DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL
(2017-2018)

Class : XII
CHEMISTRY

Under the Guidance of

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SUBJECTWISE SUPPORT MATERIAL

PREFACE

It is a matter of great pleasure for me to present the Support Material for various subjects prepared for the students of classes IX to XII by a team of dedicated and sincere teachers and subject experts from the Directorate of Education.

The subject wise Support Material is designed to enhance the academic performance of the students and improve their understanding of the subject. It is hoped that this comprehensive study material will be put to good use by both the students and the teachers in order to achieve academic excellence.

I commend the efforts of the team of respective subject teachers and their group leaders who worked sincerely and tirelessly under the able guidance of the officers of the Directorate of Education to complete this remarkable work in time.

Punya Salila
(Punya S Srivastava)

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प्रिय विद्यार्थियों,

इस पुस्तक के माध्यम से आपके साथ सीधे संवाद का अवसर मिल रहा हैं । और अपने विद्यार्थियों के साथ जुड़ने के इस अवसर का मैं पूरा लाभ उठाना चाहती हूँ ।

दिल्ली में आपके विद्यालय जैसे कोई १०३० राजकीय विद्यालय हैं , जिनका संचालन 'शिक्षा निदेशालय' करता हैं । शिक्षा निदेशालय का मुख्यालय पुराना सचिवालय (ओल्ड सेक्रेटेरिएट), दिल्ली-५४ में स्थित हैं ।

इस निदेशालय में सभी अधिकारी दिन रात कार्य करते हैं तांकि हमारे स्कूल और अच्छे बन सकें; हमारे शिक्षक आपको नए-नए व बेहतर तरीकों से पढ़ा सकें; परीक्षा में हमारे सभी विद्यार्थी और अच्छे अंक ला सकें तथा उनका भविष्य सुनिश्चित हो ।

इसी क्रम में पिछले कुछ वर्षों से शिक्षा निदेशालय ने कक्षा नवीं से बारहवीं तक के अपने विद्यार्थियों के लिए विभिन्न विषयों में 'सहायक सामग्री' उपलब्ध करवाना प्रारंभ किया है।

प्यारे बच्चो, आपके हाथ में यह जो पुस्तक है, इसे कई उत्कृष्ठ अध्यापकों ने मिलकर विशेष रूप से आप ही के लिए तैयार किया है । इसे तैयार करवाने में काफी मेहनत और धन खर्च हुआ है । इसलिए अपनी मुख्य पाठ्यपुस्तक के साथ-साथ यदि आप इस सहायक सामग्री का भी अच्छे से अभ्यास करेंगे तो परीक्षा में आपकी सफलता तो सुनिश्चित होगी ही, आपको बाजार में बिकने वाली महंगी सहायक पुस्तकें भी खरीदने की जरूरत नही पड़ेगी । और हाँ, इस पुस्तक को हर साल हम CBSE के पाठ्यक्रम के अनुसार संवर्धित और परिमार्जित भी करते हैं ताकि छात्र छात्राओं की परीक्षा-तैयारी अध्यतन रहे ।

अंततः, एक बात और । अपने विद्यार्थी काल के जिस पड़ाव से आप आज गुजर रहे हैं, यह आपके शेष जीवन की नींव के निर्माण का समय है । मुझे आप पर पूरा विश्वास है कि आप इस समय का सदुपयोग करेंगे, खूब अध्ययन करेंगे तथा अपने एवं अपने देश के लिए एक सार्थक भविष्य की नींव डालेंगे ।

मेरी ढ़ेरो शुभकामनाएं ।

सौम्या गुप्ता

आपकी
सौम्या गुप्ता

Dr. Sunita S. Kaushik
Addl. Director of Edn. (School)/Exam

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D. O. No. PA/Addl.DE/Sch/38
Dated. 14/09/2017

SUBJECTWISE SUPPORT MATERIAL

FOREWORD

I take pride in presenting latest Support Material for the students of classes IX to XII developed and prepared by a team of subject experts and dedicated teachers from different schools of the Directorate of Education.

The Support Material, over the years, has proved to be a blessing for the students of our schools who are unable to purchase quality subject material from the market unlike their public school counter parts. It gives them a fair chance to do well in the public exams . The comprehensive support material presents the material contained in the prescribed texts in a lucid and comprehensible manner.

While the teachers are expected to give ample practice to the students to enhance their academic performance, the students are also expected to utilize the material to the maximum so that they have a better understanding of the concepts of each subject.

I express my sincere appreciation to all team leaders and their respective teams for their valuable contribution to this commendable task.

14/9/17
Dr. Sunita S. Kaushik
Addl D.E. (School & Exam)

DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL
(2017-2018)

CHEMISTRY

Class : XII

NOT FOR SALE

PUBLISHED BY : DELHI BUREAU OF TEXTBOOKS

CHEMISTRY
CLASS-XII

LIST OF MEMBERS WHO REVIEWED AND REVISED SUPPORT MATERIAL OF CHEMISTRY AS PER LATEST SYLLABUS PRESCRIBED BY CBSE FOR CLASS XII (2017-18)

S. No.	Name	Designation
1.	Roop Narain Chauhan Group Leader (9868373636)	Vice Principal R. P. V. V., Sector-19 Dwarka
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Chemistry (Code No. 043) Question Paper Design

Class XII (2016-17)

Time : 3 Hours **Max. Marks : 70**

Sr. No.	Typology of Questions	Very Short Answer (VSA) 1 Mark	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	% Weigh-tage
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	10%
2.	**Understanding.** (Comprehension-to be familiar with meaning and to understand conceptually, interpret, compare, contrast, explain, paraphrase, or interpret information)	-	2	4	-	1	21	30%
3.	**Application** (Use abstract information in concrete situations, 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, Organise and / or integrate unique places of information from a variety of sources)	2	-	1	-	1	10	14%
5.	Inferential and Evaluation and Multi-Disciplinary (Appralse, 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	5×1=5	5×2=10	12×3=36	1×4=4	3×5=15	70(26)	100%

CONTENTS

CLASS XII (2016-17)
(THEORY)

Total Periods (Theory 160 + Practical 60)

Time : 3 Hours

70 Marks

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

QUESTION-WISE BREAK UP

Type of Question	Mark per Question	Total No. of Question	Total Marks
VSA	1	5	05
SA-I	2	5	10
SA-II	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 in 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.

UNIT I

THE SOLID STATE

Points to Remember

1. HCP and CCP have equal efficiency *i.e.,* 74% of space is occupied and coordination number is 12. CCP arrangement has FCC lattice.
2. Coordination number is the number of nearest neighbouring points surrounding a particular lattice point (point may be atom, ions or molecules).
3. Packing efficiency in simple cubic unit cell is 52.4%, in bcc arrangement is 68% and in fcc is 74%.
4. Unoccupied spaces in solids are called interstitial voids or interstitial sites.
5. Two types of interstitial voids are :
   (i) tetrahedral void
   (ii) octahedral void
      * No. of tetrahedral voids = 2 × N (where N is number of closed packed particles).
      * No. of octahedral voids = N.
6. Vacancy defect lowers the density of a crystal.
7. Interstitial defect increases the density of a crystal.
8. Point defects in the ionic crystal may be classified as :
   (i) Stoichiometric defect also known as intrinsic or thermodynamic defect. Ratio of cations and anions is the same in defective crystal as in ideal crystal.
   (ii) In non-stoichiometric defect ratio of cations to anions is the difference in defective crystal from the ideal crystal.
   (iii) Impurity defect (due to presence of some other ions at the lattice sites).
9. Schottky defect arises due to missing of equal number of cations and anions from lattice sites in the crystalline solid of the type A^+B^- and it lowers and density of alkali metal halides, *e.g.,* NaCl, KCl etc.
10. Frenkel defect is the combination of vacancy and interstitial defects. Cations leave their actual lattice sites and occupy the interstitial space in the solid. Density remains the same in Frenkel defect.

$^{+}$AgBr is the compound which shows both Schottky defect as well as Frenkel defect.

11. Non-stoichiometric defect

    (i) Metal excess defect due to anion vacancies.

    (ii) Metal excess defect due to presence of extra cations.

    (iii) Metal deficiency due to absence of cations.

12. **F-Center :** In metal excess defect, electrons are trapped in the anion vacancies which act as colour centres, *e.g.,* NaCl gives yellow colour when heated in sodium vapour.

13. Doping is the process of increasing the conductivity of intrinsic semiconductors by adding an appropriate amount of suitable impurity in Si or Ge.

*** n-type semiconductors :** Silicon or Germanium (group 14) doped with electron rich impurity (group 15 element like P or As). Here, conductivity is due to the extra electrons or delocalized electrons.

*** p-type semiconductors :** Silicon or Germanium (group 14) doped with group 13 elements like B or Al. Here, conductivity is due to positively charged electron holes.

* 13-15 group compounds, *e.g.,* InSb, AlP, GaAs.

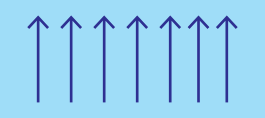
* 12-16 group compounds, *e.g.,* ZnS, CdS, CdSe, HgTe.

* These compounds have average valence of four and are used in semiconductor devices.

14. Magnetic Properties

*** Ferromagnetic substances :** A few substances like iron, cobalt, nickel and CrO_2 etc. are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances.

All molecular domains are arranged permanently in the same direction under influence of magnetic field.



*** Antiferromagnetism :** Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetism substances, but their domains are oppositely oriented and cancel out each other's magnetic moment and so cannot be attracted towards magnet.

*** Ferrimagnetism :** When the magnetic moments of the domains in the substances are aligned in parallel and antiparallel directions in unequal number.

These are weakly attracted by magnetic field as compared to ferromagnetic substances. For example, Fe_3O_4, MgF_2O_4 etc.

* Paramagnetic substances are weakly attracted by a magnetic field. Examples are O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} which are paramagnetic due to the presence of unpaired one or more electrons. They lose their magnetism in the absence of magnetic field.

* Diamagnetic substances are weakly repelled by a magnetic field. Examples are H_2O, NaCl, C_6H_6 because they have all the electrons paired.

1. Calculation of number of particles/atoms/ions in a unit cell :

Type of unit cell	Number of particles per unit cell	Relationship between edge length (a) and radius (r) of atom/ion
Simple cubic (SC)	1	$a = 2r$
Body centred cubic (BCC)	2	$a = \frac{4}{\sqrt{3}}r$
Face centred cubic (FCC)	4	$a = 2\sqrt{2}r$

2. Density of unit cell :

$$d = \frac{ZM}{a^3 N_A}$$

where Z is rank of unit cell (number of atoms per unit cell), M is molar mass/atomic mass, a is edge length of the cube, a^3 is volume of cubic unit cell and N_A is Avogadro constant.

3. **Packing efficiency,** $\mathbf{PE} = \dfrac{Z\times\frac{4}{3}\pi r^3}{a^3}\times 100$

Here, M is molar mass, r is radius of atom, d is density and N_A is Avogadro's constant (6.022×10^{23} mol^{-1}).

Rank of unit cell can be computed by packing efficiency value :

Type of unit cell	Packing efficiency	Rank of unit cell (Z)
SC	52.4%	1
BCC	68%	2
FCC	74%	4

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What do you mean by paramagnetic substance ?

Ans. Weakly attracted by magnetic field and these substances are made of atoms or ions with unpaired electrons.

Q. 2. Which substance exhibit both Schottky and Frenkel defects ?

Ans. AgBr.

Q. 3. Name a salt which is added to AgCl so as to produce cationic vacancies.

Ans. $CdCl_2$

Q. 4. Why Frenkel defects not found in pure alkali metal halides ?

Ans. Due to larger size of alkali metal ion, these cannot shift in interstitial space.

Q. 5. What is the use of amorphous silica ?

Ans. Used in photovoltanic cell.

Q. 6. Analysis shows that a metal oxide has the empirical formula $M_{0.98}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.

Ans. Let the M^{2+} ion in the crystal be x and $M^{3+} = 0.98 - x$

Since, total charge on the compound must be zero,

So, $2x + 3(0.98 - x) - z = 0$

Or $x = 0.94$

$$\% \text{ of } M^{2+} = \frac{0.94}{0.98} \times 100 = 97.9\%$$

$$\% \text{ of } M^{3+} = 100 - 97.9 = 2.1\%$$

Q. 7. What is the co-ordination number of cation and anion in Caesium chloride (bcc arrangement) ?

Ans. 8 and 8.

Q. 8. What is F-centre ?

Ans. It is the anion vacancy occupied by free electron in metal excess defect.

Q. 9. What makes alkali metal halides sometimes coloured, which are otherwise colourless ?

Ans. Due to presence of F-centre.

Q.10. How does silica differ from quartz ?

Ans. Silica is amorphous form, while quartz is crystalline form of SiO_2.

Q.11. Which point defect lowers the density of a crystal ?

Ans. Schottky defect/Vacancy defect.

Q.12. Why glass is called super cooled liquids ?

Ans. *Hint :* Its molecules move under gravity.

Q.13. Some of the very old glass objects appear slightly milky instead of being transparent. Why ?

Ans. Reallignment of molecules takes place due to movement because of constant heating and cooling.

Q.14. What is anisotropy ?

Ans. Physical properties show different values when measured along different axis in crystalline solids.

Q.15. What is the coordination number of atoms in :

(a) fcc structure (b) bcc structure ?

Ans. (a) 12 (b) 8

Q.16. How many lattice points are there in one unit cell of :

(a) fcc

(b) bcc

(c) simple cubic arrangement ?

Ans. (a) 14 (b) 9 (c) 8

Q.17. What are the co-ordination numbers of octahedral voids and tetrahedral voids ?

Ans. 6 and 4 respectively.

Q.18. Why common salt is sometimes yellow instead of being pure white ?

Ans. Due to the presence of electrons in some lattice sites in place of anions these sites act as F-centres. These electrons when excited impart colour to the crystal.

Q.19. A compound is formed by two elements X and Y. The element Y forms ccp arrangement and atoms of X occupy octahedral voids. What is the formula of the compound ?

Ans. No. of Y (ccp) = 4

No. of X (octahedral void) = 4

$$X : Y = 4 : 4$$

$$XY$$

SA-(I) Type Question (2 Marks)

Q.20. Define F-centres and how it is formed in lattice of crystal ?

Q.21. What type of stoichiometric defect is shown by

(a) ZnS

(b) AgBr

Q.22. What are the differences between Frenkel and Schottky defect ?

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

(a) Ferromagnetism

(b) Paramagnetism

(c) Ferrimagnetism

(d) 12-16 and 13-15 group compounds

Q.24. In terms of band theory, what is the difference :

(a) between conductor and an insulator ?

(b) between a conductor and a semi-conductor ?

Q.25. Explain how electrical neutrality is maintained in compounds showing Frenkel and Schottky defect.

Ans. In compound showing Frenkel defect, ions just get displaced within the lattice, while in compounds showing Schottky defect, equal number of anions and cations are removed from the lattice. Thus, electrical neutrality is maintained in both cases.

Q.26. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.

Ans. 8 corner × 1/8 atom per unit cell = 1 atom

There are four body diagonals in a cubic unit cell and each has two body centre atoms.

So, $4 \times 2 = 8$ atoms therefore, total number of atoms per unit cell $= 1 + 8 = 9$.

Q.27. Gold crystallizes in an FCC unit cell. What is the edge length of unit cell (r = 0.144 mm) ?

Ans.

$$r = 0.144 \text{ nm}$$

$$a = 2\sqrt{2}r$$

$$= 2 \times 1.414 \times 0.144 \text{ nm}$$

$$= 0.407 \text{ nm}$$

Q.28. Classify each of the following as either a p-type or n-type semi-conductor :

(a) Ge doped with In

(b) Si doped with P

Ans. *Hint :* (a) Ge is group 14 element and In is group 13 element. Therefore, an electron deficit hole is created. Thus semi-conductor is p-type.

(b) Since P is group 15 element and Si is group 14 element, there will be a free electron, thus, it is n-type semi-conductor.

Q.29. In terms of band theory, what is the difference between a conductor, an insulator and a semi-conductor ?

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

Q.30. $CdCl_2$ will introduce impurity defect if added to AgCl crystal. Explain.

Ans. Two Ag^+ ions will be replaced by one Cd^{2+} ion to maintain electrical neutrality. Thus, a hole is created at the lattice site for every Cd^{2+} ion introduced.

Q.31. The electrical conductivity of a metal decreases with rise in temperature while that of a semi-conductor increases. Explain.

Ans. In metals with increase of temperature, the kernels start vibrating at faster rate and thus offer resistance to the flow of electrons. Hence, conductivity decreases. In case of semi-conductors, with increase of temperature, more electrons can shift from valence band to conduction band. Hence conductivity increases.

Q.32. What type of substances would make better permanent magnets – ferromagnetic or ferrimagnetic? Why ?

Ans. Ferromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called domains. Each domain acts as tiny magnet and get oriented in the direction of magnetic field in which it is placed. This persists even in the absence of magnetic field.

Q.33. In a crystalline solid, the atoms A and B are arranged as follows :

(a) Atoms A are arranged in ccp array.

(b) Atoms B occupy all the *octahedral* voids and half of the *tetrahedral* voids.

What is the formula of the compound ?

Ans. No. of A (ccp) = 4

$$\text{No. of B} = \text{octahedral voids} + \frac{\text{Tetrahedral}}{2}$$

$= 4 + \frac{8}{2}$

$= 8$

A : B therefore, formula of the compound is AB_2

4 : 8

1 : 2

AB_2

Q.34. In compound atoms of element Y forms ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. What is the formula of the compound ?

Ans. No. of Y atoms per unit cell in ccp lattice = 4

No. of tetrahedral voids = 2 × 4 = 8

No. of tetrahedral voids occupied by X = 2/3 × 8 = 16/3

Therefore, Formula of the compound $= X_{16/3}Y_4$

$= X_{16}Y_{12}$

$= X_4Y_3$

Q.35. How many lattice points are there in one unit cell of the following lattices :

(a) FCC (b) BCC (c) SCC

Q.36. A cubic solid is made of two elements X and Y. Atom Y are at the corners of the cube and X at the body centres. What is the formula of the compound ?

Ans. [Hint : XY]

Q.37. Silver forms ccp lattice and X-ray studies of its crystal show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic wt. = 107.9u).

Q.38. A cubic solid is made up of two elements P and Q. Atoms of the Q are present at the corners of the cube and atoms of P at the body centre. What is the formula of the compound ? What are the co-ordination number of P and Q ?

Q.39. What happens when :

(a) CsCl crystal is heated. (Hint : Changes to NaCl type crystal)

(b) Pressure is applied on NaCl crystal. (Hint : Changes to CsCl type crystal)

SA-(II) Question (3 marks)

Q.40. The density of chromium is 7.2 g cm^{-3}. If the unit cell is a cubic with length of 289 pm, determine the type of unit cell. (Atomic mass of Cr = 52 *u* and N_A = 6.022 × 10^{23} atoms mol^{-1}).

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

Here, $Z = ?$, $a = 289 \text{ pm} = 289 \times 10^{-10}$, $M = 52 \text{ g mol}^{-1}$, $d = 7.2 \text{ g cm}^{-3}$

So, $$Z = \frac{d \times a^3 \times N_A}{M}$$

$$Z = \frac{7.2 \text{ g cm} \times \left(289 \times 10^{-10} \text{ cm}\right)^3 \times 6.022 \times 10^{23} \text{ atom mol}^{-1}}{52 \text{ g mol}^{-1}} = 2.01 \simeq 2$$

Hence type of unit cell in BCC.

Q.41. An element crystallizes in FCC structure; 200 g of this element has 4.12×10^{24} atoms. If the density of A is 7.2 g cm^{-3}, calculate the edge length of unit cell.

Q.42. Niobium crystallizes in bcc structure. If its density is 8.55 cm^{-3}, calculate its atomic radius. (Atomic mass of Niobium = 92.9 *u*, $N_A = 6.022 \times 10^{23}$ atoms mol^{-1})

Q.43. Non-stoichiometric cuprous oxide can be prepared in the laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that the substance is a p-type semiconductor ?

Q.44. The unit cell of an element of atomic mass 50 *u* has edge length 290 pm. Calculate its density. The element has bcc structure. ($N_A = 6.022 \times 10^{23}$ atoms mol^{-1})

Q.45. Calculate the density of silver which crystallizes in face centred form. The distance between nearest metal atoms is 287 pm. (Ag = 107.87 g mol^{-1}, $N_A = 6.022 \times 10^{23}$ atoms mol^{-1})

Q.46. What is the distance between Na^+ and Cl^- ions in NaCl crystal if its density is 2.165 gm cm^{-3}. NaCl crystallizes in FCC lattice.

Q.47. Analysis shows that Nickel oxide has $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} ions and Ni^{3+} ions ?

Q.48. Find the type of lattice for cube having edge length of 400 pm. Atomic weight = 60g mol^{-1} and density = 6.25 g/cc.

Q.49. Aluminium crystallizes in cubic closed pack structure. Its metallic radius is 125 pm.

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

(b) How many unit cell are there in 100 cm^3 of Aluminium ?

Q.50. Zinc oxide is white but it turns yellow on heating. Explain.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.51. A metal has cubic lattice. It is face centered cubic lattice. Edge length of lattice cell is 2 Å. The density of metal is 2.4 g cm^{-3}. How many unit cells are present in 200 g of metal ?

Q.52. A metal crystallizes as face centered cubic lattice with edge length of 450 pm. Molar mass of metal is 50 g mol^{-1}. What is the density of metal ?

Q.53. A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it ? How many of these are tetrahedral voids ?

Q.54. Copper crystallizes into FCC lattice with edge length 3.61×10^{-8} cm. Show that calculated density is in arrangement with measured value of 8.92 g/cc.

Q.55. Niobium crystallizes in bcc structure with density 8.55 g/cc. Calculate atomic radius using atomic mass *i.e.,* 93 *u*.

Q.56. The compound CuCl has FCC structure like ZnS. Its density is 3.4 g cm^{-3}. What is the length of the edge of unit cell ?

Hint : $$d = \frac{ZM}{a^3 \times N_A}$$

$$a^3 = \frac{4 \times 99}{3.4 \times 6.022 \times 10^{-23}}$$

$$a^3 = 193.4 \times 10^{-24} \text{ cm}^3$$

$$a = 5.78 \times 10^{-8} \text{ cm}$$

Q.57. If NaCl is doped with 10^{-3} mol% $SrCl_2$. What is the concentration of cation valancies ?

Q.57. The edge length of the unit cell of metal having molecular weight 75 g/mol is A° which crystallizes into cubic lattice. If the density is 2 g/cm^3, then find the radius of metal atom. ($N_A = 6.022 \times 10^{23}$ mol^{-1})

Q.58. The density of KBr is 2.75 g cm^{-3}. The length of edge of the unit cell is 654 pm. Predict the type of cubic lattice to which unit cell of KBr belongs. ($N_A = 6.022 \times 10^{23}$ mol^{-1}, Atomic mass of K = 39 g mol^{-1}, Br = 80g mol^{-1})

Hint : Calculate the value of z = 4 so it has fcc lattice.

