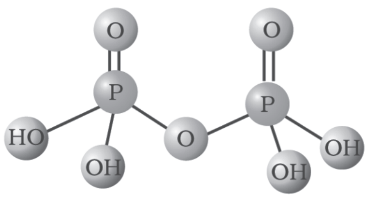
Ans: a. In the refinery / petrochemical industry hydrogen gas is evolved as a byproduct. Hence to recycle this hydrogen a fertilizer unit is established nearby.

b. Recycling of industrial waste keeps the environment clean.

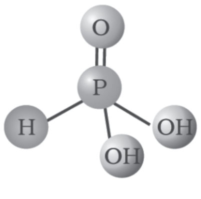
Structure of some important oxoacids of phosphorous



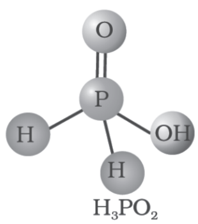
H_3PO_4
Orthophosphoric acid



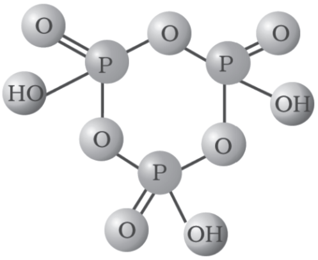
$H_4P_2O_7$
Pyrophosphoric acid



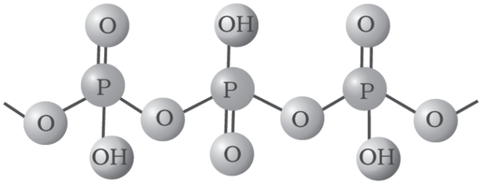
H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid

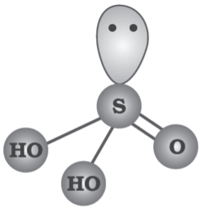


Cyclotrimetaphosphoric acid, $(HPO_3)_3$

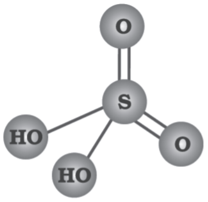


Polymetaphosphoric acid, $(HPO_3)_n$

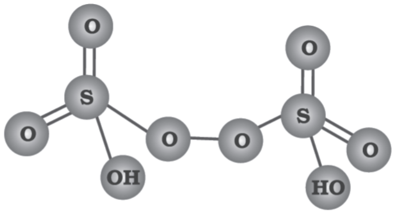
Oxoacids of Sulphur



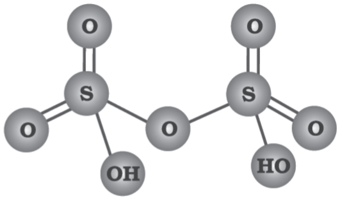
Sulphurous acid (H_2SO_3)



Sulphuric acid (H_2SO_4)



Peroxodisulphuric acid ($H_2S_2O_8$)

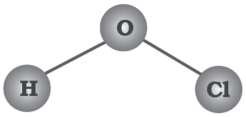


Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

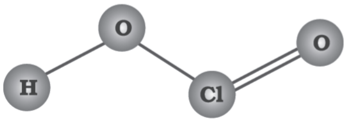
Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**HOCl** (Hypochlorous acid)	**HOBr** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	– –	HOCIO (chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	$HOCIO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	– –	$HOCIO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)

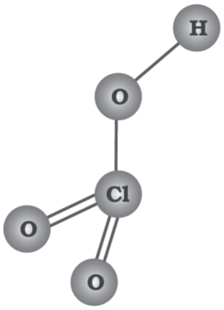
Oxoacids of chlorine



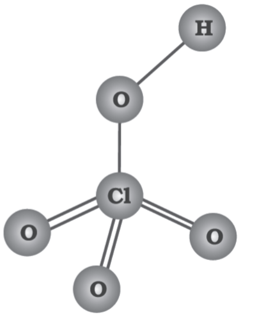
Hypochlorous acid



Chlorous acid

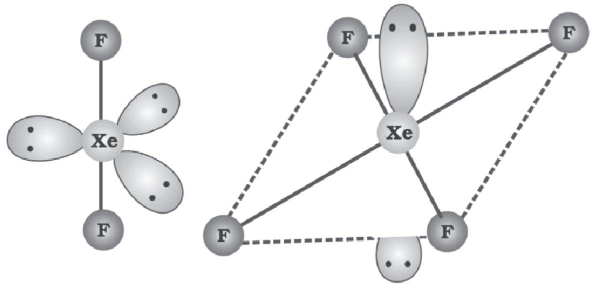


Chloric acid

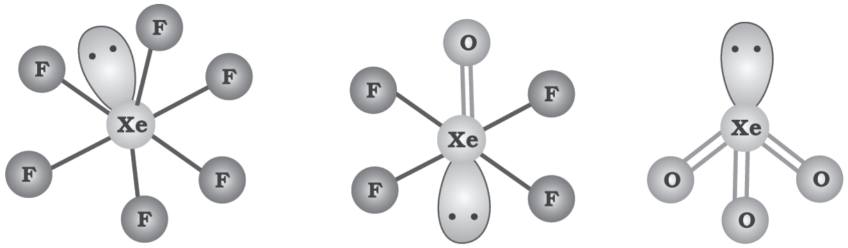


Perchloric acid

The structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ and (e) XeO_3



(a) Linear (b) Square planar



(c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

d & f BLOCK ELEMENTS (UNIT 8)

KEY CONCEPTS

- d-block consists of elements belonging to group 3-12.
- The general electronic configuration of these elements in (n-1) d^{1-10} ns^{1-2}. They contain unpaired d electron either in elementary or most commonly occurring oxidation state.
- Transition elements exhibits metallic character, high densities s, high melting and boiling point due to strong interatomic interaction between partially filled d orbits.'
- Transition elements show variable oxidation state due to small energy difference between (n-1)d & ns orbital.
- Transition metal elements show colour due to presence of unfazed electron in (n-1)d orbital of penultimate shell which undergoes d-d transit generally
- Transition metal elements are paramagnetic due to presence of unpaired e^- .
- Most of transition form complex compounds due to (I) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.
- Transition elements have lower value of reduction potential due to high ionization potential, high heat of sublimation and low enthalpy of hydration.
- Transition elements form interstitial compounds because as small atoms like C, N, O, H. occupy the voids and get bonded to the atom of Transition metals.
- Transition elements form alloys due to similar ionic radii as they can mutually substitute their position in the crystal lattice.
- The oxides of transition of transition metals in lower oxidation states are BASIC, intermediate oxidation state are amphoteric, highest oxidation state are acidic.
- The highest oxidation state of an element is equal to no. of unpaired electrons present in (n-1) d & ns orbital.

LANTHANOIDS

- In lanthanoids filling of electrons take place in 4f orbital which is 3rd last shell or antipenultimate shell.
- General electronic configuration is $[x_e]4f^{1-14}5d^{0-1}6s^2$.
- Elements after lanthanum having atomic number 58 to 71 are called lanthanoids .
- Principal oxidation state is +3 although Ce shows +4 and Eu +2 due to stable configuration. So Ce (IV) is good oxidizing and Sm (II) is good reducing agent.
- Due to poor shielding effect of electrons. There is a steady decrease in lanthanoids and its trivalent ions known as lanthanoid contraction.

ACTINOIDS

- The 14 elements after actinium having atomic number 90 to 113 are collectively known as Actinoids
- The general electronic configuration of these elements is $[Rn]5f^{1-14}, 6d^{0-1}, 7s^2$.
- The size of actinoids and its trivalent ion decreases from Ac to Lw due to poor shielding of 5f electrons. It is known as actinoids contraction.
- Chemical of actinoids is very complex due to their ability that exist is different oxidation state. More so they are radioactive.

POTASSIUM DICHROMATE Preparation: - from chromite ore $FeCr_2O_4$

I. Conversion of chromite ore to sodium chromate.

II. Conversion of sodium chromate to sodium dichromate.

III. Conversion of sodium dichromate to potassium dichromate.

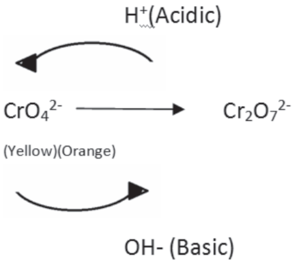
Following reaction takes place:-

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2Cr_2O_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

$Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

EFFECT OF pH



Chemical properties

Sodium and potassium dichromates acts as strong oxidising agents in acidic medium.

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

Oxidation Reaction

$6I^- \rightarrow 3I_2 + 6e^-$, $3H_2S \rightarrow 6H^+ + 3S + 6e^-$, $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$, $3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$

POTASSIUM PERMANGANETE Preparation: - From pyrolusite ore

I. Conversion of pyrolusite ore into potassium magnate

II. Conversion of potassium magnate to potassium permanganate

Following reactions takes place:-

$2MnO_2 + 4KOH + O_2 \rightarrow 2\,K_2MnO_4 + 2H_2O$

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

Chemical Properties

Potassium permanganate is a powerful oxidising agent.

Neutral solution

$2KMnO_4 + H_2O \longrightarrow 2\,KOH + 2MnO_2 + 3\,(O)$

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

Alkaline solution

$2KMnO_4 + 2KOH \longrightarrow 2\,K_2MnO_4 + H_2O + (O)$

$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

Acidic solutions

$2KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

FREQUENTLY ASKED QUESTION

(1 mark)

Q.1. Cu^+ is not stable in aqueous solution. Why?

Ans. In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

The higher stability of Cu^{2+} in aqueous solution may attributed to its greater negative $\Delta_{hyd.}H^\circ$ than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

Q.2. Which is a stronger reducing agents – Cr^{2+} or Fe^{2+} and why?

Ans. Cr^{2+} is a stronger reducing agent than Fe^{2+} because after the loss of one electron Cr^{2+} becomes Cr^{3+} which has more stable t^3_{2g} (half filled) configuration in medium like water.

Q.3. Arrange the following increasing of acidic character:

CrO_3, CrO , Cr_2O_3

Ans. $CrO < Cr_2O_3 < CrO_3$. Higher the oxidation, more will be acidic character.

Q.4. Calculate the 'spin only' magnetic moment of M^{2+}(aq) ion.(Z=27)

Ans. Electronic configuration of the M^{2+} ion (Z=27) would be M^{2+}(aq): (Ar) $3d^7$

It would contain three unpaired electrons. The 'spin only' magnetic moment is given by the relation :

$\mu = \sqrt{n\,(n+2)}\ \text{BM} = \sqrt{3\,(3+2)}\ \text{BM} = 3.87\ \text{BM}$

2 marks questions

Q 1. Why do Zr and Hf exhibit almost similar properties?

Ans. Zr and Hf have similar ionic size due to its lanthanoid contraction. So they exhibit similar properties.

Q 2. Why are Zn, Cd and Hg not regarded as transition elements?

Ans. Zn, Cd, Hg neither in their ground state nor in oxidized state have partially filled d-orbital. Thus they are not regarded as transition elements.

Q 3. What are alloys? Name one important alloy which contains some of the lanthanoid metals. Mention its use.

Ans. Alloys are homogeneous mixtures of metals with metals or non-metals.

Misch metal (pyrophoric alloy) consists of lanthanoid metal Ce= 40.5%, neodymium 44%, iron 4-5% and traces of S, C, Ca and Al. Misch metal is used to make bullets, shells and light flints.

Q 4. La(OH)$_3$ is a stronger base than Lu(OH)$_3$. Why?

Ans. Lu^{3+} is smaller in size than La^{3+} due to lanthanoid contraction. Due to smaller size of Lu^{3+}, Lu-O bond is stronger than La-O bond in the respective hydroxides. Due to weaker La-O bond, La(OH)$_3$ behaves as a strong base.

Q5. Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.

Ans. Lanthanoids exhibit oxidation state of +2, +3 and +4. This is because of large energy gap between 4f, 5d and 6s subshells. Actinoids show +3, +4, +5, +6 and +7 oxidation states because 5f, 6d and 7s energy levels are nearly same.

3 marks questions

Q 1. What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

Ans. Lanthanoid contraction: Steady decrease in the size of the lanthanoids with increase in the atomic number across the period. The electrons of 4f orbitals offer imperfect/poor shielding effect in the same subshell.

Consequence:

i) Due to this 5d series elements have nearly same radii as that of 4d series.

ii) Decrease in the basic strength from La(OH)$_3$ to Lu(OH)$_3$.

iii) Due to similar atomic size there is difficulty in separation of lanthanides.

Q 2. Compare lanthanoids and actinoids with reference to their:

a. Electronic configuration of atoms

b. Oxidation states of elements

c. General chemical reactivity of elements.

a.	Electronic configuration	[Xe]$4f^{1-14}5d^{0-1}6s^2$	[Rn]$5f^{1-14}6d^{0-1}7s^2$
b.	Oxidation states	Besides +3 OS lanthanoids show +2 and +3 only in a few cases.	Besides +3 OS actinoids show higher OS of +4, +5, +6, +7 also because of smaller energy gap between 5f, 6dand 7s subshell.
c.	General chemical reactivity of elements	These are less reactive metals. Lesser tendency towards complex formation. Do not form oxocation. Compounds are less basic.	These are highly reactive metals. Greater tendency towards complex formation. Form oxocation. Compounds are more basic.

Q 3. How would you account for the following:

a. Mn(III) undergoes disproportionation reaction easily.

b. Co(II) is easily oxidized in the presence of strong ligands.

Ans. a. Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled d-orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

b. Co(II) has electronic configuration $3d^7 4s^0$, i.e., it has three unpaired electrons. In the presence of strong ligands, two unpaired electrons in 3d-subshell pair-up and third unpaired electron shifts to higher energy subshell from where it can be easily lost and hence oxidized to Co(III).

Q.4 Give reasons for the following:

i) First ionisation energies of 5d elements are higher than those of 3d and 4d elements. Actinoid conctraction is greater from element to element than lanthanoid contraction.

Ans. i) Because of weak shielding(or screening) effect of 4f electrons, the effective nuclear charge acting on the valence electrons in 5d elements is quite high. Hence, the first ionisation energies of 5d elements are higher than those of 3d and 4d elements.

ii) This is because the 5f electrons themselves provide poor shielding from element to element in the series.

Q.5. Explain the following observations about the transition/inner transition elements:

i) There is in general an increase in density of element from titanium (Z=22) to copper (Z=29).

ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements(3rd series).

iii) The greatest number of oxidation states are exhibited by the members in the middle of a transition series.

Ans i) Because of decrease in atomic size from titanium to copper.

ii) Because of high enthalpies of atomization of heavy transition elements.

iii) Because of the involvement of both (n-1)d and ns electrons in bonding.

VALUE BASED QUESTIO

Q. While travelling on DND flyway towards Delhi from Bulandshahr, Himanshu drunk some alcoholic liquor. When he reached at toll plaza, suddenly a policeman stopped him and he did some activity by usingan orange coloured compound to detect the presence of alcohol in air breathed out. Instantly the colour of compound was changed due to the traces of alcohol and he was fined.

Now answer the following questions

Name the transition metal which was present in that orange coloured compound.

What was the changes in orange coloured compound after detecting the traces of alcohol?

Write the instrument used in testing alcohol traces.Write the values associated with it.

Ans- i) Chromiumii) Blue-green colour. Depending on the amount of alcohol changes accordingly.

ii) Alcometer

iii) Social responsibility, awareness and social justice

5 marks question

Q.1- Assign reasons for the following:

a) The enthalpies of atomization of transition elements are high.

b) The transition metals and many of their compounds act as good catalysts.

c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic number.

d) The transition elements have great tendency for complex formation.

e) Transition metals generally form coloured compounds.

Ans- a) This is because transition elements have strong metallic bonds as they have large number of unpaired electrons, therefore they have greater interatomic overlap.

b) The catalytic activity of transition metals is attributed to the following reasons-

i) Because of their variable oxidation state, transition forms unstable intermediate compounds and provide a new path with lower activation energy for the reaction.

ii) In some cases, the transitions metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers due to poor shielding effects of the d-electrons, the net electrostatic attraction between the nucleus and the outermost electrons increases.

d) orbital's of suitable energy, small size of cations and higher nuclear charge.

e) Due to presence of unpaired electrons in d-orbitals which undergoes d-d transition.

Q.2 a) Complete and balanced the following reactions:

i) $Cr_2O_7^{2-} + I^- + H^+ \rightarrow$

ii) $MnO_4^- + SO_3^{2-} + H^+ \rightarrow$

b) With reference to structural variability and chemical reactivity, write the difference between lanthanoids and actinoids.

c) Name a member of lantanoids series which is well known to exhibit +4 oxidation state.

Ans. a) i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

ii) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

b) Lanthanoids-

i) Atomic or ionic radii does not show much variation.

ii) Besides +3 oxidation state, they show +2 and +4 oxidation states in few cases.

Actinoids-

i) Atomic or ionic radii show many variations.

ii) Besides +3 oxidation states, they show higher oxidation states of +4, +5, +6, +7, also.

c) Cerium.

ASSIGNMENT

Q.1 Which of the 5d series of the transition metals exhibit the largest number of oxidation state and why?

Q.2 Why is the highest oxidation state of a metal exhibited in its oxide and fluoride only?

Q.3 Explain why Cu^+ ion is not stable in aqueous solution?

Q.4 What are interstitial compounds? Why are such compounds well known as transition metals?

Q.5 Describe the preparation of potassium dichromate from chromite ore. What is the effect of increasing pH on the solution of potassium dichromate?

Q.6 Draw the structure of following: a)CrO_4^{2-} b)MnO_4^- c)$Cr_2O_7^{2-}$

Q.7 What are the characteristics of the transition elements and why are they called transition elements? Which of the d-block elements may not be regarded as the transition metals?

Q.8 What is meant by the disproportionation? Give 2 examples of disproportionation.

Q.9 The halides of transition metals become more covalent with increasing oxidation state of the metal. Why?

[Hint: Fajan's rule]

PROPERTIES OF d-BLOCK ELEMENTS	COMPOUND OF d-BLOCK ELEMENTS	f-BLOCK ELEMENTS
Physical Properties 1. They have high mp, bp, conductivity, ductility etc. 2. They are hard and volatile except Zn, Cd and Hg[due to absence of (n-1)d electrons.]	**Potassium Dichromate** 1.Prepared as Chromite $\xrightarrow{Na_2CO_3}$ Chromate $\downarrow H^+$ $K_2Cr_2O_7 \xleftarrow{KCl}$ Dichromate of Na 2. $Cr_2O_7^{2-} \xrightarrow{OH-\ \&\ H+} CrO_4^{2-}$ 3. It oxides I^- to I_2, H_2S to S, Fe^{2+} to Fe^{3+} and itself reduced to Cr^{3+}	**Lanthanoids** 1. EC = $5d^{0-1}$, $6s^2$, $4f^{1-14}$ 2. Atomic and Ionic radii decrease from La to Lu and this decrease is called **lanthanoid contraction.** It is due to poor shielding of f-orbitals. 3. Common OS = +3 4. They are paramagnetic, coloured, have IE comparable to Ca.
Enthalpy of Atomisation 1. It is the energy required to convert the metallic crystal into atom. 2. It first increases upto middle and then decreases.	**Potassium Permanganate** 1. Prepared as Pyrolusite(MnO_2) $\xrightarrow{KOH\ \&\ O2}$ MnO_4^{2-} $\downarrow$ H^+ Mno_4^- 2. In acidic medium it oxides I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, H_2S to S and itself reduced to MnO_4^-	**Consequences of lanthanoid contraction** 1. Decrease in basic character of oxide and hydroxides from La to Lu. 2. Same size of Zr and Hf, Nb and Ta, etc.
Atomic and Ionic Radii 1. It usually decreases with increase in atomic number across a series due to increase in effective nuclear charge. 2. At the end of the series, it increases due to increased repulsive forces.		**Actinoids** 1. EC = $6d^{0-1}$, $7s^2$, $5f^{1-14}$ 2. Show actinoid contraction. 3. Show large number of OS due to less difference in energy of 6d, 7s and 5f orbitals. 4. Mostly Radioactive. 5. They are also coloured and paramagnetic.
Ionisation Enthalpy It increases with decrease in size.	**Catalytic Property** They act as good catalyst due to their variable valency and vacant d-orbitals.	
Oxidation State(OS) Show oxidation state from +2 to +7 but +3 is most common. Maximum OS = (n-1)d unpaired e^- + ns e^-.	**Alloy Formation** They form alloy with other metals. Alloy of Hg is called Amalgam.	
Standard Reduction Potential Its negative value decreases from left to right with exception of Mn, Zn and Ni.	**Complex Formation** They all form complex due to their small size, high charge density and vacant d orbitals.	
Magnetic Property and Colour These are generally paramagnetic and coloured due to the presence of unpaired d-electrons.	**Interstitial Compounds** They trap small atoms like C, H, N etc., in their crystals to modify properties.	

COORDINATION COMPOUNDS (UNIT-9)

Ky Concepts :

Difference between coordination compound and double bond:

Coordination compound	Double salt
A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules re bonded to the metal atom or ion by a coordinate bond.	When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called doubie salts
Example: $K_4[Fe(CN)_6]$	Example: $FeSO_4.(NH4)_2SO_4.\ 6H_2O$ (Mohr's salt)
They do not dissociate into simple ions when dissolved in water.	They dissociate into simple ions when dissolved in water.

Werner's coordination theory: Werner was able to explain the nature of bonding in complexes. The postulates of Werner's theory are:

a. Metal shows two different kinds of valencies: primary valence and secondary valence.

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

b. The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

c. The most common geometrical shapes in coordination compounds are octahedral!, square planar and tetrahedral.

Isomers : Two or more compounds which have same chemical formula but different arrangement of atoms are called Isomers, Types of isomerism:

a. Structural isomerism

i.	Linkage isomerism	ii.	Solvate isomerism or hydrate isomerism
iii.	lonisation isomerism	iv.	Coordination isomerism

b. Stereoisomerism

   I. Geometrical isomerism

   ii. Optical isomerism

Structural isomerism: This type of isomerism arises due to the difference in structures of coordination compounds. Structural isomerism, or constitutional isomerism, is a form of isomerism in which molecules with the same molecular formula have atorns bonded together in different orders.

a. **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex: salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

   Example: $[Co\{NH_3\}_5Brj\ SO_4$ and $[Co(NH_3)_5\ SO_4]\ Br$

b. **Solvate isomerism:** It is isomerism in which solvent is involved as ligand. If solvent is water it is called hydrate Isomerism.

   e.g. $[CrCH_2O)_6]CI_3$ and $[CrCl_2(H_2O)_4]\ Cl_2..\ 2H_2O$

c. **Linkage isomerism:** Linkage isomerisni arises in a coordination compound containing ambidentate ligand. In the isomerism, a Iigand can form linkage with metal through different atoms.

   Example: $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_sNO_2]Cl_2$

d. **Coordination isomerism:** This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

   Example: $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_s][Co(C_2O_4)_3]$

Stereoisomerism: This type of isomerism arises because of different spatial arrangement.

a. Geometrical isomerism: It arises In heteroleptic complexes due to different possible geometrical arrangements of ligands.

b. Optical isomerism: Optical isomers are those Isomers which are *nan* superimposable mirror images.

VALENCE BOND THEORY

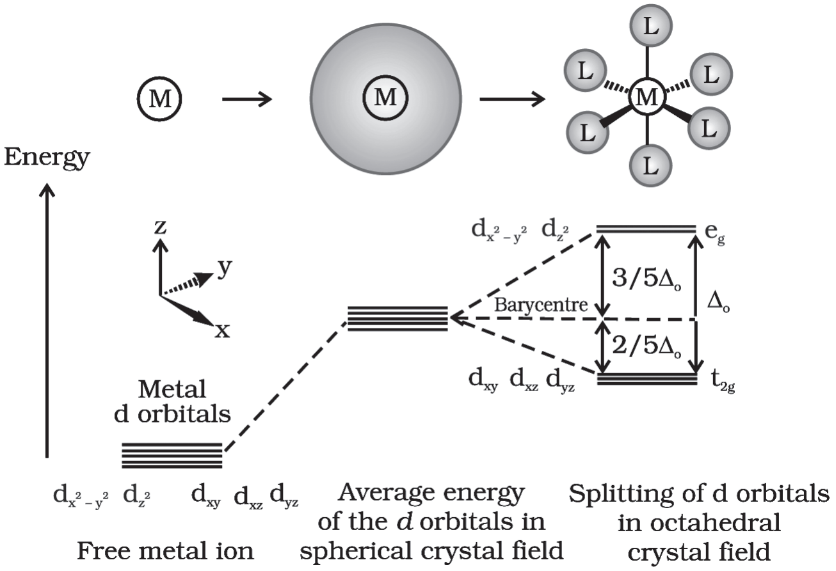
Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	tetrahedral
4	dsp^3	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2 (nd orbitals are involved - outer orbital complex or high spin or spin free complex)	Octahedral
6	d^2sp^3 (n–1) d orbitals are involved -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

Magnetic properties of coordination compounds: A coordination compound is paramagnetic In nature If it has unpaired electrons and cliamagnetic if ail the electrons in the coordination compound are paired.

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

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

Crystal field splitting in octahedral coordination complexes:



NEGATIVE LIGANDS		CHARGE	NEUTRAL LIGANDS		CHARGE
CN^-	Cyano	-1	NH_3	Ammine	0
Cl^-	Chlorido	-1	H_2O	Aqua/aquo	0
Br^-	Bromido	-1	NO	Nitrosyl	0
F^-	Fluoride	-1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	-2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	-2	CH_2-NH_2	(1,2-Ethanediamine)	0
NH_2^-	Amido	-1	POSITIVE LIGANDS		
NH^{2-}	Imido	-2	NH_2-NH_3^+	Hydrazinium	+1
ONO^-	Nitrito-O	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitro	-1	NO_2^+	Nitronium	+1
NO_3^-	Nitrato	-1			
SCN^-	Thiocyanato	-1			
NCS^-	Isothiocyanato	-1			
$CH_2(NH_2)COO^-$	Glycinato	-1			

Question of 1 Marks only

Q.1 The Spin only magnetic moment of $[MnBr]^{2-}$ is 5.9BM. Predict the geometry of the complex ion.

Ans. Mn^{2+} -Co-ordination No.4 so tetrahedral geometry 5.9 BM.

Q.2 $CusO_4$ $5H_2O$ Is Blue in Color white $CuSO_4$ is Colorless Why?

Ans. d-d Transition is possible in $CuSO_4$ $5H_2O$ so it shows Color. $CuSO_4$ due to the absence of water (ligand) CFT Is not – possible so colored.

Q3. 4 Write the State of hybridisation of the Compound$[Cr(NH_3)_6]^{3+}$

Ans. $d^2 sp^3$ geometry octahedral

Q.5 Give the formula of the given Co-ordination compound

Ni ion is bound to two water molecules and two oxalate ions.

Ans. $[Ni(H_2O)_2(OX)_2]^{2-}$

Diaquadioxalato nickelate (II)

Two marks Question

Q.1 Arrange the following complexes the order of increasing electrical conductivity

$[Co(NH_3)_3 Cl_3]$, $Co(NH_3)_5Cl]Cl_2$,

$[Co(NH_3)_6] Cl_3$, $[Co(NH_3)_4Cl_2]Cl$

Ans. $[Co\ (NH_3)_3 Cl_3] < [Co(NH_3)_4 Cl_2]Cl$

$<[Co\ (NH_3)_5 Cl]Cl_2 <[Co(NH_3)_6]Cl_3$

Q.2 How many geometric isomers are possible in the following co-ordination entities:

$[Cr(C_2O_4)_3]^3$- $[CoCl_3(NH_3)_3]$.

Ans. (i) Nil

(ii) 2 (fac-and mer-isomer).

Three marks question

Q.1 Discuss nature of bonding in the following co-ordination entities on the basis of valence bond theory.

i) $[Fe(CN)_6]^{4-}$

(ii) $[FeF_6]^{3-}$

(iii) $[CoF_6]^{3-}$.