Q.59. CsCl has bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance of CsCl.

Ans. 346.04 pm

Q.60. The radius of an iron atom is 1.42 Å. It has rock salt structure. Calculate the density of unit cell.

Ans. 5.74 g cm^{-3}

Q.61. What is the distance between Na^+ and Cl^- in a NaCl crystal if its density is 2.165 g cm^{-3} ? NaCl crystallizes in fcc lattice.

Ans. 281 pm

Q.62. Copper crystallizes with fcc unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. Atomic mass of Cu = 63.55u, $N_A = 6.022 \times 10^{23}$.

Ans. $a = 2\sqrt{2}r$, $a^3 = 4.723 \times 10^{-23}$, $d = 8.95$ g cm^{-3}

Q.63. The density of lead is 11.35 g/cm^3 and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (Atomic mass of Pb = 207 g/mol, $N_A = 6.02 \times 10^{23}$)

Ans. 174.95 pm

Q.64. Explain the following with suitable examples :

(a) Ferromagnetic substances

(b) 12-16 group compounds

(c) Paramagnetism

(d) Impurity defects

(e) Diamagnetism

Q.65. The well-known mineral fluorite is chemically calcium fluoride. In one unit of this mineral, there are $4Ca^{2+}$ and $8F^-$ ions arranged in fcc lattice. The edge of the unit cell is 5.46×10^{-8} cm. The density of the solid is 3.18 g/cm^3. Calculate Avogadro's number. (Molar mass of CaF_2 = 78.08 g/mol)

Ans. 6.03×10^{23} mol^{-1}

Q.66. Metallic magnetism has a hexagonal close-packed structure and its density is 1.74 g/cm^3. Assuming magnetism atoms to be spherical, calculate the radius of magnetism atom. (Mg = 24.3 amu)

Ans. 1.6×10^{-8} cm

VALUE BASED QUESTIONS (4 Marks)

Q.67. Radha suggested that the conductivity of the semiconductors can be increased by heating. Her friend Mira advised her to dope the semiconductor with either group 13 or group 15 elements to increase the conductivity.

(a) Explain the cause of increase in conductivity by doping.

(b) Which type of semiconductor is formed if it is doped with group 13 or group 15 elements ?

(c) What are intrinsic semiconductors ?

(d) What values are associated with the suggestion of Mira ?

Q.68. Students of class XII Chemistry wanted to prepare magnets. They have substances like iron, cobalt, nickel, CrO_2 and MnO. Kapil tried best to prepare the magnets from MnO but attempt failed. Veena suggested that except MnO, all the above mentioned substances can be used to prepare magnets.

(a) Why did Kapil fail to prepare magnet from MnO ?

(b) What values are associated with the suggestion of Veena ?

(c) Define antiferromagnetism.

(d) How can a ferromagnetic substance be made a permament magnet ?

Q.69. Vinay and Manish are provided with 50 oranges each with a tray. They are asked to arrange them in an ordered manner within 5 minutes. Vinay successfully arranged the oranges with minimum empty space but Manish does not.

(a) What type of crystal packing had Vinay attempted ?

(b) What is the % empty space that remains in such type of arrangement of oranges ?

(c) Name the values associated with the Vinay's attempt for arranging oranges.

(d) How many tetrahedral and octahedral voids are formed in the packing of 50 oranges ?

✦✦

UNIT 2

SOLUTIONS

Points to Remember

1. The component that is having more number of moles is known as solvent. Solvent determines the physical state of the solution. Water is an universal solvent.

2. Mole fraction (X) is a unitless quantity.

3. Molality (m) and mole fraction are temperature independent quantities whereas molarity decreases with increase in temperature.

4. As the temperature increases Henry's law constant, K_H increases so the lower is the solubility of the gas in the liquid.

5. 11.7% w/w Helium is added to air used by scuba divers due to its low solubility in the blood.

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

7. Azeotropes having the same composition in liquid and vapour phase and boil at a constant temperature and therefore can't be distilled.

8. Azeotropes arise due to very large deviation from Raoult's law. Maximum boiling azeotropes form when solutions exhibit negative deviation from Raoult's law whereas minimum boiling azeotropes form when solutions exhibit positive deviation from Raoult's law.

9. Relative lowering in vapour pressure is a colligative property but lowering in vapour pressure is not.

10. Van't Hoff factor (i) is the ratio of the observed value of the colligative property in solution to the theoretically calculated value of the colligative property.

    (a) A non-volatile solute undergoes dissociation, then $i > 1$.

    (b) A non-volatile solute undergoes association, then $i < 1$.

Some Important Formulae

1. Mole fraction (X)

If the number of moles of A and B are n_A and n_B respectively, the mole fractions of A and B will be

$$X_A = \frac{n_A}{n_A + n_B} \text{ and } X_B = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

2. **Molarity (M)** = $\dfrac{\text{Moles of solute}}{\text{Volume of solution in litres}} \text{mol L}^{-1}$

3. **Molality (*m*)** = $\dfrac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}} \text{mol kg}^{-1}$

4. **Parts per million (ppm)**

$$= \frac{\text{Number of parts of the compound}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

5. Raoult's law for a solution of volatile solute in volatile solvent :

$$p_A = p_A{}^0 X_A$$

$$p_B = p_B{}^0 X_B$$

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

6. Raoult's law for a solution of non-volatile solute and volatile solvent :

$$\frac{p_A{}^0 - p_A}{p_A{}^0} = iX_B = i\frac{n_B}{n_A} = i\frac{W_B \times M_A}{W_A \times M_B} \text{ (for dilute solutions)}$$

Where X_B is mole fraction of solute, *i* is van't Hoff factor and $\dfrac{p_A{}^0 - p_A}{p_A{}^0}$ is relative lowering of vapour pressure.

7. Elevation in boiling point (ΔT_b) :

$$\Delta T_b = i.K_b m$$

Where $\Delta T_b = T_b - T_b{}^0$

K_b = molal boiling point elevation constant

m = molality of solution

T_b = Boiling point of solution

T_b^0 = Boiling point of solvent

8. Depression in freezing point (ΔT_f) :

$\Delta T_f = i.K_f m$

Where $\Delta T_f = T_f^0 - T_f$

K_f = molal freezing point depression constant

m = molality of solution

T_f^0 = Freezing point of solvent

T_f = Freezing point of solution

9. Osmotic pressure (π) of a solution :

$\pi V = i\,nRT$ or $\pi = i\,CRT$

where π = osmotic pressure in bar or atm

V = volume in litres

i = van't Hoff factor

C = molar concentration in moles per litres

n = number of moles of solute

T = Temperature on Kelvin scale

$R = 0.083\ \text{L bar mol}^{-1}\ \text{K}^{-1}$

$R = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}$

10. Van't Hoff factor (i)

$$= \frac{\text{Number of particles in solution after association or dissociation}}{\text{Number of particles actually dissolved in solution}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Theoretically calculated colligative property}}$$

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

$i > 1$ For dissociation of solute

$i < 1$ For association of solute

$i = 1$ For ideal solution undergoing no association or dissociation

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What is Van't Hoff factor ?

Ans. It is the ratio of normal molecular mass to observed molecular mass. It is denoted as *i*.

i = normal molecular mass/observed molecular mass

= no. of particles after association or dissociation/no. of particles before dissociation or association

Q. 2. What is the Van't Hoff factor in $K_4[Fe(CN)_6]$ and $BaCl_2$?

Ans. 5 and 3

Q. 3. Why the molecular mass becomes abnormal ?

Ans. Due to association or dissociation of solute in given solvent.

Q. 4. Define molarity. How it is related with normality ?

Ans. N = M × Basicity or acidity

Q. 5. How molarity is related with mass percentage and density of solution ?

Ans. $M = \frac{\text{Mass\%} \times d \times 10}{M_B}$ Here *d* is density of the solution in gmL^{-1}

Q. 6. What role does the molecular interaction play in the solution of alcohol and water ?

Ans. Positive deviation from ideal behaviour.

Q. 7. What is van't Hoff factor ? How is it related with :

(a) degree of dissociation **(b) degree of association**

Ans. (a) $\alpha = i - 1/n - 1$ (b) $\alpha = i - 1/1/n - 1$

Q. 8. Why NaCl is used to clear snow from roads ?

Ans. It lowers freezing point of water.

Q. 9. Why the boiling point of solution is higher than pure liquid ?

Ans. Due to lowering in vapour pressure.

Q.10. Out of 1 M and 1 m aqueous solution which is more concentrated ?

Ans. 1 M as density of water is 1 gm/ml.

Q.11. Henry law constant for two gases are 21.5 and 49.5 atm, which gas is more soluble ?

Ans. K_H is inversely proportional to solubility.

Q.12. Define azeotrope. Give an example of maximum boiling azeotrope.

Q.13. Calculate the volume of 75% of H_2SO_4 by weight (d = 1.8 gm/ml) required to prepare 1 L of 0.2 M solution.

Hint :
$$M_1 = \frac{\text{Mass}\ \% \times d \times 10}{98}$$
$$M_1V_1 = M_2V_2$$
$$= 14.5 \text{ ml}$$

Q.14. Why water cannot be completely separated from aqueous solution of ethyl alcohol ?

Ans. Due to formation of azeotrope at (95.4%).

Q.15. What is the molarity of pure water ?

Ans. 55.5

Q.16. Calculate the moles of PO_4^{-3} present in 4L of 10^{-5} M$Ca_3(PO_4)_2$.

Ans. 8×10^{-5}

Q.17. Why anhydrous salts like NaCl or $CaCl_2$ are used to clear snow from roads on hills ?

Hint : They depress freezing point of water.

Q.18. What is the effect on boiling and freezing point of a solution on addition of NaCl ?

Hint : Boiling point increases and freezing point decreases.

Q.19. Out of M and *m*, which is better concentration term and why ?

Hint : m, it is independent of temperature change.

Q.20. Why osmotic pressure is considered as colligative property ?

Hint : It depends upon number of moles of solute present in solution.

Q.21. Liquid A and B on mixing produce a warm solution. Which type of deviation does this solution show ?

Hint : – ve deviations

Q.22. Give an example of a compound in which hydrogen bonding results in the formation of a dimer.

Hint : Carboxylic acids or other example

Q.23. What role does the molecular interaction play in solution containing chloroform and acetone ?

Hint : H-bonding formed, results in negative deviation from Raoult's law.

SHORT ANSWER TYPE QUESTIONS (2 Marks)

Q. 1. Molecular weight of a solute X is greater than that of solute Y. Their equal weights are dissolved separately in the equal quantity of same solvent. Which solution will show greater relative lowering of vapour pressure and why ?

Q. 2. Out of the following three solutions, which has the highest freezing point and why ?

(a) 0.1 M urea (b) 0.1M $BaCl_2$ (c) 0.1M Na_2SO_4

Q. 3. Which of the following solutions have highest boiling point and why ?

(a) 1M glucose (b) 1M KCl (c) 1M aluminium nitrate

Q. 4. Equal moles of liquid P and Q are mixed. What is the ratio of their moles in the vapour phase ? Given that $P_P^0 = 2 \times P_Q^0$.

Q. 5. On mixing liquid X and Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution ? What change in temperature would you observe after mixing liquids X and Y ?

Q. 6. Explain the significance of Henry's constant (K_H). At the same temperature, hydrogen is more soluble in water than helium. Which of them will have higher value of K_H and why ?

Q. 7. How many grams of KCl should be added to 1 kg of water to lower its freezing point to – 8.0ºC ? (K_f = 1.86 K kg/mol)

Ans. Since KCl dissociate in water completely, $i = 2$.

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

$$m = \frac{\Delta T_f}{iK_f}$$

$$m = \frac{8}{2 \times 1.86}$$

$$= 2.15 \text{ mol/kg}$$

Grams of KCl = 2.15 × 74. = 160.2 g/kg

Q.8. With the help of diagram, show the elevation in boiling point colligative properties ?

Q. 9. What do you mean by colligative properties ? Which colligative property is used to determine molar mass of polymer and why ?

Q.10. Define reverse osmosis. Write its one use.

Ans. Desalination of water.

Q.11. Why does an azeotropic mixture distills without any change in composition ?

Hint : It has same composition of components in liquid and vapour phase.

Q.12. Under what condition Van't Hoff factor is :

(a) equal to 1 ? (b) less than 1 ? (c) more than 1 ?

Q.13. If the density of some lake water is 1.25 gm/ml and contains 92 gm of Na^+ ions per kg of water, calculate the molality of Na^+ ion in the lake.

Ans. $$n = \frac{92}{23} = 4$$

$$m = \frac{4}{1} = 4m$$

Q.14. An aqueous solution of 2% non-volatile exerts a pressure of 1.004 Bar at the normal boiling point of the solvent. What is the molar mass of the solute ?

Hint : $$\frac{P^0{}_A - P_A}{P^0{}_A} = \frac{w_B \times m_A}{m_B \times w_A}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{m_B \times 98}$$

$$m_B = 41.35 \text{ gm/mol}$$

Q.15. Why is it advised to add ethylene glycol to water in a car radiator in hill station ?

Hint : Anti-freeze.

Q.16. Calculate the molarity of pure water (d = 1 g mL^{-1}).

Ans. Desity of water = 1 g mL^{-1}

Mass of 1000 ml of water $= V \times d$

$= 1000 \text{ mL} \times 1 \text{ gm}^{-1}$

$= 1000$ g

Moles of water $= \frac{1000}{18} = 55.55$ mol

Now, mole of H_2O present in 1000 mL or 1 L of water.

So, molarity = 55.55M

Q.17. Define Henry's law. Give their two application.

Q.18. The dissolution of ammonium chloride in water is endothermic process. What is the effect of temperature on its solubility ?

Ans. Since dissolution of NH_4Cl in water is endothermic process, its solubility increases with rise in temperature (*i.e.,* Le-Chatelier process).

Q.19. Two liquids A and B boil at 145ºC and 190ºC respectively. Which of them has higher vapour pressure at 80ºC ?

Ans. Lower the boiling point more volatile is the respective compound. Therefore, liquid A will have higher vapour pressure at 80ºC.

Q.20. Why is liquid ammonia bottle first cooled in ice before opening it ?

Ans. At room temperature, the vapour pressure of liquid ammonia is very high. On cooling vapour pressure decreases, therefore the liquid ammonia will not splash out.

Q.21. Which colligative property is preferred for the molar mass determination of macromolecules ?

Ans. Osmotic pressure measurement is preferred for molar mass determination because :

(a) even in dilute solution the osmotic pressure values are appreciably high and can be measured accurately.

(b) osmotic pressure can be measured at room temperature.

Q.22. Define osmotic pressure determined from the measurement of osmotic pressure of a solution.

Ans. **Osmotic pressure :** The excess pressure applied to solution side to stop the process of osmosis is known as osmotic pressure.

$$\pi \propto C$$

$$\pi \propto T$$

$$\pi \propto CT$$

$$\pi = CRT$$

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

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

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

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Determine the amount of $CaCl_2$ dissolved in 2.5L at 27ºC such that its osmotic pressure is 0.75 atm at 27ºC. (*i* for $CaCl_2$ = 2.47)

Ans. For $CaCl_2$, $i = 2.47$

$$\pi = iCRT$$

$$= i\frac{n_B}{V} \times RT$$

$$0.75 = \frac{2.47 \times n_B \times 0.082 \times 300}{2.5}$$

$$n_B = \frac{0.75 \times 2.5}{2.47 \times 0.082 \times 300}$$

$$n_B = 0.0308 \text{ mol}$$

$$\text{Amount} = 0.0308 \text{ mol} \times 111\text{g mol}^{-1}$$

$$= 3.418\text{g}$$

Q. 2. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25ºC assuming that it is completely dissociated.

Ans. If K_2SO_4 is completely dissociated,

$$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$$

$$i = 3$$

$$\text{Mol mass of } K_2SO_4 = 2 \times 39 + 32 + 4 \times 16 = 174 \text{ g mol}^{-1}$$

$$\pi = iCRT$$

$$= i\frac{W_B \times RT}{M_B \times V}$$

$$= \frac{3 \times 25 \times 10^{-3} \times 0.082 \times 298}{174 \times 2.0}$$

$$= 5.27 \times 10^{-3} \text{ atm}$$

Q. 3. If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Ans. K_{sp} of CuS $= 6 \times 10^{-16}$

If S is the solubility, then

$$CuS \rightarrow Cu^{2+} + S^{2-}$$

$$[Cu^{2+}] = S, [S^{2-}] = S$$

$$K_{sp} = [Cu^{2+}][S^{2-}]$$

$$= S \times S = S^2$$

$$\text{Solubility } S = \sqrt{K_{sp}} = \sqrt{6\times10^{-6}}$$

$$= 2.45 \times 10^{-8} \text{ M}$$

Highest molarity $= 2.45 \times 10^{-8}$ M

Q. 4. Suggest the most important type of intermolecular attractive interaction in the following pairs :

(a) n-hexane and n-octane **(b) I_2 and CCl_4**

(c) $NaClO_4$ and water

Ans. (a) Vander Waals interaction

(b) Vander Waals interaction

(c) Ion-dipole interaction

Q. 5. The vapour pressure of water is 12.3 Kpa at 300K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Ans. Mole fraction of solute $= \dfrac{1}{1+\dfrac{1000}{18}} = 0.0177$

$$\frac{P^0 - P_A}{P^0} = 0.0177$$

$$\frac{12.3 - P_A}{12.3} = 0.0177$$

$$P_A = 12.08 \text{ Kpa}$$

Q. 6. 6.90M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the KOH solution. (Molar mass of KOH = 56 g mol^{-1})

Ans. Mass of KOH = 30 g

$$M = \frac{n_B}{V(\text{ml})} \times 1000$$

$$= \frac{W_B}{M_B \times V(\text{ml})} \times 1000 = \frac{30}{56 \times V} \times 1000$$

$$6.90 = \frac{30 \times 1000}{56 \times V}$$

$$V = \frac{30 \times 1000}{56 \times 6.90} = 81.43 \text{ mL}$$

$$\text{D} = \frac{\text{M}}{\text{V}}$$

$$= \frac{100}{81.43} = 1.28 \text{ g mL}^{-1}$$

Q. 7. An anti-freeze solution is prepared from 222.6 g of ethylene glycol $C_2H_4(OH)_2$ and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g mL^{-1}, what will be the molarity of the solution ?

Ans. M_B of $C_2H_4(OH)_2$ = 62 g mol^{-1}

$$\text{Molality} = \frac{n_B}{W_A} \times 1000 = \frac{W_B}{M_B \times W_B} \times 1000 = \frac{222.6 \times 1000}{62 \times 200}$$

$$= 17.95\text{m}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

So, $$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{422.6}{1.072} = 394.22 \text{ ml}$$

$$\text{M} = \frac{n_B}{\text{V}} \times 1000$$

$$= \frac{222.6}{394.22 \times 62} \times 1000 = 9.11\text{M}$$

Q. 8. What would be the molar mass of compound if 6.21 g of it is dissolved in 24.0 g of $CHCl_3$ from a solution that has a boiling point of 68.04ºC. The boiling point of pure chloroform is 61.7ºC and the boiling point elevation constant K_b for chloroform is 3.63ºC/m.

Ans. Elevation in boiling point ΔT_b = 68.04 – 61.7 = 6.31ºC

Mass of substance W_B = 6.21 g

Mass of CHCl3 W_A = 24.0 g

K_B = 3.63 ºC/m

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A} = \frac{3.63 \times 6.21 \times 1000}{6.34 \times 24}$$

$$= 148.15 \text{ g mol}^{-1}$$

Q. 9. A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42ºC while pure water boils at 100ºC. What mass of glycerol was dissolved to make the solution ? (K_b = 0.512 K kg mol^{-1})

Ans. 37.73 g

Q.10. 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 ? (Kb for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.1 K)

Ans. 373.202 K

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (a) Define Raoult's law of binary solution containing non-volatile solute in it.

(b) On dissolving 3.24 g of sulphur in 40 g of benzene, boiling point of solution was higher than that of benzene by 0.81K (K_b = 2.53 K kg mol^{-1}). What is molecular formula of sulphur ? (Atomic mass s = 32 g mol^{-1})

Ans. (a) At a given temperature, the vapour pressure of a solution containing non-volatile solute is directly proportional to the mole fraction of the solvent.

(b)
$$M_B = \frac{K_b \times W_b \times 1000}{\Delta T_b \times W_A} = \frac{2.53 \times 3.24 \times 10^3}{0.81 \times 40}$$

$$= 253 \text{ g mol}^{-1}$$

Let the molecular formula of sulphur = S_x

Atomic mass of sulphur = 32

Molecular mass = $32 \times x$

$32x = 253$

$x = 7.91 \approx 8$

Molecular formula of sulphur = S_8

Q. 2. (a) Outer shells of two eggs are removed. One of the egg is placed in pure water and the other is placed in saturated solution of NaCl. What will be observed and why ?

(b) A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 ml of water has an osmotic pressure of 0.335 ton at 25ºC. Assuming the gene fragment is a non-electrolyse, determine the molar mass.

Ans. (a) In pure water the egg swells and in saturated solution of NaCl it will shrinks.

(b) Mass of gene fragment $= 8.95$ mg

$= 8.95 \times 10^{-3}$ g

Volume of water $= 35.0$ ml $= 35 \times 10^{-3}$ L

$\pi = 0.335$ ton $= 0.335/760$ atm

Temp $= 25 + 273 = 298$ K

$$\pi = \frac{W_B RT}{M_B \times V}$$

$$\frac{0.335}{760} = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298}{M_B \times 35 \times 10^{-3}}$$

$$M_B = 141933 \text{ g mol}^{-3}$$

Q. 3. (a) Define van't Hoff factor.

(b) Calculate the freezing point depression expected for 0.0711M aqueous solution of Na_2SO_4. If this solution actually freezes at – 0.320°C, what would be the value of van't Hoff factor ? (K_f = 1.86°C mol^{-1})

Ans. (a) **Van't Hoff factor :** It is the ratio of the normal molar mass to the observed molar mass of the solute.

(b) $\Delta T_f = K_f \times M$

$\Delta T_f = 1.86 \times 0.0711 = 0.132$

Observed freezing point $= 0 - (-0.320) = 0.320$°C

$$i = \frac{\text{Observed freezing point}}{\text{Calculate freezing point}}$$

$$= \frac{0.320}{0.132} = 2.42$$

Q. 4. (a) What is the value of *i* when solute is associated and dissociated ?

(b) Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184, K_f = 1.86 K kg mol^{-1})

Ans. (a) $i < 1$ when solute is associated and

$i > 1$ when solute is dissociated.

(b) $$m = \frac{n_g \times 1000}{W_A(g)}$$

$$= \frac{W_B \times 1000}{M_B \times W_A} = \frac{10.50 \times 1000}{184 \times 200} = 0.2853\text{M}$$

$MgBr_2$ ionizes as $MgBr_2 \rightarrow Mg^{2+} + 2Br^-$

$$i = 3$$

$$\Delta T_f = i \times K_f \times M$$

$$= 3 \times 1.86 \times 0.2855$$

$$= 1.59$$

Freezing point $= 0 - 1.59°C = - 1.59°C$

Q. 5. (a) What is the value of *i* for $Al_2(SO_4)_3$ when it is completely dissociated ?

(b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250 g of water. (K_b = 0.512 K kg mol^{-1} and molar mass of NaCl = 58.44 g mol^{-1})

Ans. (a) $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

$$i = 5$$

(b)

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

$NaCl \rightarrow Na^+ + Cl^-$

$$i = 2$$

$$\Delta T_b = \frac{2 \times 0.512 \times 1000 \times 15}{250 \times 58.44}$$

$$= 1.05$$

Boiling point of solution = 100 + 1.05

= 101.05°C

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Sauba divers when come towards the surface, pressure gradually decreases resulting in release of dissolved gases leading to formation of bubbles of N_2 gas in the blood which block the capillaries and thus bends are created. To avoid bends and toxic effect of high concentration of N_2 gas, the air is diluted with helium.

After the above passage, answer the following :

(a) Why is the harmful condition of bends overcome by the use of helium ?

(b) Which law is used to calculate the concentration of gases in solution ?

(c) Mention the value associated with providing divers air diluted with helum.

(d) Which gas has less value of K_H , O_2 or He, and why ?

Q. 2. Ram takes an open pan to cook vegetables at a hill station while Shyam cooked the same in a pressure cooker at the same place.

(a) Define normal boiling point of a liquid.

(b) Explain the reason who will cook vegetables faster.

(c) Mention the reason for delay in cooking.

(d) Which value is learnt by the student in the process of cooking food in pressure cooker ?

Q. 3. Sneha's grandmother lives in Manali. In winter, there is a lot of snow in front of the house. She asked Sneha to clear the snow. Sneha added NaCl to snow to clear it.

(a) Why Sneha does so ?

(b) Is the addition of $Ca(NO_3)_2$ a better choice than NaCl ? If yes, why ?

(c) What is the value in Sneha's thinking ?

(d) Define molal freezing point, depression constant, K_f.

Q. 4. Ira Singh, a student of class XII Chemistry stated that normal saline solution having 0.9% (mass/volume) NaCl is isotonic with the fluid inside the cell. Therefore, it is safe to inject normal saline solution intravenously.

(a) Define isotonic solutions. What would happen if the concentration of saline solution is (a) more, (b) less than 0.9% (mass/volume) NaCl ?

(b) What values are associated with the statement of Ira Singh ?

✧✧

UNIT 3

ELECTROCHEMISTRY CONCEPTS

Points to Remember

Electrochemistry may be defined as the branch of chemistry which deals with the quantitative study of inter-relationship between chemical energy and electrical energy and inter-conversion of one form into another relationships between electrical energy taking place in redox reactions.

A cell is of two types :

I. Galvanic cell

II. Electrolytic cell

In Galvanic cell, the chemical energy of a spontaneous redox reaction is converted into electrical work.

In Electrolytic cell, electrical energy is used to carry out a non-spontaneous redox reaction.

1. Conductivity (*k*) :

$$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

where R is Resistance, l/A = cell constant (G*) and ρ is resistivity.

2. Relation between *k* and Λ_m

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

where Λ_m is molar conductivity, k is conductivity and C is molar concentration.

Kohlrausch's law :

(a) In general, if an electrolyte on dissociation give y_+ cations and γ_- anions, then its limiting molar conductivity (Λ^o_m) is given by

$$\Lambda^o_m = \gamma_+ {}^o_+ + \gamma_- {}^o_-$$

Here, ${}^o_+$ and ${}^o_-$ are the limiting molar conductivities of cation and anion respectively and v_+ and v_- are the number of cations and anions furnished by one formula unit of the electrolyte.

(b) Degree of dissociation (α) is given by :

$$\alpha = \frac{\Lambda^{c}_{m}}{\Lambda^{o}_{m}}$$

Here, Λ^{c}_{m} = is molar conductivity at the concentration C and Λ^{o}_{m} is limiting molar conductivity of the electrolyte.

(c) Dissociation constant (K) of weak electrolyte :

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\frac{\Lambda^{c}_{m}}{\Lambda^{o}_{m}}\right)^2}{\left(1-\frac{\Lambda_{m}}{\Lambda^{o}_{m}}\right)}$$

Dry cell :

At anode (Oxidation)

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

At cathode (Reduction)

$$2NH_4^{+} + 2MnO_2 + 2e^{-} \rightarrow 2MnO\,(OH) + 2NH_3$$

Overall $Zn\,(s) + 2NH_4^{+} + 2MnO_2 \rightarrow Zn^{2+} + 2MnO\,(OH) + 2NH_3$

Mercury cell :

At anode (Oxidation)

$$Zn\,(Hg) + 2OH^{-} \rightarrow ZnO\,(s) + H_2O + 2e^{-}$$

At cathode (Reduction)

$$HgO\,(s) + H_2O + 2e^{-} \rightarrow Hg\,(l) + 2OH^{-}$$

Overall $Zn\,(Hg) + HgO\,(s) \rightarrow ZnO\,(s) + Hg\,(l)$

Lead storage cell

At anode (Oxidation)

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

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$$

At cathode (Reduction)

$$PbO_2 + 4H^{+} + 2e^{-} \rightarrow Pb^{2+} + 2H_2O$$

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

Overall

$$Pb(s) + PbO_2\,(s) + 2H_2SO_4\,(aq) \underset{\text{Recharging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O_{(l)}$$

3. **Nernst Equation for electrode reaction :**

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

$$E = E^\theta - \frac{2.303RT}{nF}\log\frac{1}{\left[M^{n+}\right]} = E^\theta - \frac{0.059}{n}\log\frac{1}{\left[M^{n+}\right]}$$

The cell potential of electrochemical reaction : $aA + bB \xrightarrow{ne^-} cC + dD$ is given by :

$$E_{cell} = E^\theta{}_{cell} - \frac{2.303RT}{nF}\log[Q_c] = E^\theta - \frac{0.059}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

4. **Relation between $E^{q}{}_{cell}$ and equilibrium constant (K_c) :**

$$E^\theta{}_{cell} = \frac{2.303RT}{nF}\log K_c = \frac{0.059}{n}\log K_c$$

5. **$\Delta G^0 = -\, nF\, E^0{}_{cell}$**

where ΔG^0 = standard Gibbs energy change and nF is the number of Faradays of charge passed. $E^0{}_{cell}$ is standard cell potential.

$$\mathbf{\Delta G^0 = -\,2.303\;RT\;\log K_c}$$

Corrosion of metals is an electrochemical phenomenon.

In corrosion, metal is oxidized by loss of electrons to oxygen and formation of oxides.

At anode (Oxidation) :

$$2Fe\,(s) \rightarrow 2Fe^{2+} + 4e^-$$

At cathode (Reduction) :

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

Atmospheric oxidation :

$$2Fe^{2+}\,(aq) + 2H_2O\,(l) + \tfrac{1}{2}O_2\,(g) \rightarrow Fe_2O_3\,(s) + 4H^+\,(aq)$$

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What is the effect of temperature on molar conductivity ?

Ans. Molar conductivity of an electrolyte increases with increase of temperature.

Q. 2. Why is it not possible to measure single electrode potential ?

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

Q. 3. Name the factor on which emf of a cell depends.

Ans. Emf of a cell depends on following factors :

(a) Nature of reactants

(b) Concentration of solution in two half cells

(c) Temperature

Nickel-Cadmium cell :

At anode : $\mathrm{Cd\ (s) + 2OH^- \underset{Recharging}{\overset{Discharging}{\rightleftharpoons}} CdO\ (s) + 2}e^-$

At cathode : $\mathrm{NiO_2 + 2H_2O + 2}e^- \underset{\mathrm{Recharging}}{\overset{\mathrm{Discharging}}{\rightleftharpoons}} \mathrm{2Ni(OH)_2 + 2OH^-}$

Overall : $\mathrm{Cd\ (s) + NiO_2 + 2H_2O \underset{Recharging}{\overset{Discharging}{\rightleftharpoons}} CdO\ (s) + 2Ni(OH)_2}$

Fuel cell :

At anode : $\mathrm{2H_{2(g)} + 2OH^- \rightarrow 2H_2O + 2}e^-$

At cathode : $\mathrm{O_{2\,(g)} + 2H_2O + 4}e^- \rightarrow \mathrm{4OH^-}$

Overall : $\mathrm{2H_{2\,(g)} + O_2 \rightarrow 2H_2O\ (}l\mathrm{)}$

$\mathrm{E^o_{cell} = 0.9V}$

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

Ans. Temperature increases, electrical conductance decreases.

Q. 5. What is the effect of temperature on the electrical conductance of electrolyte ?

Ans. Temperature increases, electrical conductance increases.

Q. 6. What is the relation between conductance and conductivity ?

Ans. $$\Lambda_m^c = \frac{k}{\mathrm{C}}$$

Q. 7. What is the Debye-Huckel-Onsager equation ?

Ans. $\Lambda_m^c = \Lambda_m^\circ - \mathrm{A}\sqrt{\mathrm{C}}$

Q. 8. Reduction potentials of 4 metals A, B, C and D are – 1.66 V, + 0.34 V, + 0.80 V and – 0.76 V. What is the order of their reducing power and reactivity ?

Ans. A > D > B > C

Q. 9. Why does a dry cell become dead even if it has not been used for a long time ?

Ans. NH_4Cl is acidic in nature. It corrodes zinc container.

Q.10. Write the overall reaction taking place in rusting.

Ans. $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

Q.11. Write the reaction taking place in the cell : $Al/Al^{3+} || Cu^{2+}/Cu$

Ans. $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$

Q.12. Why Na cannot be obtained by the electrolysis of aqueous NaCl solution ?

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

Q.13. What is the use of platinum foil in the hydrogen electrode ?

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

Q.14. Why Λ_m^o for CH_3COOH cannot be determined experimentally ?

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

Q.15. Why is it necessary to use a salt bridge in a galvanic cell ?

Ans. To complete the inner circuit and to maintain electrical neutrality of the electrolytic solutions of the half cells.

Q.16. Why does mercury cell gives a constant voltage throughout its life ?

Ans. This is because the overall cell reaction does not have any ionic can concentration in it.

Q.17. What is the role of $ZnCl_2$ in a dry cell ?

Ans. $ZnCl_2$ combines with the NH_3 produced to form a complex salt $[Zn(NH_3)_2]Cl_2$.

Q.18. Why does the conductivity of a solution decrease with dilution ?

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

Q.19. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methane and methanol.

Q.20. How does the pH of Al-NaCl solution be affected when it is electrolysed ?

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

Q.21. Which reference electrode is used to measure the electrode potential of other electrodes.

Ans. SHE, whose electrode potential is taken as zero.

Q.22. Out of zinc and tin, which one protects iron better even after cracks and why ?

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

Q.23. Define corrosion. What is the chemical formula of rust ?

Ans. Corrosion is the slow eating away of the surface of the metal due to attack of atmospheric gases. $Fe_2O_3.xH_2O$.

Q.24. What is the EMF of the cell when the cell reaction attains equilibrium ?

Ans. Zero.

Q.25. What is the electrolyte used in a dry cell ?

Ans. A paste of NH_4Cl.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

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

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

Ans. Nernst equation is :

$$E_{M^{n+}/M} = E_{M^{n+}/M} - \square\,\frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

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

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

(b) By increasing the temperature.

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

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

[Given : E^{θ}_{cell} = 3.17 V]

Ans. $n = 2$

The Nernst equation for the cell is :

$$E = E^{\theta} - \frac{0.059}{2}\log\frac{\left[Mg^{2+}\right]}{\left[Ag^{+}\right]^{2}}$$

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

$$= 3.17 - 0.21 = 2.96V$$

Q. 3. Suggest a way to determine the Λ_m^{o} value of water.

Ans. $\Lambda_m^{\circ}\left(H_2O\right) = \Lambda_{m\ H^+}^{\circ} + \Lambda_{m\ OH^-}^{\circ}$

It can be determine from the value of Λ_m^{o} (HCl), Λ_m^{o} (NaOH) and Λ_m^{o} (NaCl). Then,

$$\Lambda_m^{o}(H_2O) = \Lambda_m^{o}(HCl) + \Lambda_m^{o}(NaOH) - \Lambda_m^{o}(NaCl)$$

Q. 4. How much electricity in term of Faraday is required to produce 40 gram of Al from Al_2O_3 ? (Atomic mass of Al = 27 g/mol)

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

27 gram of Al require electricity = 3F

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

$= 4.44$ F

Q. 5. Predict the product of electrolysis of an aqueous solution of $CuCl_2$ with an inert electrode.

Ans. $CuCl_2(s) + Aq \rightarrow Cu^{2+} + 2Cl^{-}$

$$H_2O \rightarrow H^{+} + OH^{-}$$

At cathode (Reduction) : Cu^{2+} will be reduced in preference to H^+ ions.

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

At anode (Oxidation) : Cl^- ions will be oxidized in preference to OH^- ions.

$$Cl^{-} \rightarrow \tfrac{1}{2}Cl_2 + 1e^{-}$$

Thus, Cu will be deposited at cathode and Cl_2 will be liberated at anode.

Q. 6. Calculate Λ_m° for $CaCl_2$ and $MgSO_4$ from the following data :

$\Lambda_{m\left(Ca^{2+}\right)}^{\circ}$ **= 119.0, Mg^{2+} = 106.0, Cl^- = 76.3 and SO_4^{2-} = 160.05 $cm^2\ mol^{-1}$**

Ans. $$\overset{\circ}{\Lambda}_{m(\mathrm{CaCl_2})} = \overset{\circ}{\Lambda}_{m(\mathrm{Ca^{2+}})} + 2\overset{\circ}{\Lambda}_{m(\mathrm{Cl^-})}$$

$$= 119 + (2 \times 76.3) = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\overset{\circ}{\Lambda}_{m(\mathrm{MgSO_4})} = \overset{\circ}{\Lambda}_{m(\mathrm{Mg^{2+}})} + 2\overset{\circ}{\Lambda}_{m(\mathrm{SO_4{}^{2-}})}$$

$$= 106 + 160 = 266 \text{ S cm}^2 \text{ mol}^{-1}$$

Q. 7. If $\overset{\circ}{\Lambda}_m$ for $AgNO_3$, KCl and KNO_3 are 133.4, 149.9 and 144.9 S cm² mol⁻¹, calculate $\overset{\circ}{\Lambda}_m$ for AgCl.

Ans. 138.4 S cm^2 mol^{-1}

Q. 8. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

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

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

$$E = 0 - \frac{0.0591}{1} \times \text{pH}$$

$$E = -\,0.0591 \times 10$$

$$E = -\,0.591\text{V}$$

Q. 9. If a current of 0.5 amp flows through a metallic wire for 2 hours, how many electrons would flow through the wire ?

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

96500 Coulombs are equal to $6.022 \times 10^{23} e^-$

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

Q.10. How much electricity is required in Coulomb for the oxidation of 1 mole of FeO to Fe_2O_3 ?

Ans. $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$

So, 1F = 1 × 96500 C = 96500 C

Q.11. The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm-1. Calculate molar conductivity.

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

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

Q.12. Define conductivity and molar conductivity for a solution of an electrolyte.

Ans. Conductivity is defined as ease with which current flows through electrolyte. It is reciprocal of specific resistance. Molar conductivity is conductance of all the ions produced by one mole of electrolyte when electrodes are at unit distance apart and have sufficient area of cross-section to hold electrolyte.

Q.13. The resistance of conductivity cell containing 0.001M KCl solution at 298K is 1500Ω. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3} S cm^{-1}.

Ans. Cell constant = Conductivity × Resistance

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

Q.14. Indicate the reactions which take place at cathode and anode in fuel cell.

Ans. At cathode : $O_2\ (g) + 2H_2O + 4e^- \rightarrow 4OH^-\ (aq)$

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

The overall reaction is : $2H_2\ (g) + O_2\ (g) \rightarrow 4H_2O\ (l)$

Q.15. Explain Kohlrausch's law of independent migration of ions.

Ans. It states that at infinite dilution, molar conductivity of an electrolyte is equal to sum of contributions due to cation as well as anion.

$$\Lambda^{\infty}_{m(\text{Na}_2\text{SO}_4)} = 2\Lambda^{\circ}_{m\left(\text{Na}^+\right)} + \Lambda^{\infty}_{m\left(\text{SO}_4{}^{2-}\right)}$$

Q.16. Write the electrode reactions for anode and cathode in a mercury cell.

Ans. At anode : $Zn\ (amalgam) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

At cathode : $HgO\ (s) + H_2O\ (l) + 2e^- \rightarrow Hg\ (l) + 2OH^-\ (aq)$

The overall reaction is : $Zn\ (amalgam) + HgO\ (s) \rightarrow ZnO\ (s) + Hg\ (l)$

Q.17. The standard reduction potential for the Zn^{2+} (aq)/Zn (s) half cell is – 0.76V. Write the reactions occurring at the electrodes when coupled with standard hydrogen electrode (SHE).

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

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

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

Q.18. Calculate the electrode potential of a copper wire dipped in 0.1M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 Volt.

Ans. The electrode reaction written as reduction potential is

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

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

Q.19. Two metals A and B have reduction potential values – 0.76 V and + 0.34 V respectively. Which of these will liberate H_2 from dil. H_2SO_4 ?

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

Q.20. How does conc. of sulphuric acid change in lead storage battery when current is drawn from it ?

Ans. Concentration of sulphuric acid decreases.

Q.21. What type of a battery is lead storage cell ? Write the anode and cathode reaction and overall reaction occurring in a lead storage battery during discharging and recharging of cell.

Ans. It is a secondary cell.

Anode reaction : $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode reaction : $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

$$Pb\,(s) + PbO_2\,(s) + 2H_2SO_4 \underset{\text{Recharging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O\,(l)$$

Q.22. Why does the cell potential of mercury cell remain constant throughout its life ?

Ans. This is because the overall cell reaction does not involve any ion in the solution whose concentration changes during its life time.

Q.23. Why is alternating current used for measuring resistance of an electrolytic solution ?

Ans. The alternating current is used to prevent electrolysis so that the concentration of ions in the solution remains constant.

Q.24. Consider a cell given below :

$$\mathbf{Cu|Cu^{2+} \,||\, Cl^{-1}|Cl_2\,(Pt)}$$

Write the reaction that occur at anode and cathode of the cell

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

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

Q.25. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

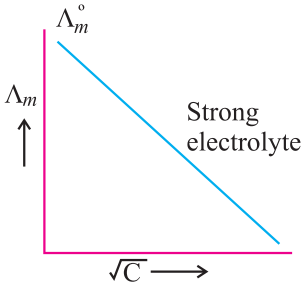
Ans. Methane and Ethane.

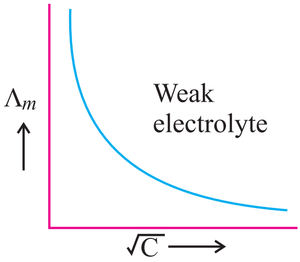
Q.26. E^θ values of MnO_4^-, Ce^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidizing agent.

Ans. $Cl_2 < MnO_4^- < Ce^{4+}$

Q.27. Draw a graph between Λ°_{m} and $\sqrt{C}$ for strong and weak electrolyte.

Ans.





Q.28. The conductivity of 0.02M solution of NaCl is 2.6×10^{-2} S cm^{-1}. What is its molar conductivity ?

Ans.

$$k = 2.6 \times 10^{-2} \text{ S cm}^{-1}$$

$$C = 0.02\text{M}$$

$$\Lambda_m = \frac{k \times 1000}{C(M)}$$

$$= \frac{2.6 \times 10^{-2} \times 1000}{0.02}$$

$$= \frac{26 \times 100}{0.02 \times 100} = \frac{26 \times 10^2}{2}$$

$$= 13 \times 10^2 \text{ S cm mol}^{-1}$$

Q.29. Give products of electrolysis of an aqueous solution of $AgNO_3$ with silver electrode.

Ans. At anode : $Ag(s) \rightarrow Ag^+ + e^-$

At cathode : $Ag^+ + e^- \rightarrow Ag(s)$

SHORT ANSWER-II TYPE QUESTIONS

Q. 1. A solution of $CuSO_4$ is electrolysed for 10 mins. with a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

Ans.

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

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

$$Q = I \times t$$

$$= 1.5 \times 600 = 900 \text{ C}$$

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

2F amount of electricity deposit copper = 63.5 g

$$900 \text{ C amount of electricity deposit copper} = \frac{63.5\times900}{2\times96500}$$

$$= 0.296 \text{ g}$$

Q. 2. Depict the galvanic cell in which the reaction

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

takes place. Further show :

(a) Which of the electrode is negatively charged ?

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

(c) Individual reaction at each electrode.

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

(a) Zn electrode (anode)

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

(c) At anode :

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

At cathode :

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

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

Ans.

$$\text{Cell constant} = k \times R$$

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

$$= 0.219 \text{ cm}^{-1}$$

Q. 4. Predict the products of electrolysis in each of the following :

(a) An aqueous solution of $AgNO_3$ with platinum electrodes.

(b) An aqueous solution of $CuCl_2$ with Pt electrodes.

Ans. (a) At anode (Oxidation)

$$4OH^{-} - 4e^{-} \rightarrow 2H_2O + O_2$$

At cathode (Reduction)

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

(b) At anode (Oxidation)

$$Cl^{-} - e^{-} \rightarrow Cl\ (g)$$

$$Cl + Cl \rightarrow Cl_2$$

At cathode (Reduction)

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

Q. 5. The standard reduction potential for Cu^{2+}/Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}.

Ans. $\text{pH} = 14$

$[H^+] = 10^{-14}$ $\{\because \text{pH} = -\log [H^+]\}$

$K_w = [H^+][OH^-]$

$$[OH^-] = \frac{k_w}{H^+} = \frac{10^{-14}}{10^{-14}} = 1$$

$$Cu(OH)_2 \rightarrow Cu^{2+} + 2\ OH^-$$

$$K_{sp} = [Cu^{2+}][OH^-]^2$$

$$1 \times 10^{-19} = [Cu^{2+}](1)^2$$

$$[Cu^{2+}] = 1 \times 10^{-19}$$

For the cell reaction,

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

$$E = E^0 - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log \frac{1}{1 \times 10^{-19}}$$

$$= 0.34 - \frac{0.059}{2} \times 19 = -0.22\ V$$

Q. 6. Determine the values of equilibrium constant K_c and ΔG^θ for the following reaction :

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

Ans. $\Delta G^\theta = -nFE^\theta_{cell}$

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

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

$\Delta G^\theta = -2 \times 1.05 \times 96500$

$= -202.650\ kJ$

$\Delta G^\theta = -RT \ln K_c$

$$\ln K_c = -\frac{\Delta G^\theta}{RT} = \frac{-202.650\times10^3}{8.314\times298}$$

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

Q. 7. The K_{sp} for AgCl at 298 K is 1.0×10^{-10}. Calculate the electrode potential for Ag^+/Ag electrode immersed in 1.0M KCl solution. Given $E^\theta_{Ag^+/Ag} = 0.80$ V.