Co-ordination	Electronic	Charge on Configuration of Central Metal ion	Hybridisation the Ion	Geometry	Magnetic Behaxion
$[F(CN)_6]^{4-}$, CN^- Strong Ligand So low spin Complex & Inner Complex	$3d^6 4s^2$	Fe^{2+}	d^2sp^3 XX XX XX XX XX XX XX $d^2 sp^3$	Octahedral	Diamagnetic
$[FeF_6]^{3-}$ F weak Ligand & High complex And outer Orbital complex	$3d^6 4s^2$	Fe^{3+}	$sp^3 d^2$ XX XX XX XX XX XX XX	octahedral	diamagnetic
$[COF_6]^{3-}$ F- is weak Ligand high spin Complex outer Orbital complex	$3d^7 4s^2$	Co^{3+}	sp^3d^2 XX XX XX XX XX XX XX sp^3d^2	octahedral	diamagnetic

Q.3 Write the formulas for the following co-ordination compounds:

(a) Tetra ammine aqua chlorido co balt (III) chloride

(b) Potassium tetra hydroxozincate (II)

(c) Potassium trioxalato aluminate (III)

Ans. (a) $[Co(NH_3)_4 H_2OCl]Cl_2$

(b) $K_2 [Zn(OH)_4]$

(c) $K_3 [Al (C_2O_4)_3]$

Q.4 Write the IUPAC names of the following co-ordination compounds:

(a) $[Pt(NH_3)_2Cl(NO_2)]$

(b) $K_3[Cr(C_2O_4)_3]$

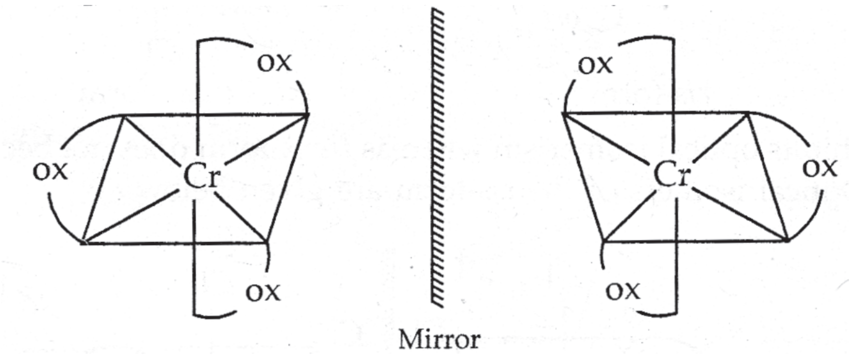
(c) $[CoCl_2(en)_2]Cl$

Ans. (a) Diammine chloridonitrito – N- Platinum(II)

(b) Potassium trioxalato chromate (III)

(c) Dichloridobis (ethane-1, 2-diammine cobalt(iii) chloride

Q-5 Draw the structures of optical isomers of: $[Cr(C_2O_4)_3]^{3-}$



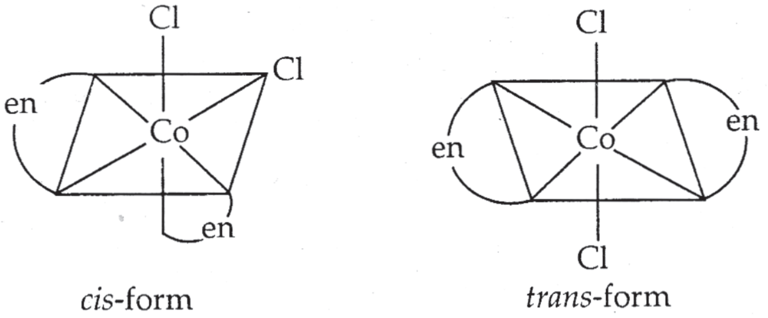
Q-6 **A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.**

ANS. In $[Ni(H_2O)_6]^{2+}$, $H_2\ddot{O}$ is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d−d transition is present. Hence, $Ni(H_2O)_6]^{2+}$ is coloured.

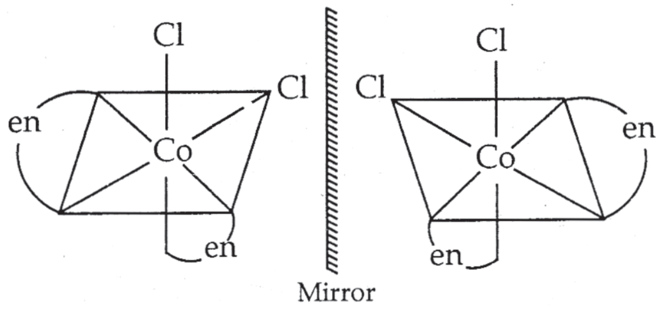
In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, d-d transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

Q-7 **Draw all the isomers (geometrical and optical) of: $[CoCl_2(en)_2]^+$**

ANS. **(i)** $[CoCl_2(en)_2]^+$



cis-form *trans*-form

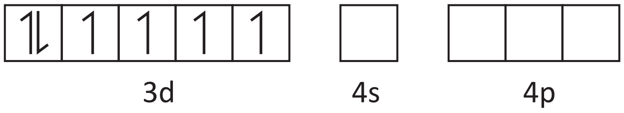


d- and *l*-forms of *cis*-$[CoCl_2(en)_2]$

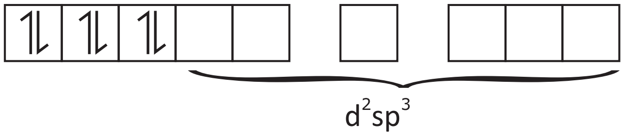
Q8. Discuss the nature of bonding in the following coordination entities on the basisof valence bond theory:

(i) $[Fe(CN)_6]^{4-}$

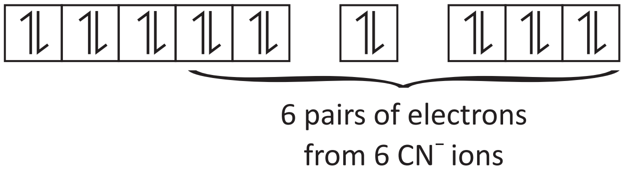
ANS. (i) $[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +II oxidation state.Fe^{2+}: Electronic configuration is $3d^6$Orbitals of Fe^{2+}ion:



As $CN^-$is a strong field ligand, it causes the pairing of the unpaired 3d electrons.Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3. d^2sp^3 hybridized orbitals of $Fe^{2+}$are:



6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3orbitals.Then, Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).



ASSIGNMENT

Q.1 Why $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic ?

Q.2 Why $Ni(CO)_4$ possesses tetrahedral geometry, while $[Pt(NH_3) Cl_2]$ is a square-planar?

Q.3 What are the factors on which the stability of a complex depends ?

Q.4 What is Spectrochemical series?

Q.5 Explain the dissociation constant.

Q.6 Explain stepwise of formation or overall stability constant with example

Q.7 How many geometrical isomers of $[Cr(en)_2Cl_2]^+$ exist? Which of these shows optical activity?

Q.8 Comment on the statement that all compounds containing carbon and metal are not organometallics.

Q.9 Outline the basis assumption of Werner co-ordination theory.

Q.10 Write the application of co-ordination compounds and organometallic compounds

HALOALKANES AND HALOARENES (UNIT 10)

Key Concept

There placement of hydrogenatom(s) in a hydrocarbon, aliphaticoraromatic, by halogenatom(s) results in the formation of alkylhalide (haloalkane) and arylhalide (haloarene), respectively

$$R\text{-}H + X_2 \longrightarrow R\text{-}X + H\text{-}X \qquad Ar - H + X_2 \longrightarrow Ar\text{-}X + H\text{-}X$$

(A) IMPORTANT NAME REACTIONS

i) **Finkelstein Reaction**

$$R\text{-} X + Na\,I \xrightarrow{\text{Dry Acetone}} R\text{-} I + Na\,X$$

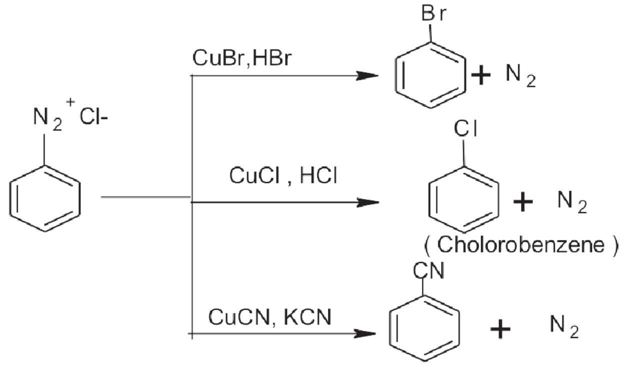
II) **Swarts Reaction**

$$R\text{-} X \xrightarrow{\text{Ag F, } Hg_2F_2\text{, Co } F_2 \text{ OR Sb } F_3} R\text{-}F$$

1. **Carbylamines reaction**

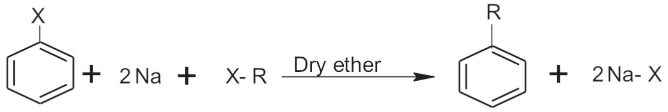
$$R - NH_2 + CHCl_3 + 3\ KOH \longrightarrow R.NC + 3KCl + 3H_2O$$
$$C_6H_5NH_2 + CHCl_3 + 3\ KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

2. **Sandmeyer's reaction**

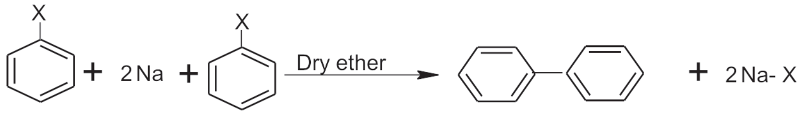


3. **Wurtz Reaction** $R - X + 2Na + RX \xrightarrow{\text{ether}} R - R + 2\ NaX$

4. **Wurtz Fittig reaction:-**



5. **Fittig reaction**



6. **Grignard reagent:** $RMgX + H_2O \longrightarrow RH + Mg(OH)X$

7. **Hunsdiecker's reaction:** $R\text{-}COOAg + Br_2 \longrightarrow R\text{- }Br + AgBr + CO_2$

(B) IMPORTANT MECHANISM

i) Nucleophilic Substitution ii) Elimination reaction iii) Electrophilic substitution

i) Nucleophilic Substitution :- it involves the replacement of an atom or group of atoms by a nucleophile (electron rich species)

$A\text{-}B + Nu \rightarrow A\text{-}Nu + B$

It is of two type:-

a) Unimolecular substitution reaction (SN^1)

b) bimolecular substitution reaction (SN^2)

a) Unimolecular substitution reaction (SN^1)

(i) it involves in two steps

(ii) in this retention/Racemization in configuration take place.

(iii) unimolecular and all are first order.

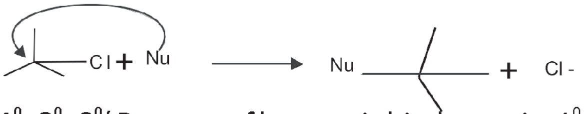
Mechanism (**step 1**) formation of carbocation.

Step 2 Attack of nucleophile on carbocation

Order of reactivity: $3^0 > 2^0 > 1^0$ (Because 3^0 carbocation is more stable)

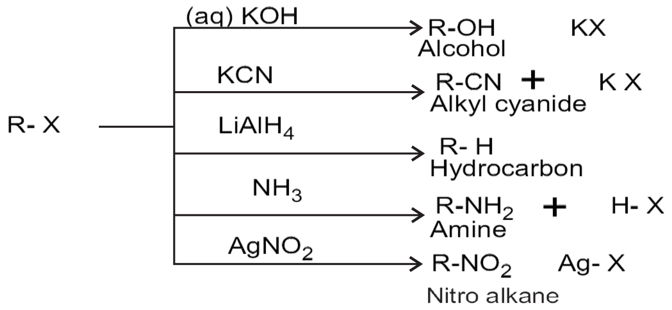
(b) Bimolecular Nucleophilic Substitution SN^2 (i) it involves in one step. (ii) in this inversion in configuration takes place.(iii) bimolecular .

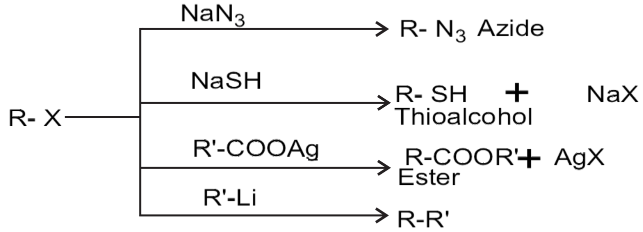
Mechanism. in this nucleophile attacks from the back side Where halogen atom is attached.



Order of reactivity:- $1^0 > 2^0 > 3^0$(Because of less steric hindrance in 1^0 alkyl hlide)

Nucleophilic substitution reaction of alkyl halides

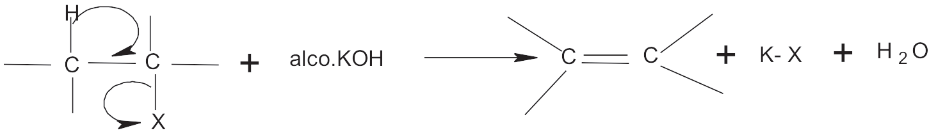




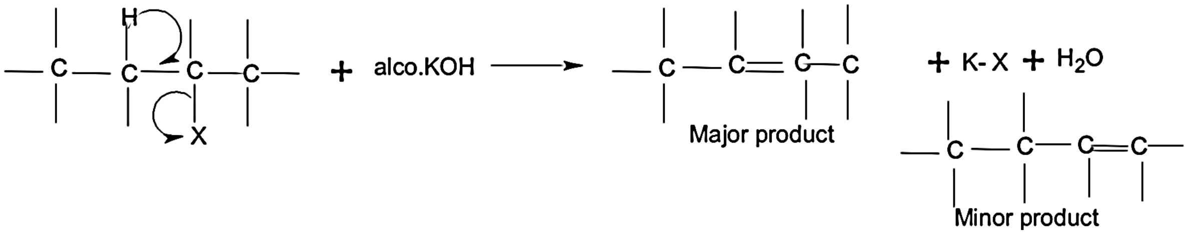
R-X + AgCN $\rightarrow$ RNC + AgX

R-X + Na-C= C-R $\rightarrow$ R-C= C-R + Na-X

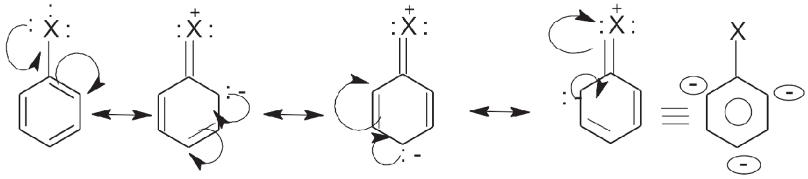
ii) **Elimination reaction** haloalkanes having -Hydrogen atom when heated with alco. KOH then there is elimination of hydrogen atom from -carbon and a halogen atom from the -carbon atom & alkene is formed.

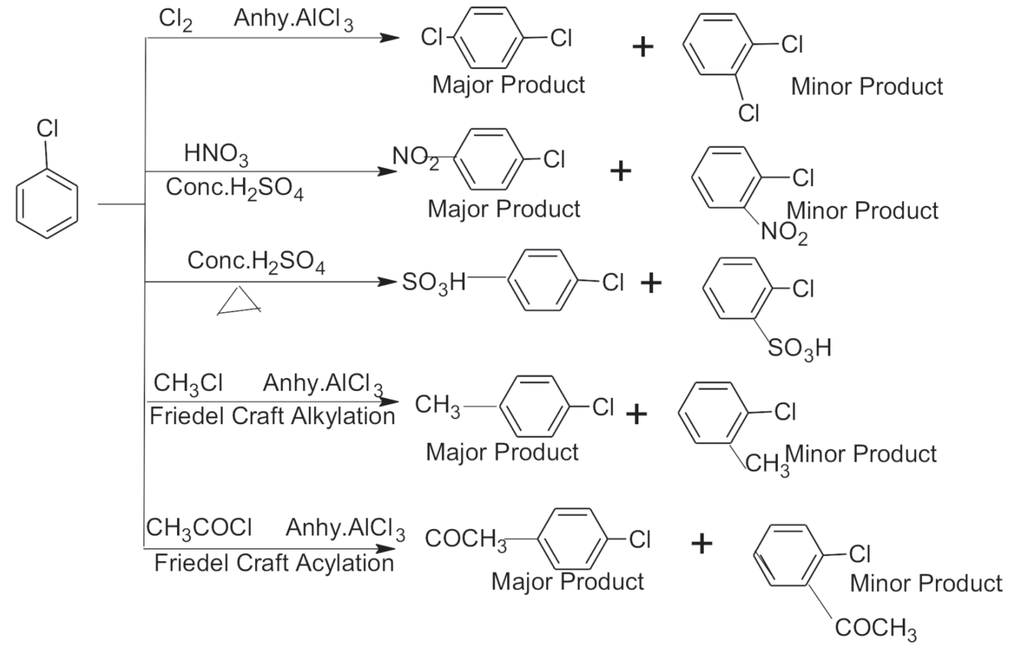


Saytzeff rule "*in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms*."



iii) **Electrophilic substitution:-** substitution occurs at *ortho*- and *para*- positions with respect to the halogen atom.





Q. 1 What are ambident nucleophiles? (1 Mark)

Ans. Nucleophiles which can attack through two different sites are called ambident nucleophiles. Example: - Cyanide ion $:CN^{-}: \leftrightarrow :C=N:^{-}$

Q. 2 Which is a better nucleophile, a bromide ion or iodide ion? (1 Mark)

Ans. Iodide ion. Because it has lower electronegativity and larger size.

Q. 3 Arrange the compounds of each set in order of reactivity towards SN^2 displacement: 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane. (1 Mark)

Ans. The reactivity in SN^2 reactions depends upon steric hindrance; more the steric hindrance slower the reaction.The order of reactivity in SN^2 reactions follows the order: $1^0 > 2^0 > 3^0$. 1-Bromopentane **>** 2-Bromopentane **>** 2-Bromo-2-methylbutane **.**

Q. 4 Arrange the following in increasing order of boiling point.

$CH_3CH_2CH_2CH_2Br$, $(CH_3)_3CBr$, $(CH_3)_2CHCH_2Br$. (1Mark)

Ans. The boiling point increases as the branching decreases, so the increasing order of boiling point is:-$(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$

Q. 5 Define optical activity? (1Mark)

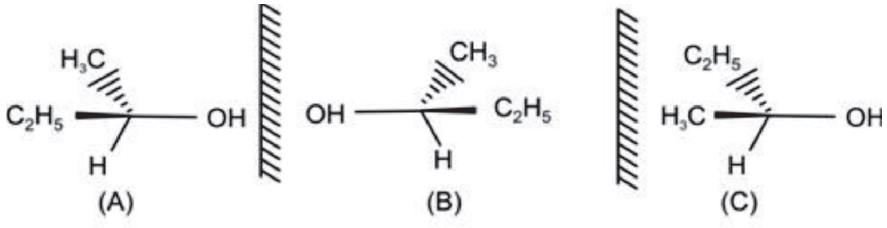
Ans. The compounds which rotate the plane of polarized light when it is passed through their solutions are called optical active compounds and this property is known as optical activity.

Q. 6 What is racemic mixture or racemic modification? (1 Mark)

Ans. A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to other isomer. Such a mixture is known as racemic mixture or racemic modification.

Q. 7 What are enantiomers? (1 Mark)

Ans. The stereoisomers related to each other as non-superimposable mirror images are called enantiomers.



(A) and (C) are non - Superimposable mirror images

Q. 8 Haloalkanes react with aq. KOH to form alcohols but react with alc. KOH to form alkenes. Why? (2 Marks)

Ans. KOH is a strong base, so it completely ionizes in aqueous solution. OH^- ions are strong nucleophile, so it replaces the halogen atoms and form alcohols. In contrast, an alcoholic solution of KOH contains alkoxide ($R-O^-$) ions which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form an alkene.

Q. 9 Haloalkanes undergo nucleophilic substitutions whereas haloarenes undergo electrophilic substitutions. Why? (3 Marks)

Ans. Haloalkanes are more polar than haloarenes. As a result the carbon atom carrying the halogen in haloalkanes is more electron-deficient than that in haloarenes. So, haloalkanes undergo nucleophilic substitutions more readily than haloarenes.

In contrast, haloarenes contain a benzene ring. Since the typical reactions of benzene are electrophilic substitutions, therefore, haloarenes undergo electrophilic substitution while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitutions.

Q. 10 Explain why?

(a) Alkyl halides, though polar, are immiscible with water.

(b) Grignard reagents should be prepared under anhydrous conditions? (3 Marks)

Ans. (a) Alkyl halides are polar in nature but it is insoluble in water because alkyl halide molecules are held together by dipole-dipole attraction and water molecules are held together by H-bonds. More energy is required to overcome these attractive forces between the haloalkanes. But less energy is released when haloalkanes and water molecules come together, so the solubility of haloalkanes are not upto the mark in water.

(b) Grignard reagents are very reactive, so they react with moisture and form alkane.

$\text{R-Mg-X} + \text{H-OH} \rightarrow \text{R-H} + \text{Mg(OH)X}$

Therefore, it must be prepared under anhydrous conditions..

VALUE BASED QUESTION

Iodoform is used as an antiseptic particularly for dressing wounds. Actually, on coming in contact with skin it decomposes and slowly loses iodine which accounts for the antiseptic properties for iodoform. Iodoform is a yellow crystalline solid with a characteristic unpleasant smell. It is insoluble in water but dissolves in alcohol, ether and other organic solvents.It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or Na_2CO_3 and I_2 in water. Yellow precipitate of CHI_3 is formed. This reaction is called iodoform reaction.

(i) What is antiseptic?

(ii) Which compound in the pair CH_3Br or CH_3I will react in S_N2 reaction?

(iii) Iodofrom is obtained by the reaction of acetone with hypoiodite but not with iodine. Why?

(iv) when iodoform is heated with silver nitrate solution a precipitate is formed, no precipitate is formed if chloroform is used in place of iodoform. Explain.

Answer

(i) Antiseptics may be defined as the chemical substance which prevent the growth of micro-organisms and may also kill them.

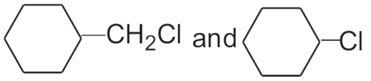
(ii) CH_3Br and CH_3I are both primary halogen compound. The reactivity will depend upon the size of the halogens. Iodine is better leaving group because of larger size. Therefore, CH_3I will react faster than CH_3Br.

(iii) The reaction is initiated by replacement of methyl protons in acetone by I^+ produced from the hypoiodite ions, OI^- $CH_3COCH_3 + 3OI^- \rightarrow CH_3COCl_3 + 3OH^-$

(iv) The C — I bonds in iodoform are much weaker than the C — Cl bonds chloroform and are, therefore, cleaved to produce iodine.

Assignment

Q1 In the following pairs of halogen compounds, which would undergo SN^2 reaction faster?



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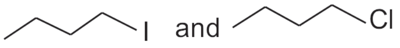
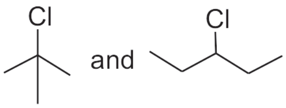


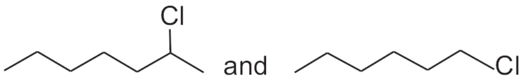
Q2 Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Q3 In the following pairs of halogen compounds, which compound undergoes faster SN^1 reaction?

(i)



(ii)



Q4 Why is sulphuric acid not used during the reaction of alcohols with KI?

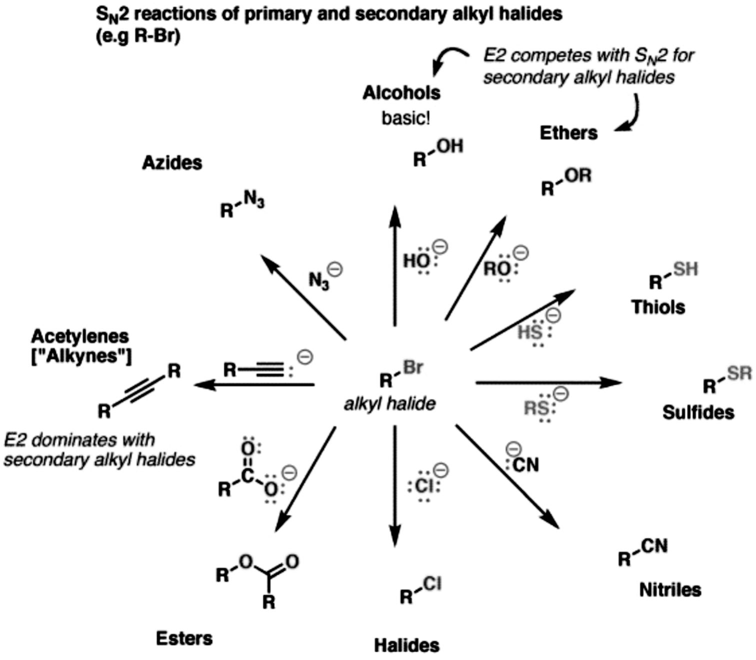
Q5 *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers. Discuss.

Q6 hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Q7 Chloroform is stored in dark coloured & sealed bottle. Why?

Q8 Aryl halides cannot be prepared by the action of sodium halide in the presence H_2SO_4. Why?

MIND MAP FOR CONVERSION

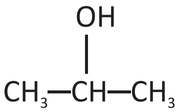


ALCOHOLS, PHENOLS AND ETHERS (Unit- 11)

Definition:

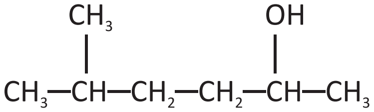
An ***alcohol*** is any organic compound in which a hydroxyl functional group (-**OH**) is bound to a carbon atom, usually connected to other carbon or hydrogen atoms.

- $CH_3—CH_2—CH_2—OH$ 1-propanol



$CH_3—\overset{\overset{OH}{|}}{C}H—CH_3$

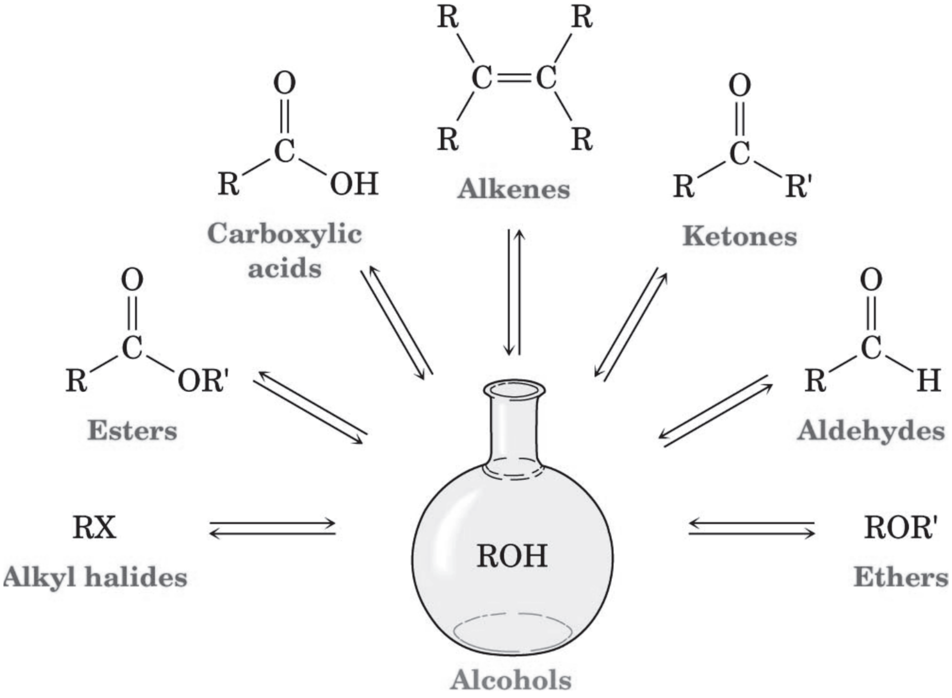
2-propanol



$CH_3—\overset{\overset{CH_3}{|}}{C}H—CH_2—CH_2—\overset{\overset{OH}{|}}{C}H—CH_3$

5-methyl-2-hexanol

MIND MAP OF PROPERTIES OF ALCOHOL

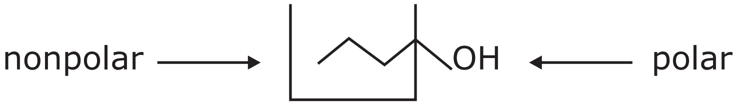


Physical Properties

1. **Alcohols are polar molecules (because of O-H and C-O).**
2. **Hydrogen bonding occurs between alcohols molecules relatively weak bond(represented by dots) O has a partially negative charge δ- & H has a partially positive charge.**
3. **They are weak acids (alkyl alcohols weaker than Phenol):**

   Although alkyl alcohols have an -OH group, they do not ionize in water, whereas phenols ionize like acids (donating a proton to water).

4. Solubility in water (Molecular weight ↑ : solubility ↓)



-As the chain of the R group increases the hydrocarbon (**non- polar)** character of the compound also increases. Consequently, the **solubility** and **boiling point** of an alcohol are affected by the

1) Length of the carbon chain and

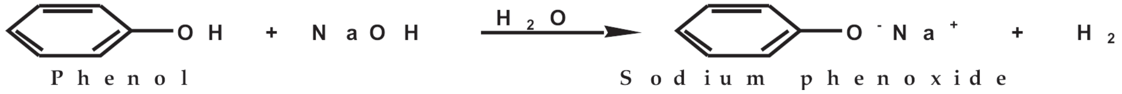
2) The shape of the molecule.

-The **short** chain alcohols are **soluble** in water, whereas the **longer** chain alcohols are **insoluble** in water.

-In general a molecule which is **more compact** (i.e., more branched) will be **more soluble** in water and will have **a lower boiling point** than the straight chain isomer.(for isomeric alcohol)

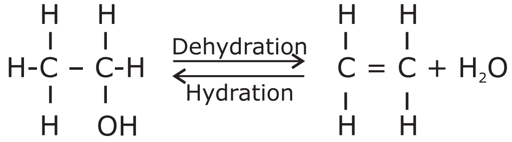
Chemical Properties of Alcohols

1. Acidity of Alcohols:



2. Acid-Catalyse Dehydration:

$$CH_3CH_2OH \xrightarrow[180°C]{H_2SO_4} CH_2{=}CH_2+H_2O$$



$$\begin{array}{c} H \quad H \\ | \quad\; | \\ H\text{-}C - C\text{-}H \\ | \quad\; | \\ H \quad OH \end{array} \underset{\text{Hydration}}{\overset{\text{Dehydration}}{\rightleftharpoons}} \begin{array}{c} H \quad H \\ | \quad | \\ C = C \\ | \quad | \\ H \quad H \end{array} + H_2O$$

3. Oxidation of Alcohols: (1°), (2°) & (3°)

Using Potassium Dichromate & Sulphuric Acid as catalysts

In the oxidation [O] of a primary alcohol(1°) , aldehyde is produced

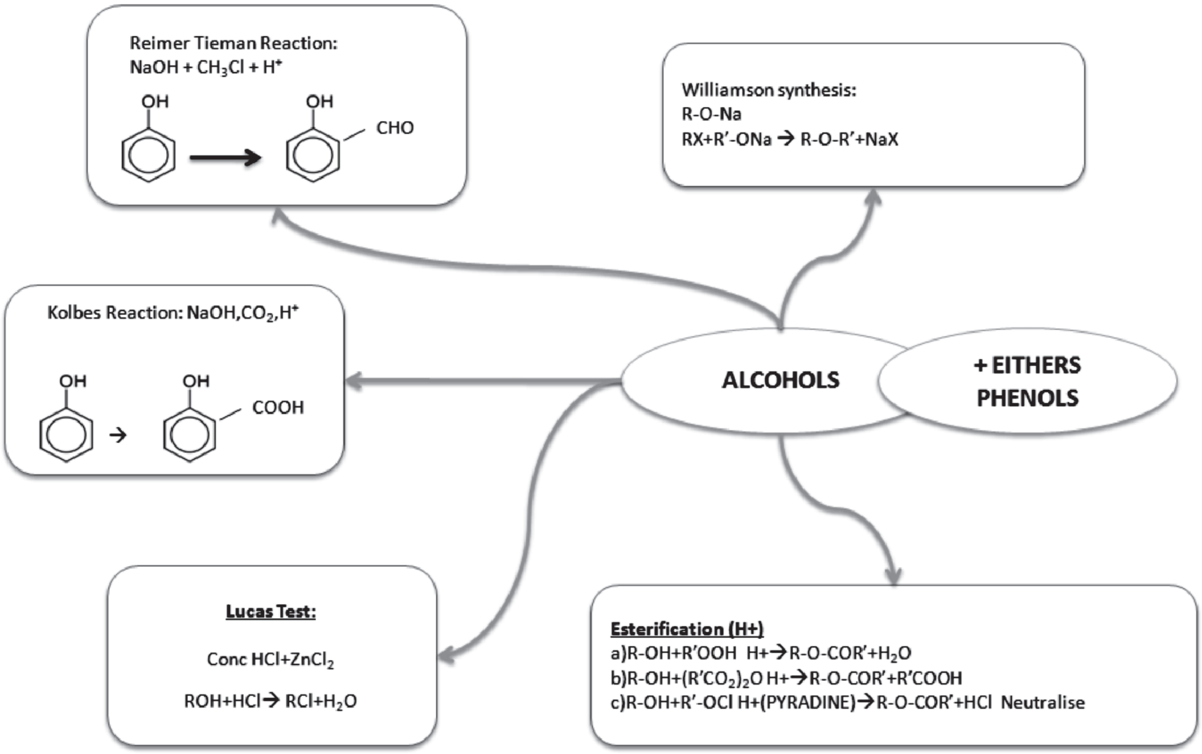
Primary alcohol → aldehyde → carboxylic acid

On oxidation of 2 alcohols a ketone is formed.

Secondary alcohol → ketone

Tertiary 3 alcohols do not oxidize.

Tertiary alcohol → No reaction



CONCEPTUAL QUESTIONS

Q1) Preparation of ethers by acid dehydration of secondary or 3^0 alcohols is not a suitable method?

Ans. The formation of ethers by dehydration of alcohol is a bimolecular reaction (SN_2) group is hindered. As a result elimination dominates substitution as 3^0 carbocation is more stable. Hence in place of ethers, alkenes are formed.

Q2) Phenols do not give protonation reactions readily. Why?

Ans. The lone pair on oxygen of O-H in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

REASONING QUESTIONS

Q1. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Ans. The molecules of Butane are held together by weak van der Waal's Forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

Q2. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

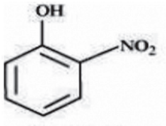
Ans. Alcohols can form hydrogen bonds with water and break the hydrogen bonds already existing between water molecules Therefore they are soluble in water. Whereas hydrocarbons cannot form hydrogen bonds with water and hence are insoluble in water.

Q3 While separating a mixture of ortho and para nitro phenols by steam distillation, name the isomer which will be steam volatile. Give reason.

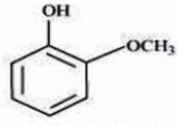
Ans. O-nitro phenol is steam volatile due to intramolecular hydrogen bonding and hence can be separated by steam distillation from p-nitro phenol which is not steam volatile because of inter-molecular hydrogen bonding.

Q4. Explain why is ortho nitro phenol more acidic than ortho methoxyphenol?

Ans. The nitro-group is an electron-withdrawing group. Therefore decreases the electron density of the ring as well as oxygen.. As a result, it is easier to lose a proton. Also, the o-nitrophenoxide ion formed after the loss of proton is stabilized by resonance. Hence, ortho-nitro phenol is stronger acid. On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density of the oxygen atom and hence, the proton cannot be given out easily. Therefor ortho-nitro phenol is more acidic than orthomethoxyphenol.



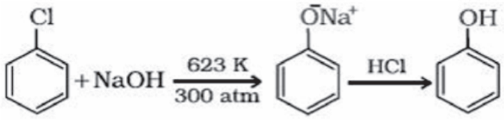
o – Nitrophenol



o – Methoxyphenol

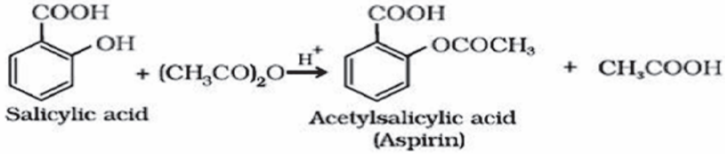
Q5. Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans. Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



Q6. How is aspirin (Acetylsalicylic acid) prepared from salicylic acid?

Ans. Acetylation of salicylic acid produces aspirin.



Q7. Which out of propan-1-ol and propan-2-ol is stronger acid?

Ans. Propan-1-ol is stronger acid than propan-2ol. The acidic strength of alcohols is in the order $1^0 > 2^0 > 3^0$.

Q8. What is denaturation of an alcohol?

Ans. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Q9. Give IUPAC name of $CH_3OCH_2OCH_3$

Ans. Dimethoxymethane

Q10. Diethyl ether does not react with sodium. Explain.

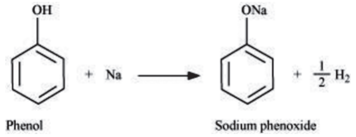
Ans. Diethyl ether does not contain any active hydrogen.

2 MARKS QUESTIONS

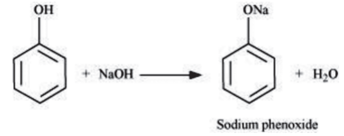
Q1. Give two reactions that show the acidic nature of Phenol. Compare acidity of phenol with that of ethanol.

Ans. The acidic nature of phenol can be represented by the following two reactions:

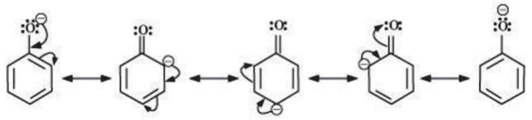
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water.

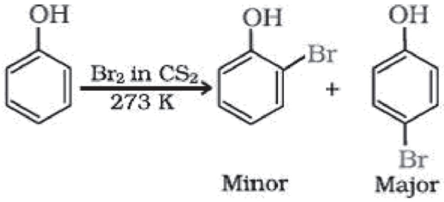


The acidity of phenol is more than that of ethanol. This is because of after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.

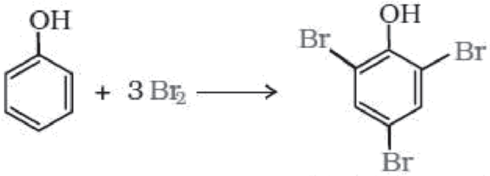


Q2. How does phenol react with Br_2 in CS_2 and Bromine water?

Ans. (i) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed i.



ii. When phenol is treated with bromine water, 2, 4,6tribromophenol is formed as white precipitate.



2,4,6-Tribromophenol

Q4. How do you account for the fact that unlike phenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous solution of sodium carbonate?

Ans. 2, 4-Dinitrophenol and 2, 4, 6-trinitrophenol are stronger acids then carbonic acid (H_2CO_3) due to the presence of electron withdrawing – NO_2 groups. Hence, they react with Na_2CO_3 to form their corresponding salts and dissolve in aq. Na_2CO_3 solution

Q5. Account for the following

a. Boiling point of the C_2H_5OH is more than that of C_2H_5Cl

b. The solubility of alcohols in water decreases with increase in molecular mass.

Ans. a. Because of hydrogen bonding.

b. With increase in molecular mass the non-polar alkyl group becomes more predominant.

Q6. Answer the following

a. What is the order of reactivity of 1^0, 2^0 and 3^0 alcohols with sodium metal?

b. How will you account for the solubility of lower alcohols in water?

Ans, a. $1^0 > 2^0 > 3^0$

b. Here --OH group is predominant and the alcohol molecules can form hydrogen bonds with water molecules.

Q7. Give reasons:

i) Nitration of phenol gives ortho- and para- products only.

ii) Why do alcohols have higher boiling points than the halo alkanes of the same molecular mass?

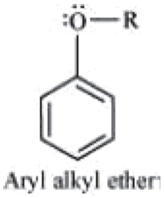
Ans. (1) -OH group increases the electron density more at ortho and para positions through its electron releasing resonance effect.

(2) Alcohols are capable of forming intermolecular H-bonds.while alkyl halide do not.

Q8. Explain the fact that in aryl alkyl ethers

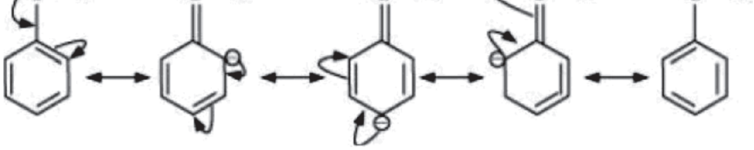
(i) The alkoxy group activates the benzene ring towards electrophilic substitution and

(ii) It directs the incoming substituents to ortho and para positions in benzene ring.



Aryl alkyl ether

(Ans. (i) In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.



Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene.

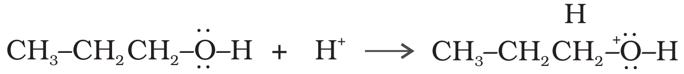
Q9. How is 1-propoxypropane synthesized from propan-1ol? Write mechanism of this reaction.

Ans. 1-propoxypropane can be synthesized from propan-1ol by dehydration. Propan-1-ol undergoes dehydration in the presence of protic acids (such as H_2SO_4, H_3PO_4) to give 1propoxypropane.

$$\underset{\text{Propane-1-ol}}{2CH_3CH_2CH_2-OH} \xrightarrow[413K]{H^+} \underset{\text{1- Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3}$$

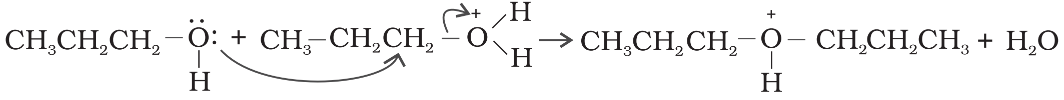
The mechanism of this reaction involves the following three steps:

Step 1: Protonation



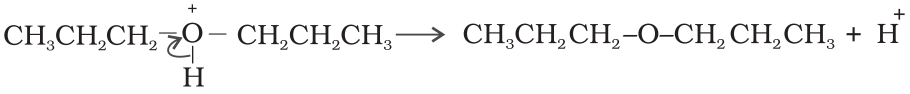
$$CH_3-CH_2CH_2-\ddot{\underset{..}{O}}-H + H^+ \longrightarrow CH_3-CH_2CH_2-\overset{+}{\underset{..}{\overset{H}{O}}}-H$$

Step 2: Nucleophilic attack



$$CH_3CH_2CH_2-\underset{H}{\underset{|}{\ddot{O}}}: + CH_3-CH_2CH_2-\overset{+}{O}\langle^{H}_{H} \longrightarrow CH_3CH_2CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_2CH_3 + H_2O$$

Step 3: Deprotonation



$$CH_3CH_2CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2-O-CH_2CH_2CH_3 + H^+$$

ASSIGNMENT

Q1. **How are primary, secondary and tertiary alcohols prepared from Grignard Reagents?**

Q2. **Give the equations of oxidation of primary, secondary and tertiary alcohols by Cu at 573 K.**

Q3. **Show how will you synthesize:**

(i) 1-phenylethanol from a suitable alkene.

(ii) Cyclohexylmethanol using an alkyl halide by an SN_2 reaction.

(iii) pentan-1-ol using a suitable alkyl halide?

Q4. **How are the following conversions carried out?**

(i) Propene → Propan-2-ol

(ii) Benzyl chloride → Benzyl alcohol

(ii) Ethyl magnesium chloride → Propan-1-ol.

Q5. **Name the reagents used in the following reactions:**

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2, 4, 6-tribromophenol.

Value based Questions

Ethyl alcohol to which another liquid has been added to make it unfit for use as beverage is called denatured alcohol. Ethyl alcohol denatured by adding methyl alcohol, is highly poisonous.

Answer the following questions:

(i) Mention another way by which alcohol is denatured.

(ii) Explain why methanol is highly toxic to human beings?

(iii) How is methanol prepared on large-scale? Give its two important use.

Aldehydes, Ketones and Carboxylic Acids (UNIT- 12)

Key Points:-

- Formaldehyde cannot be prepared by Rosenmund's reaction since formyl chloride is unstable at room temperature.
- Benzaldehyde is less reactive than aliphatic aldehydes towards nucleophilic addition reaction.
- In reaction of toluene with CrO_3, acetic anhydride is used to protect benzaldehyde as benzylidenediacetate to avoid further oxidation to benzoic acid.
- Aromatic ketones are less reactive , they do not react with $NaHSO_3$.
- In reaction of aldehydes and ketones with ammonia derivatives, the medium should be slightly acidic (pH=4.5). In too highly acidic medium, ammonia derivatives being acidic form salts and not act as nucleophile
- Benzaldehyde although reduce Tollens' reagent, it does not reduce Fehling's and Benedict's solution.
- Ketones do not give Tollens reagent and Fehling solution test.
- Only CH_3CHO and all methyl ketones give Iodoform test
- A stronger acid has higher K_a but lower pK_a.
- Benzoic acid is a stronger acid than acetic acid.
- -CHO and –COOH group , attached to benzene ring, are deactivating and m-directing.
- Methanoic acid decolouries the pink colouer of acidified $KMnO_4$ solution but acetic acid not.
- A 40% aqueous solution of fomaldehyde is known as formalin and is used to preserve biological specimens an to prepare bakelite.
- Bezaldehyde is used in perfumery and in dye industries.

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

Q1. Arrange the following compounds in an increasing order of their reactivity towards nucleophilic addition reaction.

CH_3CHO, CH_3CH_2CHO ,CH_3COCH_3, $CH_3COCH_2CH_3$.

Ans. $CH_3COCH_2CH_3 < CH_3COCH_3 < CH_3CH_2CHO < CH_3CHO$

Q2. Name the reagent which is used to convert allyl alcohol to propanol.

Ans. PCC (Pyridinium Chlorochromate)

Q3. Name the aldehyde which does not give Fehling solution test.

Ans. Benzaldehyde.

Q4. Write IUPAC name of the compound $CH_2 = CHCOCH_2COOH$

Ans. 3-Oxopent-4- enoic acid

Q5. Complete the reaction:-

$$CH_3\text{-}C\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4}$$

Ans. $$CH_3\text{-}C\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3COCH_3$$

SHORT ANSWER TYPE QUESTIONS (2- MARKS)

Q1. Write chemical equation to illustrate following name reactions:-

(a) Cannizzaro's reaction

(b) Hell-Volhard- Zelinsky reaction

Ans. (a) Cannizzaro's reaction

$$HCHO \xrightarrow{NaOH} CH_3OH + HCOONa$$

(OR)

$$C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$

(b) Hell-Volhard- Zelinsky reaction

$$R\text{-}CH_2\text{-}COOH \xrightarrow[(ii)H_2O]{(i)X_2/P(red)} R\text{-}CH(X)\text{-}COOH \qquad (X = Cl, Br)$$

Q2. Give a chemical test to distinguish between the following pairs:-

(i) Phenol and bezoic acid

(ii) Benzaldehyde and Acetophenone

Ans. (i) Benzoic acid reacts with$NaHCO_3$ giving CO_2 gas with effervescence where as phenol does not .

$$C_6H_5\,COOH + NaHCO_3 \rightarrow C_6H_5COONa + H_2O + CO_2$$

(ii) Acetophenone on reacting with hot NaOH / I_2 gives yellow ppt of CHI_3while Benzophenone does not .$CH_3COC_6H_5 \xrightarrow{NaOH/I_2} CHI_3 + C_6H_5COONa$

Q3. Account for the following :-

(i) Chloroacetic acid $Cl\text{-}CH_2COOH$ is a stronger acid than acetic acid CH_3COOH.

(ii) Carboxylic acids do not give the reaction of carbonyl group.

Ans. (i) The –I effect of Cl atom in $ClCH_2COOH$ stabiles the $ClCH_2COO^-$ ion while +I effect of CH_3- group in CH_3COOH destabilizes the CH_3COO^-.

(ii) In the resonating structures of carboxylic acid and carbonyls, the carbonyl carbon of carboxylic acid is less electro-positive (less electrophile) than carbonyl carbon in aldehydes and ketones. Therefor carboxylic acids do not give the reaction of carbonyl group

Q4. Arrange the following.

(i) C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH(decreasing order of their acidic character)

(ii) Ethanal, Propanal, Propanone, Butanone reaction(increasing order of their nucleophilic addition reaction)

Ans. (i) $NO_2\text{-}CH_2\text{-}COOH > F\text{-}CH_2\text{-}COOH > C_6H_5\text{-}COOH$

(ii) Butanone < Propanone < Propanal < Ethanal

Q5. An organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iododorm test. It does not reduce Tollens' or Fehling's reagent and does not decolourise bromine water also . On oxidation with chromic acid, it gives a carboxylic acid 'B' with molecular formula $C_7H_6O_2$. Deduce the structures A and B.

Ans. Since A does not give Fehling's or Tollens' test but gives iodoform test and 2,4- DNP test so it has CH_3 CO- group. Hence:

$$\underset{(A)}{C_6H_5COCH_3} \xrightarrow{H_2CrO_4} \underset{(B)}{C_6H_5COOH}$$

OR

Write chemical equation for the following conversion (not more than two steps)

(i) Acetaldehyde to butane -1,3 –diol

(ii) Acetone to propene

Ans. (i) $CH_3\text{-}CHO \xrightarrow{NaOH} CH_3\text{-} CHOH\text{-}CH_2\text{-}CHO \xrightarrow{NaBH_4} CH_3\text{-} CHOH\text{-}CH_2\text{-}CH2OH$

(ii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3 \xrightarrow{H_2SO_4/heat} CH_3CH = CH_2$

SHORT ANSWER TYPE QUESTIONS (3- MARKS)

Q1. Explain the following name reaction by giving one suitable example of each:-

(i) Wolff-kishner reduction (ii) Aldol condensation (iii) Clemensen's reduction

Ans. (i) Wolff-kishner reduction

$R_2CO \xrightarrow{(i)NH_2NH_2} R_2C{=}NNH_2 \xrightarrow{KOH/Glycol} RCH_2R$

(ii) Aldol condensation

Carbonyl compounds with α- hydrogen in basic medium undergo condensation to give Hydroxy aldehydes and ketones.

$CH_3CHO \xrightarrow{NaOH} CH_3\text{-}CHOH\text{-}CH_2\text{-}CHO \xrightarrow{heat} CH_3\text{-}CH{=}CH\text{-}CHO + H_2O$

(iii) Clemensen's reduction

$R_2CO \xrightarrow{Zn–Hg.Con.–HCl} RCH_2R$

Q2. Write the products of the following reactions

(i) $CH_3COCH_3 \xrightarrow{Zn–Hg/.Con.–HCl}$?

(ii) $CH_3\text{-}CO\text{-}Cl + H_2 \xrightarrow{Pd – BaSO_4/S}$?

(iii) $C_6H_5COOH \xrightarrow{Br_2/FBr_3}$?

Ans. (i) $CH_3COCH_3 \xrightarrow{Zn–Hg/.Con.–HCl} CH_3CH_2CH_3 + H_2O$

(ii) $CH_3\text{-}CO\text{-}Cl + H_2 \xrightarrow{Pd – BaSO_4/S} CH_3CHO + HCl$

(iii) $C_6H_5COOH \xrightarrow{Br_2/FBr_3} C_6H_4(m\text{-}Br)\ COOH$

Q3. Arrange the following in the order of indicated property

(i) CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ (increasing order of boiling points)

(ii) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ (increasing acid srength)

(iii) Benzaldehyd,p-Tolualdehyde, p-Nitrobenzaldehyde,Acetophenone (increasing nucleophilic addition)

Ans. (i) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

(ii) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

(iii) Acetophenone < p-Tolualdehyde < Benzaldehyde< p-Nitrobenzaldehyde

Q4. How do you convert the following ?

(i) Benzoic acid to Benzaldehyde

(ii) Ethyne to Ethanol

(iii) Acetic acid to Methane

Ans. (i) $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl + H_2 \xrightarrow{Pd-BaSO_4} C_6H_5CHO$

(ii) $CH\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} [CH_2{=}CH\,OH] \rightarrow CH_3CHO$

(iii) $CH_3COOH + NaOH \rightarrow CH_3COONa \xrightarrow{(NaOH + CaO)/\Delta} CH_4$

Q5. Give reasons for the following:

(i) Ethanal is more reactive than acetone towards nucleophilic addition reaction.

(ii) $(CH_3)_3C$-CHO does not undergo aldol condensation.

(iii) Carboxylic acids are higher boiling liquids than alcohols.

Ans. (i) The presence of two alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon , and reduce the positivity of carbonyl carbon more effectively in ketones than in aldehydes.

(i) Due to unavailability of α-hydrogen in the given compound it does not undergo aldol condensation.

(ii) Due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding,(exits as dimer)

LONG ANSWER TYPE QUESTIONS (5-MARKS)

Q1. (a) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.

(b) How will you bring about the following conversions?

(i) Acetic acid to Acetaldehyde

(ii) Propylene to Acetone

(iii) Ethanal to but-2-enal

Ans. (a) (i) resonating structures of carboxylate ion are more stable than phenoxide ion.

(ii) Negative charge is dispersing on two electronegative oxygen in carboxylate ion whereas in phenoxide ion it is on one oxygen .

(b) Conversions:

(i) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{H_2/Pd-BaSO_4} CH_3CHO$

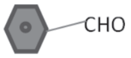
(ii) $CH_3\text{-}CH{=}CH_2 \xrightarrow{H_2O/H^+} CH_3\text{-}CHOH\text{-}CH_3 \xrightarrow{Cu/573k} CH_3COCH_3$

(iii) $CH_3CHO \xrightarrow{NaoH(dil.)} CH_3\text{-}CHOH\text{-}CH_2\text{-}CH \xrightarrow{heat} CH_3\text{-}CH{=}CH\text{-}CHO$

Q2. (a) Write the structures of A,B, C and D in the following reactions:

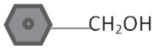
$$\begin{tikzcd} C_6H_5COCl\ A \arrow[r, "H_2/Pd-BaSO_4"] & {} \arrow[r, "Conc.NaOH"] & B + C \\ & A \arrow[d] \arrow[r, "CH_3MgBr", "H_3O^+"'] & {} \\ & D & \end{tikzcd}$$

(A)

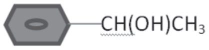


(B)

(C)



(D)



(b) Distinguish between: (i) Acetone and Acetaldehyde (ii) Benzaldehyde and Benzophenone

Ans. (i) Acetaldehyde on warming with Fehling solution,gives red precipitate of cuprous oxide, while acetone does not.

$$CH_3CHO + 2Cu(OH)_2 + NaOH \rightarrow \underset{\text{(Red ppt)}}{CH_3COONa + Cu_2O} + 3H_2O$$

(ii) Bezaldehyde gives Tollens' test, while benzophenone not.

$$C_6H_5CHO + 2[Ag(NH_3)_2] \rightarrow C_6H_5COONH_4 + 2Ag + 3NH_3 + H_2O$$

VALUE BASED QUESTION (4-MARKS)

Q1. Ram and Rahim went to Kullu in Himachal Pradesh on a hiking trip. On the way, Ram brushed against a certain plant and it resulted in severe itching. Rahim recognized the plant as stinging nettle. Rahim went to nearby shop and bought a soap cake. He rubbed the soap cake on the skin of Ram after wetting it with water. It helped Ram and the itching stopped within very short time. After reading the above passage answer the following questions.

(a) Which chemical compound caused itching on Ram's skin?
(b) Why itching stopped when some rubbed on it?
(c) What are the values are associated with Rahim's initiatives?

Ans. (a) The cause of itching on Ram's skin is formic acid.
(b) Soap contains some free alkali (NaOH or KOH) which neutralized the formic acid as a result itching stopped.
(c) The values associated with Rahim's initiative

Friendship, Knowlodge of chemistry put to use , General awareness.

ASSIGNMENT

1. Arrange the following :
   - (i) (a) Benzoic acid
     - (b) 4-Nitrobenzoic acid
     - (c) 3,4-Dintrobenzoic acid
     - (d) 4-Methoxybenzoic acid (increasing acidic character)
   - (ii) CH_3CHO, C_6H_5CHO,$HCHO$ (reactivity towards nucleophilic addition reaction)
2. Write the reaction mechanism for the reaction.

   $R\text{-}CHO + HCN \rightarrow R\text{-}CHCN\text{-}OH$
3. Draw the molecular structure of the compounds:-
   - (i) 4- methylpent-3-en-2-one.
   - (ii) 3-Methylbutanal
   - (iii) Hexane-1,6-dioic acid
4. How will you prepare benzyl alcohol from benzaldehyde without using a reducing agent?

   Identify the compounds A,B and C in the following reaction

   $CH_3\text{-}Br \xrightarrow{Mg/ether} (A) \xrightarrow{(i)CO_2/(ii)H_2O} (B) \xrightarrow{(i)CH_3OH/H^+(ii)\Delta} (C)$

   1. How do you convert the following?
      - (i) Benzoic acid to Benzaldehyde
      - (ii) Ethyne to Ethanoic acid
   2. (a) Account for the following-
      - (i) The boiling points of aldehydes and ketones are lower than their corresponding carboxylic acids.
      - (ii) The aldehydes and ketones undergo a number of addition reactions
      - (iii) In the reaction of ammonia derivatives with carbonyl compounds the pH should not be lesser than 4.5.

      (b) Give chemical test to distinguish between:
      - (i) Acetaldehyde and Benzaldehyde (ii) Propanone and propanol
   3. Distinguish between the following:
      - (a) (i) Butanone and Butanal
        - (ii) Ethanal and ethanoic acid
      - (b) Write a suitable example of each:
        - (i) Rosenmund reaction
        - (ii) Etard reaction

VALUE BASED QUESTION (4-MARKS)

4. Radha wants to clean old brass lamp used for Pooja. It badly tarnished. Her husband Shyam advised her to use vinegar to clean the brass lamp.
   - (a) Can vinegar bring back the old shine on brass lamp in a shorter time and lesser labour?
   - (b) Name the active compound present in vinegar. Give its IUPAC name.
   - (c) What values are associated with Shyam advise to Radha?

Concept Map

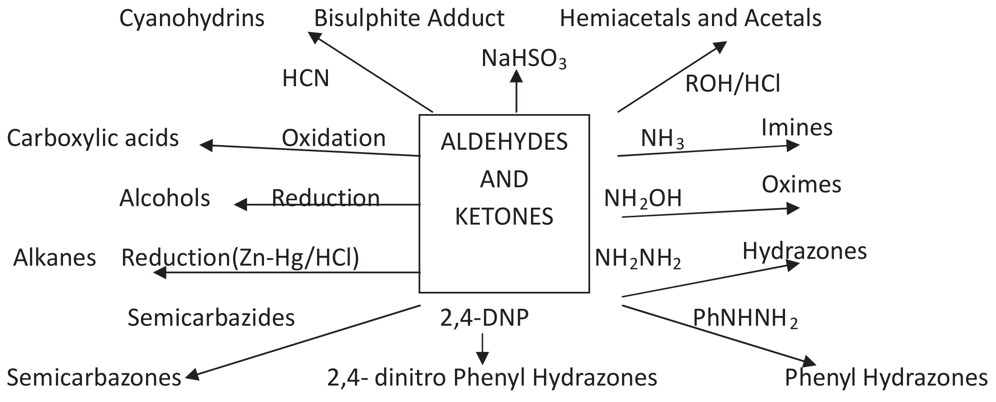
PREPARATION OF ALDEHYDES AND KETONES:

Alcohols	oxidation or hydrogenation →	ALDEHYDES AND KETONES
Alkene	ozonolysis followed by reduction →	
Alkynes	hydrolysis in presence of Hg^{2+} →	

Acyl Halides + H_2	Pd- $BaSO_4$ (Rosenmund's reaction) →	ALDEHYDES
Nitriles (Redn)	$SnCl_2$ and HCl(Stephen reaction) →	
Alkyl Benzene	CrO_2Cl_2followed by hydrolysis (Etard's Reaction) →	
Benzene	CO,HCl Anhydrous $AlCl_3$(Gattermann Koch Reaction) →	

Acyl Halides +	$(CH3)_2Cd$ →	KETONES
Nitriles	Addition of Grignard's Reagent followed by hydrolysis →	
Benzene and substituted benzene	Friedal Kraft's Acylation →	

PROPERTIES OF ALDEHYDES AND KETONES:



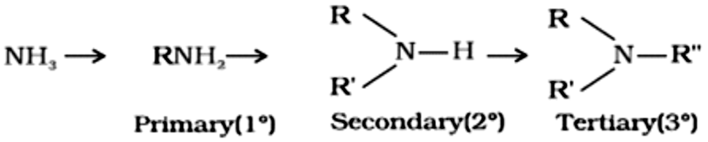
PREPARATION OF CARBOXYLIC ACID:

Acid derivatives	H_2O /NaOH →	CARBOXYLIC ACIDS
Nitriles	H_2O /NaOH or H^+ →	
Alkyl Benzene	oxidation ($KMnO_4/K_2Cr_2O_7$) →	
Alcohols and Aldehydes	oxidation ($KMnO_4/K_2Cr_2O_7$) →	
Grignard's Reagent	CO_2 followed by hydrolysis →	

AMINES (UNIT 13)

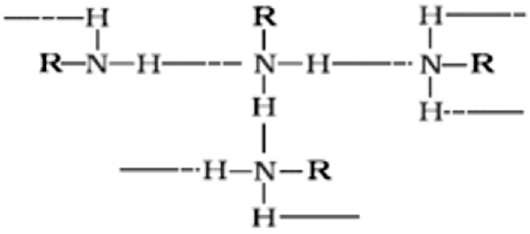
KEY CONCEPTS

Classification:- Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three.