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

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

$$[Cl^-] = 1.0 \text{ M}$$

$$[Ag^+] = \frac{k_{sp}}{\left[Cl^-\right]} = \frac{1\times10^{-10}}{1} = 1 \times 10^{-10} \text{ M}$$

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

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

$$= 0.80 - \frac{0.059}{1}\log\frac{1}{10^{-10}}$$

$$= 0.80 - 0.059 \times 10 = 0.21 \text{ V}$$

Q. 8. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction :

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

Ans.

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

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

$$\Delta G = -nFE$$

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

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

$$E = -2.487 \text{ V}$$

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

Q. 9. Two electrolytic cells containing silver nitrate solution and copper sulphate solution are connected in series. A steady current of 2.5 amp was passed through them till 1.078 g of Ag were deposited. How long did the current flow ? What weight of copper will be deposited ? (Ag = 107.8 u, Cu = 63.5 u)

Ans.

$$w = z \times i \times t$$

$$t = \frac{w}{z \times i}$$

$$t = \frac{1.078 \times 1 \times 96500}{107.8 \times 2.5} = 386 \text{ seconds}$$

$$\mathrm{Cu^{2+} + 2e^- \rightarrow Cu}$$

$$w = \frac{63.5}{2 \times 96500} \times 2.5 \times 386 = 0.3175 \text{ gram}$$

Q.10. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 amp for 20 minutes. What mass of the nickel will be deposited at the cathode ? (Ni = 58.7 u)

Ans.

$$w = z \times i \times t$$

$$z = \frac{58.7}{2 \times 96500}$$

$$w = 1.825 \text{ gram}$$

Q.11. The cell in which the following reaction occurs :

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

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

Ans.

$$n = 2$$

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

$$\Delta G^o = -2.303 \, RT \log K_c$$

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

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

Q.12. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\Lambda^o(H^+)$ = 349.6 S cm^2 mol^{-1}, $\Lambda^o(HCOO^-)$ = 54.6 S cm^2 mol^{-1}.

Ans.

$$\Lambda^o_m\,(\text{HCOOH}) = \Lambda^o_m\,(\text{H}^+) + \Lambda^o_m\,(\text{HCOO}^-)$$

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

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

$$\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$$

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

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

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

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

Q.13. Calculate the standard cell potentials of galvanic cells in which the following reaction take place :

$$\mathbf{2Cr\,(s) + 3Cd^{2+}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + 3Cd\,(s)}$$

Also calculate ΔG^o and equilibrium constant of the reaction.

Ans.

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= -0.40 - (-0.74) = 0.34 \text{ V}$$

$$\Delta G^o = -nFE^0_{\text{cell}} = -6 \times 96500 \times 0.34 = -196860$$

$$= -196860 \text{ J mol}^{-1} = -196.86 \text{ kJ/mol}$$

$$-\Delta G^o = 2.303 \text{ RT} \log K_c$$

$$196860 = 2.303 \times 8.314 \times 298 \log K_c$$

Or $\log K_c = 34.5014$

$$K_c = \text{antilog } 34.5014 = 3.192 \times 10^{34}$$

Q.14. Calculate the potential of the following cell Sn^{4+} (1.5 M) + Zn → Sn^{2+} (0.5 M) + Zn^{2+} (2M).

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

Will the cell potential ↑ or ↓ if the concentration of Sn^{4+} is increased ?

Ans.

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

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

$$= 0.89 - \frac{0.0591}{2}\log\frac{1}{1.5}$$

$$= 0.895 \text{ V}$$

On increasing the concentration of Sn^{4+}, EMF of the cell will increase.

Q.15. E° (Cu^{2+}/Cu) and E° (Ag^+/Ag) is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is +ve. If the concentration of Cu2+ is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag^+.

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

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

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

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

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

Q.16. Calculate the potential of the cell at 298 K :

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

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

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

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

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

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

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

Q.17. The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Ans. Diameter = 1 cm, radius = 0.5 cm

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

$$\rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \times 0.785}{50}$$

$$= 87.135 \text{ ohm cm}$$

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

$$= 0.01148 \text{ ohm cm}$$

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

Q.18. The measured resistance of a conductance cell containing 7.5×10^{-3} M solution of KCl at 25ºC was 1005 ohms. Calculate (a) specific conductance, (b) molar conductance of the solution.

Ans. 1.247×10^{-3} S cm^{-1}, 165.83 S cm^2 mol^{-1}

Q.19. Conductivity of saturated solution of $BaSO_4$ at 315 K is 3.648×10^{-6} ohm^{-1} cm^{-1} and that of water is 1.25×10^{-6} ohm^{-1} cm^{-1}. Ionic conductance of Ba^{2+} and SO_4^{2-} are 110 and 136.6 ohm^{-1} cm^2 mol^{-1} respectively. Calculate the solubility of $BaSO_4$ in g/L.

Ans.

$$\Lambda^o_m (BaSO_4) = \Lambda^o_m Ba^{2+} + \Lambda^o_m SO_4^{2-} = 110 + 136.6 = 246.6 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$K_{BaSO4} = K_{BaSO4} \text{ (solution)} - K_{water} = 3.648 \times 10^{-6} - 1.25 \times 10^{-6}$$

$$= 2.398 \times 10^{-6} \text{ S cm}^{-1}$$

$$\Lambda_m^c = \frac{K \times 1000}{\text{Solubility}} = \frac{2.398 \times 10^{-6} \times 1000}{246.6} = 9.72 \times 10^{-6} \text{ mol/L}$$

$$\text{Solubility} = 9.72 \times 10^{-6} \times 233 = 2.26 \times 10^{-3} \text{ g/L}$$

LONG ANSWER TYPE QUESTIONS (5 Marks)

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

Ans.

$$\Lambda^o_m = \frac{k \times 1000}{M}$$

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

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

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

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

$$= 1.86 \times 10^{-5}$$

Q. 2. Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively all connected in series. A steady current of 1.5 amperes was passed through then until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow ? What mass of copper and of zinc were deposited ?

Ans.

$$Ag^+ + e^- \longrightarrow Ag\,(s)$$

108 g of silver is deposited by 96500 C.

$$1.45 \text{ g silver is deposited by} = \frac{96500 \times 1.45}{108}$$

$$= 1295.6 \text{ C}$$

$$Q = I \times t$$

$$1295.6 = 1.5 \times t$$

$$t = \frac{1295.6}{1.5} = 863 \text{ s}$$

In cell A, the electrode reaction is

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

$$\text{2F of electricity deposit Zn} = 65.3 \text{ g}$$

$$\text{1295.6 of electricity deposit Zn} = \frac{65.3 \times 1295.6}{2 \times 96500}$$

$$= 0.438 \text{ g}$$

In cell C, the electrode reaction is

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

$$\text{2F of electricity deposit Cu} = 63.5 \text{ g}$$

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

$$= 0.426 \text{ g}$$

Q. 3. (a) Define Kohlraush's law.

(b) Suggest a way to determine the Λ^{o}_{m} for CH_3COOH.

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

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

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

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

$$\Lambda^{o}_{m}\ CH_3COOH = \Lambda^{o}\ CH_3COONa + \Lambda^{o}\ HCl - \Lambda^{o}\ NaCl$$

(c)
$$\Lambda^{o}_{m}\ CH_3COOH = \Lambda^{o}\ CH_3COONa + \Lambda^{o}\ HCl - \Lambda^{o}\ NaCl$$
$$= 91.0 + 425.9 - 126.4$$
$$= 390.5\ S\ cm^2\ mol^{-1}$$

Q. 4. (a) Define weak and strong electrolytes.

(b) The E^{θ} values corresponding to the following two reduction electrode processes are :

(i) $Cu^{+}/Cu = 0.52$ V (ii) $Cu^{2+}/Cu^{+} = 0.16$ V

Formulate the galvanic cell for their combination. Calculate the cell potential and ΔG^{o} for the cell reaction.

Ans. (a) **Weak electrolyte :** The substance which partially ionized in solution is known as weak electrolyte. Example : NH_4OH.

Strong electrolyte : The substance which completely ionized in solution is known as strong electrolyte. Example : NaCl.

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

Overall cell reaction : $2Cu^{+} \rightarrow Cu + Cu^{2+}$

$$Cu^{+}/Cu^{2+}||Cu^{+}/Cu$$

$$E^{\theta}_{cell} = 0.52 - 0.16 = 0.36\ V$$
$$\Delta G^{o} = -nFE^{\theta}_{cell}$$
$$= -1 \times 96500 \times 0.36$$
$$= -34740\ J\ mol^{-1}$$

Q. 5. (a) Give anode and cathode reaction of mercury cell.

(b) Calculate emf of the cell for the cell reaction at 25°C for the cell :

$$\mathbf{Zn/Zn^{2+}\ (0.0004M)\ ||\ Cd^{2+}\ (.2M)/Cd\ (s)}$$

Given : $E^{o}_{cell} = 0.36$ V

Ans. (a) At anode : $Zn + 2OH^{-} \rightarrow ZnO + 2e^{-} + H_2O$

At cathode : $HgO\ (s) + H2O + 2e^{-} \rightarrow Hg\ (l) + 2OH^{-}$

(b) $Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd$

$n = 2$

According to Nernst equation :

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cd^{2+}]}$$

VALUE BASED QUESTIONS (4 Marks)

Q. 1. People are advised to limit the use of fossil fuels resulting in Green House Effect leading to a global rise in temperature of earth. Hydrogen provides an ideal alternative in fuel cells.

(a) Write electrode reactions in H_2-O_2 fuel cells.

(b) Can we use CH_4 in place of H_2 ? If yes, then write the electrode reaction at anode.

(c) How is green house effect reduced by the use of fuel cells ?

(d) Write the values associated with preference to fuel cells.

Q. 2. In Apollo space programs, H_2-O_2 fuel cell was used.

(a) Explain why fuel cell is preferred in space programme.

(b) Mention the values associated with the decision of using fuel cells.

(c) Can we use the fuel cells in automobiles ?

(d) How can we increase efficiency of fuel cells ?

Q. 3. Ira, a student of science, went with her father to buy a battery for their invertor and camera. They found two types of batteries, one a lead storage and other a Ni-Cd storage battery. Later was more expensive but lighter in weight. Ira insisted to purchase costlier Ni-Cd battery.

(a) In your opinion, why Ira insisted for Ni-Cd battery ? Give reasons.

(b) Write the values associated with above decision.

(c) Write overall cell reaction during the discharge.

(d) Can this cell be sealed unlike lead storage cell ?

Q. 4. Shyam bought a dry cell which was very old. He puts it in torch. The torch did not glow. He found that the cell was dead.

(a) Why did this happen ?

(b) Write the overall cell reaction during discharge.

(c) What value did you derive from it ?

(d) Why is dry cell not rechargeable ?

Q. 5. Sakshi, a student of Chemistry of class XII, found that some kitchenwares made of iron or copper were galvanized. Sakshi told her mother not to use these cookwares and advised her mother to get them plated with tin instead of zinc.

(a) Why Sakshi was against using the cookwares plated with zinc ?

(b) What would happen if cookwares plated with zinc were used in kitchen ?

(c) Can the cookwares be plated with tin ?

(d) What values are associated with the advice of Sakshi ?

(e) What would happen if the tin plating on cookwares made of copper or iron is broken ?

* * *

UNIT 4

CHEMICAL KINETICS

CONCEPT

Chemical Kinetics : The branch of physical chemistry which deals with the study of rate of reaction and factors affecting rate.

Rate of chemical reaction : The change in concentration of any reactant or product per unit time is called rate of reaction.

Types of Rate of Reaction :

1. **Average rate of reaction :** The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \frac{\Delta x}{\Delta t} = \frac{-\Delta[\mathrm{R}]}{\Delta t} = \frac{\Delta[\mathrm{P}]}{\Delta t}$$

2. **Instantaneous rate of reaction :** The rate of reaction measured at a particular time is called instantaneous rate of reaction.

$$(\text{Rate})_i = (\text{Instantaeous rate})\ dx/dt = -d[\mathrm{R}]/dt = +d[\mathrm{P}]/dt$$

Factors affecting Rate of Reaction

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation in photochemical reaction

Rate constant (k) : It is equal to the rate of reaction when molecular concentration of reactant is at unity.

Rate law : The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.

For a reaction, $aA + bB \rightarrow cC + dD$

$$\text{Rate law} = k[A]^p[B]^q$$

where powers p and q are determined experimentally.

Molecularity : The total number of reactants taking part in elementary chemical reaction is called molecularity.

Order of reaction : The sum of powers to which the concentration terms are raised in a rate law expression is called order of reaction.

For above case, $\text{Order} = P + Q$

Orders of reaction is determined experimentally.

Half-life period : The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

Activation energy : The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – Kinetic energy

Temperature coefficient : The ratio of rate constant at two temperatures having difference of 10ºC is called temperature coefficient.

Temperature coefficient = Rate constant at T + 10ºC/Rate constant at TºC

Arhenius Equation :

$$K = Ae^{-Ea/RT}$$

where, K = Rate constant

A = Arrhenius energy (Frequency factor or pre-exponential factor)

E_a = Activation energy

R = Rate constant

T = Temperature

$\frac{Ea}{RT}$ = Fraction of molecules having energy equal to or more than activation energy

$$\log K = \log A - \frac{Ea}{2.303RT}$$

$$\log \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{K_2}{K_1}=\frac{E_a}{2.303\times 8.314}\left[\frac{T_2-T_1}{T_2-T_1}\right]$$ Where R = 8.314 JM^{-1} mol^{-1}

$$\log\frac{K_2}{K_1}=\frac{E_a}{19.147}\left[\frac{T_2-T_1}{T_2-T_1}\right]=0.0522E_a\left[\frac{T_2-T_1}{T_2-T_1}\right]$$

1. Integrated rate law equation for zero order reaction is given as below :

(a) $k=\frac{[R]_0-[R]_t}{t}$

Where k is rate constant and $[R]_0$ is initial molar concentration.

(b) $t_{1/2}=\frac{[R]_o}{2k}$, $t_{1/2}$ is half-life period of zero order reaction.

2. Integrated rate law equation for first order reaction :

(a) $k=\frac{2.303}{t}\log\frac{[R]_0}{[R]_t}$

where k is rate constant, $[R]_0$ is initial molar concentration and $[R]_t$ is final concentration at time 't'.

(b) Half-life period ($t_{1/2}$) for first order reaction :

$$t_{½}=\frac{0.693}{k}$$

Pseudo chemical reaction : The chemical reaction which looks like higher order reaction but in real it follows lower order reaction.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k[CH_3COOC_2H_5]^1$$

$$\boxed{\text{Order} = 1}$$

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. The gas phase decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO$$

follows the rate law, Rate = $k(P_{CH3CHO})^{3/2}$, unit of P is atm and time is second. What are the units of its rate constant ?

Ans. $Atm^{-½}$ sec^{-1}

Q. 2. State the order with respect to each reactant and overall reaction.

$$H_2O + 3I^- + 2H^+ \rightarrow 2H_2O + I^{3-}$$

Rate = $k[H_2O_2]^1[I^-]^1$

Ans. Order of reaction = 1 + 1 = 2

Q. 3. Give one example of pseudo first order reaction.

Ans. Hydrolysis of an ester :

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Q. 4. The rate law for a reaction is

$$\textbf{Rate} = \mathbf{K\,[A]\,[B]^{3/2}}$$

Can the reaction be an elementary process ? Explain.

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

Q. 5. For the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expressions $-\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ inter-related ?

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

Q. 6. Identify the order of a reaction from the following rate constant :

$$k = 2.3 \times 10^{-5}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

Ans. Second order

Q. 7. After five half-life periods for a first order reaction, what fraction of reactant remains ?

Ans. $\frac{1}{32}$

Q. 8. Give the damaging effect of photochemistry.

Ans. The colour of fabrics fades away on exposure to sunlight.

Q. 9. What is the effect of adding catalyst on the free energy of a reaction ?

Ans. No change in ΔG.

Q.10. What value of *k* is predicted for the rate constant by Arrhenius equation is T → ∞ ? Is this value physically reasonable ?

Ans. From the equation $k = Ae^{-E_a/RT}$ if $T \rightarrow \infty$ $k \rightarrow A$ so that Ea = 0. This is not feasible.

Q.11. Determine the order of reaction :

Step 1. $2NO + H_2 \rightarrow N_2 + H_2O_2$ **Slow**

Step 2. $H_2O_2 + H_2 \rightarrow 2H_2O$ **Fast**

Ans. Rate $= k\,[NO]^2\,[H_2]$

Order $= 2 + 1$

$= 3$

Q.12. What is the order of reaction whose rate constant has the same units as the rate of reaction ?

Ans. Zero order

Q.13. Why are reactions of higher order less in number ?

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

Q.14. What will be the effect of temperature on rate constant ?

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

Q.15. State a condition under which a bimolecular reaction is kinetically first order reaction.

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

Q.16. Why can't molecularity of any reaction be equal to zero ?

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

Q.17. Give an example of zero order reaction.

Ans. $H_2 + Cl_2 \xrightarrow{hv} 2HCl$ or any other example

Q.18. The rate constant of a reaction is 3×10^2 min^{-1}. What is its order of reaction ? (On the basis of units of rate constant)

Ans. First order reaction.

Q.19. Three-fourth of a reaction is completed in 32 minutes. What is the half life period of this reaction ?

Ans. 16 minutes.

Q.20. What is meant by an elementary reaction ?

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

Q.21. Give one example of a reaction where order and molecularity are equal ?

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

Q.22. For a reaction R → P, the rate becomes 2 times when the concentration of the reactant A is increased 4 times. What is the order of reaction ?

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

Q.23. The rate constant of a zero order reaction in A is 0.003 mol L^{-1} sec^{-1}. How long will it take for the initial concentration of A to fall from 0.10M to 0.075 M ?

Ans. $t = \frac{[A]_0 - [A]}{k} = \frac{0.10 - 0.075}{0.003} = 8.3 \text{ sec}$

Q.24. In a reaction 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Average rate = $\frac{-\Delta[A]}{2\Delta t} = -\frac{1}{2}\left(\frac{0.4 - 0.5}{10}\right) = 5 \times 10^{-3} \text{ M min}^{-1}$

Q.25. In some cases large number of colliding reactant molecules have energy more than threshold energy even then the reaction is slow. Why ?

Ans. Because resultant molecules do not collide in proper orientation.

Q.26. Give an example of a reaction having fractional order.

Ans. Decomposition of acetaldehyde (order = 1.5).

$$CH_3CHO \xrightarrow{723K} CH_4 + CO$$

Q.27. Decomposition reaction of ammonia on Pt surface has rate constant = 2.5 × 10^{-1} mol L^{-1} sec^{-1}. What is order of reaction ?

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

Q.28. What is order of radioactive decay ?

Ans. First order

Q.29. For a reaction A + B → Product, the rate low is given by $r = k[A]^{1/2} [B]^2$. What is the order of the reaction ?

Ans. Order of reaction = ½ + 2 = 2.5

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

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

Ans. $K_2/K_1 = 4$

$T_1 = 293 \text{ K}, T_2 = 313 \text{ K}$

$$\log\frac{K_2}{K_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Thus, on calculating and substituting values, we get :

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

Q. 2. If the decomposition of nitrogen oxide as

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

follows a first order kinetics.

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

Ans. Rate $= K[N_2O_5]$

$$K = \frac{\text{Rate}}{[N_2O_5]}$$

$$= \frac{1.5\times10^{-6}}{0.05}$$

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

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

Ans. Rate $= 2.45 \times 10^{-5}$ mol L^{-1} s^{-1}

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

$$= 0.82 \text{ M}$$

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

Ans.

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

Q. 4. The rate constant for a reaction of zero order A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial conc. of A to fall from 0.10M to 0.075M ?

Ans. For a zero order reaction,

$$K = 0.0030 \text{ mol } L^{-1} s^{-1}$$

$$[A]_0 = 0.10M \qquad [A] = 0.075M$$

$$K = \frac{[A]_0 - [A]}{t}$$

$$t = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s}$$

Q. 5. For the reaction :

Write : $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

(a) Rate of reaction expression.

(b) Molecularity

Ans. (a) $$\text{Rate} = -\frac{d[C_{12}H_{22}O_{11}]}{dt} = -\frac{d(H_2O)}{dt}$$

$$= \frac{d[C_6H_{12}O_6]}{dt} = \frac{d[C_6H_{12}O_6]}{dt}$$

(b) Molecularity = 2

Q. 6. Consider the decomposition reaction :

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

This reaction takes place in two steps as given below :

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

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

(a) Determine rate law expression.

(b) Determine the order of reaction.

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

(b) Order = 1 + 1 = 2

Q. 7. The decomposition of hydrocarbon follows the equation $K = (4.5 \times 10^{11} s^{-1}) e^{-28000k/T}$. Calculate E_a.

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

Comparing the equation with Arrhenius equation,

$$K = Ae^{-Ea/RT}$$

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

$$E_a = 28000 \times 8.314$$

$$= 232192\ J\ mol^{-1}$$

Q. 8. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the conc. of the reactant is reduced to half. What is the unit of rate constant for such a reaction ?

Ans. $$\text{Rate} = k[A]^2$$

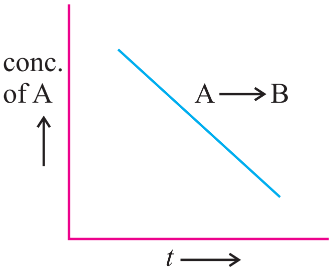
$$\text{Unit of } k = \frac{\text{mol L}^{-1}}{\text{S}} = k(\text{mol}^{-1})^2$$

$$k = \text{mol}^{-1}\ \text{L S}^{-1}$$

Q.9. For a first order reaction time taken for half of the reaction to complete is t_1 and ¾ of the reaction to complete is t_2. How are t_1 and t_2 related ?

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

Q. 10.



(a) What is the order of the reaction ?

(b) What is the slope of the curve ?

Ans. (a) Zero order reaction.

(b) $[R] = [R_0] - kt$

$\therefore$ Slope $= -k$

Q.11. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction,

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

For completion of the reaction [R] =0

$\therefore \quad kt = [R]_0$

Or $\quad t = \dfrac{[R]_0}{k}$

Q.12. For the reaction N_2 (g) + $3H_2$ (g) → $2NH_3$ (g)

How is the rate of formation of ammonia related to the rate of disappearance of H_2 ?

Ans. Rate of reaction $= -\dfrac{1}{3}\dfrac{\Delta[H_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[NH_3]}{\Delta t}$

Or $\quad \dfrac{\Delta[NH_3]}{\Delta t} = -\dfrac{2}{3}\dfrac{\Delta[H_2]}{\Delta t}$

Q.13. The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

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

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

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

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

Dividing equation (i) by equation (ii),

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

Or $\quad n = 1$

Q.14. A reaction which is first order with respect to A has rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 ML^{-1} ?