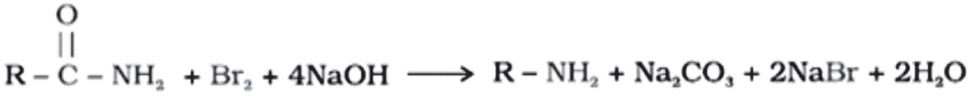
Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
2. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
3. Boiling points order: primary amine> secondary amine> tertiary amine



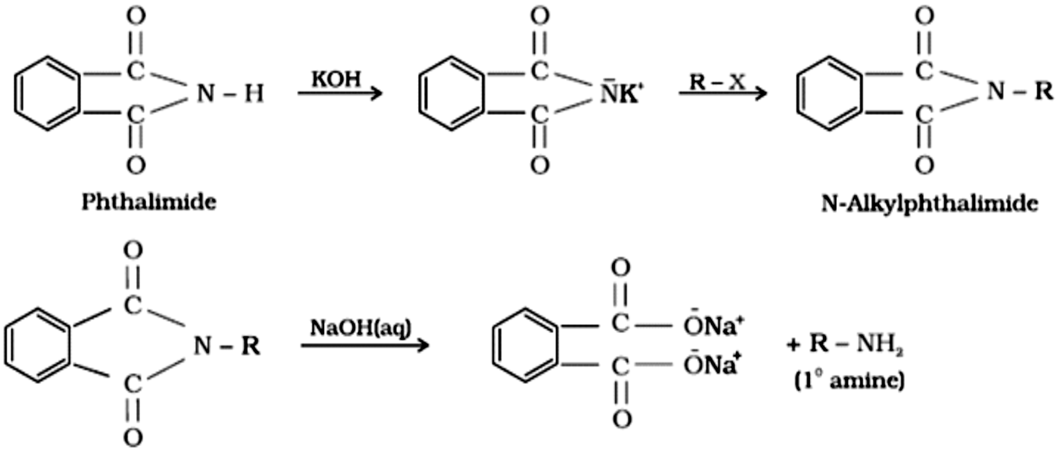
Preparation

HOFFMANN BROMAMIDE REACTION:-



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

GABREIL PHTHALIMIDE SYNTHESIS:-



Chemical Properties

Basic Strength of Amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom. More the K_b (dissociation constant of base), higher is the basicity of amines. Lesser the pK_b higher is the basicity of amines. Aliphatic amines ($R\text{-}NH_2$) are stronger bases than NH_3due to the electron releasing +I effect of the alkyl group. Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Aromatic amines are weaker bases than aliphatic amines and NH_3, due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π-electron pairs of the ring.

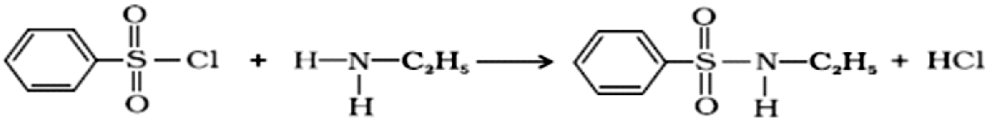
BENZOYLATION:

$$\underset{\textbf{Methanamine}}{CH_3NH_2} + \underset{\textbf{Benzoyl chloride}}{C_6H_5COCl} \rightarrow \underset{\textbf{N – Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

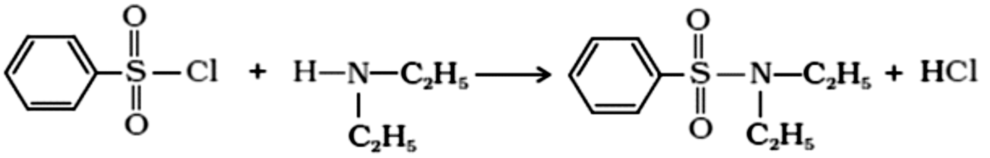
CARBYLAMINE REACTION:

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

HINSBERG'S TEST:



N-Ethylbenzenesulphonamide
(soluble in alkali)

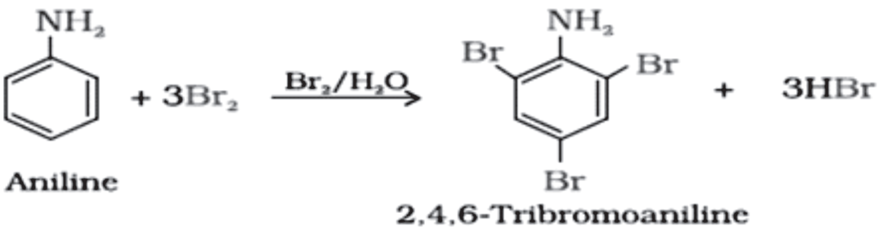


N.N-Diethylbenzenesulphonamide (Insoluble in KOH)

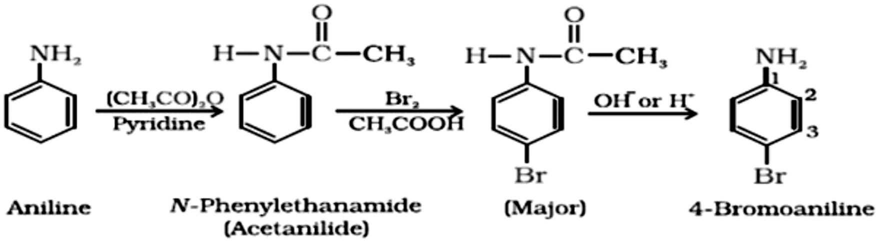
Tertiary amines do not react with benzene sulphonyl chloride.

ELECTROPHILIC SUBSTITUTION REACTIONS:-

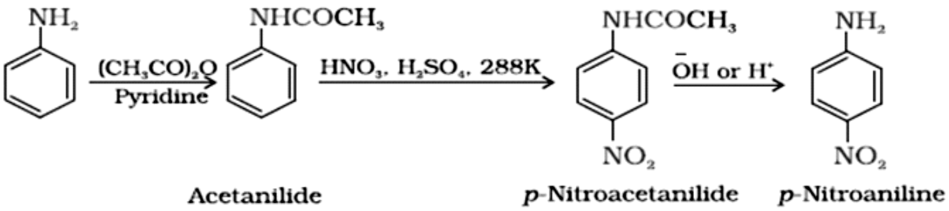
BROMINATION:-



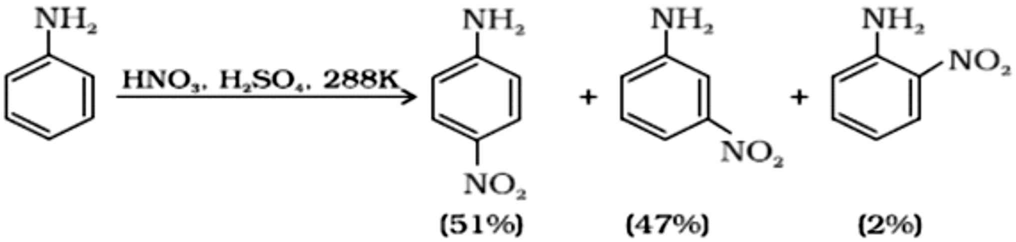
To prepare monosubstituted derivative, activating effect of $–NH_2$ group must be controlled by protecting$–NH_2$ by acetylation with acetic anhydride.



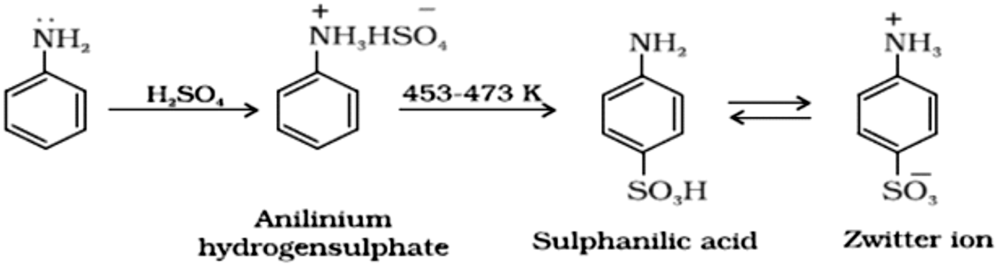
NITRATION: Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strongly acidic medium, aniline is protonated to form anilinium ion which is meta directing so it gives meta product also



SULPHONATION:



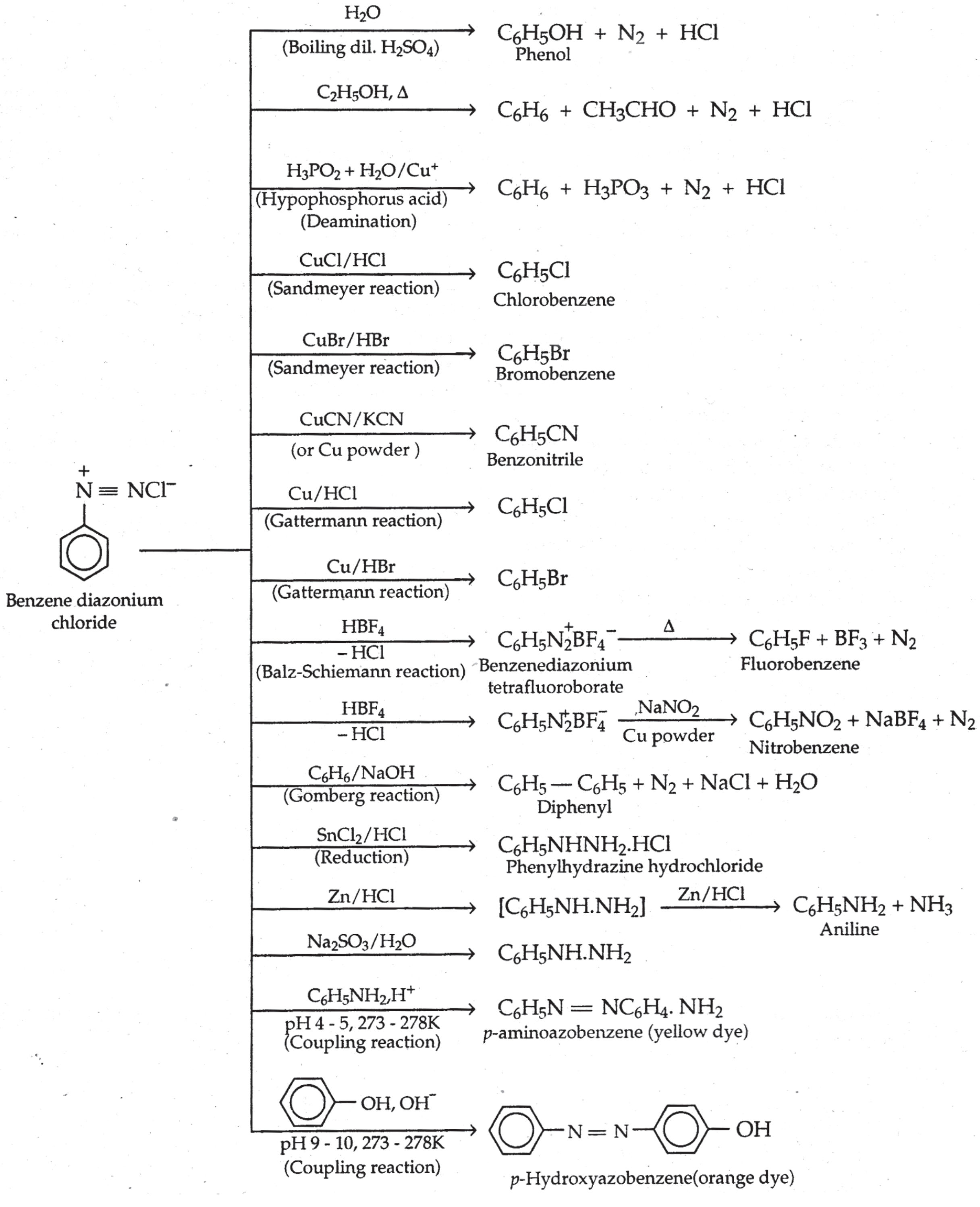
Aniline does not undergo Friedel Craft reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst.

DIAZOTISATION:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5\overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

Properties of benzene diazonium chloride

Reactions of benzene diazonium chloride are summarised as below :



Very Short Answer questions: (1 Mark)

Q.1 What is Hinsberg's reagent?

Ans. Benzene sulphonyl chloride

Q.2 Why is aniline acylated before its nitration?

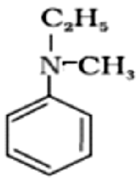
Ans. To prevent it from oxidation

Q.3 Ethylamine is soluble in water but aniline is not, why?

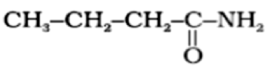
Ans. Ethylamine forms intermolecular H-bond with water, but aniline does not form H-bond to a very large extent due to the presence of large hydrophobic $-C_6H_5$ group.

Q.4 Write the structure of N-Ethyl-N-methylaniline.

Ans.



Q.5 Write structures and IUPAC names of the amide which gives propanamine by Hoffmann bromamide reaction.

Ans.  $CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-NH_2$, Butanamide

Short Answer questions: (2 Mark)

Q.6 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $C_6H_5NHCH_3$ (ii) $(CH_3CH_2)_2NCH_3$

Ans. (i) N-Methyl aniline 2^0 (ii) N-Ethyl-N-methylethanamine 3^0

Q.7 Give plausible explanation for each of the following:

(i) Why do primary amines have higher boiling point than tertiary amines?

(ii) Why are aliphatic amines stronger bases than aromatic amines?

Ans. (i) Due to strong intermolecular H-bonding in primary amines.

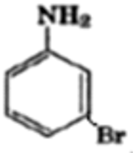
(ii) In aromatic amines lone pair is engaged with benzene in resonance.

Q.8 How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.

Ans. By using Hoffmann bromamide reaction

Q.9 Write the structures of: (a) 3-Bromobenzenamine (b) 3-Chlorobutanamide

Ans: (a)



(b) $CH_3CH(Cl)CH_2CONH_2$

Q.10 Arrange the following:

(i) In decreasing order of the p$K_b$values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

Aniline, *p*-nitroaniline and *p*-toluidine

Ans: (i) $C_6H_5NH_2$, $C_6H_5NHCH_3$,$C_2H_5NH_2$,$(C_2H_5)_2NH$

(ii) *p*-Nitroaniline , aniline, *p*-toluidine

Short Answer questions: (3 Marks)

Q.11 Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine

(ii) Ethylamine and aniline

(iii) Aniline and benzylamine

Ans: (i) Carbylamine reaction

(ii) Azo dye Test

(iii) Azo dye Test

Q.12 Account for the following:

(i) Although amino group is o, p− directing in aromatic electrophilic substitution reactions,aniline on nitration gives a substantial amount of m-nitroaniline.

(ii) Aniline does not undergo Friedel-Crafts reaction.

(iii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Ans. (i) Because nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion which is meta-directing.

(ii) Friedel-Craft reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ acts as a Lewis acid, while aniline acts as a Lewis base. Thus, aniline reacts with $AlCl_3$ to form a salt.

(iii) Gabriel phthalimide synthesis results in the formation of primary amines only. Secondary and tertiary amines are not formed in this synthesis. Thus, a pure primary amine can be obtained. Therefore,Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q.13 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH_2Br_2} C$

(ii) $C_6H_5N_2Cl \xrightarrow[CuCH]{NaCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAH_4} B \xrightarrow[0°C]{HNO_2} C$

Ans: (i) (A) CH_3CH_2CN (B) $CH_3CH_2CONH_2$ (C) $CH_3CH_2NH_2$

(ii) (A) C_6H_5CN (B) C_6H_5COOH (C) $C_6H_5CONH_2$

(iii) (A) CH_3CH_2CN (B) $CH_3CH_2CH_2NH_2$ (C) $CH_3CH_2CH_2OH$

Q.14 How will you convert:

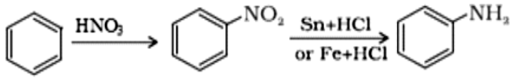
(i) Benzyl chloride to 2-phenylethanamine

(ii) Benzene to Aniline

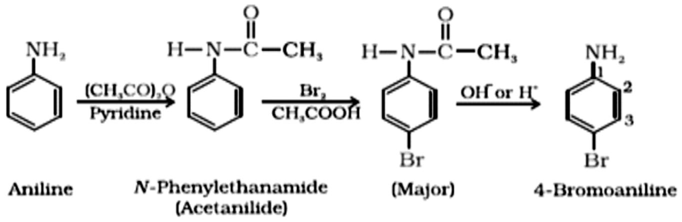
(iii) Aniline to *p*-bromoaniline

Ans: (i) $C_6H_5CH_2Cl \xrightarrow{\text{Ethanolic NaCN}} C_6H_5CH_2CN \xrightarrow{H_2/N_1} C_6H_5CH_2CH_2NH_2$

(ii)



(iii)



Q.15 An organic compound [A] $C_3H_6O_2$ on reaction with ammonia followed by heating yield B. Compound B on reaction with Br_2 and alc. NaOH gives compound C (C_2H_7N). Compound C forms a foul smelling compound D on reaction with chloroform and NaOH. Identify A, B, C, D and the write the equations of reactions involved.

[Hint: (A) CH_3CH_2COOH (B) $CH_2CH_2CONH_2$ (C) $CH_3CH_2NH_2$ (D) CH_3CH_2NC.]

VALUE BASED QUESTION

Ethyl amine is used in making some photographic dyes and emulsifying agents. Ethylamine is colourless liquid with an ammoniacal odour and biting taste. It is also highly soluble in water.

It is formed during putrefaction of yeast and flour. In the laboratory it is obtained by hoffman's reaction using propionamide. Industrially it is prepared by passing a mixture of ethylene and ammonia over cobalt catalyst at about 450^{O}C under 20 atm-pressures.

(i) Give a chemical test and reagent used to distinguish between ethylamine and diethylamine.

(ii) Ethylamine is a stronger base than ammonia. Give reason.

(iii) How ethylamine is prepared from acetonenitrile?

(iv) Give 2 uses of ethylamine.

Answers

(i) Ethylamine reacts with benzene sulphonyl chloride and forms a product which is soluble in alkali. Diethylamine reacts with benzene sulphonyl chloride and forms a product which is insoluble in alkali.

(ii) Ethylamine is more basic than ammonia because the ethyl group is electron releasing and therefore tend to push the electrons towards nitrogen. This makes the lone pair of N more readily available for sharing with a proton than NH_3 in which neither any electron releasing nor any electron withdrawing group is present.

(iii) $CH_3CN + 2H_2 \rightarrow CH_3\text{-}CH_2\text{-}NH_2$

(iv) Uses of ethylamine:

(a) It is used in making some photographic dyes.

(b) It is used in making emulsifying agents.

ASSIGNMENTS

1 MARK QUESTIONS

1. Arrange the following in decreasing order of their basic strength: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$and $C_6H_5NH_2$
2. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?
3. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?
4. Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
5. Write structures and IUPAC names of the amine produced by the Hoffmann degradation of benzamide.

2 MARKS QUESTIONS

Q1. Write short notes on the following:

(i) Carbylamine reaction

(ii) Diazotisation

(iii) Hofmann's bromamide reaction

(iv) Coupling reaction

Q2. Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.KOH \rightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

Q3. Give a chemical test to distinguish between:

(a) $C_6H_5NH_2$ & CH_3NH_2

(b) CH_3NHCH_3 & $(CH_3)_3N$

Q4. Give the IUPAC names of: (a) $(CH_3)_2CHNH_2$ (b) $(CH_3CH_2)_2NCH_3$

3 MARKS QUESTIONS

Q1. How will you convert?

- (i) Benzene into N, N-dimethylaniline
- (ii) Aniline to phenol
- (iii) Aniline into benzene

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C'of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

BIOMOLECULES (UNIT 14)

KEY POINTS	EXPLANATIONS
Monosaccharides	Cannot be hydrolyzed further. eg- glucose, fructose, ribose
Disaccharides	Sucrose (α-D- glucose + β-D-fructose) , Maltose(α-D- glucose + α-D- glucose) Lactose(β-D-galactose + β-D-glucose)
Polysaccharides	*Starch* (two components—Amylose and Amylopectin) polymer of α-D- glucose
Amylose	Water soluble, 15-20% of starch., unbranched chain, C1– C4 glycosidic linkage.
Amylopectin	Water insoluble , 80-85% of starch., branched chain polymer, C1–C4 & C1–C6 glycosidic linkage
Cellulose	Straight chain polysaccharide of β -D-glucose units/ joined by C1-C4glycosidic linkage (β-link), not digestible by human / constituent of cell wall of plant cells
Glycogen	Highly branched polymer of α-D- glucose .found in liver, muscles and brain.
Reducing sugars	Aldehydic/ ketonic groups free so reduce Fehling's/ Tollens solution and. Eg- maltose and lactose
Non reducing sugars	Aldehydic/ ketonic groups are bonded so can not reduce Fehling's solution and Tollens' reagent. Eg- Sucrose
Anomers.	The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* Such isomers, i.e., α –form and β -form, are called anomers.
Invert sugar	Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar
Glycosidic linkage	Linkage between two mono saccharide
Importance of Carbohydrates	Major portion of our food. / used as storage molecules as starch in plants and **glycogen** in animals/. Cell wall of bacteria and plants is made up of cellulose./wood and cloth are cellulose / provide raw materials for many important industries like textiles, paper, lacquers and breweries.
essential amino acids	Which cannot be synthesised in the body and must be obtained through diet, eg- Valine, Leucine

Nonessential amino acids	Which can be synthesised in the body, eg - Glycine, Alanine
zwitter ion.	In aqueous solution, amino acids exist as a dipolar ion known as *zwitter ion*.
peptide linkage	peptide linkage is an amide formed between –COOH group and –NH2 group of two successive amino acids in peptide chain.
1^0- str. Of proteins:	sequence of amino acids that is said to be the primary structure of protein
2^0- str. of proteins:	secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two types of structures viz. α -helix and β -pleated sheet structure.
Tertiary structure of proteins:	further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular.
Fibrous proteins	Polypeptide chains run parallel, held together by hydrogen and disulphide bonds, fibre– like structure. Water insoluble . Eg- are keratin(in hair, wool, silk) and myosin (present in muscles).
Globular proteins	chains of polypeptides coil around to give a spherical shape. water soluble. Eg-Insulin and albumins
Stab. forces 2°& 3°	Hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
Denaturation of Proteins	When a protein is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of protein. (During denaturation 2° and 3° structures are destroyed but 1°structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk
Fat soluble vit	These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues
Water soluble vit	B , C . these vitamins must be supplied regularly in diet because they are readily excreted in urine
Vitamins –sources- Deficiency diseases	Vit- A (Fish liver oil, carrots)- Night blindness / Vitamin B1 (Yeast, milk,)- Beri beri
	Vit-B2 (Milk, eggwhite)- Cheilosis / Vit- B6 (Yeast, milk,)- Convulsions / Vit- B12 (Meat, fish,)- anaemia
	Vit C(Citrus fruits)- Scurvy, / Vit D(Exposure to sunlight, fish and egg yolk)- Rickets, osteomalacia
	Vit E(wheat oil, sunflower oil)- fragility of RBCs / Vit K(leafy vegetables)- Increased blood clotting time

DNA	pentose sugar (D-2-deoxyribose) + phosphoric acid + nitrogenious bases (A , G , C, T)
RNA	pentose sugar (ribose) + phosphoric acid + nitrogenious bases (A, G , C, U)
Nucleoside / tides	Nucleoside → sugar + base Nucleotides → sugar + base + phosphate
Phosphodiester link	Linkage between two nucleotides in polynucleotides
Functions of Nucleic Acids	DNA reserve genetic information, maintain the identity of different species e is capable of self duplication during cell division, synthesizes protein in the cell.

QUESTIONS

(Q.) What is difference between Reducing and non-reducing sugars or carbohydrates? (1 Mark)

(**Ans**) All those carbohydrates which contain aldehydic and ketonic group in the hemiacetal or hemiketal form and reduce Tollen's reagent or Fehling's solution are called reducing carbohydrates while others which do not reduce these reagents are called non-reducing sugars.

(Q.) Explain the term mutarotation? (1 Mark)

(**Ans**) Mutarotation is the change in the specific rotation of an optically active compound with time, to an equilibrium mixture.

(Q.) Define glycosidic linkage? (1 Mark)

(**Ans**) The two monosaccharide units are joined together through an ethereal or oxide linkage formed by the loss of a molecule of H_2O. Such a linkage between two monosaccharide units through oxygen atoms is called glycosidic linkage.

(Q.) Give a chemical equation for obtaining Maltose? (1 Mark)

(**Ans**) Maltose is obtained by partial hydrolysis of starch by the enzyme diastase present in malt i.e., sprouted barley seeds.

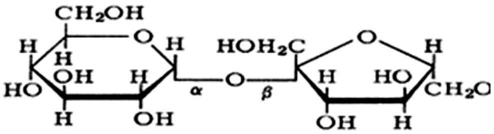
$$2(C_6H_{10}O_5)_n + n\ H_2O \xrightarrow{\textit{Diastase}} n\ C_6H_{12}O_6$$

(Q.) What do you understand by denaturation of proteins? (2 Marks)

(**Ans**) When a protein in its native form, is subjected to physical change like in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

(Q.) **Give the chemical structure of sucrose & explain why sucrose is non reducing sugar. (2 Marks)**

(**Ans**)



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

(Q.) **Give a broad classification of vitamins? (2 Marks)**

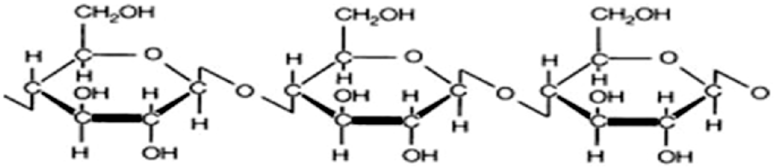
(**Ans**) Vitamins are complex organic molecules. They can be broadly classified as:

(i) Water soluble vitamins: These include vitamin B-complex and vitamin C.

(ii) Fat soluble vitamins: These are oily substances that are not readily soluble in water. However, they are soluble in fat. These include vitamins A,D,E and K.

(Q.) **Write a short note on cellulose and give its chemical structure. (3 Marks)**

(**Ans**)



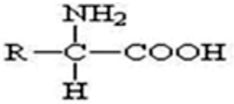
Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of β– D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of t he next glucose unit

(Q.) **Give a short note on Zwitter ion? (3 Marks)**

(**Ans**) Amino acids are usually colourless, crystalline solids. These are water soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxylic group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion.

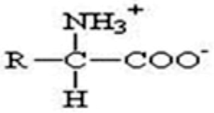
(Q.) **How are peptides formed. Show the formation of peptide bond with diagram. (3 Marks)**

(**Ans**) Peptides are amides formed by the condensation of amino group of one α– amino acid with the carboxyl group of another molecule of the same or different

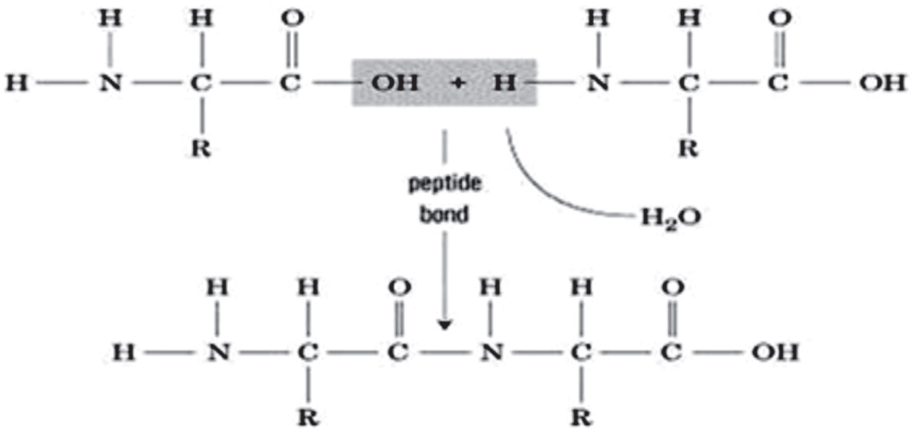


$$R-\overset{NH_2}{\underset{H}{C}}-COOH$$

R is the functional group of the amino acid



$$R-\overset{NH_3^+}{\underset{H}{C}}-COO^-$$



VALUE BASED QUESTION

1-Vitamins are organic compounds which are essential for maintenance of normal growth and health of the organism. Certain vitamins cannot be stored in our body and have to be supplied regularly in diet while others can be stored in the body. Vitamins are required only in small amounts and should not be taken in excess. Answer the following questions:

(i) Out of water soluble and fat soluble vitamins which can be stored in our body?

(ii) Name any two water soluble and two fat soluble vitamins.

(iii) Which of the vitamin belonging to B-complex series can be stored in our body?

(iv) What are the values associated with it.

Ans. (i) Fat soluble

(ii) (Water soluble) B and C, (fat soluble) A,D,E,K

(iii) B_{12}

(iv) Concern for health, awareness about vitamins etc.

Biomolecules

These are the macromolecules essential for survival of life, e.g. carbohydrates, proteins, etc.

Carbohydrates

These are polyhydroxy aldehydes or ketones or their derivatives, e.g. glucose.

Sugars

These are the carbohydrates having sweet taste.
They may be reducing or non-reducing.