Ans. $\quad k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]}$

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

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

Q.15. The conversion of the molecules X to Y follows second order kinetics. If the concentration of X is increased to three times, how will it affect the rate of formation of Y ?

Ans. 9 times

Q.16. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 gram of this reactant take to reduce to 3 grams ?

Ans. t = 444 seconds

Q.17. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. If rate of formation of NO is 6×10^{-4} atm min^{-1}, calculate the rate of formation of H_2O.

Ans. 9.0×10^{-4} atm min^{-1}

Q.18. A first order reaction is 75% completed in 60 min. Find the half life of this reaction.

Ans. 30 mins.

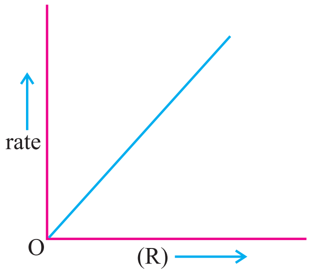
Q.19. The composition of a hydrocarbon follows the equation $K = (4.5 \times 10^{11}\ sec^{-1})\ e^{-28000K/T}$. Calculate the value of E_a.

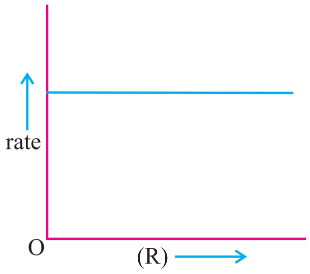
Ans. 232.79 kJ/mol

Q.20. Consider a certain reaction A → Product with $K = 2.0 \times 10^{-2}\ s^{-1}$. Calculate the concentration of A remaining after 100 s, if the initial concentration of A is 1.0 mol L^{-1}.

Ans. [A] = 0.135 M

Q.21. Explain with an example, what is a pseudo first order raction ? The graphs (A and B) given below are plots of rate of reaction Vs concentration of the reactant. Predict the order from the graphs.





Q.22. Differentiate between :

(a) Average rate and instantaneous rate of a chemical reaction.

(b) Molecularity and order of reaction.

Q.23. Show that in case of first order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction.

Q.24. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimentally determined rate expression below 400 K is rate = $k[NO_2]^2$. What mechanism can be proposed for this reaction ?

Q.25. The half life period of a first order reaction is 60 min. What % will be left after 240 mins. ?

Ans. 6.25%

Q.26. Time for half change for a first order reaction is 25 min. What time will be required for 99% reaction ?

Ans. 166.16 mins.

SHORT ANSWER TYPE-II QUESTIONS

Q. 1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value ?

Ans.

$$t = \frac{2.303}{K}\log\frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{\frac{1}{10}}\log\frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{60}\log 10$$

$$t = \frac{2.303}{60}$$

$$= 3.38 \times 10^{-2}\ s^{-1}$$

Q. 2. The rate of most of reaction double when their temperature is raised from 298 K to 308 K. Calculate the activation energy of such a reaction.

Ans.

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89 \text{ KJ/mol}$$

Q. 3. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion.

Ans.

$$K = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{69.3} \text{ min}$$

$$= 10^{-2} \text{ min}^{-1}$$

$$T = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$= \frac{2.303}{10^{-2}} \log 5$$

$$= 160.9 \text{ min}$$

Q. 4. The rate constant of a reaction is 1.2 × 10^{-3} sec^{-1} at 40° C. Calculate the energy of activation of the reaction.

Ans. $K_1 = 1.2 \times 10^{-3}\ sec^{-1}$ $T_1 = 30 + 273 = 303$ K

$K_2 = 2.1 \times 10^{-3}\ sec^{-1}$ $T_2 = 40 + 273 = 313$ K

Using,
$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Rightarrow \quad \log \frac{2.1 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{313 - 303}{313 \times 303}\right)$$

$$\log \frac{2.1}{1.2} = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{10}{313 \times 303}\right)$$

$$E_a = 44.13 \text{ KJ mol}^{-1}$$

Q. 5. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is 1.8 × 10^{-1} sec^{-1}. Calculate the frequency factor A.

Ans. Given, $E_a = 94.14 \times 10^3$ J mol^{-1}, T = 40 + 273 = 313 K, K = 1.8 × 10^{-1} sec^{-1}

By using, $$K = Ae^{-E_a/RT} \quad \Rightarrow \quad \ln K = \ln A - \frac{E_a}{RT}$$

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

Or $$\log\left(1.8\times10^{-1}\right) + \frac{94.19\times10^3}{2.303\times8.314\times313} = \log A$$

Or A = antilog (10.9635) = 9.194 × 10^{10} sec^{-1}

Q. 6. The rate constant of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of E_a and A.

Ans. 18.23 KJ mol^{-1}, 1.603

Q. 7. The rate constant of a reaction at 700 K and 760 K are 0.011 M^{-1} s^{-1} and 0.105 M^{-1} s^{-1} respectively. Calculate the value of Arrhenius parameters.

Ans. 2.824 × 10^{10}

Q. 8. The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + ½O_2$ was 1.24 × 10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20 × 10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

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

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

$$= 0.0304 \text{ min}^{-1}$$

Q. 9. The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :

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

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

Calculate rate constant.

Ans. 4.98 × 10^{-4} sec^{-1}

Q. 10. A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion.

Ans. 144.3 minutes

Q. 11. For a first order reaction, calculate the ratio between the time taken to complete ¾ of the reaction and the time taken to complete half of the reaction.

Ans. Two

Q. 12. The following results have been obtained during the kinetics studies of the reaction :

$$2A + B \rightarrow C + D$$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of formation of D mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-1}

Determine the rate law and the rate constant for the reaction.

Ans. Rate = $K[A][B]^2$

Q. 13. The rate of reaction triples 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.

Q. 14. The decomposition of A into product has value of K as 4.5×10^3 sec^{-1} at 10° C and energy of activation 60 kJ/mol. At what temperature would K be 1.5×10^4 sec^{-1}.

Ans. 24° C

Q. 15. The rate of formation of NO is 3.6×10^{-3} mol L^{-1} sec^{-1}. Calculate the rate of disappearance of NH_3 and rate of formation of H_2O.

Ans. 3.6×10^{-3} Ms^{-1}, 5.4×10^{-3} Ms^{-1}

Q. 16. (a) Write rate law and order of the following reaction :

$$AB + C_2 \rightarrow AB_2C + C \text{ (slow)}$$

$$AB_2 + C \rightarrow AB_2C \text{ (fast)}$$

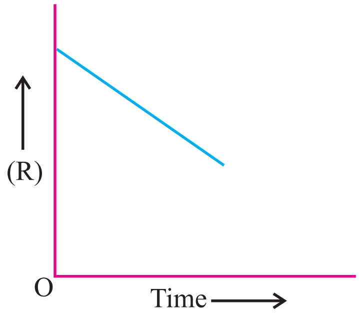
(b) Define energy of activation of a reaction.

(c) What is the relationship between rate constant and activation energy of a reaction ?

Ans. (a) Rate = $K[AB][C_2]$, Order = 1 + 1 = 2

(c) $K = Ae^{-E_a/RT}$

Q. 17. For a chemical reaction R → P, the variation in the concentration (R) vs time (t) plot is given :



(a) Predict the order of reaction.

(b) Write down its rate law.

(c) What is the slope of the curve ?

Q. 18. What do you understand by a first order reaction ? Show that for a first order reaction time required to complete a definite fraction of the reaction is independent of initial concentration.

Q. 19. In a pseudo first order reaction of hydrolysis of an ester in H_2O, the following results were obtained :

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

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

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

Ans. (a) Average rate during 30-60 sec. $= \frac{0.17-0.31}{60-30} = 4.67\times10^{-3}$ mol L^{-1} sec^{-1}

(b)

$$K_{30} = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{30}\log\frac{0.55}{0.31}$$

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

$$K_{90} = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

Average K = 1.98×10^{-2} sec^{-1}

Q. 20. Following reaction takes place in one step :

$$\mathbf{2NO + O_2 \rightarrow 2NO_2}$$

How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume ? Will there be any change in the order of reaction with reduced volume ?

Ans. $2NO + O_2 \rightarrow 2NO_2$

$dx/dt = K^*[NO]^2[O_2]^1$

[Since it is one step.]

If the volume of reaction vessel is diminished to 1/3, conc. of both NO and O_2 will become 3 times, the rate of reaction increased 27 times in the order of reaction with the reduced volume.

Q. 21. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2 ? [K = 2.5 × 10^{-4}]

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

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

$$\frac{d[NH_3]}{dt} = \text{rate} = k\times[NH_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$= \frac{1}{2}\times 2.5\times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2}\times 2.5\times 10^{-4}$$

$$= 3.75 \times 10^{-44} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{Rate} = -\frac{d[NH_3]}{dt} = k\times[NH_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

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

LONG ANSWER TYPE QUESTIONS

Q. 1. (a) Define order of reaction.

(b) Rates of reaction double with every 10° rise in temperature. If this generalization holds for a reaction in the temperature ranges 298 K to 308 K, what would be the value of activation energy for their reaction ? $R = 8.314\ J\ K^{-1}\ mol^{-1}$.

Ans. (a) **Order of Reaction :** It is the sum of powers to which the conc. terms are raised in rate law expression.

(b) $$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Here, $T_1 = 298\ K$, $T_2 = 308\ K$, $R = K^{-1}\ mol^{-1}$

$$\frac{K_2}{K_1} = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 52898\ J\ mol^{-1}$$

$$= 52.898\ KJ\ mol^{-1}$$

Q. 2. (a) What are pseudo order reaction ? Give example.

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

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

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

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

For example,

$$\underset{\text{excess}}{CH_3COOC_2H_5 + H_2O} \xrightarrow{H^+} CH_5COOH + C_2H_5OH$$

Rate $= K[CH_3COOC_2H_5]$

Order $= 1$

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

So, $E_a = -2.303 \times R \times \text{Slope}$

$= -2.303 \times 8.314\ J\ K^{-1}\ mol^{-1} \times 4250$

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

$= 81.375\ KJ\ mol^{-1}$

Q. 3. (a) Determine the units of rate constant for first and zero order reaction.

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

Ans. (a) $K = (mol)^{1-n}\ L^{n-1}\ S^{-1}$

For zero order, $n = 0$

So, $K = (mol)^{1-0}\ L^{0-1}\ S^{-1} = S^{-1}\ mol\ L^{-1}$

For first order, $n = 1$

$K = (mol)^{1-n}\ L^{n-1}\ S^{-1}$

So, $K = (mol)^{1-1}\ L^{1-1}\ S^{-1}$

$= S^{-1}$

(b) For a first order reaction,

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

$$[A]_0 = a,\ [A] = a - \frac{a \times 99}{100} = 0.01\ a$$

$$t(99\%) = \frac{2.303}{K}\log\frac{a}{0.01a}$$

$$= \frac{2.303}{K}\log 100$$

$$= \frac{2.303}{K} \times 2 \qquad \text{...(i)}$$

For 90% completion of reaction,

$$[\mathrm{A}] = a - \frac{a \times 99}{100} = 0.1a$$

$$t(90\%) = \frac{2.303}{\mathrm{K}} \log \frac{a}{0.1a}$$

$$= \frac{2.303}{\mathrm{K}} \times 1 \qquad \text{...(ii)}$$

Dividing equation (i) by equation (ii), we get

$t(99\%) = 2 \times t(90\%)$

Q. 4. (a) Define rate constant of reaction.

(b) A first order reaction takes 40 mins for 30% decomposition. Calculate $t_{1/2}$.

Ans. (a) **Rate constant :** It is the rate of chemical reaction when the concentration of reactant taken as unity at a given temperature.

(b) Let initial conc. = a

$$\text{Conc. after 40 mins.} = a - \frac{a \times 30}{100}$$

$$= 0.70\, a$$

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

$$= \frac{2.303}{40} \log \frac{a}{0.70a}$$

$$= \frac{2.303}{40} \log \frac{1}{0.70}$$

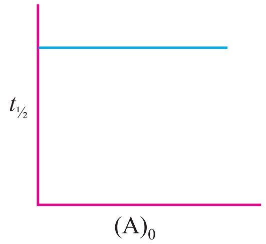
$$= \frac{2.303}{40} \times 0.1549$$

$$= 8.92 \times 10^{-3}\ \mathrm{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{\mathrm{K}}$$

$$= \frac{0.693}{8.92 \times 10^{-3}} = 77.7\ \mathrm{min}$$

Q. 5. (a) Determine the order of reaction and also determine the units of rate constant.



(b) The following data were given for thermal decomposition of SO_2Cl_2 at a constant volume :

$$SO_2Cl_2\ (g) \rightarrow SO_2\ (g) + Cl_2\ (g)$$

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Ans. (a) First order reaction

$$K = mol^{1-n}\ L^{n-1}\ S^{-1}$$

$$n = 1$$

$$K = (mol)^{1-1}\ L^{1-1}\ S^{-1}$$

$$= S^{-1}$$

(b)

$$k = \frac{2.303}{t}\log\frac{P_1}{(2P_1 - P_t)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{(2\times0.5-0.6)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{0..4}$$

$$= \frac{2.303}{100}\times0.969 = 2.23\times10^{-3}\ s^{-1}$$

Now, Rate = $P_{SO_2Cl_2}$

Pressure of SO_2Cl_2 when total pressure = 0.65 atm

$$P_{SO_2Cl_2} = 2P_1 - P_t$$

$$= 2 \times 0.5 - 0.65$$

$$= 0.35\ atm$$

$$\text{Rate} = 2.23 \times 10^{-3} \times 0.35$$
$$= 7.8 \times 10^{-4} \text{ atm S}^{-1}$$

Q. 6. (a) The activation energy of a reaction is 100 kJ/mol. In the presence of catalyst the activation energy is decreased by 75%. What is the effect on rate constant of the reaction at 20º C ?

(b) $A + 2B \rightarrow 3C + 2D$

The rate of disappearance of B is 1×10^{-2} mol L^{-1} sec^{-1}. What will be (i) rate of reaction (ii) rate of change in the concentration of A and C ?

Ans. (a) 2.35×10^{13} times

[*Hint :* $\log\frac{K_2}{K_1} = \frac{E_a - E_p}{2.303RT} \Rightarrow \log\frac{K_2}{K_1} = \frac{75\times10^3}{2.303\times8.314\times293}$]

(b) $(5 \times 10^{-3}, 5 \times 10^{-3}, 15 \times 10^{-3})$ M L^{-1} sec^{-1}

Q. 7. (a) For the reaction $2A + B$ □ A_2B

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 sec^{-1}. Calculate the initial rate of reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

(b) (i) The activation energy for the reaction $2HI \rightarrow H_2 + I_2$ is 209.5 KJ/mol at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

(ii) The activation energy of a reaction is zero. Will the rate constant of the reaction depend upon temperature ? Give reason.

Ans. $K = Ae^{-E_a/RT}$ if $E_a = 0$, then K = A. Frequency factor (A) does not depend upon temperature, therefore, rate constant and rate does not depend on temperature.

Q. 8. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained :

[R] molar	1.0	0.75	0.40	0.10
t (in min)	0.0	0.05	0.12	0.18

Calculate the order of the reaction.

[*Hint :* Determine the rate of reaction at different intervals of time. It comes out to be constant. Hence, it is a zero order reaction.]

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Food and dairy products get spoiled more quickly in summer. Therefore, use of refrigerator has became very common in almost every house. Sita, a class XII Chemistry student, suggested her mother to store milk and other dairy products in refrigerator and not in open on kitchen slab.

(a) Why Sita suggested her mother to store milk and dairy products in the refrigerator ?

(b) Mention the relationship to express how rate of reaction is related with temperature.

(c) What values are learnt by Sita's advice ?

(d) Name the food preservative used to prevent spoilage of food.

Q. 2. Ramesh tried his best to carry out the reaction between the pure hydrogen with pure oxygen but he failed. Mohan, a friend of Ramesh, suggested that the reaction must be carried out in the presence of Pt catalyst. As he placed platinum in the reaction mixture, the reaction took place explosively.

(a) Mention the role of catalyst in the above chemical reaction.

(b) What values are associated with the suggestion of Mohan ?

Define (c) activity and (d) selectivity of a catalyst.

Q. 3. Sudha's mother received a phone call on Monday morning from a close relative stating that three of them would be coming over for lunch. Sudha's mother noticed that she did not have enough curd to serve the guests. Sudha, a class XII chemistry student, suggested to her mother to take warm milk and keep it under direct sunlight and curdle it.

(a) Why do you think Sudha suggested the above method ?

(b) Will it be helpful if her mother followed Sudha's suggestion ?

(c) What values are associated with Sudha's suggestion ?

(d) Name the bacteria responsible for curdling of milk.

✧✧

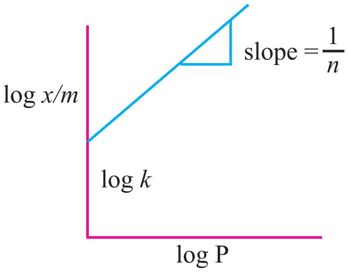
UNIT 5

SURFACE CHEMISTRY

Points to Remember

1. Adsorption occurs because of unbalanced forces acting inwards on the surface of the solid or a liquid.
2. The substance adsorbed is called **adsorbate** and substance on which adsorption takes place is **adsorbent.**
3. In physical adsorption, adsorbate is held to adsorbent by weak van der Waals forces. In chemisorptions, adsorbate is held to adsorbent by strong chemical bond type of foces.
4. Water vapours are adsorbed in silica gel but absorbed in $CaCl_2$.
5. If the concentration of adsorbate is more on the surface with respect to bulk, it is called **positive adsorption.** If it is less on the surface with respect to bulk, it is called **negative adsorption**.
6. Greater the surface area of the adsorbent, the more is the extent of adsorption.
7. Higher the critical temperature of a gas, greater is its extent of adsorption.
8. Physical adsorption is due to van der Waals forces and is reversible. Chemisorption involves the formation of compounds on the surface and is irreversible.
9. At constant temperature, adsorption generally increases with pressure. The lower the temperature, the greater is the effect of pressure.
10. Freundlich adsorption isotherm is

$$\frac{x}{m} = kP^{1/n}\,(n > 1) \qquad i.e., \qquad \log\frac{x}{m} = \log k + \frac{1}{n}\log P$$



The plot of log x/m vs log P gives a straight line with slope = $1/n$ and y-intercept = log k.

11. Adsorption is generally temperature dependent. Generally adsorption is **exothermic** and, therefore, adsorption decreases with the increase in temperature.

12. For adsorption from solution, pressure (P) is replaced by equilibrium concentration (C).

13. A catalyst is a substance that increases the rate of reaction without being consumed in the reaction. In general, a catalyst functions by lowering the energy of activation which in turn makes the rate constant larger and, hence, the rate of reaction higher. (The catalysts take part in reaction but get regenerated during course of reaction.)

14. In **homogeneous catalysis,** the catalyst is in the same phase as that of reactants and in **heterogeneous catalysis,** the catalyst is in the different phase from the reactants.

15. **Enzymes** are biological catalysts. Their main characteristics are their high *specificity,* efficiency (even in traces) and activity at physiological temperature of 37° C and pH of 7.4.

16. Enzyme catalysed reaction takes place in two steps :

    $E+S \rightarrow [ES]$ (fast and reversible)

    $[ES] \rightarrow E + P$ (slow and rate determining)

    (E is enzyme, S is substrate and P is product.)

17. **Colloidal solutions** are intermediate between true solutions and suspensions. Their size ranges in the order 1 nm to 1000 nm.

18. A colloidal system consists of two phases : the dispersed phase and dispersion phase.

19. **Lyophilic sols :** There is strong attraction between dispersed phase and dispersion medium. These are formed by organic substances like gum, starch, protein etc. These are reversible and more stable.

20. **Lyophobic sols :** There is very little interaction between dispersed phase and dispersion medium and are formed by inorganic substances like metals, their sulphides etc. These are irreversible and less stable.

21. The stability of lyophilic sols is due to their greater hydration in the solution.

22. The colloidal systems show Brownian movement, Tyndall effect and electrophoresis.

23. Aggregate of ions in an associated colloidal sol is called **ionic micelle.** The concentration above which these are formed is called **critical micelle concentration** (CMC) and the temperature above which these are formed is called **Kraft temperature** (T_k).

24. Conversion of a freshly precipitated substance into colloidal sol by shaking with a suitable electrolyte is called **peptization.**

25. The movement of colloidal particles under the influence of an electric field is called **electrophoresis.**

26. The process of changing the colloidal particles in a sol into the insoluble precipitate by the addition of some suitable electrolytes is known as **coagulation.**

27. According to Hardy Schulze rule, greater the valency of the flocculating ion of the electrolyte, the faster is the coagulation.

28. The minimum number of millimoles of the electrolyte required for complete coagulation of one litre of a colloidal sol is called its **coagulation or flocculation value.**

29. The minimum number of milligrams of a lyophilic sol needed to protect 10 mL of gold sol by the addition of 1 mL of 10% NaCl is called **gol number.** Protective power is the reciprocal of gold number.

30. **Emulsions** are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of (i) oil in water (o/w) and (ii) water in oil (w/o) type.

31. The process of making emulsion is called emulsification.

32. To stabilize an emulsion, an emulsifying agent or emulsifier is added. Soap and detergents are most frequently used as **emulsifiers.**

33. The potential difference between the fixed layer and the diffused layer of opposite charges in colloids is called electrokinetic potential or zeta potential.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Why does a gas mixed with another gas not form a colloidal system ?

[*Hint :* Gaseous mixture is homogeneous.]

Q. 2. Why are adsorbate particles attracted and retained on the surface of adsorbent ?

[*Hint :* The unbalanced forces of the adsorbent are responsible for attracting adsorbate particles at adsorbent surface.]

Q. 3. Explain the terms sorption and desorption.

[*Hint :* Sorption is used to describe the process when adsorption and absorption take place simultaneously.

Desorption : Removal of adsorbate from the surface of adsorbent.]

Q. 4. "Chemisorption is highly specific." Illustrate with an example.

[*Hint :* As it involves chemical bonding between adsorbent and adsorbate.]

Q. 5. "Adsorbents in finely divided form are more effective." Why ?

[*Hint :* Due to their more surface area in finely divided form.]

Q. 6. Name two compounds used as adsorbent for controlling humidity.

Ans. Silica gel, Alumina gel

Q. 7. Mention one shape selective catalyst used to convert alcohol directly into gasoline.

[*Hint :* ZSM-5]

Q. 8. 'Generally high temperature is favourable for chemisorption.' Why ?

[*Hint :* To provide energy of activation.]

Q. 9. Name the catalyst used in the following process :

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

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

[*Hint :* (a) Finely divided Fe/FeO, MO as promoter.

(b) Pt (Platinised asbestos)]

Q. 10. Write Freundlich adsorption isotherm relation.

[*Hint :* $\frac{x}{m} = kP^{1/n} \left(n > 1\right)$, $\log\frac{x}{m} = \log k + \frac{1}{n}\log P$]

Q. 11. Which group elements show maximum catalytic activity for hydrogenation reactions ?

[*Hint :* 7-9 group elements.]