Glucose

- It is obtained by hydrolysing starch or cane sugar.
- Its reactions are as:

$\text{Glucose} \xrightarrow[\Delta]{HI} n\text{-hexane}$

$\xrightarrow[3\ mol]{NH_2OH}$ Oxime

$\xrightarrow{Br_2\ water}$ Gluconic acid

$\xrightarrow[CH_3COCl]{Acetylation}$ Pentaacetate

$\xrightarrow{HNO_3}$ Saccharic acid

Sucrose

- It contains D-(+)-glucose and D(–)-fructose joined together by β-1,2-glycosidic linkage.
- It is also called invert sugar.

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.

Proteins

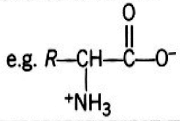
These are polymers of α-amino acids.

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. 

$R{-}\underset{{}^{+}NH_3}{\underset{|}{CH}}{-}\overset{O}{\overset{\|}{C}}{-}O^-$

Denaturation

- It is the process of destroying 2° or 3° 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 protein).

Secondary Structure

(It is formed due to hydrogen bonding and may be α-helix or β-pleated sheet structure).

Enzymes

These are the proteins which catalyse reaction occurring in human body, so also called biocatalysts, e.g. maltase, zymase, etc.

Vitamins, Nucleic Acids and Hormones

Vitamins

These are essential but in very small amounts. Vitamins 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

Nucleic Acids

These are the polymer of nucleotides (sugar + base + phosphoric acid).

Deoxyribonucleic Acid (DNA)

It contains pentose sugar (deoxyribose), purine base (adenine, A and guanine, G) pyrimidine base (Thymine, T and cytosine, C) and phosphoric acid.

Ribonucleic Acid (RNA)

It contains sugar (ribose), purine base (adenine and guanine) and pyrimidine base (uracil, U and cytosine) and phosphoric acid.

Hormones

These are the reactions of endocrine glands.

Steroid Hormones

e.g. sea hormones, bile acids, etc.

Non-steroid Hormones

These do not have steroid ring, e.g. insulin.

POLYMERS (UNIT 15)

KEY POINTS

Polymer:

It is a very large molecule having high molecular mass (10^3 - 10^7 u). They are formed by joining of repeating structural units on large scale.

Classification of polymers:

Based on Source

(i) Natural: Found in plants and animals, e.g. proteins, cellulose, natural rubber,.

(ii) Synthetic: Man-made e.g. nylon, polyester, neoprene, Bakelite, Teflon, PV.C,

Semi-synthetic: Cellulose derivatives as cellulose acetate and cellulose nitrate.

Based on structure:

Linear polymers: This consist of long and straight chain repeating units. e.g. polythene (HDPE), PVC, nylon, polyester.

Branched polymers: This contain linear chains having some branches

e.g. amylopectin.

Cross linked polymers: Strong covalent bonds are present between various linear polymer chains. e.g Bakelite, urea-formaldehyde polymer, melamine etc.

Based on mode of polymerization:

Addition Polymers: These areformed by the repeated addition of monomer molecules possessing multiple bonds, e.g., Polythene, polypropene, polystyrene, etc.

Condensation Polymers: These are formed by the repeated condensation reaction of different bifunctional or trifunctional monomers, with the elimination of small molecules like water, HCl, NH_3, alcohol etc. e.g. Bakelite, nylon, urea-formaldehyde resin etc.

Based on molecular forces:

Elastomers: Forces of interaction between polymer chains is weakest, e.g. buna -S , buna- N, neoprene etc.

Fibers: Strong hydrogen bonds are present between the polymer chains. They have high tensile strength e.g., nylon, polyester, silk, wool, orlon, rayon etc.

Thermoplastics: They are linear/slightly branched chain molecules capable of repeatedly softening on heating and hardening on cooling, e.g. polythene, PVC, polystyrene, etc.

Thermosetting Plastics: They are coss-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g, bakelite, urea formaldehyde resin etc.

e) Based on growth of polymerization: Depending upon the mechanism of polymerization, polymers are classified as ;

(I) Addition polymers or chain growth polymers: This mode of polymerization leads to an increase in chain length through the formation of free radicals.

(ii) Condensation Polymers or step growth polymers : They are formed in gradual steps,the product of each step is again a bifunctional species and the sequence of condensation goes on.

POLYMERS AT A GLANCE

Polymer	Monomer	Uses
(a) Polythene	Ethene	Insulation of wires, toys, manufacture of dustbins etc.
(b) Polytetra fluroethene (Teflon)	Tetrafluroethene	Oil seal and gasket and non-stick kitchen Wares.
(c) Polyarcylonitrile	Acrylonitirile	Substitute for wool.
(d) Terylene or Decron	Ethylene glycol + Terephthalic acid	Safety helmets, used in blending with cotton and wool fibers.
(e) Nylon-6,6	Hexamethylenediamine + adipic acid	Stocking, Socks, ropes, parachutes, fabrics, bristles of tooth brush.
(f) Novalac	Phenol + Formaldehyde	Used for binding glue, paints.
(g) Bakelite	Formaldehyde + Phenol	Combs, records, Switches boards
(h) Melamine	Melamine + Formaldehyde	Manufacture of unbreakable crockery.
(i) Polypropene	Propene	Ropes, toys, pipes, fibres etc.
(j) Polystyrene	Styrene	As insulator, wrapping material, radio and television cabinets.
(k) Glyptal	Ethylene glycol + phthalic acid	Manufacture of paints and lacquers.
(l) Buna-N	1,3-Butadiene+Acrylonitrile	In making oil seals,tank lining, etc.
(m) Nylon-2-Nylon6	Glycine + aminocaproic acid	it is biodegradable polymer
(n) Buna-S copolymer	1,3-Butadiene+Styrene	Autotyress floor tiles foot-wear components
(o) Natural Rubber	2-methyl-1,3-butadiene	Used for tyres
(p) Neoprene	2-chloro-1,3-butadiene	Conveyor belts, gasket, hoses
(q) (PHBV) poly-β hydroxybutyrate-co-β hydroxy valerate (Biodegradable)	3-hydroxybutanoic acid + 3-hydroxypantanoic acid	Speciality packaging, orthopaedic devices.

1 MARKS QUESTIONS

Q.1 What does the designation 6,6 mean in the name nylon -6,6 ?

Ans. The acid and amine parts ,which condense to give the polymer both contain 6 carbons each .

Q.2 Give an example of elastomers .

Ans. Buna -S , Buna -N and neoprene are example of elastomers .

Q.3 Name the polymers used in laminated sheets and give the name of monomeric units involved in its function .

Ans. Urea - formaldehyde resins . Monomer units are Urea and formaldehyde .

Q.4 Explain the difference between Buna-N and Buna-S .

Ans. Both are copolymers . Buna-N is a copolymer of 1,3 -butadiene and and acrylonitrile while Buna-S is a copolymers of 1,3-butadiene and styrene .

Q.5 Why are rubbers called elastomers ?

Ans. Rubbers are stretched on application of force and regain its original state after the force is removed , therefore these are called elastomers .

2 Marks Questions

Q1 Arrange the following polymers in increasing order of their intermolecular forces .

(i) Nylon 6 ,6 ,Buna-S , polythene .

(ii) Nylon 6, neoprene , polyoinyl chloride .

Ans. The increasing intermolecular forces of attraction follows the order : Elastomer, Thermo plastic, Fibre .

(i) Buna-S , polythene , Nylon 6, 6 .

(ii) Neoprene , polyvinyl chloride , Nylon 6 .

Q.2 Distinguish between the terms homopolymers and copolymers and give an example of each

Ans. Homopolymers :- Polymers whose repeating structural units are derived from only one type of monomer units are called Homopolymers . For example , Polythene , PVC, PAN , teflon , etc .

Copolymers :- Polymers whose repeating structural units are derived from different types of monomer molecules . For examples , Buna-S , nylon 6 ,6 , polyester , bakelite , etc .

Q.3 Differentiate the following pairs of polymers based on the property mentioned against each

(i) Novalac and bakelite (structure)

(ii) Buna-S and terylene (intermolecular force of attraction)

Ans. (i) Novalac is a linear condensation polymer formed by reaction between phenol and formaldehyde . Bakelite is a cross linked condensation polymer formed by reaction between phenol and formaldehyde .

(ii) Buna-S has weak intermolecular forces of attraction. terylene has stronger intermolecular force of attraction (dipole- dipole attraction).

Q.4 Write the name of monomers used for getting the polymers PVC and PMMA . state one use for each of these polymers .

Ans. **PVC:-** Vinyl chloride is the monomers used in PVC . It is used for making pipes and electrical insulators .

PMMA:- Poly methyl methacrylate is the monomer used in PMMA . It is used as substitute of glass .

Q.5 Write one difference between chain growth and step growth polymerisation . Give one example of each .

Ans. Chain growth polymerisation involves addition of monomers by free radical mechanism . Generally unsaturated monomers react by this mode of polymerisation to give polymers . Example Polythene , polypropene .

Step growth polymerisation involves repetitive condensation reaction between two bifunctional monomers. Ex Terylene.

3 Marks questions

Q.1 How does the presence of double bonds in rubber molecules influence their structure and reactivity?

Ans. Natural rubber is cis- 1,4 -polyisoprene and is obtained by linear polymerisation of isoprene units. The cis-configuration at double bonds does not allow the polymer chains to come closer for effective interactions and hence intermolecular forces are quite weak. As a result, Natural rubber, i.e, cis-polyisoprene has a randomly coiled structure and hence shows elasticity.

Q.2 How is bakelite made and what is its major use ? Why is bakelite a thermosetting polymer?

Ans. Bakelite is obtained by condensation reaction of phenol and formaldehyde. It is used in making electrical switches and switch boards. It is thermosetting polymer because on heating it undergoes extensive cross linking in the mould.

Q.3 Draw the structures of the monomers of the following polymers :

(i) Polythene (ii) PVC (iii) Teflon

Ans (i) Polythene :- The structure of the monomer of polythene is :

$$CH_2 = CH_2$$

(ii) PVC (polyvinyl chloride) :- The structure of monomer of PVC is given below :

$$CH_2=CH-Cl$$

(iii) Teflon :-The structure of the monomer of teflon is :

$$CF_2=CF_2$$

Q.4 (a) Give an example of synthetic rubber and mention its main advantages

(b) Write the monomers of Dacron

(c) Arrange the following polymers in increasing order of tensile strength :

Nylon-6 , Buna-S , Polythene

Ans. (a) An example of synthetic rubber is Buna-S. Main Advantage : It is resistant to the action of petrol , lubricating oil and organic solvents .

(b) Monomers of Dacron are : Ethylene glycol and Terephthalic acid

(c) Increasing order of tensile strength of the given polymers is

Buna-S < Polythene < Nylon -6

Q.5 Write the names of monomers of the following polymers and classify them as addition or condensation polymers (a) Teflon (b) Bakelite (c) Natural rubber

Ans. (a) Monomer of Teflon is tertraflouroethene ($CF_2=CF_2$). It is an addition polymer .

(b) Monomer of bakelite are formaldehyde and phenol . It is a condensation polymer .

(c) Monomer of natural rubber is isoprene (2-methyl-1 , 3-butadience). It is an addition polymer .

VALUE BASED QUESTION

Q.1 After watching a program onTV about the problem of disposal of carry home bags and packaging material, Ankit a clss XII student suggested that instead of using synthetic polymer carry home bags & packaging materials, use should be made up of paper/cardboard . After reading the passage, answer the following question

i. Name the polymer used to make carry home bags and packaging material.

ii. What values are expressed by Ankit.

iii. Give the name, structure of one biodegradable polymer.

A1 i. Carry home bags and packaging material is made up of low density polythene (LDP)

ii. Carry home bags are made of LDP which is a non biodegradable polymer & create disposal problem while paper/cardboard is boidegradable polymer which saves the environment from getting polluted, further paper/cardboard can be recycled easily.

iii. Biodegradable polymer is(PHBV) Poly β- hydroxybutyrate-coβ-hydroxyvalerate.

ASSIGNMENT QUESTIONS

1. Name a synthetic polymer which is a amide.
2. How are addition polymers different from condensation polymers?
3. What is the basic difference between following pairs:
   (a) Elastomers and fibres
   (b) Thermo setting polymer & thermo plastic polymers.
4. Explain the mechanism of polymerisation of ethene.
5. Differentiate between LDP and HDP.
6. Give preparation of polyacrylonitrile.
7. Write one use of each – Teflon and polyacrylonitrile.

8. Why is condensation polymerisation also called on step – growth polymerisation?
9. Give monomers and preparation of Nylon – 6, 6 and Dacron.
10. How is Nylon – 6, 6 different from Nylon -6?
11. Write uses of bakelite and melamine.
12. How are neoprene & Buna – N prepared? Which one is a copolymer?
13. Classify following on Homopolymer and copolymer-

    PVC, Polystyrene, Buna – S, Neoprene, Buna – N, Teflon.
14. Classify following an addition and condensation polymer-

    Bakelite, Polythene, Nylon – 6, 6, Polyacrylonitrile
15. Write monomers of polystyrene and PVC.

CHEMISTRY IN EVERYDAY LIFE (UNIT 16)

KEY CONCEPTS

1. DRUGS- Drugs are chemical of low molecular masses, which interact with macromolecular targets and produces a biological response.
2. CHEMOTHERAPY- The use of chemicals for therapeutic effect is called chemotherapy.
3. CLASSIFICATION OF DRUGS-
    a) ON THE BASIS OF PHARMACOLOGICAL EFFECT- Useful for doctors as it provides whole range of drugs for treatment of particular kind of disease.
    b) ON THE BASIS OF DRUG ACTION- Action of drug on a particular biochemical process.
    c) ON THE BASIS OF CHEMICAL STRUCTURE- Drugs having similar chemical structure.
    d) ON THE BASIS OF MOLECULAR TARGETS- Drugs interacting with biomolecules as lipids, proteins.
4. ENZYMES AS DRUG TARGETS
    i) CATALYTIC ACTION OF ENZYMES-
        a) Enzymes have active sites which hold the substrate molecule. It can be attracted by reacting molecules.
        b) Substrate is bonded to active sites through hydrogen bonds, ionic bonds, Vander waal or dipole-dipole interactions.
    ii) DRUG –ENZYME INTERACTIONS-
        a) Competitive inhibitors- Drug compete with natural substrate for their attachments on the active sites of enzymes. They are called competitive inhibitors.
        b) Allosteric sites -Some drugs binds to a different site of the enzyme called allosteric sites which changes the shape of active sites.
5. ANTAGONISTS- The drugs that bind to the receptor site and inhibit its natural function.
6. AGONISTS-Drugs mimic the natural messenger by switching on the receptor.
7. ANTACIDS- These are compounds which neutralize excess acid of stomach. eg-Aluminium Hydroxide, Magnesium Hydroxide.
8. ANTI HISTAMINES – The drugs which interfere with the natural action of histamines and prevent the allergic reaction e.g.- Ranitidine, Brompheniramine.
9. TRANQULIZERS- The class of chemical compound used for the treatment of stress , mild or even severe mental diseases e.g.- derivatives of Barbiturates, Luminal, Equanil.
10. ANALGESICS- They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system. E.g.- Aspirin, Phenacetin.
11. ANTIMICROBIALS – They tend to prevent/ destroy or inhibit the pathogenic action of microbes as bacteria, virus, fungi etc. They are classified as.

(i) ANTIBIOTICS – those are the chemical which are produced by the micro-organisms e.g. – Penicillin, Ofloxacin.

NARROW SPECTRUM ANTI-BIOTICS – These are effective mainly against gram positive and gram negative bacteria. Eg. Penicillin, streptomycin.

BROAD SPECTRUM ANTI-BIOTICS – They kill or inhibit a wide range of gram positive and gram –ve bacteria. Eg. Chloramphenicol, tetracydine.

(ii) ANTISEPTICS OR DISINFECTANT—These are which either kill/inhibit the growth of micro-organisms.antiseptic are applied to the living tissues such as wounds, cuts, ulcers etc. Eg. Boric acid, terpinol (Dettol) . disinfectant are applied to inanimate objects such as floors, drainage system. Eg. Cl_2 , SO_2

(0.2% solution of phenol is an antiseptic while 1% solution is disinfectant.)

12. ANTIFERTILITY DRUGS – These is the chemical substances used to control pregnancy. They are also called oral contraceptives or birth control pills. Eg. Mifepristone, norethindrone.
13. ARTIFICIAL SWEETING AGENTS – These are the chemical compounds which give sweeting effect to the food without increasing calories to the body. They are good for diabetic people. Eg. Aspartame, saccharin, alitame, sucralose.
14. FOOD PRESERVATIVES – They prevent spoilage of food to microbial growth. Eg. Salt, sugar and sodium benzoate.
15. CLEANSING AGENTS-

    (i) SOAPS- They are sodium or potassium salts of long chain fatty acids. They are obtain by the saponification reaction, when fatty acids are heated with aqueous sodium hydroxide.

16. SYNTHETIC DETERGENTS – They are cleaning agent having properties of soaps, but actually contain no soap. They can used in both soft and hard water. They are-

    (i) ANIONIC DETERGENT – They are sodium salts of sulphonated long chain alcohols or hydrocarbon. E.g. –sodium lauryl sulphonate. They are effective in acidic solution.

    $CH_3(CH_2)_{10}CH_2OH \quad H_2SO_4 \quad \rightarrow \quad CH_3(CH_2)_{10}CH_2OSO_3H$ (laurylalchol)

    (ii) CATIONIC DETERGENTS- They are Quaternary NH_4 salts of amines with acetates, Cl^- or Br^{--}. They are expensive. E.g.- Cytyltrimethylammoniumbromide

    (iii) NON-IONIC DETERGENTS – They does not contain any ions, some liquid dish washing detergents which are of non-ionic type.

17. NON-BIODEGRADABLE – The detergents which are branched and cannot be decomposed by microorganisms are called non-biodegradable. It creates water pollution. E.g. - sodium 4(1, 3 tetramethyloctl)-benzene sulphonate.

FAQ

Q. 1. What is meant by narrow spectrum antibiotics?

Ans. Those antibiotics which are effective against only one particular micro-organisms are called narrow spectrum antibiotics.

Q. 2. Define the term Chemotherapy?

Ans. The branch of chemistry which deals with the treatment of disease using chemicals is called chemotherapy.

Q. 3. What is tincture of iodine?

Ans. A 2-3% solution of iodine in alcohol – water mixture is known as tincture of iodine. It is used as an antiseptic.

Q. 4. Name the substance that can be used as an antiseptic as well as disinfectant.

Ans. 0.2% solution of phenol act as an antiseptic and 1% of the solution acts as a disinfectant.

Q. 5. What is BHA and BHT?

Ans. BHA is butylated hydroxyl anisole whereas BHT is butylated hydroxyl toluene. Both are used as antioxidant in food.

2 Marks

Q. 1. Why are cimetidine and ranitidine better antacids than sodium bi-carbonate or aluminium hydroxide?

Ans. $NaHCO_3$ or $Mg(OH)_2$ or $Al(OH)_3$; if taken in excess makes the stomach alkaline and thus triggers the release of even more HCl causing ulcers in stomach , whereas cimetidine and ranitidine prevent the interaction of histamine with the receptor cells in the stomach wall, resulting in release of lesser amount of HCl.

Q. 2. What are analgesics? How are they classified?

Ans. The drugs which give relief from the pain are known as analgesics. They are classified as:

1.) Non-Narcotics: They do not cause addiction.

Eg. Aspirin

2.) Narcotics: They are habit forming.

Eg. Morphine

Q. 3. What are biodegradable and non- biodegradable detergents? Give one example of each.

Ans. Biodegradable detergents are decomposed by microorganisms like bacteria into harmless product.

They do not create water pollution. Detergents having linear alkyl chains are biodegradable. Eg. Sodium lauryl sulphate.

Non-Biodegradable are not decomposed by microorganisms. They create water pollution.eg. Cetymethyl, Ammonium bromide.

Q. 4. How antiseptics are different from disinfectant. Give one example of each.

Ans.

Antiseptics	**Disinfectant**
Do not harm the living tissues.	Tonic to living tissues.
Applied to wounds, Ulcers, diseased skin etc.	Used for disinfecting instruments, floors, toilet, drains etc.
Examples. Phenol(0.2%), Boric acid, Tincture of Iodine	Example. Phenol(1%), Chlorine, DDT etc.

Q. 5. A) Why is Bithional added to soap?

B) Give the composition of Dettol.

Ans. A) Bithional is an antiseptic which reduces the odour produced by bacteria decomposition of organic matter on skin.

B) Dettol is a mixture of chloroxyenol and terpineol.

3 marks

1. Explain the following terms with suitable examples (a) cationic detergents (b) anionic detergents (c) neutral detergents.

Ans. (a) Cationic detergents are generally quaternary Ammonium salts as Chlorides, Bromides or acetates. These detergents are quite expensive and find limited use. Some of these detergents have germicidal properties and are used as germicides.

(b) Anionic detergents: - A detergent whose hydrophilic activity hinges on an anionic group. Fatty acids are natural anionic detergents (AD), but are neither used as detergents nor functional in biological systems; the main synthetic ADs are aliphatic Sulphate esters (e.g., Sodium dodecylsulphate).

(c) **Neutral Detergent**is the most common measure of fibre used for animal feed analysis, but it does not represent a unique class of chemical compounds. NDF measures most of the structural components in plant cells (i.e. Lignin, Hemicellulose and Cellulose)

Q. 2. What are the following substances, give one example of each.
(a) Tranquilizers (b) Food preservatives (c) Antihistamines.

Ans. (a) Tranquilizers: - These chemicals are used for the treatment of stress, fatigue and mental diseases. They release anxiety, stress irritability, etc.
example- Equanil, Luminal.

(b) Food preservatives: - These chemical substances are added to the food materials to prevent their spoilage due to microbial growth.
example: - Sodium benzoate, Sodium chlorate.

(c) Antihistamines: - These drugs interfere with the natural action of histamine by competing with histamine for bonding sites of receptor with histamine exerts its effects.

example: - Cetirizine

Q. 3. Define: (a) Receptors (b) Agonists (c) Antagonists.

Ans. (a) Receptors: - Proteins which are crucial to communication system in the body are called receptors. Receptors are embedded in cell membrane.

(b) Agonists: - Drugs that mimic the natural messenger by switching on the receptor are called agonists.

(c) Antagonists: - Drugs that bind the receptors site and inhibit its natural function are called antagonist.

Q. 4. (a) Name two artificial sweetness used in food materials.

(b) Give one examples of (i) bactericidal antibiotic (ii) bacteriostatic antibiotic

(c) Give an example of sulpha drug.

Ans. (a) Aspartame and Alitame

(b) (i) Penicillin (ii) Tetracycline

(c) Sulpha pyridine or Sulpha guanidine

Value Based Question

Q. 1. Punit, a class 12 student read the composition of detergent which their housemaid was using for washing clothes. He found that beside the cleansing agent, the other ingredient of the detergent was polyphosphates. He told his mother about the pollution that detergents cause to our rivers.

Answer the following questions:–

(i) What values are expressed by Punit?

(ii) What are the cleansing agents usually present in domestic detergent?

(iii) Why does polyphosphate added to detergents?

Ans. (i) Punit expressed concern about environmental protection for rivers

(ii) Detergents usually contains sodium or potassium salt of benzene sulphonic acids.

(iii) Polyphosphates are added to soften the water as they form soluble complex with Ca^{2+} and Mg^{2+} ions thereby making them ineffective.

ASSIGNMENT

1. Which site of an enzyme is called allosteric site?
2. Which class of drugs is used in sleeping pills?
3. Explain soaps do not work in hard water.
4. Why is the use of sweetener aspartame limited to cold food and drinks only?

5. Mention one important use of each of the following: (i) Equanil (ii) Sucralose.
6. What is the cause of a feeling of depression in human beings? Name a drug which can be useful in treating this depression.
7. Account for the following : -
   - (i) Aspirin drug helps in prevention of heart attack.
   - (ii) Diabetic patients are advised to take artificial sweeteners instead of natural sweeteners.

MIND MAP

Chemistry in healthcare	**Classes of drugs**	**Chemicals in other industries**
DRUGS-Chemicals of low molecular masses.(n=100-500u)	Antacids- removes excess acid and raise pH to an appropriate level.Eg: $Mg(OH)_2$, Histamine	**Chemicals in food** Artificial sweeteners- provide sweetness without calories. Eg: Aspartame, Alitame.
Medicines are drugs which produce useful biological response.	Antihistamines- interfere with natural action of histamine.Eg: Chloropheniramine	Food preservatives- prevent spoilage of food.Eg: Sodium Benzoate.
Chemotherapy-disease is treated with chemicals.	Analgesics- drugs used to reduce body pain. Eg: aspirin, paracetamol.	Antioxidants-retard the oxidation of food. Eg: BHT, BHA.
Drug target interactions	Antimicrobials- prevent development of micro organisms.	Cleansing agents- improve the cleansing property of water.
Receptors-protiens used for communication in body.	Antibiotics-inhibit the growth of microorganisms or may destroy it.Eg:Penicillin, tetracycline	Soaps- Na or K salts of long chain fatty acids.
Inhibitors-drugs that block binding site of enzymes.	Antiseptics-check the growth of micro organisms.Eg: Furacin, Iodine tincture.	Synthetic detergents- soapless soaps.
Antagonists- drugs that bind the receptor site.	Antifertility drugs-used to prevent unwanted pregnancies. Eg:progesterone	Anionic Detergents- Na salt of sulphonated long chain alcohol or hydrocarbon.Eg: Sodium Lauryl Sulphates.
Agonists- drugs which mimic the natural messengers.	Disinfectant-applied to inanimate objects like floors, drainage.Eg: 100% solution of phenol	Non ionic detergents-don't contain ions.Eg:detergents obtained from steric acids and polyethylene glycol. Cationic detergents-quaternary ammonium saltsEg: Cetyltrimethyl ammonium bromide.

APPENDIX –A

Important formula (from unit 1 - 4)

SOLID STATE (UNIT 1)

- Let the number of close packed spheres be N, then:
  The number of octahedral voids generated = N
  The number of tetrahedral voids generated = 2N

CALCULATION OF DENSITY OF THE UNIT CELL: = $Z \times M \ / \ N_A \times a^3$

Where Z = No. of atoms per Unit cell, M = Atomic mass / Molecular mass in gm

N_A = Avagadro number = 6.023×10^{23}, a = Cell edge in cm

= Density of the unit cell in gm cm^{-3}

VALUES OF Z AND a :

Name of the unit cell with Example	Value of Z	Relation of 'a' with 'd'	Relation of 'a' with 'r'	Inter ionic Distance
Simple cubic	1	$d = 2r = a$	$a = 2r \Rightarrow r = a / 2$	
B.C.C(CsCl type)	2	$d = 2r = (\sqrt{3}\ a) / 2$	$r = (\sqrt{3}\ a) / 4$	$r^+ + r^- = (\sqrt{3}a) /2$
F.C.C(NaCl type	4	$d = 2r = (\sqrt{2}\ a) / 2$	$r = a / (2\sqrt{2})$	$r^+ + r^- = a / 2$

Where d → Distance between the nearest neighbor. r → Radius of the atom.

r+ → Radius of the cation r → Radius of the Anion.

UNIT 2 SOLUTIONS

HENRY'S LAW $P = K_H X$ K_H is Henry's law constant .

RAOULT'S LAW :- $P_A = P^0_A X_A$; $P_B = P^0_B X_B$ $P_{total} = P_A + P_B$

5. **RELATIVE LOWERING OF VAPOUR PRESSURE**

   $P^0_A - P_A / P^0_A = X_B$ $X_B = n_A / n_A + n_B$

   For dilute solution, $n_B << n_A$, hence n_B is neglected in the denominator.