Q. 12. Why gas masks are used by miners in coal mines while working ?

[*Hint :* To absorb poisonous gases.]

Q. 13. Write the chemical reaction involved in the preparation of sulphur sol.

[*Hint :* $SO_2 + H_2S \xrightarrow{\text{oxidation}} 2S_{(sol)} + 2H_2O$]

Q. 14. Name the enzyme which converts milk into curd.

[*Hint :* Lactobacilli.]

Q. 15. What are the optimum temperature and pH at which enzymes are highly active ?

[*Hint :* Temperature 298-310 K and pH 5 to 7]

Q. 16. What are the physical states of dispersed phase and dispersion medium in foam rubber ?

[*Hint :* Dispersed phase : Gas; Dispersion medium : Solid]

Q. 17. What is the composition of colloidion solution ?

[*Hint :* 4% solution of nitrocellulose in a mixture of alcohol and ether.]

Q. 18. Why do colloidal particles show Brownian movement ?

[*Hint :* Due to unbalanced bombardment of the dispersed phase particles by the molecules of the dispersion medium.]

Q. 19. State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface.

[*Hint :* $S = -$ ve]

Q. 20. Why does sky appear blue to us ?

[*Hint :* Due to scattering of blue light by dust particles and water suspended in air.]

Q. 21. What happens when hydrated ferric oxide and arsenious sulphide sols are mixed in almost equal proportions ?

[*Hint :* Mutual precipitation/coagulation took place.]

Q. 22. Gelatin is generally added to ice-cream. Why ?

[*Hint :* Ice-cream is water in oil type emulsion and gelatin acts as emulsifier.]

Q. 23. How is lake test for aluminium ion based upon adsorption ?

[*Hint :* $Al_2O_3.xH_2O$ has the capacity to adsorb the colour of blue litmus from the solution.]

Q. 24. What is saturation pressure in Freundlich's isotherm ?

[*Hint :* High pressure]

Q. 25. Mention the two conditions for the formation of micelles.

[*Hint :* CMC and T_k.]

Q. 26. How is Brownian movement responsible for the stability of sols ?

[*Hint :* Stirring effect due to Brownian movement does not allow the particles to settle down.]

Q. 27. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol : (i) KCl, (ii) $CaSO_4$, (iii) $K_3[Fe(CN)_6]$?

[*Hint :* $K_3[Fe(CN)_6]$]

Q. 28. State the purpose of impregnating the filter paper with colloidion solution.
[*Hint :* To reduce pore size of filter paper, so that colloidal particles cannot pass through.]

Q. 29. Mention one use of ZSM-5 catalyst.

[*Hint :* In dehydration of alcohols in formation of synthetic gasoline.]

Q. 30. Name the enzyme which convert starch into maltose.

Ans. Diastase/Salivary amylase.

Q. 31. Why is it necessary to remove CO (carbon monoxide) when ammonia is obtained by Haber's process ?

Ans. CO acts as poison catalyst for Haber's process therefore, it will lower the activity of the Fe catalyst.

Q. 32. Explain the terms : (i) CMC, (ii) Kraft temperature (T_k).

[*Hint :* CMC : Concentration above which micelle formation took place.

Kraft Temperature : It is the temperature above the micelle formation took place.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

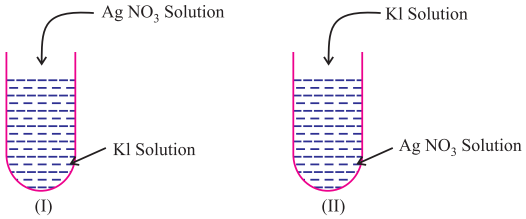
Q. 1. Explain the effect of temperature on the extent of physical and chemical adsorption.

[*Hint :* Physical adsorption decreases with increase of temperature, while chemical adsorption increases with increase of temperature.]

Q. 2. Define the term peptization and mention its cause.

[*Hint :* It is the process of converting a ppts into a colloidal sol by shaking it with small amount of electrolyte with dispersion medium. Ppts adsorb one of the ions of the electrolyte on its surface.]

Q. 3. What will be the charge on colloidal solutions in the following cases ?



Give reasons for the origin of charge.

Ans. (i) Ag^+ ions are adsorbed on AgI, forming positively charged colloid.

(ii) I^- ions are adsorbed on AgI forming negatively charged colloid.

Reason for origin of charge is the preferential adsorption of common ions of the electrolyte present in excess.

Q. 4. Write the factors upon which the catalytic reaction of shape-selective catalyst depends ?

[*Hint :* (a) Pore structure of the catalyst.

(b) Size and shape of the reactant and product molecules.]

Q. 5. Mention two examples of emulsifying agents for o/w emulsions and w/o emulsions.

[*Hint* : For o/w emulsions : Proteins, gums, soaps.

For w/o emulsions : Fatty acids, long chain alcohols, lampblack.]

Q. 6. Suggest a mechanism of enzyme catalysed reaction.

[*Hint* : (a) Binding of enzyme and substrate : $E + S \rightarrow [ES]$

(b) Decomposition of activated complex to product : $[ES] \rightarrow E + P$]

Q. 7. A small amount of silica gel and a small amount of anhydrous calcium chloride are placed separately in two beakers containing water vapour. Name the phenomenon that takes place in both the beakers.

[*Hint* : Silica gel : Adsorption, Anhydrous $CaCl_2$: Absorption, as it forms $CaCl_2.2H_2O$]

Q. 8. Write the differences between adsorption and absorption.

[*Hint* : Adsorption is surface, while absorption is bulk phenomenon.]

Q. 9. How can physisorption be distinguished from chemisorptions ?

[*Hint* : Physisorption arises because of van der Waal's forces, not specific and reversible while chemisorptions is caused by chemical bond formation, highly specific and irreversible.]

Q. 10. Classify the following reactions as homogeneous and heterogeneous catalysis :

(a) Vegetable oil (l) + H_2 (g) $\xrightarrow{\text{Ni (s)}}$ Vegetable ghee (s)

(b) $C_{12}H_{22}O_{11}$ (aq) + H_2O (l) $\xrightarrow{H_2SO_4\text{ (aq)}}$ $C_6H_{12}O_6$ (aq) + $C_6H_{12}O_6$ (aq)

[*Hint* : (a) : Heterogeneous catalysis

(b) : Homogeneous catalysis

Q. 11. In what ways these are different : (a) a sol and a gel (b) a gel and an emulsion ?

[*Hint* :

(a) For a sol : Dispersed phase : Solid, Dispersion medium : Liquid

For a gel : Dispersed phase : Liquid, Dispersion medium : Solid

(b) For a gel : Dispersed phase : Liquid, Dispersion medium : Solid

For an emulsion : Dispersed phase : Liquid, Dispersion medium : Liquid]

Q. 12. State 'Hardy Schulze Rule' with one example.

[*Hint* : It states that greater the valency of the flocculating ion of the electrolyte, the faster is the coagulation.]

Q. 13. What is an emulsifying agent ? What role does it play in forming an emulsion ?

[*Hint :* Those agents which stabilize emulsions. It acts as binding agent between two immiscible liquid phases.]

Q. 14. Define the terms :

(a) Helmholtz electrical double layer

(b) Zeta potential

[*Hint :* (a) The combination of the two layers of opposite charges around the colloidal particles. *E.g.,* AgI/I^-K^+.

(b) The potential difference between the fixed layer and diffused layer of opposite charges is called zeta potential.]

Q. 15. A graph between *x/m* and log p is a straight line at an angle of 45º with intercept on the y-axis *i.e.,* (log k) equal to 0.3010. Calculate the amount of the gas absorbed per gram of the adsorbent under a pressure of 0.5 atmosphere.

$$\left[\begin{array}{l} \textit{Hint}: \text{ Refer to NCERT Textbook page 125, Fig. 5.2} \\ \dfrac{1}{n} = \tan 45° = 1, \log k = 0.3010, k = 2, p = 0.5 \text{ atm} \\ \hfill \dfrac{x}{m} = kp^{1/n} = 2\times(0.5)^1 = 1.0 \end{array}\right]$$

Q. 16. Mention the two necessary conditions for the observation of Tyndall effect.

[*Hint :* (a) The size of dispersed phase particles is not much smaller the wavelength of light used.

(b) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.]

Q. 17. Account for the following :

(a) Artificial rain can be caused by spraying electrified sand on the clouds.

(b) Electrical precipitation of smoke.

Q. 18. Write chemical equations for the preparation of sols :

(a) Gold sol by reduction

(b) Hydrated ferric oxide sol by hydrolysis.

[*Hint :* (a) $2AuCl_3 + 3SnCl_2 \xrightarrow{\text{Reduction}} 2Au\text{ (sol)} + 3SnCl_4$

(b) $FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\text{ (sol) (Or }Fe_2O_3.xH_2O) + 3HCl$]

Q. 19. How can the two emulsions can be distinguished :

(a) oil in water type (o/w) and

(b) water in oil type (w/o)

[*Hint :* (a) By dilution test

(b) By dye test]

Q. 20. Leather gets hardened after tanning. Why ?

Ans. Animal hide is colloidal in nature and has positively charged particles. When it is soaked in tanning which has negatively charged colloidal particles, it results in mutual coagulation. This results in the hardening of leather.

Q. 21. Why are some medicines more effective in the colloidal form ?

Ans. Medicines are more effective in the colloidal form because of large surface area and are easily assimilated in this form.

Q. 22. What happens when dialysis is prolonged ?

Ans. When dialysis is prolonged the traces of electrolyte which stabilies the colloids are removed completely. This makes the colloid unstable and therefore coagulation takes place.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Write the difference between :

(a) catalysts and enzymes

(b) promoters and poisons

[*Hint :* (a) Catalyst is a substance that alters the rate of reaction without consuming itself in the reaction. Ezymes are biocatalysts, they are highly specific than catalysts.

(b) Promoters enhance the activity of a catalyst while poisons decrease the activity of catalysts.]

Q. 2. Write the steps of 'Modern Adsorption Theory of Heterogenous Catalysis'.

[*Hint :* (a) Diffusion and adsorption of reactant molecules on the surface of catalyst.

(b) Formation of intermediate on the surface of catalyst.

(c) Desorption of the products from catalysts surface.

(d) Diffusion of products away from the catalyst surface.]

Q. 3. Mention two important features of solid catalysts and explain them with the help of suitable examples.

[*Hint :* Heterogeneous catalyst, activity and selectivity of catalysts. Example, Hydrogenation of unsaturated hydrocarbons in presence of Raney Ni or any other example.]

Q. 4. How are the following colloids different from each other in respect of dispersion medium and dispersed medium ? Give one example of each type.

(a) An aerosol (b) A hydrosol (c) An emulsion

[*Hint :*	**D.P.**	**D.M.**	**Example**
(a)	Solid/liquid	Gas	Smoke, dust, fog, cloud
(b)	Solid	Water	Muddy water
(c)	Liquid	Liquid	Milk, hair cream]

Q. 5. What happens :

(a) By persistent dialysis of a sol.

(b) When river water meets the sea water.

(c) When alum is applied on cuts during bleeding.

[*Hint :* (a) Coagulation of sol takes place.

(b) Delta formation takes place due to coagulation of river water.

(c) Clot is formed due to coagulation of blood which stops further bleeding.]

Q. 6. Distinguish between multimolecular, macromolecular and associated colloids with the help of one example of each.

[*Hint :* (i) Multimolecular colloids formed by aggregation of small atoms or molecules. Example, gold sol, sulphur sol.

(ii) Macromolecular colloids formed by dispersing macromolecules having colloidal size in proper dispersion medium. Example, protein, starch colloid.

(iii) Associated colloids are formed by aggregation of particles at higher concentration to colloidal range. Example, micelles.]

Q. 7. (a) Which property of colloids is responsible for the sun to look red at the time of setting ?

(b) C_2H_2 on addition with H_2 forms ethane in presence of palladium catalyst but if reaction is carried in the presence of barium sulphate and quinoline, the product is ethane and not ethane. Why ?

Ans. (a) Sun is at horizon and blue part of the light is scattered away by the dust particles as light has to travel a long distance through the atmosphere.

(b) $$CH \equiv CH + H_2 \xrightarrow{Pd} CH_2 = CH_2 \xrightarrow{Pd} CH - CH$$

$$CH \equiv CH + H_2 \xrightarrow[BaSO_4,\ quinoline]{Pd} CH_2 = CH_2$$

($BaSO_4$ in presence of quinoline act as poison. The catalyst in this case is not effective in further reduction.)

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Describe some features of catalysis by Zeolites.

Ans. **Features of catalysis by Zeolites :**

(i) Zeolites are hydrated alumino silicates which have a three dimensional network structure containing water molecules in their pores.

(ii) To use them as catalysts, they are heated so that water of hydration present in the pores is lost and the pores become vacant.

(iii) The size of the pores varies from 260 to 740 pm. Thus, only those molecules can be adsorbed in these pores and catalyzed whose size is small enough to enter these pores. Hence, they act as molecular sieves or shape selective catalysts.

An important catalyst used in petroleum industries is ZSM-5. It converts alcohols into petrol by first dehydrating them to form a mixture of hydrocarbons.

$$\text{Alcohols} \xrightarrow[\text{Dehydration}]{\text{ZSM-5}} \text{Hydrocarbons}$$

Q. 2. Comment on the statement that "colloid is not a substance but state of a substance."

Ans. The given statement is true. This is because the statement may exist as a colloid under certain conditions and as a crystalloid under certain other conditions. E.g., NaCl in water behaves as a crystalloid while in benzene, behaves as a colloid (called associated colloid). It is the size of the particles which matters *i.e.,* the state in which the substance exist. If the size of the particles lies in the range 1 nm to 1000 nm it is in the colloid state.

Q. 4. Write short notes on the following :

(a) Tyndall Effect

(b) Brownian Movement

(c) Hardy Schulze Rule

Ans. (a) **Tyndall Effect :** Scattering of light by colloidal particles by which part of beam becomes clearly visible. This effect is known as tyndall effect.

(b) **Brownian Movement :** Zig-zag motion of colloidal particles.

(c) **Hardy Schulze Rule :** Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

E.g., $Na^+ < Ca^{++} < Al^{3+}$ For negatively charged sol

$Cl^- < CO^{2-}_3 < PO^{3-}_4 < [Fe(CN)_6]^{4-}$ For positive sol

MATCHING TYPE

Match the items of Column I and Column II in the following questions :

Q. 1. Method of formation of solution is given in Column I. Match it with the type of solution given in Column II.

Column I	Column II
(i) Sulphur vapours passed through cold water	(a) Normal electrolyte solution
(ii) Soap mixed with water above critical micelle concentration	(b) Molecular colloids
(iii) White of egg whipped with water	(c) Associated colloid
(iv) Soap mixed with water below critical micelle concentration	(d) Macro molecular colloids

Q. 2. Match the statement given in Column I with the phenomenon given in Column II.

Column I	Column II
(i) Dispersion medium moves in an electric field	(a) Osmosis
(ii) Solvent molecules pass through semi permeable membrane towards solvent side	(b) Electrophoresis
(iii) Movement of charged colloidal particles under the influence of applied electric potential towards oppositely charged electrodes	(c) Electro osmosis
(iv) Solvent molecules pass through semi permeable membranes towards solution side	(d) Reverse osmosis

Q. 3. Match the items given in Column I and Column II.

Column I	Column II
(i) Protective colloid	(a) $FeCl_3$ + NaOH
(ii) Liquid-liquid colloid	(b) Lyophilic colloids
(iii) Positively charged colloid	(c) Emulsion
(iv) Negatively charged colloid	(d) $FeCl_3$ + hot water

Q. 4. Match the types of colloidal systems given in Column I with the name given in Column II.

Column I	Column II
(i) Solid in liquid	(a) Foam
(ii) Liquid in solid	(b) Sol
(iii) Liquid in liquid	(c) Gel
(iv) Gas in liquid	(d) Emulsion

Q. 5. Match the items of Column I and Column II.

Column I	Column II
(i) Dialysis	(a) Cleansing action of soap
(ii) Peptisation	(b) Coagulation
(iii) Emulsification	(c) Colloidal sol formation
(iv) Electrophoresis	(d) Purification

Q. 6. Match the items of Column I and Column II.

Column I	Column II
(i) Butter	(a) Dispersion of liquid in liquid
(ii) Pumice stone	(b) Dispersion of solid in liquid
(iii) Milk	(c) Dispersion of gas in solid
(iv) Paints	(d) Dispersion of liquid in solid

Answers

1.	(i) – (b)	(ii) – (c)	(iii) – (d)	(iv) – (a)
2.	(i) – (c)	(ii) – (d)	(iii) – (b)	(iv) – (a)
3.	(i) – (b)	(ii) – (c)	(iii) – (d)	(iv) – (a)
4.	(i) – (b)	(ii) – (c)	(iii) – (d)	(iv) – (a)
5.	(i) – (d)	(ii) – (c)	(iii) – (a)	(iv) – (b)
6.	(i) – (d)	(ii) – (c)	(iii) – (a)	(iv) – (b)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. A factory was situated very close to the residential area where Sita lived. The smoke coming out from the chimney was causing a lot of health problems to people living in the area. Sita and few others decided to meet the top officials of factory and gave idea of installing Cottrell's smoke precipitator.

(a) Name the principle used in Cottrel precipitator.

(b) How does precipitator cause precipitation and settling of smoke particles ?

(c) What values do you attribute to Sita's concern ?

(d) What happens when a strong beam of light is passed through the smoke ?

Q. 2. Ramesh, living in Ooty, was washing clothes in cold water during winter. He found that the clothes were not getting clean properly. Geetu, his niece, suggested that he should wash clothes in warm water because washing of clothes with soaps/detergents is easier in warm water than cold water.

(a) Why is it so ?

(b) Why do we get lathers easily in warm water ?

(c) Define CMC.

(d) What values do you derive from this ?

Q. 3. Nandita observed that the barber applied alum on the face of his customer. He also observed her mother dissolving alum to purify muddy water.

(a) Which concept of colloidal solutions is observed by Nandita ?

(b) How are deltas formed ?

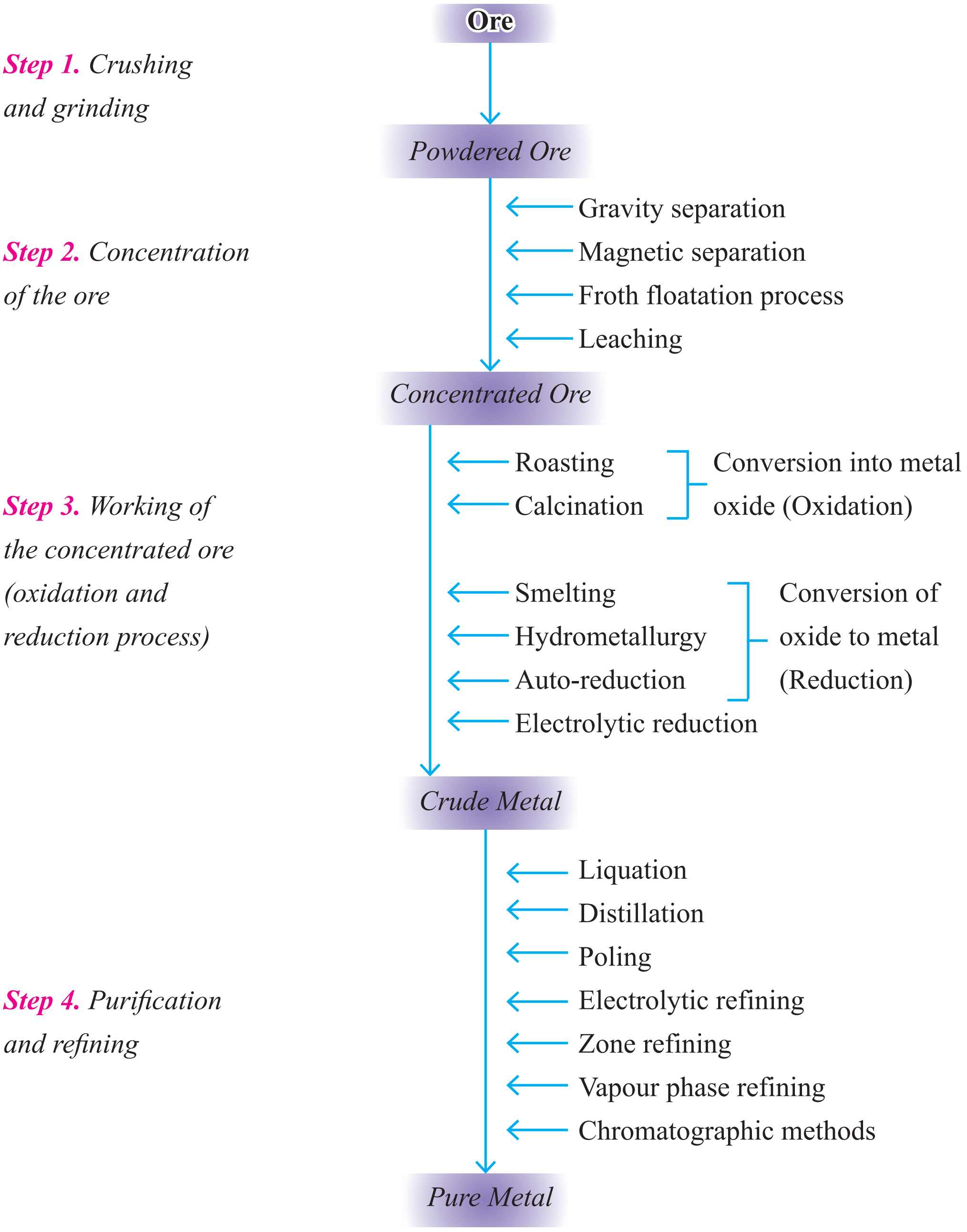
(c) State Hardy Schulze Rule.

(d) Write the value associated with the observation.

UNIT-6

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Flow-sheet diagram of metallurgical process is given below :



General Types of Ores of Metals

Type of Ore	Metal	Name of ore
1. Oxides	Iron	Haematite, Fe_2O_3
	Aluminium	Bauxite, $Al_2O_3.2H_2O$
	Copper	Cuprite, Cu_2O
	Zinc	Zincite, ZnO
	Manganese	Pyrolusite, MnO_2
2. Sulphides	Copper	Copper pyrites, $CuFeS_2$
	Lead	Galena, PbS
	Zinc	Zinc blende, ZnS
	Mercury	Cinnabar, HgS
3. Carbonates	Iron	Siderite, $FeCO_3$
	Copper	Malachite, $CuCO_3.Cu(OH)_2$
	Calcium	Limestone, $CaCO_3$
	Magnesium	Dolomite, $MgCO_3.CaCO_3$
4. Chloride	Sodium	Rock salt, NaCl
	Magnesium	Carnallite, KCl, $MgCl_2.6H_2O$
	Silver	Horn silver, AgCl
5. Sulphates	Calcium	Gypsum, $CaSO_4.2H_2O$
	Lead	Anglesite, $PbSO_4$
6. Silicates	Magnesium	Calcium magnesium silicate, $CaSiO_2.3MgSiO_2$ (Asbestos)

Various Types of Steel

Type of Steel	Carbon content	Properties	Uses
Mild Steel (Medium carbon	0.2-0.5%	(i) It can be hardened by heat treatment. (ii) It has a good machining property. (iii) It is very good for welding.	(i) Lightly stressed machine fittings, turbine, motors, steel) railway axels, crank shafts, fish plates, cross heads, etc.
Hard Steel	0.5-0.7%	(i) It can be imparted desired hardness by heat treatment. (ii) It can be welded with a great care.	Wheels for railways service, cushion springs, clutch springs, dies, set screws, etc.
Chrome Steel	1.5-2% Cr	Extremely hard	For making armour – piercing projectiles, crushing machinery and cutlery.
Stainless Steel	11.5% Cr 2% Ni	Resists corrosion	For making cutlery, utensils, surgical instruments, automobile parts and cycle parts.

Note : NaCN is used as depressant when an ore contains both ZnS and PbS. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth in froth floatation process.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Name three metals which occur in native state in nature.

Ans. Au, Ag and Pt.

Q. 2. What are collectors in froth floatation process ? Give one example.

Ans. Pine oil.

Q. 3. Give the names and formulae of three ores which are concentrated by froth floatation process.

Ans. Galena (PbS), Zinc blende (ZnS), Cinnabar (HgS).

Q. 4. Among Fe, Cu, Al and Pb, which metal(s) cannot be obtained by smelting ?

Ans. Al.

Q. 5. What is the thermodynamic criteria for the feasibility of a reaction ?

Ans. ΔG should be –ve or log K = + ve.

Q. 6. Why can't aluminium be reduced by carbon ?

[*Hint :* Al is stronger reducing agent than carbon.]

Q. 7. Name the most important form of iron. Mention its one use.

Ans. Cast iron is used for making gutter pipes, castings, railway sleepers, toys etc.

Q. 8. Name the impurities present in bauxite ore.

Ans. SiO_2, Fe_2O_3 and TiO_2.

Q. 9. What is the composition of copper matte ?

[*Hint :* Cu_2S and FeS]

Q. 10. Which form of copper is called blister copper ?

[*Hint :* The solidified copper obtained has blistered appearance due to the evolution of SO_2, so it is called blistered copper.]

Q. 11. What are froth stabilizers ? Give two examples.

[*Hint :* Examples are cresol and aniline.]

Q. 12. A sample of galena is contaminated with zinc blende. Name one chemical which can be used to concentrate galena selectively by froth floatation method.

Ans. NaCN

Q. 13. What are the constituents of German silver ?

Ans. Cu = 25-30%, Zn = 25-30%, Ni = 40-50%]

Q. 14. Why is froth floatation process selected for concentration of the sulphide ore ?

Ans. Sulphide ore particles are wetted by oil (Pine oil) and gangue particles by water.

Q. 15. Write the reaction involved in the extraction of copper from low grade ores.

Ans. First step is leaching of ore with acid or bacteria then,

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

Q. 16. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Why ?

[*Hint :* Due to formation of inert oxide Al_2O_3.]

Q. 17. Which method of purification is represented by the following reaction :

$$\underset{\text{impure}}{Ti_{(s)}} + 2I_{2(g)} \rightarrow TiI_{4(g)} \xrightarrow{\Delta} \underset{\text{pure}}{Ti_{(s)}} + 2I_{2(g)}$$

[*Hint :* Van Arkel method]

Q. 18. Zinc is used but not copper for the recovery for metallic silver from the complex $[Ag(CN)_2]^-$, although electrode potentials of both zinc and copper are less than that of Ag. Explain why ?

[*Hint :* Zinc reacts at faster rate as compared with copper, further zinc is cheaper than copper.]

Q. 19. Write the composition of moleten mixture which is electrolysed to extract aluminium.

[*Hint :* Molten $Al_2O_3 + Na_3AlF_6$ or CaF_2]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. What is hydrometallurgy ? Give one example where it is used for metal extraction.

Ans. Leaching followed by reduction is called hydrometallurgy. It is used in extraction of copper.

Q. 2. Name the process for the benefaction/concentration of (i) an ore having lighter impurities, (ii) sulphide ore.

[*Hint :* (i) Gravity separation
(ii) Froth floatation]

Q. 3. Mention the role of cryolite in the extraction of aluminium.

[*Hint :* It lowers the melting point of the mixture and brings conductivity.]

Q. 4. Mention the role of following :

(a) SiO_2 in the metallurgy of Cu.

(b) $CaCO_3$ in the metallurgy of Fe.

(c) CO in the metallurgy of iron.

(d) I_2 in the purification of zirconium.

[*Hint :* (a) Flux
(b) $CaCO_3$ decomposed to CaO, which acts as flux.
(c) Reducing agent
(d) To form a volatile complex with Zr.]

Q. 5. Extraction of copper directly from sulphide ore is less favourable than from its oxide through reduction. Explain.

Ans. $2CuS\ (s) + C\ (s) \rightarrow CS_2\ (l) + 2Cu\ (s)$

$CuO\ (s) + C\ (s) \rightarrow CO\ (g) + Cu\ (s)$

G value is more –ve in second case as compared with first case.

Q. 6. The graphite electrodes in the extraction of 'aluminium' by Hall-Heroult process need to be changed frequently. Why ?

Q. 7. Write the chemical formulae of the following ores :

(a) Haematite **(b) Magnetite**

(c) Limonite **(d) Siderite**

Ans. (a) Fe_2O_3 (b) Fe_3O_4

(c) $Fe_2O_3.2H_2O$ (d) $FeCO_3$

Q. 8. Give equations for the industrial extraction of zinc from calamine.

Ans. $ZnCO_3 \rightarrow ZnO + CO_2$ (Calcination)

$ZnO + C \rightarrow Zn + CO$ (Reduction)

Q. 9. Name the elements present in anode mud during refining of copper. Why does it contain such elements ?

Ans. Au and Ag. They are not oxidized at anode. They are less electropositive than copper.

Q. 10. Write the chemical reactions taking place in different zones in the blast furnace for the extraction of iron from its ore.

[*Hint :* (i) $C + CO_2 \rightarrow 2CO$

(ii) $3Fe_2O_3 + CO \rightarrow 2Fe_2O_4 + CO_2$

(iii) $Fe_3O_4 + CO \rightarrow 2FeO + CO_2$

(iv) $FeO + CO \rightarrow Fe + CO_2$

(v) $CaCO_3 \rightarrow CaO + CO_2$

(vi) $CaO + SiO_2 \rightarrow CaSiO_3$

Q. 11. How are impurities separated from bauxite ore to get pure alumina ?

[*Hint :* By leaching.

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

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

(iii) $Al_2O_3.xH_2O \rightarrow \underset{\text{(alumina)}}{Al_2O_3}\ (s) + xH_2O\ (g)$

Q. 12. Why is the reduction of a metal oxide easier if metal formed is in liquid state at the temperature of reduction ?

[*Hint :* Entropy is more positive when the metal is in liquid state as compared with solid state, so ΔG becomes more –ve.]

Q. 13. What is pyrometallurgy ? Explain with one example.

Ans. A process of reducing a metal oxide by heating with either coke or some other reducing agent. *E.g.,* Al, Mg etc.

$$\mathrm{ZnO + C \xrightarrow{975\ K} Zn + CO}$$

Q. 14. Write the method to produce copper matte from copper pyrites.

[*Hint :* Froth floatation.]

Q. 15. Copper can be extracted by hydrometallurgy but not zinc. Explain why ?

[*Hint :* $\mathrm{E^o}_{2n^{2+}} / 2n$ = – ve, $\mathrm{E^o}_{\mathrm{cu}^{+2}}$ /cu = + ve

Q. 16. Gibbs energy of formation G_f^G of MgO (s) and CO (g) at 1273 K and 2273 K are given below :

G_f [MgO (s)] = – 941 kJ mol^{-1} at 1273 K

G_f [CO (g)] = – 439 kJ mol^{-1} at 1273 K

G_f [MgO (s)] = – 314 kJ mol^{-1} at 2273 K

G_f [CO (g)] = – 628 kJ mol^{-1} at 2273 K

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO (s).

Ans. For the reaction, $\mathrm{MgO\ (s) + C\ (s) \rightarrow Mg\ (s) + CO\ (g)}$

At 1273 K, G_r = G_f[CO (g)] – G_f[MgO (s)] = – 439 – (– 941) kJ mol^{-1} = 502 kJ mol^{-1}

At 2273 K, G_r = – 628 – (– 314) kJ mol^{-1} = – 314 kJ mol^{-1}

The temperature is 2273 K.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. State the principle of refining of metal by the following methods :

(a) Zone refining

(b) Electrolytic refining

(c) Vapour phase refining

[*Hint :*(a) The impurities are more soluble in the melt than in the solid state of the metal.

(b) Impure metal is made to act as anode, while the strip of same metal in pure form as cathode.]

Q. 2. How is pure copper obtained from its principle ore ? Write the chemical reactions occurring during the extraction.

[*Hint :* (i) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + O_2$

(ii) $Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(iii) $Cu_2O + C \rightarrow 2Cu + CO$

(iv) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$]

Q. 3. Name the method of refining of the following metals :

(a) Hg (b) Sn (c) Cu (d) Ge (e) Ni (f) Zr

Ans. (a) Distillation, (b) Liquation, (c) Electrolytic refining, (d) Zone refining, (e) Mond process, (f) Van Arkel process]

Q. 4. The native silver forms a water soluble compound (B) with dilute aqueous solution of NaCN in the presence of a gas (A). The silver metal is obtained by the addition of a metal (C) to (B) and complex (D) is formed as a byproduct. Write the structures of (C) and (D) and identify (A) and (B) in the following sequence :

$Ag + NaCN + [A] + H_2O\ [B] + OH^- + Na^+\ [C] + [B][D] + Ag$

Ans. $[A] = O_2$

$[B] = Na[Ag(CN)_2]$

$[C] = Zn$

$[D] = Na_2[Zn(CN)_4]$

Q. 5. In the cynamide extraction process of silver pon argentite ore, name the oxidizing and reducing agents. Write the chemical equations of the reactions involved.

[*Hint :* $4Ag + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Ag(CN)_2] + 4NaOH$

$2[Ag(CN)_2]^-\ (aq) + Zn\ (s) \rightarrow [Zn(CN)_4]^{2-}\ (aq) + 2Ag\ (s)$

MATCHING TYPE QUESTIONS

Match the items given in Column I and Column II in the following questions.

Q. 1. Match the items of Column I with items of Column II and assign the correct code :

Column I	Column II
(A) Pendulum	(1) Chrome steel
(B) Malachite	(2) Nickel steel
(C) Calamine	(3) Na_3AlF_6
(D) Cryolite	(4) $CuCO_3.Cu(OH)_2$
	(5) $ZnCO_3$

Q. 2. Match the items of Column I with items of Column II and assign the correct code :

Column I	Column II
(A) Coloured bands	(1) Zone refining
(B) Impure metal to volatile complex	(2) Fractional distillation
(C) Purification of Ge and Si	(3) Mond process
(D) Purification of mercury	(4) Chromatography
	(5) Liquation

Q. 3. Match the items of Column I with items of Column II and assign the correct code :

Column I	Column II
(A) Cyanide process	(1) Ultrapure Ge
(B) Froth floatation process	(2) Dressing of ZnS
(C) Electrolytic reduction	(3) Extraction of Al
(D) Zone refining	(4) Extraction of Au
	(5) Purification of Ni

Q. 4. Match the items of Column I with items of Column II and assign the correct code :

Column I	Column II
(A) Sapphire	(1) Al_2O_3
(B) Sphalerite	(2) NaCN
(C) Depressant	(3) Co
(D) Corundum	(4) ZnS
	(5) Fe_2O_3

Q. 5. Match the items of Column I with items of Column II and assign the correct code :

	Column I		Column II
(A)	Blistered Cu	(1)	Aluminium
(B)	Blast furnace	(2)	$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$
(C)	Reverberatory furnace	(3)	Iron
(D)	Hall-Heroult process	(4)	$FeO + SiO_2 \rightarrow FeSiO_3$
		(5)	$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

Answers

1.	(A) – (2)	(B) – (4)	(C) – (5)	(D) – (3)
2.	(A) – (4)	(B) – (3)	(C) – (1)	(D) – (2)
3.	(A) – (4)	(B) – (2)	(C) – (3)	(D) – (1)
4.	(A) – (3)	(B) – (4)	(C) – (2)	(D) – (1)
5.	(A) – (2)	(B) – (3)	(C) – (4)	(D) – (1)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Ram and Shyam were extracting aluminium from purified Al_2O_3. Ram used electrolytic cell for the reduction of Al_2O_3 but Shyam added cryolite in Al_2O_3 in the electrolytic cell to obtain aluminium.

(a) Who will obtain aluminium easily ?

(b) Mention two functions of cryolite in this reduction process.

(c) What is the role of graphite anode in the metallurgy of Al ?

(d) What values are learnt by the use of cryolite (Na_3AlF_6) in the extraction of aluminium ?

Q. 2. Steel finds different uses and alloy steel is obtained when other metal like Cr, Ni are added to form nickel steel, chrome steel and stainless steel.

(a) What is alloy steel ?

(b) Why do transition metals form alloys ?

(c) A person wants to manufacture cycles and motor cycles in his factory. Name the alloy steel he should use for manufacturing the same.

(d) Name the value learnt by the selection of a proper type of steel.

Q. 3. A person met to a housewife and motivated her for cleansing of gold ornaments at very low cost. Housewife gave gold ornaments to him. He placed them into a solution containing 1 part conc. HNO_3 and 3 parts conc. HCl. After sometime he showed the shiny gold ornaments to her. In the mean time, housewife's daughter

Pinki, a student of chemistry of Class XII, returns from school. She took the cleansing solution in her custody and the cleaner ran away. She explained all the chemistry behind the incident to her mother.

(a) Name the solution used by cleaner for cleansing of gold ornaments.

(b) How can we recover the gold from the solution used for cleansing purpose ?

(c) Write the reaction that takes place between the solution and gold ornaments.

(d) What values are learnt from the incident ?

UNIT 7

p-BLOCK ELEMENTS

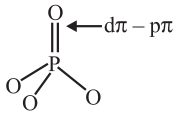
Anomalous behavior of first element in the p-block elements is attributed to small size, large (charge/radius) ratio, high ionization enthalpy, high electronegativity and unavailability of d-orbitals in its valence shell.

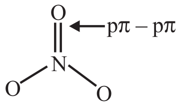
Consequences :

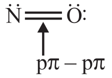
1. The first element in p-block element has four valence orbitals *i.e.,* one 2s and three 2p. Hence maximum covalency of the first element is limited to four. The other elements of the p-block have vacant d-orbitals in their valence shell, *e.g.,* three 3p and five three 3d orbitals. Hence, these elements show maximum covalence greater than four. Following questions can be answered :
   - (i) Nitrogen (N) does not form pentahalide while P forms PCl_5, PF_5 and PF_6^-. Why ?
   - (ii) Sulphur (S) forms SF_6 but oxygen does not form OF_6. Why ?
   - (iii) Though nitrogen forms pentoxide but it does not form pentachloride. Why ?
   - (iv) Fluorine forms only one oxoacid while other halogens form a number of oxoacids. Why ?
2. The first member of p-block elements displays greater ability to form pπ-pπ bond(s) with itself, (*e.g.,* C=C, C≡C, N=N, N≡N) and with the other elements of second period, for example, C=O, C≡N, N=O compared to the subsequent members of the group.

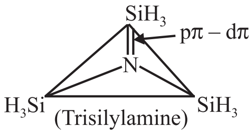
   This is because p-orbitals of the heavier members are so large and diffuse that they cannot have effective sideways overlapping. Heavier members can form p π-dπ bonds with oxygen.

   Nitrogen rarely forms pπ-dπ bonds with heavier elements as in case of trisilylamine $(SiH_3)_3N$.

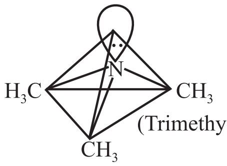








(Trisilylamine)



(Trimethylamine)

Now, the following questions can be explained using the above mentioned reasoning :

(i) Nitrogen forms N_2 but phosphorus forms P_4 at room temperature. Why ?

(ii) Oxygen exists as O_2 but sulphur as S_8. Why ?

(iii) Explain why $(CH_3)_3P{=}O$ is known but $(CH_3)_3N{=}O$ is not known.

3. Due to small size and high electronegativity and presence of lone pair(s) of electrons, elements N, O, F when bonded to hydrogen atom, forms hydrogen bonds which are stronger than other intermolecular forces. This results in exceptionally high m.p. and b.p. of the compounds having N–H/O–H/F–H bonds.

Isostructural species have same number of bond pairs and lone pairs if present around the central atom in a molecule/ion. Thus, they have the same geometry/ shape/structure and the same hybridisation scheme. For example, ICl_4^-/XeF_4, BrO_3^-/XeO_3, BH_4^-/NH_4^+ are the pairs of isostructural species.

Inert pair effect : Due to poor shielding effect of intervening d and/or f-electrons, the effective nuclear charge increases. This increased nuclear charge holds the ns^2 electrons of heavier elements strongly and the tendency of ns^2 electrons to take part in bonding is more and more restricted down the group. Consequently, more stable lower oxidation state which is two units less than higher oxidation state, becomes more and more stable than the higher oxidation state. Following questions can be explained with the help of inert pair effect :

(i) For N and P, + 5 oxidation state is more stable than + 3 oxidation state but for Bi + 3 oxidation state is more stable than + 5. Explain why ?

(ii) $NaBiO_3$ is a strong oxidizing agent. Why ? [*Hint :* Bi (V) is least stable.]

(iii) In group 16, stability of +6 oxidation state decreases and the stability of + 4 oxidation state increases down the group. Why ?

(iv) SO_2 acts as reducing agent. Explain why ?

(v) Why is BrO_4^- a stronger oxidizing agent than ClO_4^- ?

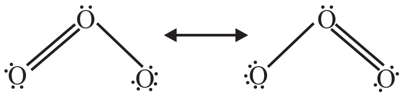
[*Hint :* It is because + 7 oxidation state is less stable in BrO_4^- due to which Br – O bond becomes weaker.]

(vi) $AsCl_5$ is less stable than $SbCl_5$.

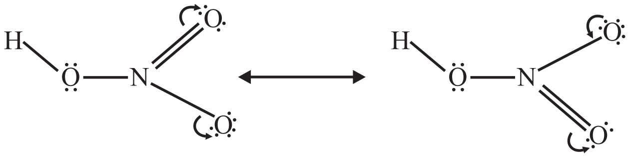
[*Hint :* More effective nuclear charge in As than Sb.]

(vii) The stability of highest oxidation state of 4p element is less than those of 3p and 5p elements of the same group. Why ?

Bond length : Resonance averages bond lengths. The two oxygen-oxygen bond lengths are identical in the O_3 molecule because it is resonance hybrid of following two canonical forms.



In case of HNO_3, two nitrogen-oxygen bonds are identical and smaller than the third nitrogen-oxygen bond. This is because the third N– OH bond is not involved in resonance.

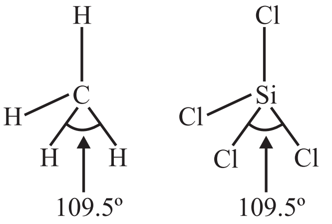


Now the following questions can be explained on the basis of this concept :

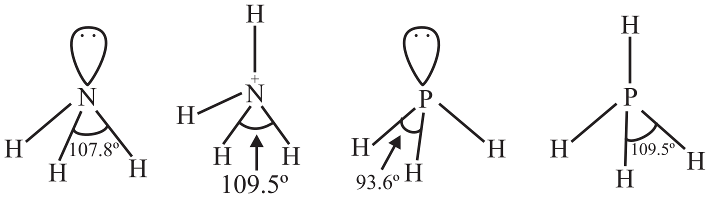
(i) In SO_2, the two sulphur-oxygen bonds are identical. Explain why ?

(ii) In NO_3^- ion, all the three N– O bonds are identical. Why ?

Bond angle : In regular structures (where no lone pairs are present in the valence shell of the central atom in a molecule/ion), the bond angle does not depend upon the size/electronegativity of the central or terminal atoms.



In presence of lone pair(s) on the central tom, the geometry is distorted and the bond angle is changed.



Comparison of HNH and HPH bond angles

Since N is more electronegative than P, the bonding electron pair of N– H bond will shift more towards N atom than the bonding electron pair of P– H bond would shift towards P atom. This results in more bond pair-bond pair repulsion in NH_3 molecule than PH_3 molecule. Because of more Ip-bp repulsion, the N– H bonds are pushed closer to a lesser extent than in PH_3. Consequently, HNH bond angle is greater than HPH angle.

Now, the following questions can be explained using the above mentioned concept :

(i) Bond angle in PH_4^+ ion is higher than in PH_3. Why ?

(ii) H– O– H bond in H_2O is greater than H– S– H angle in H_2S. Why ?

Boiling and melting points of hydrides depends upon the molar mass (or surface area) of molecules. More the molar mass, the higher is the m.p. and b.p. Hydrides forming intermolecular hydrogen bonds have exceptionally high m.p. and b.p. since intermolecular hydrogen bonds are stronger than the van der Waals forces.

Increasing order of melting point and boiling point of hydrides is as given below :

$PH_3 < AsH_3 < SbH_3 < NH_3$	Melting point
$PH_3 < AsH_3 < NH_3 < SbH_3$	Boiling point
$H_2S < H_2Se < H_2Te < H_2O$	Melting point and boiling point
$HCl < HBr < HI < HF$	Boiling point
$HCl < HBr < HF < HI$	Melting point

(i) NH_3 has higher boiling point than PH_3.

(ii) H_2O is liquid and H_2S is gas or H_2S is more volatile than H_2O.

Thermal stability, reducing power and acid strength of hydrides depend upon bond dissociation enthalpy of E– H bond (E = group 15, group 16, and group 17 element). Due to the increase in size down the group, bond dissociation enthalpy of E–H bond decreases. Consequently, thermal stability, reducing power and acid strength of hydrides increases down the group.

The following questions can be explained using the above concepts.

Explain why :

(i) HF is weaker acid than HCl.

(ii) Among hydrogen halides, HI is the strongest reducing agent.

(iii) H_2Te is more acidic than H_2S.

(iv) NH_3 is mild reducing agent while BiH_3 is the strongest reducing agent among the group-15 hydrides.

(v) H_2S is weaker reducing agent than H_2Te.

Basic nature of hydrides EH_3 of group 15 elements

All the hydrides EH_3 of group 15 elements has one lone pair of electrons. In ammonia, the lone pair of electrons is present in sp^3 hybrid orbital of the N-atom. The sp^3 hybrid orbital is directional and further N is more electronegative than H, the bond pair of N – H is shifted towards N atom which further increases the electron density on N atom. In PH_3, the lone pair of electrons is present in large and more diffuse 3s orbital which is non-directional. As a result, PH_3 is less basic than NH_3 and basic character decreases down the group. NH_3 donates electron pair more readily than PH_3. $(SiH_3)_3N$ has less Lewis basic nature than that of $(CH_3)_3N$ because lone pair of electrons in p-orbital of N atom in $(SiH_3)_3N$ is transferred to the vacant d-orbital of Si atom forming $d\pi$-$p\pi$ bond.