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

   $P^0_A - P_A / P^0_A = W_B * M_A / M_B * W_A$

6. **ELEVATION OF BOILING POINT**

   $\Delta T_b = k_b m$

   Where , $\Delta T_b = T_b - T^0_b$

   $M = k_b \times 1000 \times W_B / \Delta T_b \times W_A$

7. **DEPRESSION IN FREEZING POINT**

$\Delta T_f = K_f m$

Where , $\Delta T_f = T^0_f - T_f$

$M = k_f \times 1000 \times W_B / \Delta T_f \times W_A$

8. **OSMOTIC PRESSURE**

$\Pi = CRT$ $\Pi = n/VRT$

$R = 0.0821$ Latm mol^{-1} ;

i = normal molecular mass/ observed molecular mass

VAN'T HOFF FACTOR (i)

i = observed colligative properties/ calculated value of colligative properties

$i<1$ (for association)

$i>1$ (for dissociation)

MODIFIED FORMS OF COLLIGATIVE PROPERTIES

5) $P^0_A - P_A / P^0_A = i \times n_B/n_A$
6) $\Delta T_b = i \times K_b m$
7) $\Delta T_f = i \times K_f m$
8) $\Pi = i \times CRT$

UNIT 3 ELECTROCHEMISTRYT

1.) P= R a\l
2.) K = 1\p
3.) K = 1\R l\a
4.) $\wedge_m$ = k100\c
5.) $E_{cell} = E^0_{cell}$-2.303R.T\nF log K
6.) At 25^0c $E_{cell} = E^0_{cell}$-0.0591\n log K
7.) At equilibrium

    E^0_{cell} = 0.0591 \n log K
8.) $\Delta G = -nFE^0$

UNIT 4 CHEMICAL KINETICS

1. Rate of reaction:- For a reaction R → P,

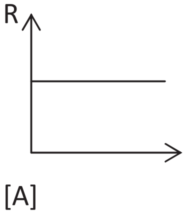
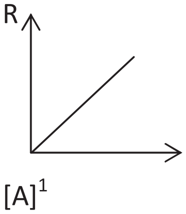
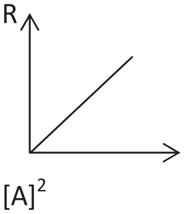
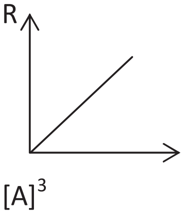
Rate of reaction = change of conc. of R or P / T time interval

$$= \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

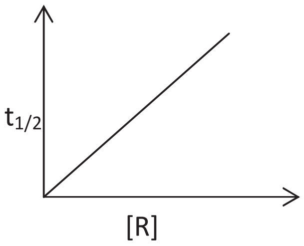
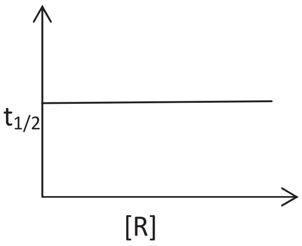
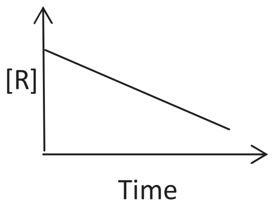
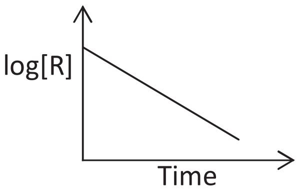
2. Order of reaction:- For the reaction $aA + bB \rightarrow cC + dD$

$$\text{Rate} = K[A]^x [B]^y$$

3. Units of rate constants and graph between rate and conc. of reactat

Order of reaction	**zero**	**first**	**second**	**third**
Unit of rate constt.	$MolL^{-1}s^{-1}$	s^{-1}	$Mol^{-1}L^{+1}s^{-1}$	$Mol^{-2}L^{+2}s^{-1}$
Relation b/w rate & conc of Reactant	$R \propto [A]^0$	$R \propto [A]^1$	$R \propto [A]^2$	$R \propto [A]^3$
Graph b/w rate & conc of Reactant				

4. Integrated rate equation for zero order and first order reaction

	for zero order reaction	**for first order reaction**
Integrated rate equation	$k = \frac{[R]_0 - [R]}{t}$	$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$
Half life	$t_{1/2} = [R]_0/2K$	$t_{1/2} = 0.693/K$
Graph b/w half-life & conc of Reactant		
Graph b/w conc .of reactant & time		

5. $t_{1/2} \propto [conc]^{1-n}$ where n = order of reaction.

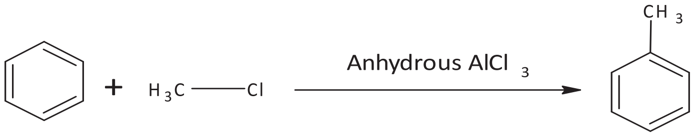
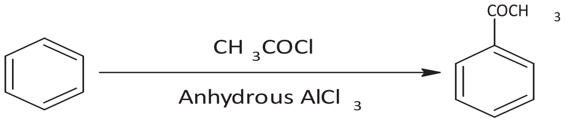
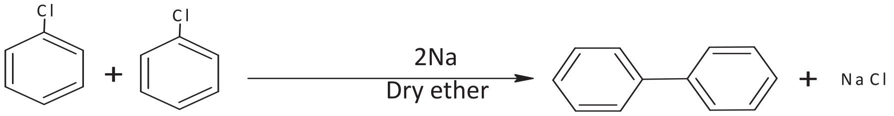
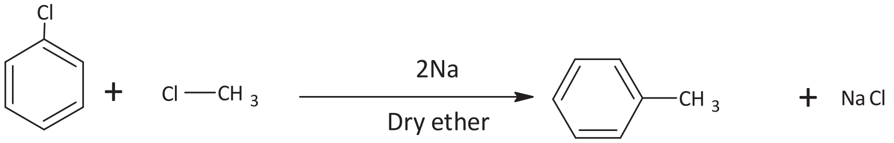
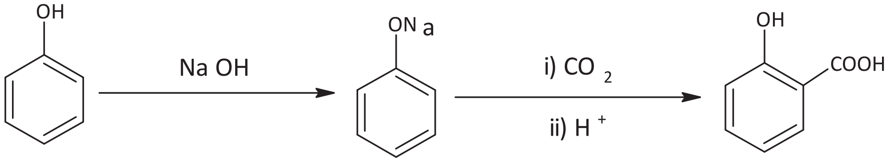
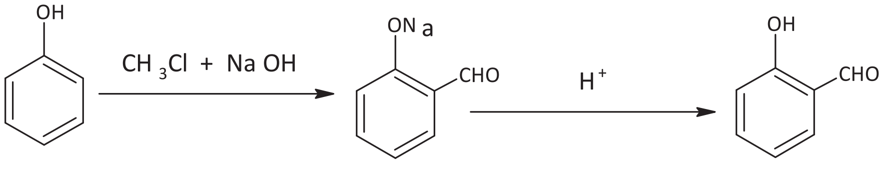
6. Arrhenius equation

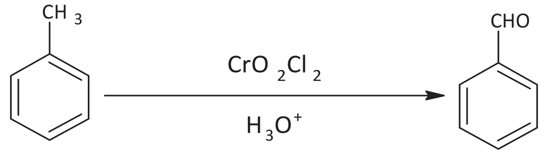
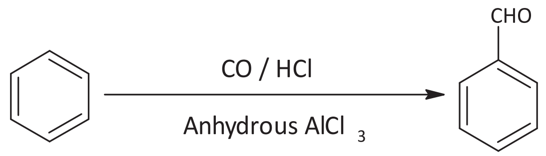
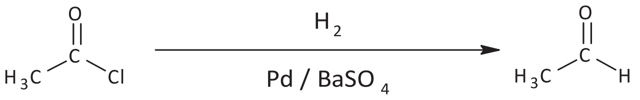
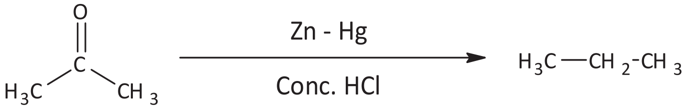
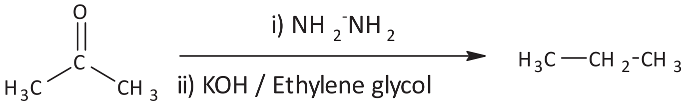
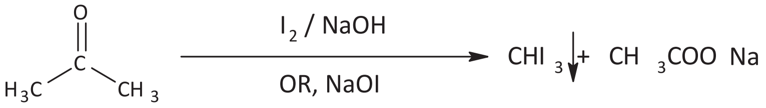
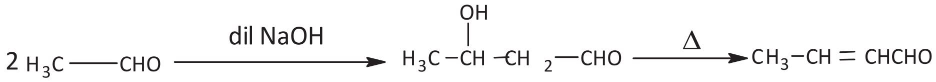
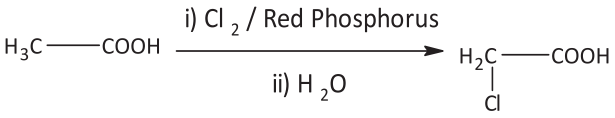
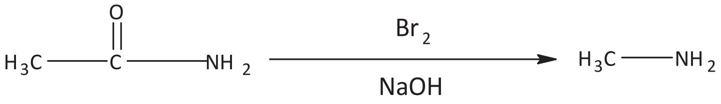
$$\log K = \log A - E_a/2.303RT$$

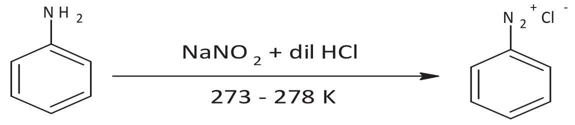
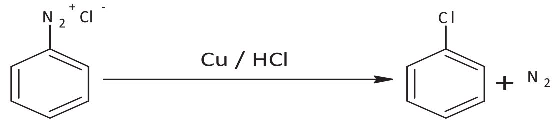
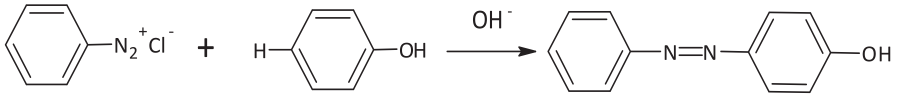
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

APPENDIX –B

NAME REACTIONS

1.	Finkelstein	$CH_3Br + NaI \xrightarrow{Acetone} CH_3\text{-}I + NaBr$
2.	Swarts	$CH_3Br + AgF \longrightarrow CH_3F + AgBr$
3.	Friedel-Crafts Alkylation	
4.	Friedel-Crafts Acylation	
5.	Wurtz	$H_3C-Cl + Cl-CH_3 \xrightarrow[\text{Dry ether}]{2Na} H_3C-CH_3 + NaCl$
6.	Fittig	
7.	Wurtz-Fittig	
8.	Kolbe	
9.	Reimer-Tiemann	
10.	Williamson	$CH_3\text{-}Br + CH_3\text{-}ONa \longrightarrow CH_3\text{-}O\text{-}CH_3 + NaBr$
11.	Stephen	$H_3C-CN + SnCl_2 + HCl \longrightarrow H_3C-CH{=}NH \xrightarrow{H_3O^+} H_3C-CHO$

12.	Etard	
13.	*Gatterman – Koch*	
14.	Rosenmund reduction	 $CH_3COCl \xrightarrow[Pd\ /\ BaSO_4]{H_2} CH_3CHO$
15.	Clemmensen reduction	 $CH_3COCH_3 \xrightarrow[Conc.\ HCl]{Zn - Hg} H_3C—CH_2\text{-}CH_3$
16.	Wolff-Kishner reduction	 $CH_3COCH_3 \xrightarrow[ii)\ KOH\ /\ Ethylene\ glycol]{i)\ NH_2\text{-}NH_2} H_3C—CH_2\text{-}CH_3$
17.	*Tollens' test*	$R\text{-}CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow R\text{-}COO^- + 2Ag\downarrow + 2H_2O + 4\,NH_3$
18.	*Fehling's test*	$R\text{-}CHO + 2\,Cu^{2+} + 5\,OH^- \longrightarrow R\text{-}COO^- + Cu_2O\downarrow + 3H_2O$
19.	*Iodoform*	 $CH_3COCH_3 \xrightarrow[OR,\ NaOI]{I_2\ /\ NaOH} CHI_3\downarrow + CH_3COO\ Na$
20.	*Aldol condensation*	 $2\ H_3C—CHO \xrightarrow{dil\ NaOH} H_3C-\overset{OH}{CH}-CH_2—CHO \xrightarrow{\Delta} CH_3-CH = CHCHO$
21.	*Cannizzaro*	$HCHO + HCHO \xrightarrow{Conc.\ NaOH} HCOONa + H_3C—OH$
22.	Hell-Volhard-Zelinsky (HVZ)	 $H_3C—COOH \xrightarrow[ii)\ H_2O]{i)\ Cl_2\ /\ Red\ Phosphorus} \underset{Cl}{H_2C}—COOH$
23.	*Hoffmann bromamide degradation*	 $H_3C—\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow[NaOH]{Br_2} H_3C—NH_2$

24.	*Carbylamine*	$R\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\Delta} R\text{-}NC + 3\ KCl + 3\ H_2O$
25.	*Diazo*	
26.	*Sandmeyer.*	
27.	*Gatterman*	
28.	*Coupling*	

Distinguish By a Single Chemical Test

1. All aldehydes (R-**CHO**) give **Tollens' Test** and produce silver mirror.
   $RCHO + 2\ [Ag(NH_3)_2]^+ + 3\ OH^- \rightarrow RCOO^- + 2\ Ag \downarrow + 2H_2O + 4\ NH_3$
   Tollens' Reagent silver ppt

   Note: HCOOH(methanoic acid) also gives this test, ketones (RCOR) do not give this test
2. All aldehydes (R-**CHO**) and ketones(R**CO**R) give **2,4-DNP test**
   $RCOR + 2,4\text{-}DNP \rightarrow$ Orange ppt
   $R\text{-}CHO + 2,4\text{-}DNP \rightarrow$ Orange ppt
3. Aldehydes and ketones having **CH_3CO**- (keto methyl) group give Iodoform Test. Alcohols having CH_3CH- OH group also give **Iodoform Test**.
   $CH_3CHO + 3I_2 + 4\ NaOH \rightarrow CHI_3 \downarrow + HCOONa + 3\ NaI + 3H_2O$
   Yellow ppt
4. The following compounds give Iodoform Test: ethanol (C_2H_5OH), propan-2-ol ($CH_3CH(OH)CH_3$), ethanal(CH_3CHO), propanone(CH_3COCH_3), butanone ($CH_3COCH_2CH_3$), pentan-2-one ($CH_3COCH_2\ CH_2CH_3$), acetophenone ($PhCOCH_3$)
5. All carboxylic acids (R-**COOH**) give **Bicarbonate Test**
   $RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2 \uparrow + H_2O$
   effervescence
6. **Phenol** gives **$FeCl_3$** Test
   $C_6H_5OH + FeCl_3 \rightarrow (C_6H_5O)_3Fe + 3\ HCl$
   (neutral) (violet color)

7. All primary amines (R/Ar -**NH_2**) give **Carbyl Amine Test**

$R\text{-}NH_2 + CHCl_3 + KOH(alc) \rightarrow R\text{-}NC + KCl + H_2O$

offensive smell

8. Aniline gives Azo Dye Test (Only for aromatic amines)

$C_6H_5NH_2 + NaNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^-$; then add β-naphthol orange dye

9. All alcohols (R**OH**) give **Na-metal test**

$R\text{-}OH + Na \rightarrow R\text{-}ONa + H_2$

bubbles

10. For esters (RCOOR) : Hydrolyses first. Then see the products (acid & alcohol) and give a test to identify them.

11. All alkenes (C=C) and alkynes (C≡C) decolorizes Br_2 – water from red to colourless

12. **Lucas Test to distinguish primary, secondary and tertiary alcohols**

Lucas reagent: $ZnCl_2/HCl$

3^0-alcohol + Lucas reagent → immediate turbidity

2^0-alcohol + Lucas reagent → turbidity after sometime

1^0-alcohol + Lucas reagent → no turbidity

APPENDIX –D

ORGANIC CHEMISTRY CONCEPT BASED QUESTION & ANSWER

1 Bond enthalpy decreases as : CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I

Because C-X bond length increases from F to I due to greater size

2 Phenol can not be converted into chlorobenzene by using HCl

Because C-O bond in phenol has partial double bond character and OH gr is attached to sp^2 carbon

3 Thionyl chloride is preferred to convert ROH into RCl

Because the side products are gases and the product can be obtained as pure

4 3^0 alcohol easily can be converted into alkyl halide

Because 3^0 carbocations are stable

5 Benzene is converted into iodobenzene in presence of oxidizing agent like HNO_3 or HIO_3

$C_6H_6 + I_2/Fe \rightleftharpoons C_6H_5I + HI$ Because HNO_3 or HIO_3 oxidises HI and prevent backward reaction

6 ROH is converted into RI by using KI inpresence of H_3PO_4 not H_2SO_4

H_2SO_4 converts KI into HI and than into I_2

7 B.pt. of alkyl halides (RX) is higher than hydrocarbons

Because R-X is polar so there is dipole dipole attraction

8 B.pt : R-I > R-Br > R-Cl > R-F

Because molecular mass decreases so van der Waals force decreases from RI to RF

9 B.pt : CH_3-CH_2-CH_2-CH_2-Br > CH_3-CH_2-CH(Br)-CH_3> (CH_3)CBr

Because as the branching increases surface area decreases so van der Waals force of attraction decreases

10 p-dichloro benzene has higher m.pt than ortho and meta isomer

Because p-dichloro benzene has symmetrical structure so it fits well in the crystal lattice

11 Alkyl halide (RX) with KCN gives alkyl cyanide (RCN) where as with AgCN it gives isocyanide(RNC)

KCN is ionic and CN^- is ambident nucleophile but it link through C because C-C bond is more stable than C-N. In the other hand AgCN is covalent and links through N only

12 S_N2 reactivity : CH_3-X > CH_3CH_2-X > CH_3-CH(X)-CH_3> $(CH_3)_3$C-X ($1^0>2^0>3^0$)

Due to steric hindrance nucleophile can not approach easily. In S_N2 path release of X and linking of Nu^- take place simultaneously

13 S_N1 reactivity : CH_3-X < CH_3CH_2-X < CH_3-CH(X)-CH_3< $(CH_3)_3$C-X ($1^0<2^0<3^0$)

Because S_N1 path involves formation of carbocation intermediate. And stability of carbocation is in the order : $CH_3^+ < CH_3CH_2^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$ ($1^0<2^0<3^0$)

14 S_N reactivity : R-I > R-Br > R-Cl > R-F

Because as the size of halogen increases C-X bond becomes weaker

15 Aryl halides (C_6H_5-X) are less reactive than alkyl halides(R-X) towards nucleophilic substitution

Because in aryl halide C-X bond has partial double bond character and X is attached to sp^2 C. there is also the repulsion between Nu- and benzene ring which is electron rich

16 Chloroform is stored in dark coloured bottle as closed and completely filled

Because in air and light it converts into poisonous phosgene gas($COCl_2$)

17 In many countries DDT has been banned now

Because of its slow metabolism and it has toxic effect on aquatic animals

18 Cyclohexyl chloride has greater dipole moment than chloro benzene

19 Alkyl halides are immiscible in water although they are polar

In water there is intermolecular H-bonding but there is less attraction between R-X and H_2O

20 Grignard reagent(RMgX) should be prepared in anhydrous condition

Because RMgX reacts with water and gives corresponding alkane

21 Alkyl halides undergo substitution when treated with aq KOH but in presence of alc KOH elimination takes place

Alcohol + KOH produces RO^- which is a strong base so it extract H^+ and elimination takes place

22 C-O-H bond angle in alcohol is less than regular tetrahedral angle

Due to lp-lp repulsion

23 In phenol the C-O bond length is less

Due to i) partial double bond character ii) O is attached to sp^2 carbon

24 In ether the R-O-R bond angle is greater

Due to repulsion between two bulkier R group

25 To convert acid into alcohol $LiAlH_4$ is not used

Because it is expensive so : $RCOOH \rightarrow RCOOR'$ then ester is reduced into RCH_2OH by using H_2/Pd

26 b.pt of alcohol(ROH) is higher than alkane(RH), ether(R-O-R), alkyl halide(R-X) and aryl halide(Ar-X)

Due to inter molecular H-bonding in R-O-H.

27 b.pt : n-butyl alcohol > sec. butyl alcohol > tert. Butyl alcohol

Because as the branching increases surface area decreases so van der Waals force of attraction decreases

28 Alcohols are highly miscible in water

Due to H-bonding with water

29 Acidity of alcohol : $R-CH_2-OH > R_2CH-OH > R_3C-OH$

Because as the R gr increases +I effect increases so alkoxide ion becomes less stable

30 Alcohol is weaker acid than water

Because $R-O^-$ is less stable than HO^-

31 Phenol (Ph-OH) is acidic in nature

Because phenoxide ion($Ph-O^-$) is resonance stabilized.

32 Acidity : nitro phenol > phenol > methyl phenol

Because $-NO_2$ group is electron withdrawing it further increases the stability of phenoxide ion where as-CH_3 group is electron donating it destabilizes phenoxide ion

33 Esterification is carried out in presence of small amount of conc. H_2SO_4

Because it absorbs the water produced and accelerate the forward reaction.

34 $R'COCl + R-OH \rightleftharpoons R'COOR + HCl$. Pyridine is used in this reaction

It is to remove HCl produced and to prevent the backward reaction

35 Tert. Alcohols are easier to dehydrate

Because the intermediate tert. carbo cation is stable.

36 -OH group in benzene ring is ortho and para directing for electrophilic substitution

Due to +R effect it increases the electron density at ortho and para positions

37 o-nitro phenol is steam volatile(low b.pt) but p-nitro phenol is not

In o-nitro phenol there is intra molecular H-bonding. But in p-nitro phenol there is inter molecular H-bonding so molecules get associated and hence it has comparatively higher b.pt

38 Phenol with aq bromine gives 2,4,6-tribromo phenol but in non polar medium mono substitution takes place

39 $CuSO_4$ and pyridine are mixed with ethanol used for industrial purpose

To prevent its misuse. $CuSO_4$ gives colour pyridine gives smell

40 Ethers (R-O-R) are polar

41 Ethers are soluble in water

Due to H-bond with water and ether

42 Aldehydes (R-CHO) and ketones (R-CO-R) have higher b.pt than hydrocarbon and ether

Because they are polar so there is dipole-dipole attraction in aldehyde and ketones

43 Lower aldehydes and ketones are miscible with water

Because they form hydrogen bond with water

44 Aldehydes (R-CHO) are more reactive than ketones (R-CO-R) in nucleophilic addition
In ketone the two alkyl groups (R) have +I effect so they reduce the electrophilicity co carbonyl carbon. Also there is steric hindrance in ketone

45 Benzaldehyde (C_6H_5CHO) is less reactive than propanal (CH_3CH_2CHO)
Due to resonance the electrophilicity of carbonyl carbon is less in benzaldehyde

46 $NaHSO_3$ is used for separation of aldehydes
It forms a soluble compound with aldehyde which on hydrolysis give back the aldehyde

47 α-H of aldehyde and ketone is acidic in nature
Because the corresponding carbanion is resonance stabilized

48 Carboxylic acids (R-COOH) do not give nucleophilic addition reaction like RCHO & RCOR although it has >C=O due to resonance the carbonyl carbon looses its electrophilicity

49 Carboxylic acids have higher b.pt than aldehyde, ketones and even than alcohols

There is extensive inter molecular H-bonding in carboxylic acid(RCOOH). Even in vapour phase it exists as dimer

50 Carboxylic acids are miscible in water
Due to H-bonding with water

51 R-COOH is acidic in nature
Because the conjugate base $R\text{-}COO^-$ (carboxylate ion) is stable due to resonance

52 Acidic Strength : $Cl\text{-}CH_2\text{-}COOH > CH_3\text{-}COOH > CH_3CH_2\text{-}COOH$
Because Cl has –I effect which stabilizes the conjugate base and ethyl gr has +I effect

53 In amines the C-N-H/C bond angle is less than 109.5°
Due to lp-bp repulsion

54 For reduction of nitro compounds into amines Fe/HCl is preferred instead of Sn/HCl
Because Fe + HCl à $FeCl_2$. on hydrolysis $FeCl_2$ gives HCl. So just small quantity of HCl is required to initiate the reaction

55 To convert alkyl halide(R-X) into amines ($R\text{-}NH_2$) ammonolysis is not suitable
Because on ammonolysis a mixture of pri, sec, tert and quaternary amine will be produced

56 Aniline on exposure to air and light turns into coloured
Due to atmospheric oxidation

57 Lower amines are soluble in water
Due to H-bonding with water. In case of higher amine alkyl group is larger which is hydrophobic

58 Amines ($R\text{-}NH_2$) are less soluble than alcohols (R-OH)

In alcohol the H-bonding with water is stronger because O is more electronegative than N

59 Amines ($R\text{-}NH_2$) are lower boiling than alcohols (R-OH)

In alcohol the inter molecular H-bonding is stronger because O is more electronegative than N

60 Order of b.pt : primary amine > sec. amine > tert. amine
The no of N-H bond decreases so extent of H-bonding also decreases

61 In gaseous phase the order os basic strength : 3^0-amine > 2^0-amine > 1^0-amine > NH3
Due to +I effect of alkyl groups the electron density on N increases. So 3° is strongest as it has 3 alkyl groups

62 In aqueous state the base strength order : $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ ($2^0 > 3^0 > 1^0 > NH_3$) : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ ($2^0 > 1^0 > 3^0 > NH_3$)
In aqueous state +I effect, steric effect and solvation effect interplay. So the order is not regular

63 R-NH_2 is stronger base than NH_3
Due to +I effect of alkyl group electron density on N increases in R-NH_2

64 Aniline (C_6H_5-NH_2) is weaker base than NH_3 and R-NH_2
In aniline the lone pair of electron of N is involved in resonance. So it is less available.

65 Base strength : p-methoxy aniline > aniline > p-nitro aniline
Methoxy group (-OCH_3) has +R effect where as –NO_2 group has –R effect so electron density in the first case increases but in the second case it decreases.

66 Acylation of aniline is carried out in presence of pyridine
Pyridine removes HCl produced and favours forward reaction

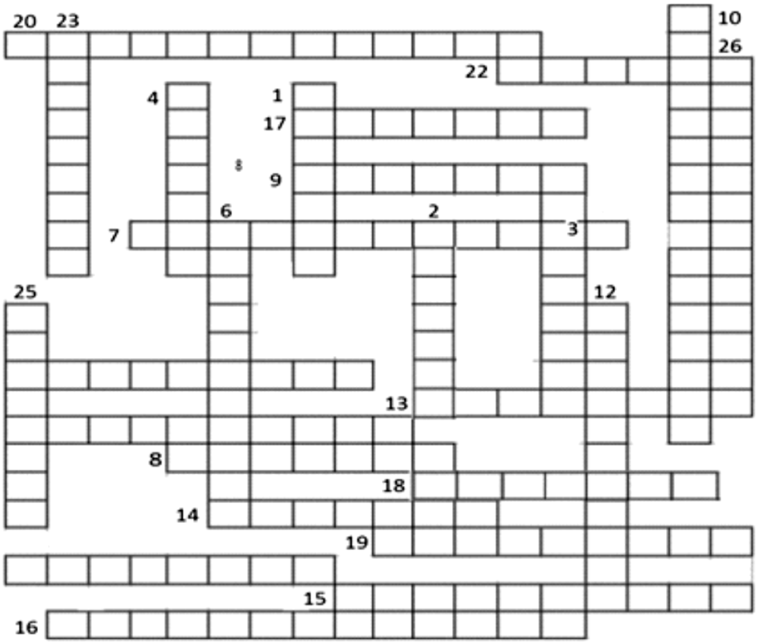
67 -NH_2 group in benzene ring is ortho –para directing for electrphilic substitution
Due to +R effect it increases the electron density at ortho and para position

68 Bromination of aniline gives 2,4,6-tribromo aniline
Because –NH_2 group activates benzene ring by +R effect. So for mono substitution –NH_2 group is acylated.

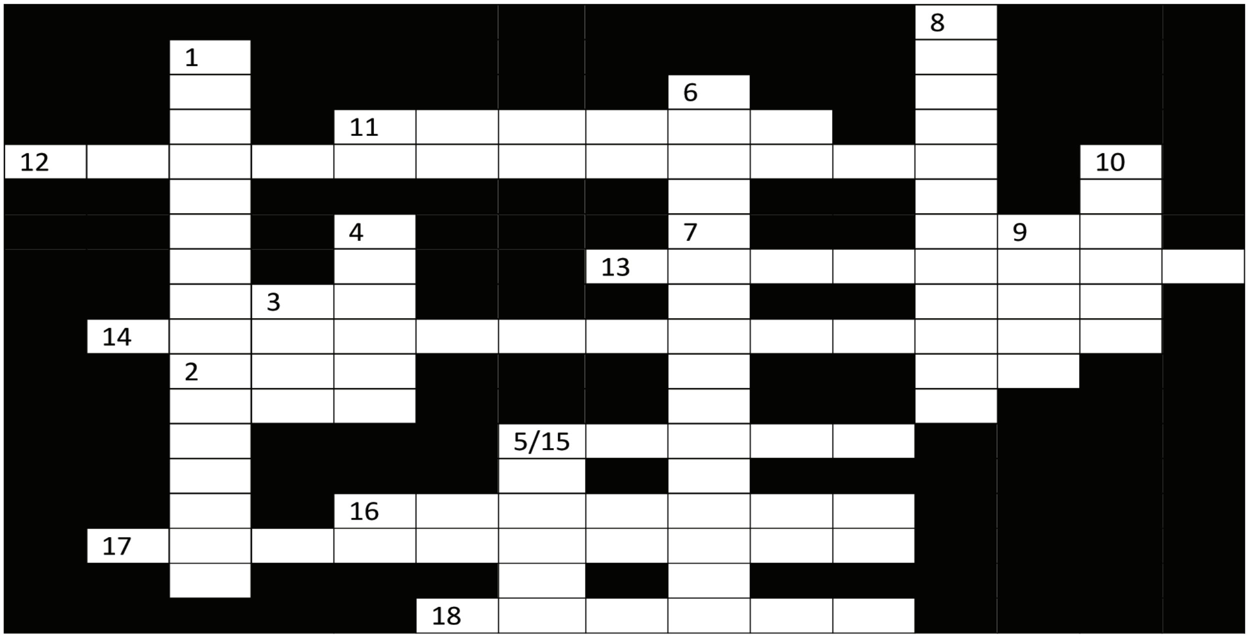
69 Nitration of aniline gives unusual meta-nitro aniline although –NH_2 group is ortho-para directing
In presence of acid –NH_2 is converted into –NH_3^+ which is meta directing

70 Aniline does not undergo Friedel Craft reaction
Aniline is base and reacts with anhydrous $AlCl_3$ so N becomes positive which deactivates benzene ring.

APPENDIX-E



TOP TO BOTTOM	LEFT TO RIGHT
1. Biological macromolecules with which drugs usually interact. 2. An analgesic prepared from salicylic acid. 3. The building blocks of a polymer are small molecules. 4. Natural Catalyst. 6. Nucleic acids are polymers in which _________ are the monomers. 12. Monomer of nylon 6 is – 23. Proteins embedded in the cell membrane to receive Chemical messenger - 25. Cetyltrimethyl ammonium chloride is an example of _____________ Detergent. 26. Soaps are safer to use from the environmental point of View because they are -	5. This type of polymer has extensive cross links between its chains. 7. Globular proteins on heating or due to pH change undergoes coagulation & loose biological activity. The Phenomenon is - 8. In DNA thymine pairs with - 9. Optically inactive amino acid – 11. Commercial name of poly totrafluroethylene is 13. Polymerization of chloroprene forms - 14. Element with Which natural rubber is heated for vulcanization- 15. The polymers in which polymer chains are held together by vander waal's forces are known as – 16. ___________ And a terpineol are the main constituents of an antiseptic Dettol. 17. Ranitidine is an - 18. A high potency artificial sweeter - 19. A sweeter that decomposes at looking temperature - 20. Drugs which reduce anxiety and produce feeling of well Being – 21. It is added to soaps to impart antiseptic properties - 22. Chloramphenicol is a _________Spectrum Antibiotic. 24. Medicines used for the relief of post-operative pain & Cardiac pain –



DOWNWARD

1. BASICITY OF ORTHOPHOSPHORIC ACID.
2. ACID MANUFACTURED BY OSTWALD PROCESS.
3. ROCKY MATERIAL THROUGH WHICH METAL CAN BE EXTRACTED PROFITABLY.
4. GAS WHICH IS ALLOTROPE OF OXYGEN AND IS PALE BLUE AND DIAMAGNETIC.
5. IT IS DIVIDED WITH WATER TO FORM SULPHURIC ACID.
6. THIS ALLOTROPE OF PHOSPHOROUS IS USED IN MAKING MATCHBOX.
7. THE FOURTEEN ELEMENTS IN WHICH ANTIPENULTIMATE 4f ORBITAL IS SUCCESSIVELY FILLED.
8. PROCESS OF HEATING ORE IN MODERATE SUPPLY OF AIR TO CONVERT CARBONATE ORE INTO OXIDES.
9. THIS NOBLE GAS MIXIED IN DISCHARGE TUBES FOR ADVERTISING.
10. THIS NOBLE GAS WAS DISCOVERED BY DORN FROM RADIUM.

ACROSS

11. THEY ARE MONOATOMIC GASES WITH STABLE ELECTRONIC CONFIGURATION.
12. COMPLEXES EXHIBITS THIS MAGNETIC PROPERTY DUE TO ABSENCE OF UNPAIRED d ELECTRON IN d ORBITAL.
13. A MOLECULE OF ION OR GROUP THAT COORDINATE TO A METAL ATOM OR IN A COMPLEX.
14. THE NUMBER OF ATOM OR MOLECULES SURROUNDING THE METAL ION.
15. THIS IRON CONTAIN 3% OF CARBON CONTENT. IT IS HARD AND BRITTLE.
16. HOMOGENEOUS MIXITURE OF METAL WITH METAL AND NON METAL.
17. PHENONMENON WITH SAME MOLECULE FORMULA BUT DIFFERENT STRUCTURAL FORMULA.
18. METAL WITH ALLOY OF CERIUM (25%) AND OF THE LANTHANIDES ELEMENT. IT IS PYROPHORIC ALLOY.

ANSWER

											8			
		1									C			
		T						6			A			
		R		11	I	N	E	R	T		L			
12	D	I	A	M	A	G	N	E	T	I	C		10	
		B						D			I		R	
		A		4				7			N	9	A	
		S		O			13	L	I	G	A	N	D	S
		I	3	Z				A			T	E	O	
	14	C	O	O	R	D	I	N	A	T	I	O	N	
		2	R	N				T			O	N		
		W	E	E				H			N			
		I				5/15	C	A	S	T				
		T				O		N						
		R		16	A	L	L	O	Y	S				
	17	I	S	O	M	E	R	I	S	M				
		C				U		D						
					18	M	I	S	C	H				

APPENDIX-F

IMPORTANT REACTIONS

p-Block Elements

1. $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$
2. $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$
3. $\underset{\text{(white ppt)}}{AgCl(s)} + 2NH_3(aq) \longrightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$
4. $3Cu + 8HNO_3 \text{ (dilute)} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
5. $Cu + 4HNO_3 \text{(conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
6. $4Zn + 10HNO_3 \text{ (dilute)} \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$
7. $Zn + 4HNO_3 \text{ (conc.)} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$
8. $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$
9. $S_8 + 48HNO_3 \text{(conc.)} \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$
10. $P_4 + 20HNO_3 \text{ (conc.)} \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
11. $NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$
    $[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(brown)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$
12. $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$
13. $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
14. $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$
15. $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$
    $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$
16. $3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$
17. $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$
18. $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
19. $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$
20. $2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$
    $Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$
21. $4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$
22. $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
23. $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$
24. $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$
25. $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
26. $2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^-(aq) + I_2(s) + O_2(g)$
27. $SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(l)$
28. $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
29. $5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

30. $2MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4$, M = Metal, X = F, Cl, NO_3

$CuF_2 + H_2SO_4 \longrightarrow CuSO_4 + 2HF$

31. $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$

32. $Cu + 2H_2SO_4 \text{ (conc.)} \longrightarrow CuSO_4 + SO_2 + 2H_2O$

33. $3S + 2H_2SO_4 \text{ (conc.)} \longrightarrow 3SO_2 + 2H_2O$

34. $C + 2H_2SO_4 \text{ (conc.)} \longrightarrow CO_2 + 2SO_2 + 2H_2O$

35. $F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br or I)

36. $2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(aq)$

37. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

38. $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

39. $S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$

40. $H_2S + Cl_2 \longrightarrow 2HCl + S$

41. $\underset{\text{(cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

42. $\underset{\text{(hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

43. $2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

44. $SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$

45. $I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$

46. $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$

47. $I_2 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow 2ICl_3$

48. $Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\text{ K}} 2ClF_3$

49. $Br_2 + \underset{\text{(excess)}}{5F_2} \longrightarrow 2BrF_5$

50. $\underset{\text{(xenon in excess)}}{Xe(g)} + F_2(g) \xrightarrow{673\text{K, 1 bar}} XeF_2(s)$

51. $\underset{\text{(1 : 20 ratio)}}{Xe(g)} + 3F_2(g) \xrightarrow{573\text{ K, 60-70 bar}} XeF_6(s)$

52. $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

53. $2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

54. $XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$; $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

55. $XeF_6 + MF \longrightarrow M^+[XeF_7]^-$ (M = Na, K, Rb or Cs)

56. $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

57. $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

58. $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$, $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

DESIGN OF THE QUESTION PAPER

Time : 3 Hours **Max. Marks : 70**

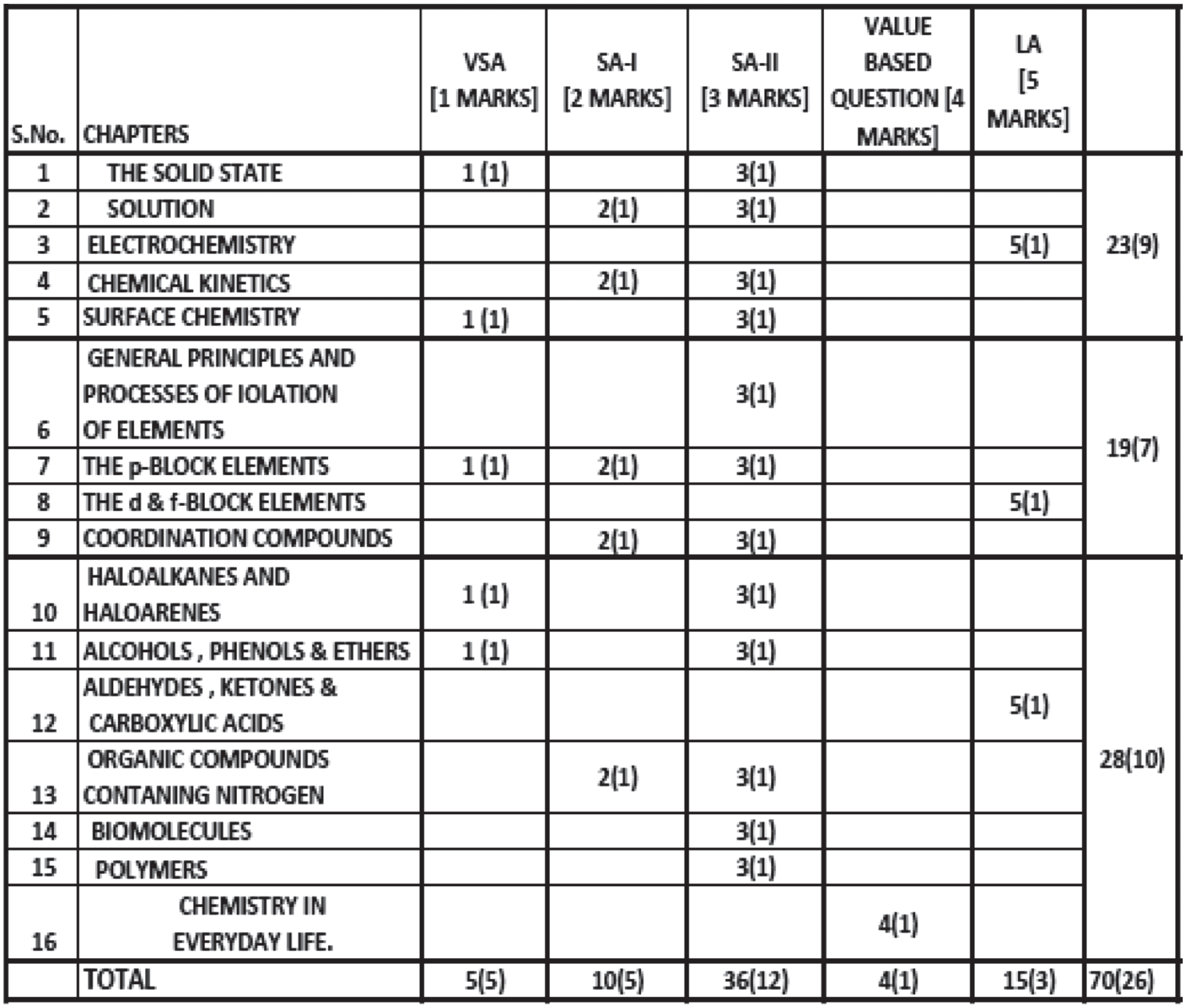
S. No.	Typology of Questions	Very Short Answer (VSA) (1 marks)	Short Answer-I (SA-I) (2 marks)	Short Answer-II (SA-II) (3 marks)	Value based question (4 marks)	Long Answer (LA) (5 marks)	Total Marks	% Weight-age
1.	Remembering (Knowledge based Simple recall questions, to know specific facts, terms, concepts, principles, or theories, Identify, define, or recite, information)	2	1	1	–	–	7	1-%
2.	Understanding comprehension- to be familiar with meaning and to understand conceptually, interpret, compare, contrast, explain, paraphrase information)	–	2	4	–	1	21	30%
3.	Application (Use abstract information in concrete situation, to apply knowledge to new situations, Use given content to interpret a situation, provide an example, or solve a problem)	–	2	4	–	1	21	30%
4.	High Order Thinking Skills (Analysis & Synthesis- Classify, compare, contrast, or differentiate between different pieces of information, Organize and/or integrate unique pieces of information from a variety of sources)	2	–	1	–	1	10	14%
5.	**Evaluation and** Multi-Disciplinary-(Appraise, judge, and/or justify the value or worth of a decision or outcome, or to predict outcomes based on values)	1	–	2	1	–	11	16%
	Total	5X1 = 5	5X2 = 10	12X3 = 36	1X4 = 4	3X5 = 15	70(26)	100%

Question Wise Break Up

Type of Question	Mark per Question	Total No. of Questions	Total Marks
VSA	1	5	05
SA-I		5	10
SA-ir	3	12	36
VBQ	4	1	04
LA	5	3	15
Total		26	70

1. **Internal Choice:** There is no overall choice in the paper. However, there is an internal choice m one question of 2 marks weightage, one question of 3 marks weightage and all the three questions of 5 marks weightage.
2. The above template is only a sample. Suitable internal variations, may be made for generating similar templates keeping the overall weightage to different **form**’of questions and typology of questions same.

BLUE-PRINT



S.No.	CHAPTERS	VSA [1 MARKS]	SA-I [2 MARKS]	SA-II [3 MARKS]	VALUE BASED QUESTION [4 MARKS]	LA [5 MARKS]	
1	THE SOLID STATE	1 (1)		3(1)			23(9)
2	SOLUTION		2(1)	3(1)			
3	ELECTROCHEMISTRY					5(1)	
4	CHEMICAL KINETICS		2(1)	3(1)			
5	SURFACE CHEMISTRY	1 (1)		3(1)			
6	GENERAL PRINCIPLES AND PROCESSES OF IOLATION OF ELEMENTS			3(1)			19(7)
7	THE p-BLOCK ELEMENTS	1 (1)	2(1)	3(1)			
8	THE d & f-BLOCK ELEMENTS					5(1)	
9	COORDINATION COMPOUNDS		2(1)	3(1)			
10	HALOALKANES AND HALOARENES	1 (1)		3(1)			28(10)
11	ALCOHOLS , PHENOLS & ETHERS	1 (1)		3(1)			
12	ALDEHYDES , KETONES & CARBOXYLIC ACIDS					5(1)	
13	ORGANIC COMPOUNDS CONTANING NITROGEN		2(1)	3(1)			
14	BIOMOLECULES			3(1)			
15	POLYMERS			3(1)			
16	CHEMISTRY IN EVERYDAY LIFE.				4(1)		
	TOTAL	5(5)	10(5)	36(12)	4(1)	15(3)	70(26)

CBSE Class 12th Chemistry Question Paper-2016

General Instructions :

*(i) **All** questions are compulsory.*

*(ii) Questions number **1** to **5** are very short answer questions **and** carry **1** mark each.*

*(iii) Questions number **6** to **10** are short answer questions and carry **2** marks each.*

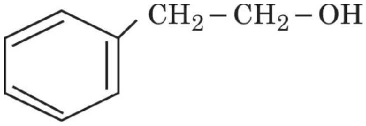
*(iv) Questions number **11** to **22** are also short answer questions and carry **3** marks each.*

*(v) Question number **23** is a value based question and carry **4** marks.*

*(vi) Questions number **24** to **26** are long answer questions and carry **5** marks each.*

*(vii) Use log tables, if necessary. Use of calculators is **not** allowed.*

1. Write the IUPAC name of the given compound :



2. Write the structure of an isomer of compound C_4H_3Br which is most reactive towards S_N1 reaction.

3. What is the reason for the stability of colloidal sols ?

4. Give an example each of a molecular solid and an ionic solid.

5. $Pb(NO_3)_2$ on heating gives a brown gas which undergoes dimerization on cooling? Identify the gas.

6. For a reaction : $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

   Rate = k

   (i) Write the order and molecularity of this reaction.

   (ii) Write the unit of k.

7. Write the chemical equations involved in the following reactions :

   (i) Hoffmann-bromamide degradation reaction

   (ii) Carbylamine reaction

8. (i) Gas (A) is more soluble in water than Gas (B) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why ?

   (ii) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes ?

9. When a coordination compound $CoCl_3.6NH_3$ is mixed with $AgNO_3$, 3 moles of AgCl are precipitated per mole of the compound. Write

   (i) Structural formula of the complex

   (ii) IUPAC name of the complex

10. Write the structures of the following :

(i) BrF_3 (ii) XeF_4

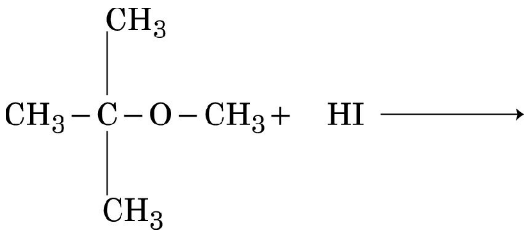
OR

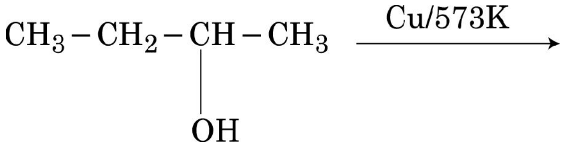
What happens when :

(i) SO_2 gas is passed through an aqueous solution Fe^{3+} salt ?

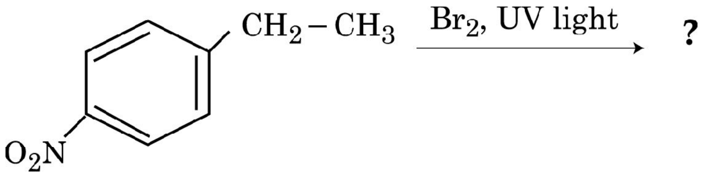
(ii) XeF_4 reacts with SbF_5 ?

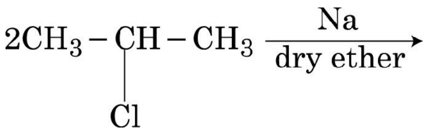
11. Write the final product (s) in each of the following reactions :

(a)

$CH_3-C(CH_3)_2-O-CH_3 + HI \longrightarrow$

(b)

$CH_3-CH_2-CH(OH)-CH_3 \xrightarrow{Cu/573K}$

(c) $C_6H_5-OH \xrightarrow[\text{(ii)} \quad H^+]{\text{(i) } CHCl_3 + aq.NaOH}$

12. (i)


(ii)

$2CH_3-CH(Cl)-CH_3 \xrightarrow[\text{dry ether}]{Na}$

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN}$ **?**

How do you convert :

(i) Chlorobenzene to biphenyl

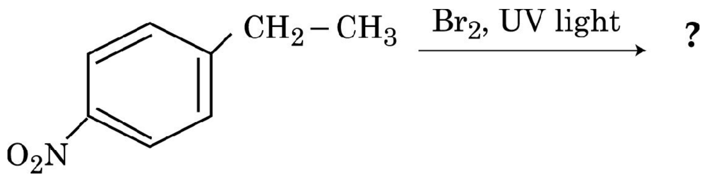
(ii) Propene to 1-iodopropane

(iii) 2-bromobutane to but-2-ene

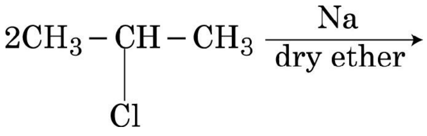
OR

Write the major product(s) in the following :

(i)



(ii)



$2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{dry ether}]{Na}$

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN}$ **?**

13. (i) Write the structural difference between starch and cellulose.

    (ii) What type of linkage is present in Nucleic acids ?

    (iii) Give one example each for fibrous protein and globular protein.

14. (i) Name the method of refining of nickel

    (ii) What is the role of cryolite in the extraction of aluminium?

    (iii) What is the role of limestone in the extranction of iron from its oxides?

15. Give reasons :

    (i) SO_2 is reducing while TeO_2 is an oxidizing agent.

    (ii) Nitrogen does not form pentahalide.

    (iii) ICl is more reactive than I_2.

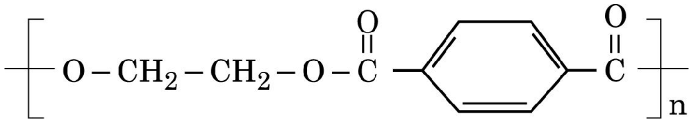
16. (a) For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number : Fe = 26)

    (b) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive.

17. An element crystallizes in a b.c.c. lattice with cell edge of 500pm. The density of the element is $7.5 g\ cm^{-3}$. How many atoms are present in 300 g of the element ?

18. (i) What is the role of Sulphur in the vulcanization of rubber ?

(ii) Identify the monomers in the following polymer :



(iii) Arrange the following polymers in the increasing order of their intermolecular forces :

Terylene, Polythene, Neoprene

19 For the first order thermal decomposition reaction, the following data were obtained :

$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

Time / sec	Total pressure / atm
0	0.30
300	0.50

Calculate the rate constant

(Given : log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

20. Give reasons for the following :

(i) Aniline does not undergo Friedal-Crafts reaction.

(ii) $(CH_3)_2$ NH is more basic than $(CH_3)_3$ N in an aqueous solution.

(iii) Primary amines have higher boiling point than tertiary amines.

21. Define the following terms :

(i) Lyophilic colloid

(ii) Zeta potential

(iii) Associated colloids

22. Calculate the boiling point of solution when 4 g of $MgSO_4$ ($M = 120$ g mol^{-1}) was dissolved in 100 g of water, assuming $MgSO_4$ undergoes complete ionization.

(K_b for water = 0.52 K kg mol^{-1})

23. Due to hectic and busy schedule, Mr. Singh started taking junk food in the lunch break and slowly became habitual of eating food irregularly to excel in his field. One day during meeting he felt severe chest pain and fell down. Mr. Khanna, a close friend of Mr. Singh. took him to doctor immediately. The doctor diagnosed that Mr. Singh was suffering from acidity and prescribed some medicines. Mr. Khanna advised him to eat home made food and change his lifestyle by doing yoga, meditation and some physical exercise. Mr. Singh followed his friend's advice and after few days he started feeling better.
After reading the above passage, answer the following :
(i) What are the values (at least two) displayed by Mr. Khanna ?
(ii) What are antacids ? Give one example.
(iii) Would it be advisable to take antacids for a long period of time ? Give reason.

24. (a) Write the structures of A and B in the following reactions :

(i) $CH_3COCl \xrightarrow{H_2,Pd-BaSO_4} A \xrightarrow{H_2N-OH} B$

(ii) $CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ CO_2} A \xrightarrow{PCl_5} B$

(b) Distinguish between :

(i) $C_6H_5-COCH_3$ and C_6H_5-CHO

(ii) CH_3COOH and $HCOOH$

(c) Arrange the following in the increasing order of their boiling points :

CH_3CHO, CH_3COOH, CH_3CH_2OH

OR

(a) Write the chemical reaction involved in Wolff-Kishner reduction.

(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction :

$C_6H_5COCH_3$, CH_3-CHO, CH_3COCH_3

(c) Why carboxylic acid does not give reactions of carbonyl group ?

(d) Write the product in the following reaction

$CH_3CH_2CH=CH-CH_2CN \xrightarrow[2.\ H_2O]{1.\ (i-Bu)_2AlH}$

(e) A and B are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

25. (a) Calculate E°_{cell} for the following reaction at 298K :

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

Given : $E_{cell} = 1.98$ V

(b) Using the E° values of A and B, predict which is better for coating the surface of iron $[E^\circ(Fe^{2+}/Fe) = -0.44V]$ to prevent corrosion and why ?

Given : $E^\circ(A^{2+}/A) = -2.37V$: $E^\circ(B^{2+}/B) = -0.14V$

OR

(a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given $\lambda^0(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^0(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

(b) Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell ?

26. (a) Account for the following :

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(ii) Cr^{2+} is a strong reducing agent.

(iii) Cu^{2+} salts are coloured while Zn^{2+} salts are white.

(b) Complete the following equations :

(i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow$

OR

The elements of 3d transition series are given as :

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following :

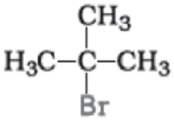
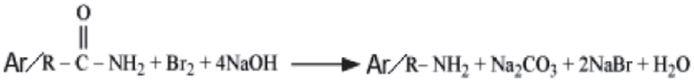
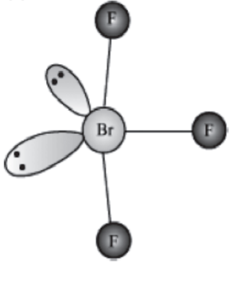
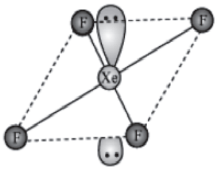
(i) Write the element which shows maximum number of oxidation states. Give reason.

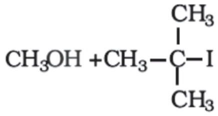
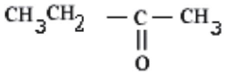
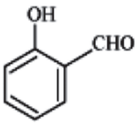
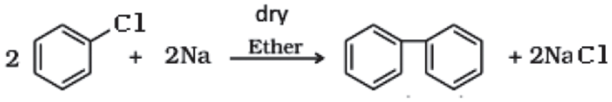
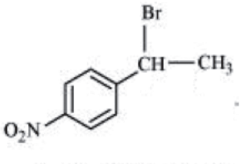
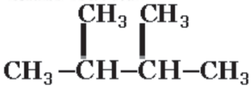
(ii) Which element has the highest m.p ?

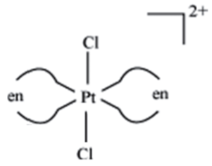
(iii) Which element shows only +3 oxidation state ?

(iv) Which element is a strong oxidizing agent in +3 oxidation state and why ?

CHEMISTRY (045) MARKING SCHEME 2016
SET-56/2/C

Q	VALUES POINTS	MARKS
1	2- Phenylethanol	1
2	 $H_3C-\underset{Br}{\overset{CH_3}{C}}-CH_3$	1
3	Like charged particles cause repulsion / Brownian movement / solvation	1
4	(i) Molecular Solid - I_2 (ii) Ionic Solid - NaCl (Any other suitable example)	½ + ½
5	NO_2	1
6	(i) Zero order reaction, Molecularity is 2 / bimolecular reaction (ii) mol L^{-1} s^{-1}	½ +½ 1
7	(i)  $Ar/R-\overset{O}{\overset{\Vert}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow Ar/R-NH_2 + Na_2CO_3 + 2NaBr + H_2O$ (ii) $Ar/R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} Ar/R-NC + 3KCl + 3H_2O$ (where R=alkyl group , Ar=aryl group)	1 1
8	(i) Gas B , Higher the value of K_H lower is the solubility of gas / $p = K_H x$ (ii) Negative deviation from Raoult's law	½ + ½ 1
9	(i) $[Co(NH_3)_6]Cl_3$ (ii) Hexaamminecobalt(III) chloride	1 1
10	(i)  ii) 	1+1
	OR	
10	(i) $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$ (ii) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$	1 1

11	(a)  $CH_3OH + CH_3-C(CH_3)_2-I$	1
	(b)  $CH_3CH_2-C(=O)-CH_3$	1
	(c) 	1
12	(i) 	1
	(ii) $CH_3CH=CH_2 \xrightarrow{HBr\ /\ peroxide} CH_3CH_2CH_2Br \xrightarrow{NaI/acetone} CH_3CH_2CH_2I$	1
	(iii)  $CH_3CH_2CH(Br)CH_3 \xrightarrow{Alc.KOH} CH_3CH=CHCH_3$	1
	OR	
12	(i) 	1
	(ii)  $CH_3-CH(CH_3)-CH(CH_3)-CH_3$	1
	(iii) CH_3CH_2NC	1

13	(i) Starch - Polymer of α –D- glucose units / Polymer of α - glucose units. Cellulose – polymer of β-D -glucose units / polymer of β -glucose units. (ii) Phosphodiester linkage (iii) Fibrous protein – Keratin / myosin / collagen Globular protein - haemoglobin / insulin	1 1 ½ +½
14	(i) Mond's Process (ii) The melting point of alumina is very high. It is dissolved in cryolite which lowers the melting point and brings conductivity / acts as a solvent. (iii) Limestone is decomposed to CaO ,which removes silica impurity of the ore as slag. OR $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ $C aO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$	1 1 1
15	i) Because stability of higher oxidation state decreases as we move down the group / S is more stable in higher (+6) oxidation state whereas Te is more stable in +4 oxidation state. (ii) Due to absence of d orbital. (iii)Because I – Cl bond is weaker than I-I bond.	1 1 1
16	(i) sp^3d^2 , paramagnetic, high spin (ii) 	1+½+½ 1
17	z= 2 $d = \frac{z \times M}{a^3 \times N_o}$ $N= z \times M/ d \times a^3$ $N= 2\times\ 300\ g / [7.5\ g\ cm^{-3}\ (5 \times\ 10^{-8}\ cm)^3]$ $N=\ 6.4 \times 10^{23}$ atoms OR $d = \frac{z \times M}{a^3 \times N_o}$ $7.5 = \frac{2 \times M}{(500)^3 \times 10^{-30} \times 6.022 \times 10^{23}}$ $M = \frac{7.5\ \times 125 \times 10^{-24} \times 6.022 \times 10^{23}}{2}$ = 282.3g/mol $282.3\ g\ =\ 6.022 \times 10^{23}$ atoms $300\ g\ =\ \frac{6.022 \times 10^{23} \times 300}{282.3}$ $= 6.4 \times 10^{23}$ atoms	½ ½ 1 1 ½ 1 ½ 1

18	(i) On vulcanization , sulphur forms cross links at the reactive sites of double bond, the rubber gets stiffened. (ii) Ethylene glycol / HO – CH_2 CH_2 – OH, Terephthalic acid /  (iii) Neoprene < Polythene < Terylene	1 1 1
19	Given: Initial pressure, $P_o = 0.30$ atm $P_t = 0.50$ atm $t = 300$ s Rate constant, $k = \frac{2.303}{t} \log \frac{P_o}{2P_o - P_t}$ $= \frac{2.303}{300\ s} \log \frac{0.30}{2 \times 0.30 - 0.50}$ $= \frac{2.303}{300\ s} \log \frac{0.30}{0.60 - 0.50}$ $= \frac{2.303}{300\ s} \log \frac{0.30}{0.10}$ $= \frac{2.303}{300\ s} \log 3$ $= \frac{2.303}{300\ s} \times 0.4771$ $= \frac{1.099}{300\ s}$ $= 0.0036\ s^{-1}$ / $3.66 \times 10^{-3}\ s^{-1}$ (deduct ½ mark if unit is not written)	1 1 1
20	(i) Aniline is a Lewis base while $AlCl_3$ is lewis acid. They combine to form a salt. (ii) Due to combined + I and solvation effects. (iii) Due to presence of H-bonding in primary amines.	1 1 1
21	i) Liquid loving/ solvent loving. ii) Potential difference between the fixed layer and diffused / double layer of opposite charges iii) Some substances at higher concentration exhibit colloidal behaviour due to formation of aggregates. The aggregated particles thus formed are called associated colloids or micelles	1 1 1

22	$\Delta T_b = i\ K_b.m$ $i=2$ $= i \times K_b \times \frac{w_2 \times 1000}{M \times W_1}$ $= 2 \times 0.52 K\ kg\ mol^{-1} \times \frac{4\ g \times 1000\ g/kg}{120\ g/mol \times 100 g}$ $= \frac{2 \times 0.52}{3}$ $= 0.346$ K Boiling point of water = 373.15 K / 373 K $T_b = T_b^\circ + \Delta T_b$ = 373.15 K + 0.346 K / 373 K + 0.346 K	½ 1 ½
	= 373.496 K / 373.346 K	1
23	(i) Caring nature, supportive, aware (or any other two suitable values) (ii) Antacids are the medicines used to control acidity in stomach. Ex – mixture of aluminium and magnesium hydroxide / sodium hydrogen carbonate / Zantac / Ranitidine (or any other suitable example) (iii) No, Excessive antacid can make the stomach alkaline and trigger the production of more acid.	½ + ½ 1+ ½ ½ + 1
24	**(a)** (i) A: CH_3CHO , B: $CH_3CH{=}N\text{-}OH$ (ii) A: CH_3COOH , B: CH_3COCl **(b)** (i) Heat both compounds with NaOH and I_2, $C_6H_5COCH_3$ forms yellow ppt of CHI_3 whereas C_6H_5CHO does not. (ii) Add ammonical solution of silver nitrate (Tollen's reagent) to both the compounds, HCOOH gives silver mirror but CH_3COOH does not. (or any other suitable test) (C) $CH_3CHO < CH_3CH_2OH < CH_3COOH$	½ + ½ ½ + ½ 1 1 1
	OR	
24	**(a)**  **(b)** $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$ **(c)** Because of resonance in carboxylic group the carbonyl group loses a double bond character. **(d)** $CH_3CH_2CH{=}CH\text{-}CH_2CHO$ **(e)** A : CH_3CH_2CHO B : CH_3COCH_3	1 1 1 1 ½ + ½

25	a) $E_{cell} = E^0_{cell} - \frac{0.0591\ V}{n} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$ $E^0_{cell} = E_{cell} + \frac{0.0591\ V}{n} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$ $E^0_{cell} = 1.98\ V + \frac{0.0591\ V}{6} \log \frac{(0.01)^2}{(0.01)^3}$ $E^0_{cell} = 1.98\ V + \frac{0.0591\ V}{6} \log 10^2$ $E^0_{cell} = 1.98\ V + \frac{0.0591\ V}{6} \times 2 \times \log 10$ [∵log 10 = 1] $E^0_{cell} = 1.98\ V + \frac{0.0591\ V}{6} \times 2$ $E^0_{cell} = 1.98\ V + 0.0197\ V$ $E^0_{cell} = 1.9997\ V$ (b) A , because its E^0 value is more negative. OR	1 1 1
	(a) $\Lambda_m^c = \kappa \times 1000/C$ $= 3.905 \times 10^{-5} \times 1000/ 0.001$ $= 39.05\ S\ cm^2/mol$ $CH_3COOH \rightarrow CH_3COO^- + H^+$ $\Lambda^\circ\ CH_3COOH = \lambda^\circ\ CH_3COO^- + \lambda^\circ\ H^+$ $= 40.9 + 349.6$ $\Lambda^\circ\ CH_3COOH = 390.5\ S\ cm^2/mol$ $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$ $= 39.05/ 390.5$ $= 0.1$ **(b)** Device used for the production of electricity from energy released during spontaneous chemical reaction and the use of electrical energy to bring about a chemical change. The reaction gets reversed / It starts acting as an electrolytic cell & vice – versa.	1+1 ½ 1 ½ 1 1 1
26	**(a)** i) Ability of oxygen to form multiple bond with Mn metal. ii) Cr^{2+} is oxidized to Cr^{3+} which has stable d^3 / t^3_{2g} orbital configuration iii) Cu^{2+} has unpaired electron while Zn^{2+} has no unpaired electron. **(b)** i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\triangle} 2K_2MnO_4 + 2H_20$ ii) $Cr_2O_7^{2-} + 14\ H^+ + 6\ I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3\ I_2$ (balanced equation is required)	1 1 1 1 1
	OR	
26	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.	½ +1 1 1 ½ +1

Board Paper-1

Time allowed: 3 hours **Maximum marks: 70**

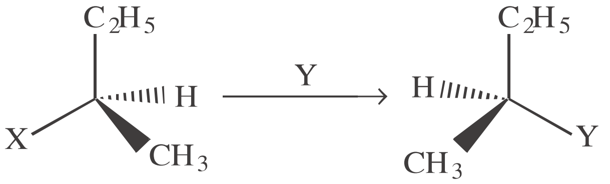
General Instructions: Same as CBSE Sample Question Paper-2016

1. Write the main reason for the stability of colloidal sols.

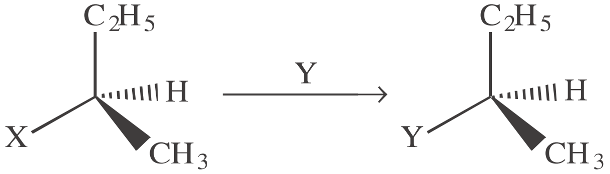
2. Glass from ancient monuments appears milky. Why ?

3. Which of the following reactions is S_N1 type ?

(i)

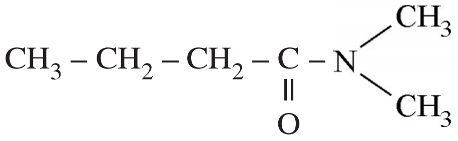


(ii)



4. On heating Cu turnings with conc. HNO_3, a brown coloured gas is evolved which on cooling dimerises. Identify the gas.

5. Write the IUPAC name of the given compound.



$$CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\parallel}}{C} - N\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$$

6. When a co-ordination compound $CoCl_3 \cdot 4NH_3$ is mixed with $AgNO_3$, 1 mole of AgC*l* is precipitated per mole of the compound. Write
   (i) Structural formula of the complex
   (ii) IUPAC name of the complex

7. Show that in a first order reaction, time required for completion of 99.9% is 10 times that of half-life ($t_{1/2}$) of the reaction.

OR

Derive integrated rate equation for rate constant for a first order reaction.

8. State Henry's law. Write its one application. What is the effect of temperature on solubility of gases in liquid ?

9. An organic compound 'X' having molecular formula C_4H_8O gives orange-red ppt. with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow ppt. of iodoform on heating with NaOI. Compound X on reduction with $LiAlH_4$ gives compound 'Y' which undergoes dehydration reaction on heating with conc. H_2SO_4 to form But-2-ene. Identify the compounds X and Y.

10. Write the structures of the following :
    (i) H_2SO_3
    (ii) XeF_4

11. For the first order thermal decomposition reaction, following data were obtained :

$$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$$

Time/sec	**Total pressure / atm**
0	0.30
300	0.50

Calculate the rate constant.

(Given : log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

12. Give reasons :
    (i) The α-hydrogen atoms of aldehydes and ketones are acidic in nature.
    (ii) Propanone is less reactive than ethanol toward addition of HCN.
    (iii) Benzoic acid does not give Friedal-Crafts reaction.

OR

How can you convert ?
(i) Toluene to Benzaldehyde
(ii) Ethanoic acid to 2-chloroethanoic acid
(iii) Acetone to Propane

13. An element crystallizes in a f.c.c. lattice with cell edge of 400 pm. Calculate the density if 200 g of this element contain 2.5×10^{24} atoms.

14. Define the following terms :
    (i) Sorption
    (ii) Zeta potential
    (iii) Kraft temperature

15. Calculate the freezing point of solution when 2 g of Na_2SO_4($M = 142$ g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionization.

(K_f for water = 1.86 K kg mol^{-1})

16. Give reasons :
    (i) PCl_5 is more covalent than PCl_3.
    (ii) O-O bond has lower bond dissociation enthalpy than S-S bond.
    (iii) F_2 is a stronger oxidizing agent than Cl_2.

17. Complete the following reactions :

(i) $C_6H_5-COO^- \overset{+}{N}H_4 \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/pyridine} C$

(ii) $C_6H_5\overset{+}{N}_2\overset{-}{B}F_4 \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3 + alc.\ KOH} C$

18. Write the name of monomers and their structures in the following :

(i) Buna-N

(ii) PVC

(iii) Neoprene

19. (i) Draw the pyranose structure of glucose.

(ii) What type of linkage is present in proteins ?

(iii) Give one example each for water-soluble vitamins and fat-soluble vitamins.

20. (i) For the complex $[Fe(CO)_5]$, write the hybridization, magnetic character and spin of the complex. (At. number : Fe = 26)

(ii) Define crystal field splitting energy.

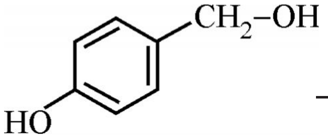
21. Write the role of

(i) I_2 in the van Arkel method of refining.

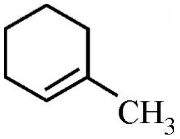
(ii) Cryolite in the extraction of aluminium.

(iii) Dilute NaCN in the extraction of silver.

22. Write the major product(s) in the following reactions :

(i) 

$\xrightarrow{PCl_5} ?$

(ii) 

$\xrightarrow{HBr} ?$

(iii) $CH_3CH_2Cl \xrightarrow{KNO_2} ?$

23. Due to hectic and busy schedule, Mr. Awasthi made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Roy, a close friend of Mr. Awasthi, advised him to stop taking sleeping pills and suggested to change his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Awasthi followed his friend's advice and after few days he started feeling better.

After reading the above passage, answer the following :

(i) What are the values (at least two) displayed by Mr. Roy ?

(ii) Why it is not advisable to take sleeping pills without consulting doctor ?

(iii) What are tanquilizers ? Give two examples.

24. (a) Calculate $\Delta G°$ and log K_c for the following reaction at 298 K :

$$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s)$$

Given : $E^{\circ}_{cell} = 0.30$ V

(b) Using the E° values of A and B, predict which is better for coating the surface of iron [$E°(Fe^{2+} | Fe) = –0.44$ V] to prevent corrosion and why ?

Given : $E°(A^{2+} | A) = –2.37$ V : $E°(B^{2+} | B) = –0.14$ V

OR

(a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given : $\lambda°(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda°(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}.

(b) What type of battery is lead storage battery ? Write the overall reaction occurring in lead storage battery.

25. (a) Account for the following :

(i) Mn_2O_7 is acidic whereas MnO is basic.

(ii) Though copper has completely filled d-orbital (d^{10}) yet it is considered as a transition metal.

(iii) Actinoids show wide range of oxidation states.

(b) Write the preparation of potassium permanganate from pyrolusite ore (MnO_2).

OR

(a) The elements of 3d transition series are given as :

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following :

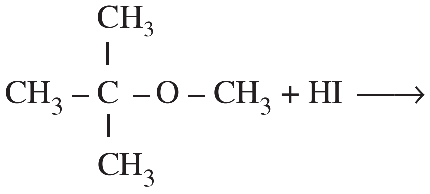
(i) Which element has the highest m.p. and why ?

(ii) Which element is a strong oxidizing agent in +3 oxidation state and why ?

(iii) Which element is soft and why ?

(b) Write the equations involved in the preparation of Potassium dichromate from Sodium chromate (Na_2CrO_4).

26. (a) Write the major product(s) in each of the following reactions :

(i) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3+HI\longrightarrow$$

(ii) 

$$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3\xrightarrow{Cu/573\ K}$$

(iii) $C_6H_5-OH\xrightarrow[\text{(ii) } H^+]{\text{(i) } CHCl_3+aq\cdot NaOH}$

(b) Write the chemical reaction involved in the following reactions :

(i) Kolbe's reaction

(ii) Friedal-Crafts acetylation of anisole

OR

(a) What happens when

(i) phenol reacts with Bromine water ?

(ii) ethanol reacts with CH_3COCl/pyridine ?

(iii) anisole reacts with HI ?

Write the chemical equations involved in the above reactions.

(b) Distinguish between :

(i) Ethanol and phenol

(ii) Propan-2-ol and 2-methylpropan-2-ol

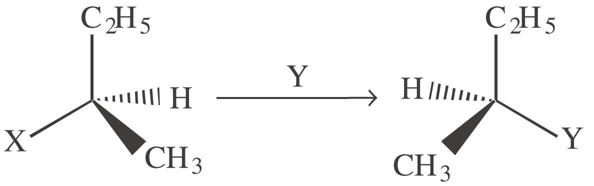
Board Paper-2

Time allowed: 3 hours **Maximum marks: 70**

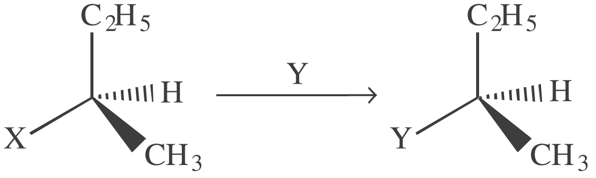
General Instructions: Same as CBSE Sample Question Paper-2016

1. Which of the following two reactions is S_N2 and why?

(i)



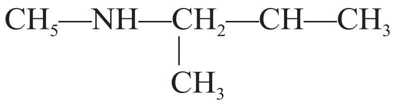
(ii)



2. On heating $Pb(NO_3)_2$ a brown gas is evolved which undergoes dimerisation on cooling. Identify the gas.

3. ZnO turns yellow on heating. Why?

4. Write the IUPAC name of the given compound:



$$CH_5—NH—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$$

5. Write the reason for the stability of colloidal sols.

6. (i) Write the colligative property which is used to find the molecular mass of macromolecules.

   (ii) In non-ideal solution, what type of deviation shows the formation of minimum boiling azeotropes?

7. Write the structures of the following:

   (i) $(HPO_3)_3$ (ii) ZeF_4

8. When a coordination compound $NiCl_2. 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write

   (i) structural formula of the complex.

   (ii) IUPAC name of the complex.

9. For a reaction : $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$, Rate = k

   (i) Write the order and molecularity of this reaction.

   (ii) Write the unit of k.

10. Write the chemical equations involved in the following reactions:

    (i) Kolbe’s reaction

    (ii) Friedal-Crafts acetylation of anisole

OR

How do you convert

(i) phenol to toluene?

(ii) formaldehyde to ethanol?

11. An element crystallises in a *fcc* lattice with cell edge of 400 pm. The density of the element is 7 g cm^{-3}. How many atoms are present in 280 g of the element?

12. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4 \mathrm{K}}{T}$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.

(Given R = 8.314 JK^{-1} mol^{-1})

13. Define the following terms :

    (i) O/W Emulsion

    (ii) Zeta potential

    (iii) Multimolecular colloids

14. (i) Name the method of refining which is based on the principle of adsorption.

    (ii) What is the role of depressant in froth floatation process?

    (iii) What is the role of limestone in the extraction of iron from its oxides?

15. Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionisation.

(K_b for water = 0.52 K kg mol^{-1})

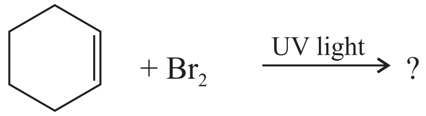
16. Assign reasons for the following:

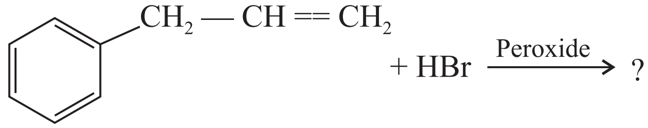
    (i) H_3PO_2 is a stronger reducing agent than H_2PO_4.

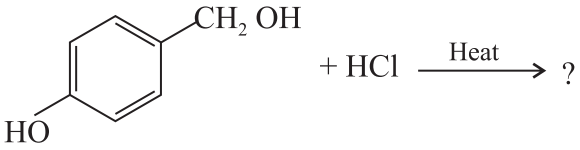
    (ii) Sulphur shows more tendency for catenation than oxygen.

    (iii) Reducing character increases from HF to HI.

17. Write the major monohalo product(s) in each of the following reactions:

(i) 

(ii) 

(iii) 

18. Give reasons for the following:

(i) Protonation of phenols is difficult whereas ethanol easily undergoes protonation.

(ii) Boiling point of ethanol is higher than that of dimethyl ether.

(iii) Anisole on reaction with HI gives phenol and CH_3—1 as main products and not iodobenzene and CH_2OH.

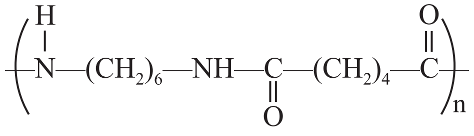
19. Write the structures of *A, B* and *C* in the following reactions:

(i) $C_6H_5-COO^-\,\overset{+}{N}H_4 \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/\text{pyridine}} C$

(ii) $C_6H_5\overset{+}{N}_2\overset{-}{B}F_4 \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3 + \text{alc. KOH}} C$

20. (i) What is the role of benzoyl peroxide in the polymerisation of ethene?

(ii) Identify the monomers in the following polymer:



$$\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-NH-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}\right)_n$$

(iii) Arrange the following polymers in the increasing order of their intermolecular forces:

Nylon-6, 6, Polythene, Buna-S

OR

Write the mechanism of free radical polymerisation of ethene.

21. (i) Write one reaction of D-Glucose which cannot be explained by its open chain structure.

(ii) What type of linkage is present in nucleic acids?

(iii) Give one example each for water-soluble vitamins and fat-foluble vitamins.

22. (i) For the complex $[Fe(CN)_6]^{4-}$, write the hybridization, magnetic character and spin type of the complex. (At. number : Fe = 26)

(ii) Draw one of the geometrical isomers of the complex $[Co(en)_2\,Cl_2]^+$ which is optically active.

23. Due to hectic and busy schedule, Mr. Awasthi made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Roy, a close friend of Mr. Awasthi, advised him to stop taking sleeping pills and suggested to change his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Awasthi followed his friend's advice and after few days he started feeling better.

After reading the above passage, answer the following :

(i) What are the values (at least two) displayed by Mr. Roy?

(ii) Why it is not advisable to take sleeping pills without consulting doctor?

(iii) What are tanquilizers? Give two examples.

24. (i) Calculate E°_{cell} for the following reaction at 298 K:

$$2Cr(s) + 3Fe^{2+}\,(0.01\ m) \rightarrow 2Cr^{3+}\,(0.01) + 3Fe(s)$$

Given : $E^\circ_{cell} = 0.261$ V

(ii) Using the E° values of A and B, predict which one is better for coating the surface of iron $[E^\circ_{Fe^{2+}/Fe} = -0.44V]$

to prevent corrosion and why?

Given : $E^\circ_{(Ae^{2+}/A)} = -2.37\,V$. $E^\circ_{(Be^{2+}/B)} = -0.14V$

OR

(i) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (a).

Given $\lambda^\circ(H^+) = 349.6\ S\ cm^2\ mol^{-1}$ and $\lambda^\circ(CH_3COO^-) = 40.9\ S\ cm^2\ mol^{-1}$.

(ii) Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?

25. (i) Account for the following :

(a) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(b) Zirconium and Hafnium exhibit similar properties.

(c) Transition metals act as catalysts.

(ii) Complete the following equations:

(a) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(b) $Cr_2O_7^{2-} + 14H^{+} + 61^{-} \longrightarrow$

OR

The elements of 3*d* transition series are given as :

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following :

(i) Write the element which is not regarded as a transition element. Give reason.

(ii) Which element has the highest m.p.?

(iii) Write the element which can show an oxidation state of +1.

(iv) Which element is a strong oxidising agent in +3 oxidation state and why?

26. (i) Write the structures of *A, B, C* and *D* in the following reactions:

$$\begin{tikzcd}
CH_3CN \arrow[r, "\text{(i) } SnCl_2\text{—}HCl", "\text{(ii) } H_2O"'] & A \arrow[r, "\text{dil.NaOH}"] \arrow[d, "HCN"] & B \arrow[r, "\text{Heat}"] & C \\
& D & &
\end{tikzcd}$$

(ii) Distinguish between:

(a) C_6H_5—CH=CH—$COCH_3$ and C_6H_5—CH=CH—$COCH_2CH_3$

(b) CH_3CH_2COOH and HCOOH

(iii) Arrange the following in the increasing order of their boiling points:

CH_3CH_2OH, CH_3COCH_3, CH_3COOH

OR

(i) Write the chemical reaction involved in the Etard reaction.

(ii) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction :

CH_3—CHO, $C_6H_5COCH_3$, HCHO

(iii) Why p*Ka* of Cl—CH_2—COOH is lower than the p*Ka* of CH_3COOH?

(iv) Write the product in the following reaction:

$CH_3CH_2CH{=}CH\text{—}CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) (i–Bu)}_2\text{AIH}}$

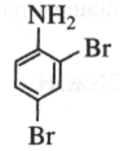
(v) *A* and *B* are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2. isomer *A* forms yellow precipitate of iodoform whereas isomer *B* does not form any precipitate. Write the formulae of *A* and *B*.

Board Paper-3

Time allowed: 3 hours **Maximum marks: 70**

General Instructions: Same as CBSE Sample Question Paper-2016

1. On heating Zn granules with conc. HNO_3, a brown gas is evolved which undergoes dimerisation on cooling. Identify the gas.
2. What is the reason for the stability of colloidal sols?
3. Write the IUPAC name of the given compound.



4. Out of $CH_2=CH—CH_2Cl$ and $CH_3—CH_2—CH_2Cl$, which is more reactive towards S_N1 reaction?
5. What type of magnetism is shown by a substance if its domains are arranged in equal number and in opposite directions?
6. When a coordination compound $PdCl_2.\ 4NH_3$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write.
   (i) structural formula of the complex.
   (ii) IUPAC name of the complex.
7. Write the chemical equations involved in the following reactions:
   (i) Clemmensen reduction
   (ii) Hell-Volhard Zelinsky reaction

OR

How do you convert

(i) toluence to benzaldehyde?

(ii) ethanoyl chloride to ethanal?

8. For a reaction : $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

   Rate = k

   (i) Write the order and molecularity of the reaction.
   (ii) Write the unit of k.

9. For the given cells :

   Lead storage cell, Mercury cell, Fuel cell and Dry cell

   Answer the following :

   (i) Which cell is used in hearing aids?

   (ii) Which cell was used in Apollo space programme?

   (iii) Which cell is used in automobiles and inverters?

   (iv) Which cell does not have long life?

10. When pyrolusite ore MnO_2 is fused with KOH in presence of air, a green coloured compound (*A*) is obtained which undergoes disproportionation reaction in acidic medium to give a purple coloured compound (*B*). Identify A and B.

11. (i) Calculate E°_{cell} for the following reaction at 298 K:

    $2Cr(s) + 3Fe^{2+} (0.01\ m) \rightarrow 2Cr^{3+} (0.01) + 3Fe(s)$

    Given : $E^\circ_{cell} = 0.261$ V

12. (i) Name the method of refining which is based on the principle of adsorption.

    (ii) What is the role of depressant in froth floatation process?

    (iii) What is the role of limestone in the extraction of iron from its oxides?

13. (i) Out of silica gel and anhydrous $CaCl_2$. Which will adsorb the water vapours?

    (ii) Out of H_2SO_4 and H_3PO_4. Which one is more effective in causing coagulation of positively charged sol? Give reason.

    (iii) Out of sulphur sol and proteins, which one forms macromolecular colloids?

14. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

    $$\log k = 14.2 - \frac{1.0 \times 10^4 K}{T}$$

    Calculate E_a for this reaction and rate constant *k* if its half-life period be 200 minutes.

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

15. An element crystallises in a *fcc* lattice with cell edge of 400 pm. The density of the element is 7 g cm^{-3}. How many atoms are present in 280 g of the element?

16. (i) For the complex $[CoF_6]^{3-}$, write the hybridization, magnetic character and spin type of the complex. (Al number : Co = 27)

    (ii) Draw one of the geometrical isomers of the complex $[Co(en)_2\ Cl_2]^+$ which is optically active.

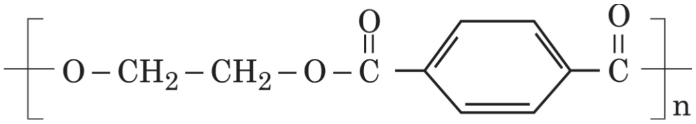
    (ii) Draw one of two monosaccharides obtained on hydrolysis of maltose sugar.

17. (i) Write the structural difference between starch and cellulose.

    (ii) What type of linkage is present in Nucleic acids?

    (iii) Give one example each for fibrous protein and globular protein.

18. (i) What is the monomers in the following polymber :



    (iii) Arrange the following polymers in the increasing order of their intermolecular forces : PVC, Nylon-6, Buna-N

OR

Write the mechanism of free radical polymerisation of ethene.

19. Complete the following reactions :

    (i) $C_6H_5-COO^-\,NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/\text{pyridine}} C$

    (ii) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3 + \text{alc. KOH}} C$

20. Give reasons for the following:

    (i) Aldehydes (R—CHO) are more reactive than ketones (R—CO—R) towards nuclephilic addition reaction.

    (ii) Benzaldehyde does not undergo aldol condensation reaction.

    (iii) Benzoic acid does not give Friedal-Crafts reaction.

21. What happens when

    (i) 2, 4, 6 - trinitrochlorobenzene is treated with warm water?

    (ii) 2-chlorobutane is treated with alcoholic KOH?

    (iii) ethyl chloride is treated with Na metal in presence of dry ether?

22. Give reasons :

    (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

    (ii) Zn is soft whereas Cr is hard.

    (iii) Eu^{2+} is a good reducing agent.

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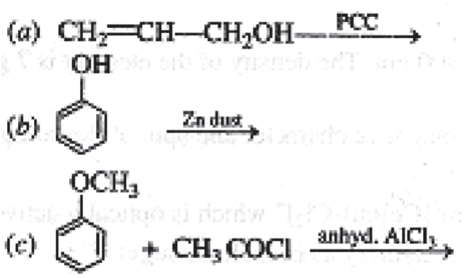
24. (i) Write the product(s) in each of the following reactions:



(ii) Write the mechanism of the following reaction :

$2CH_3CH_2OH \xrightarrow{\text{Coec } H_2SO_4/413K} CH_3CH_2—O—CH_2CH_3$

OR

(i) Write equations of the following reactions:

- (a) Bromine in CS_2 with phenol
- (b) Treating phenol with chloroform in the presence of aq. NaOH
- (c) Anisole reacts with HI

(ii) Distinguish between

- (a) Ethanol and Diethyl ether
- (b) Propanol and *t*-butyl alcohol

25. (i) Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionisation.

    (K_b for water = 0.52 K kg mol^{-1})

(ii) Define the following terms:

 (a) Colligative properties

 (b) Ideal solution

OR

(i) When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).

(K_f for CS_2 = 3.83 K kg mol^{-1}, Atomic mass of sulphur = 32 g mol^{-1})

(ii) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing.

 (a) 1.2% sodium chloride solution?

 (b) 0.4% sodium chloride solution?

26. (i) Account for the following:

 (a) H_2Te is more acidic than H_2S.

 (b) PCl_5 is more covalent than PCl_3.

 (c) Boiling points of interhalogens are little higher as compared to pure halogens.

(ii) Draw the structure of :

 (a) $HClO_4$

 (b) $XeOF_4$

OR

(i) Arrange the following in the increasing order of their reducing character :

H_3PO_3, H_3PO_4, H_3PO_2

(ii) Out of He and Xe, which one can easily form compound and why?

(iii) Write the conditions to maximise the yield of ammonia in Haber's process.

(iv) Write two uses of chlorine gas.

(v) How can you detect the presence of SO_2 gas?

TIPS FOR STUDENTS

Self motivation- Honestly write down your aim and all the desires in your life. It will propel you towards success.

Set up a routine- Prepare smart and successful studying programme.

Find a **quiet place**, away from distractions and figure out time of the day you can contribute best and that fits into your schedule.

Make a good time table-A schedule of every subject should be made with different priorities like tough subjects and the one in which you are week should be given more hours. Study at the same place & at the same time every day.

Sit in an **alert posture**.

Stay **healthy** mentally and physically_ get adequate rest, exercise and balanced nutrition.

Manage distractions like cellphones, friends, sms, TV, video games, surfing etc which are biggest time drains.

Avoid doing “marathon” session (i.e. larger than 1 hour) as it is least productive. Our attention span ranges from 30-60 minute.

Unwind and relax- 10 to 15 min break after every study session.

Study difficult topics first. When mentally fresh, brain can process information more quickly. Short term planning is more achievable than long term plans.

Don't spend more than three days a week in coaching/tution as **self study is the only real study**. **Therefore atleast** four days for uninterrupted self study.

Prepare a competitive study group- share useful concepts and questions, your knowledge, skills and resources, clarify doubts, take help of a friend who is an expert in that topic/unit.

Give yourself enough time to study. dont leave until the last minute.

Use flow charts & mind maps.

Test yourself before actual test –practice previous year's examination papers.

Review- clear doubts- revise- attempt questions of textbook and previous year CBSE papers.

NIGHT BEFORE THE EXAM - don't cram.

Reduce stress and anxiety.. avoid stressful friends....relax.. eat some brain snacks.. sleep..review main points.

Prepare to be prepared: before going to bed before an exam make sure to collect everything that you will need fo r exam – stationery , admit card, wrist watch....

Ensure location of exam centre.

ON EXAMINATION DAY.. leave home in time and ensure your arrival at centre in time..so that you go into your exam calmly rather than in a frantic rush sweaty.

DURING TEST-

Focus on your exam and not on what other students are doing

Start strategically..begin your exam by skimming through the question quickly and note down any initial thoughts or related memorised facts beside each question.

Start with the question you know best. This will boost your confidence and give you a good start.

- Read the instructions carefully and follow.
- Answer as per marking scheme.
- Write neat and present well.
- Attempt the easiest part and the units you are most confident. Manage time so that extra time can be allotted to difficult portion.
- Attempt complete question paper.
- Never cheat
- Review and make sure you have not left out any question unattempted.

CHASE YOUR GOALS.

ALL THE BEST