Covalent/Ionic Character of Halides

Pentahalides are more covalent than trihalides since the element (E) in higher oxidation state (+ 5) in pentahalides has more polarizing power than element (E) in lower oxidation state (+ 3) in trihalides, similarly, $SnCl_4$, $PbCl_2$, $SbCl_3$ and UF_4 respectively. Compounds having more ionic character have more m.p. and b.p. than the compounds having more covalent character.

Following questions can be explained by using this concept.

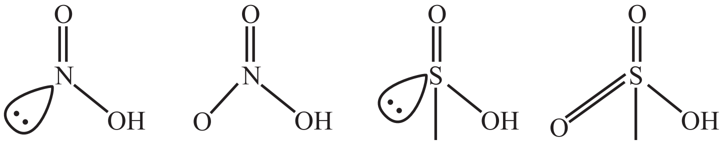
Explain why :

(i) $SnCl_2$ has more b.p. than $SnCl_4$.

(ii) $SbCl_5$ is more covalent than $SbCl_3$.

(iii) PCl_5 has lower boiling point than that of PCl_3.

Oxoacids of N, P and halogens :

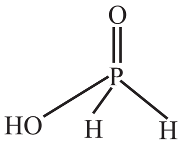


(HNO_3)

Stronger than HNO_3

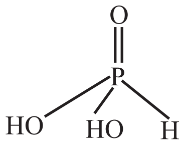
H_2SO_3

Stronger than H_2SO_3



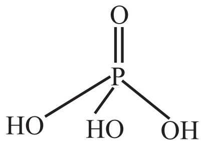
(Monophonic)

(H_3PO_2)



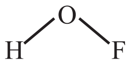
(Diprotic)

(H_3PO_3)

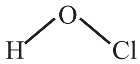


(Triprotic)

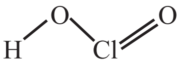
(H_3PO_4)



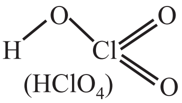
(HOF)



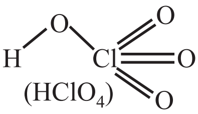
(HClO)



($HClO_3$)



($HClO_4$)



($HClO_4$)

Strength of Oxo Acids

Strength of oxoacids depends upon the polarity of O– H bond which in turn, depends on the electron withdrawing power (or electronegativity) of the element E. Strength of oxoacids increases if the number of oxygen atoms bonded with E increases.

Strength of oxoacids of halogens in the same oxidation state depends on the electronegativity of the halogen. The more the electronegativity, stronger is the oxoacid.

Strength of oxoacid of a halogen in different oxidation state increases with the increase in oxidation state. This is because the stabilization of the oxoanion increases with the number of the oxygen atoms bonded to the halogen atom. More the number of oxygen atoms, the more the dispersal of –ve charge present on the oxoanion and stronger will be the oxoacid.

Oxidising Power of Halogens

$$\begin{tikzcd}
X(g) \arrow[r, "-\Delta_{eg}H"] & X(g) \arrow[d, "aq"', "-\Delta_{hyd}H^\theta"] \\
\frac{1}{2}X_2(g) \arrow[u, "+\frac{1}{2}\Delta_{diss}H^\theta"'] \arrow[r, "\Delta_r H^\theta"] & X(aq)
\end{tikzcd}$$

The more negative the value of $\Delta_r H^\theta = \frac{1}{2}\Delta_{diss}H^\theta - \Delta_{eg}H^\theta - \Delta_{hyd}H^\theta$ the higher will be oxidizing property of the halogen and more positive will be standard reduction potential E^θ_{red} of the halogen.

Following questions can be explained on the basis of parameters, like $\Delta_{diss}H^\theta$, $\Delta_{eg}H^\theta$ and $\Delta_{hyd}H^\theta$.

(i) Why does F_2 have exceptionally low bond dissociation enthalpy ?

(ii) Although electron gain enthalpy of fluorine (F) is less negative as compared to chlorine (Cl), Fluorine gas (F_2) is a stronger oxidizing agent than Cl_2 gas. Why ?

Some Important Reactions

1. $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$
2. $FeCl_3\,(aq) + NH_4OH\,(aq) \rightarrow Fe_2O_3.xH_2O\,(s) + NH_4Cl\,(aq)$
3. $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
4. $AgCl\,(s) + 2NH_3\,(aq) \rightarrow [Ag(NH_3)_2]Cl$
5. $2Pb(NO_3)_2 \xrightarrow{673\text{ K}} 4NO_2 + 4PbO + O_2$
6. $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$
7. $3Cu + 8HNO_3\,(dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
8. $Cu + 4HNO_3\,(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
9. $4Zn + 10HNO_3\,(dil.) \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
10. $Zn + 4HNO_3\,(conc.) \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
11. $I_2 + 10HNO_3\,(conc.) \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$
12. $S_8 + 48HNO_3\,(conc.) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$
13. $P_4 + 20HNO_3\,(conc.) \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
14. Chemistry of ring test :

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

    $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$
15. $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
16. $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
17. $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
18. $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
19. $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 3HCl$
20. $4H_3PO_3 \xrightarrow{heat} 3H_3PO_4 + PH_3$
21. $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
22. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
23. $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
24. $2F_2\,(g) + 2H_2O\,(l) \rightarrow 4H^+\,(aq) + 4F^-\,(aq) + O_2\,(g)$
25. $X_2\,(g) + H_2O\,(l) \rightarrow HX\,(aq) + HXO\,(aq)$ (X = Cl, Br)
26. $4I^-\,(aq) + 4H^+\,(aq) + O_2 \rightarrow 2I_2\,(s) + 2H_2O\,(l)$

27. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

28. $2NaOH\ (dil) + X_2 \xrightarrow{Cold} NaX + NaOX + H_2O$

29. $6NaOH\ (conc) + 3X_2 \xrightarrow{heat} 5NaX + NaXO_3 + 3H_2O$ $(X_2 = Cl_2, Br_2, I_2)$

30. $2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

31. $NaCl + H_2SO_4 \xrightarrow{heat} NaHSO_4 + HCl$

32. $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$

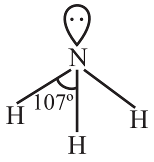
33. $XeF_6 + MF \rightarrow M^+[XeF_7]^-$ (M = Na, K, Rb or Cs)

34. $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

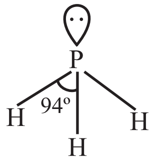
35. $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

36. $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

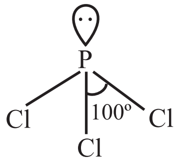
37. $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$



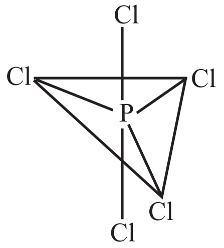
NH_3
Sp_3 (Pyramidal)



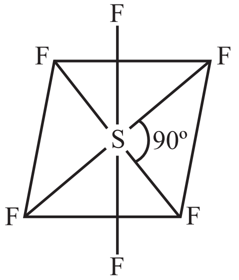
PH_3
Sp^3 (Pyramidal)



Sp^3 (Pyramidal)
PCl_3

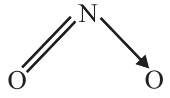


Sp^3d (Trigonalbiphyramidal)



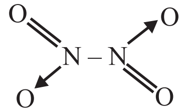
SF_6
Sp^3d (octahedral)

Oxides of Nitrogen
:N = 0
Nitric oxide (colourless)
paramagnetic

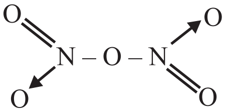


Sp^2 (NO_2) Bentmolecule
(brown) Paramagnetic

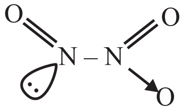
$N \equiv N \rightarrow O$
(N_2O) Colourless
Linear



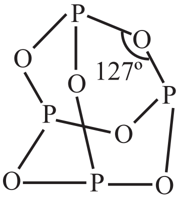
N_2O_4 (Colourless)
(diamagnetic)



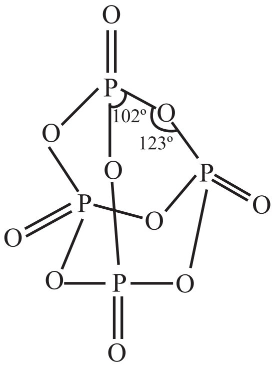
N_2O_5 (Colourless)
(diamagnetic)



(N_2O_3)
Pale blue solid

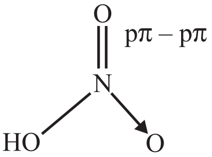


dimer P_2O_3

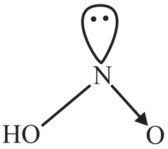


dimer of P_2O_5

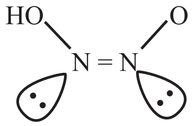
Oxy-acids of Nitrogen



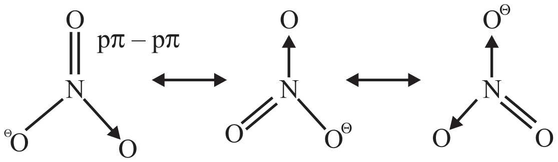
(HNO_3)
Colourless



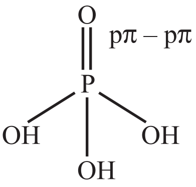
(HNO_3)
Para blue



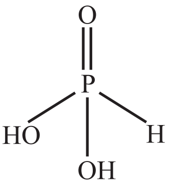
Hyponitrous acid



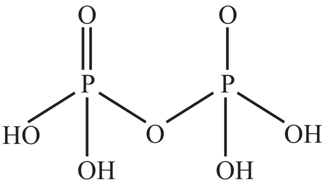
Resonating structure of NO_3^-



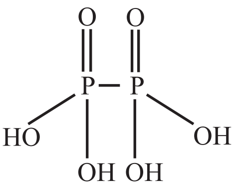
H_3PO_4
(Phosphoric acid)
tribasic



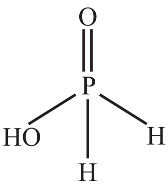
H_3PO_3
Phosphoric acid
(Dibasic)



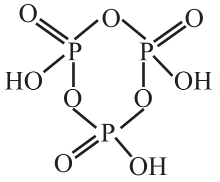
$H_4P_2O_7$
Pyrophosphoric acid
(tetrabasic)



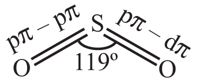
Hypophosphoric acid
$H_4P_2O_6$ (tetrabasic)



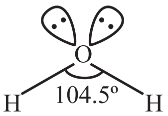
H_3PO_2
(Hypophosphoric acid)
(Monobasic)



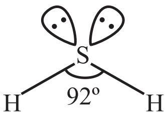
Cyclic meta phosphoric
acid $(HPO_3)_n$



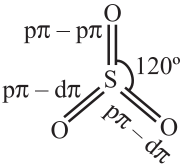
sp^3
Bent molecules



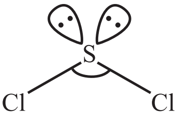
H_2O (sp^3)
V-shape

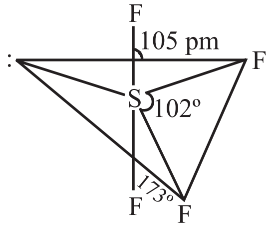


H_2O (sp^3)
V-shape

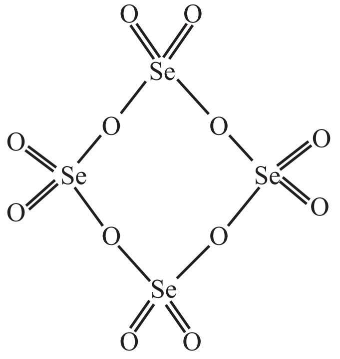


Planer Sp^2

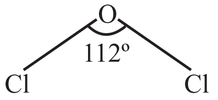




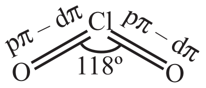
SF_4
Trigonal pyramidal sp3d
Oxy-acids of sulphur



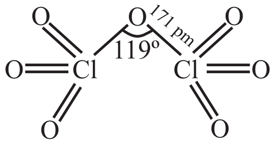
Cyclic tetramer of SeO_2



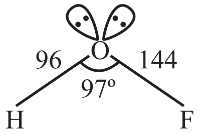
Cl_2O



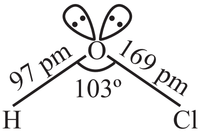
ClO_2

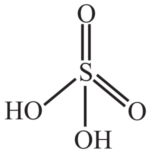


Cl_2O_7

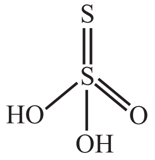


Cl_2O

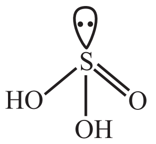




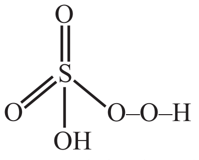
(H_2SO_4)
Sulphuric acid



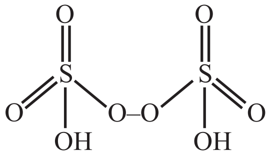
$(H_2S_2O_3)$
(Thiosulphuric acid)



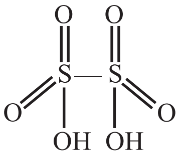
(H_2SO_3)
(Sulphurous acid)



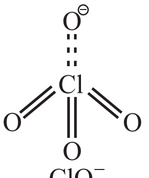
Peroxomonosulphuric acid
(Caro's acid)



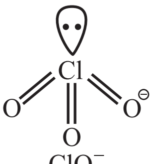
Peroxodisulphuric acid
$(H_2S_2O_3)$ Marshall's acid



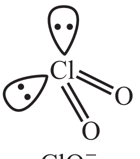
Dithionic acid $(H_2S_2O_5)$



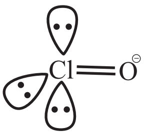
ClO_4^-



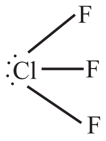
ClO_3^-



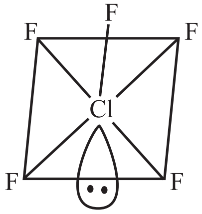
ClO_2^-



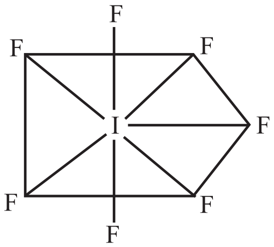
ClO^-



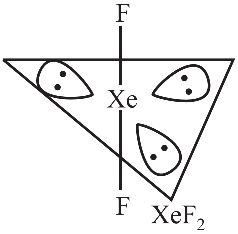
Bent- T-shaped (sp^3d) CIF_3



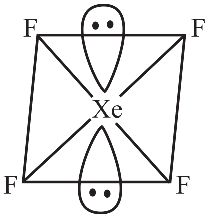
Square pyramidal
CIF_5 (sp_3d^2)



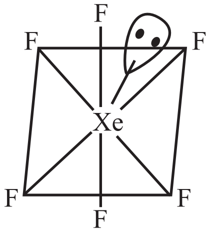
Pentagonal bipyramidal
IF_5 (sp^3d^3)



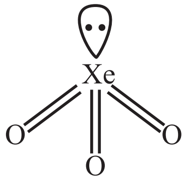
XeF_2 Linear (sp^3d)



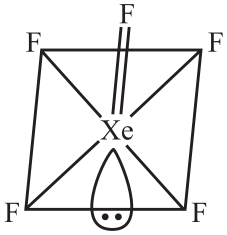
XeF_4 Square Planer
(sp^3d^2)



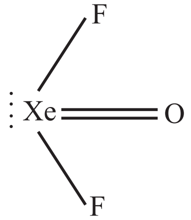
XeF_6 (sp^3d^2)
Distorted octahedral



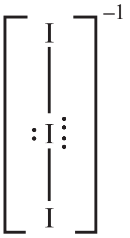
sp^3 Pyramidal
XeO_3



Square pyramidal
$XeOF_4$ (sp^3d^2)



$XeOF_2$ Linear (sp^3d)
Bent-T-shaped



[I_3^{-1} sp^3d, Linear]

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. In group 15 elements, there is considerable increase in covalent radius from N to P but small increase from As to Bi. Why ?

[*Hint :* Due to completely filled d- and/or f-orbitals in As, Sb and Bi.]

Q. 2. The tendency to exhibit – 3 oxidation state, decreased down the group in group 15 elements. Explain.

[*Hint :* Due to increase in size and decrease in electronegativity down the groups.]

Q. 3. Maximum covalence of nitrogen is '4' but the heavier elements of group 15 show covalence greater than '4'. Why ?

[*Hint :* Nitrogen is not having vacant d- orbitals in its octet, hence cannot expand its octet, while heavier members have vacant d-orbitals to expand their octet.]

Q. 4. Nitrogen exists as a diatomic molecule with a triple bond between the two atoms, whereas the heavier elements of the group do not exist as E_2 at room temperature. Assign a reason.

[*Hint :* p-p multiple bonds are formed by N due to its small size.]

Q. 5. The ionization enthalpies of group 15 elements are higher than those of corresponding members of group 14 and 16 elements. Assign the reason.

[*Hint :* Due to their stable electronic configuration (ns^2np^3).]

Q. 6. The boiling point of PH_3 is lesser than NH_3. Why ?

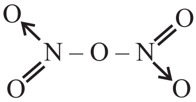
[*Hint :* NH_3 molecules are stabilized by intermolecular H-bonding, while PH_3 by weak van der Waals's forces.]

Q. 7. NO_2 dimerises to form N_2O_4. Why ?

[*Hint :* Due to presence of odd electron on N.]

Q. 8. Draw the structure of N_2O_5 molecule.

Ans.



Q. 9. How does ammonia solution react with Ag^+ (aq) ? Write the balanced chemical equation.

[*Hint :* $Ag^+ (aq) + 2NH_3 (aq) \rightarrow [Ag(NH_3)_2]^+ (aq)$]

Q. 10. Why does NH_3 forms intermolecular hydrogen bonds whereas PH_3 does not ?

[*Hint :* Due to strong electronegativity, small size of nitrogen atom and presence of lone pair of electrons on N atom.]

Q. 11. Write disproportionation reaction of H_3PO_3 ?

[*Hint :* $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$]

Q. 12. How does NH_3 acts as a complexing agent ?

[*Hint :* Metal hydroxides are dissolved in excess of NH_4OH. Ammonia acts as a Lewis base. It can donate electron pair to central metal atom or ion.]

Q. 13. Write the reaction of PCl_5 with heavy water.

[*Hint :* $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$]

Q. 14. What is laughing gas ? How is it prepared ?

[*Hint :* N_2O, $NH_4NO_3 \rightarrow N_2O + 2H_2O$]

Q. 15. Why is white phosphorus kept under water ?

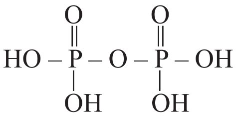
[*Hint :* Due to high angular strain, it is highly reactive and catches fire in air, hence kept under water.]

Q. 16. "Hydrophosphorus acid is a good reducing agent." Justify with an example.

[*Hint :* $4AgNO_3 + H_3PO_2 + 2H_2O \rightarrow 4Ag + 4HNO_3 + H_3PO_4$]

Q. 17. Draw the structure of $H_4P_2O_7$ and find out its basicity.

[*Hint :*



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$$

As four –OH groups are present, hence basicity is 4.]

Q. 18. Why is Bi (V) a stronger oxidant than Sb (V) ?

[*Hint :* Due to inert pair effect; + 3 oxidation state is more stable than + 5 oxidation state in Bi.]

Q. 19. How many P – O – P bonds are there in cyclotrimetaphosphoric acid ?

[*Hint :* 3 bonds]

Q. 20. Give reason : In the solid state, PCl_5 behaves as an ionic species.

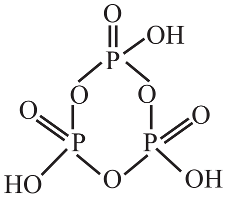
[*Hint :* It exists as an ionic solid $[PCl_4]^+[PCl_6]^-$]

Q. 21. Give reason : $BiCl_3$ is less covalent than PCl_3.

[*Hint :* Due to more polarization power of P^{3+} ion than Bi^{3+} ion.]

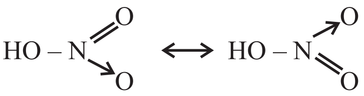
Q. 22. Draw the structure of $(HPO_3)_3$.

Hint :



Q. 23. In the structure of HNO_3 molecule, the N – O bond (121 pm) is shorter than N – OH bond (140 pm).

[*Hint :* Due to resonance N – O bond is having partial double bond character hence shorter than N – OH bond which is pure single bond character.]



Q. 24. Write the name and formula of neutral oxide of nitrogen.

[*Hint :* (i) Nitrous oxide/Dinitrogen oxide/Nitrogen (I) oxide N_2O.

(ii) Nitrogen monoxide/Nitrogen (II) oxide/Nitric oxide NO.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Complete the following reactions :

1. (i) $(NH_4)\,G_2O_7 \xrightarrow{heat}$

   (ii) $NH_4Cl\ (aq) + NaNO_2\ (aq) \rightarrow$

2. (i) $NH_2CONH_2 + H_2O \rightarrow$

   (ii) $FeCl_3\ (aq) + NH_4OH\ (aq) \rightarrow$

3. (i) $Ca_3P_2 + H_2O\ (l) \rightarrow$

   (ii) $I_2 + HNO_3$ (conc.) $\rightarrow$

4. (i) $Ba(N_3)_2 \xrightarrow{heat}$

   (ii) $4H_3PO_3 \xrightarrow{heat}$

5. (i) $PH_4I + KOH \rightarrow$

   (ii) $HgCl_2 + PH_3 \rightarrow$

6. (i) $PCl_3 + 3H_2O \rightarrow$

   (ii) $PCl_5 + H_2O \rightarrow$

7. (i) $NO_3^- + Fe^{2+} + H^+ \rightarrow$

   (ii) $Zn + HNO_3$ (dil.) $\rightarrow$

8. (i) $Zn + HNO_3$ (conc.) $\rightarrow$

   (ii) $P_4 + HNO_3$ (conc.) $\rightarrow$

9. (i) $NH_3 + O_2 \xrightarrow[\text{500K, 9 bar}]{\text{pt/Rh}}$

   (ii) $P_4 + NaOH + H_2O \rightarrow$

10. (i) NH_3 (excess) $+ Cl_2 \rightarrow$

    (ii) $NH_3 + Cl_2$ (excess) $\rightarrow$

11. (i) $P_4 + HNO_3$ (conc.) $\rightarrow$

    (ii) $Cu + HNO_3$ (conc.) $\rightarrow$

Q. 12. Why is red phosphorus denser and less chemically reactive than white phosphorus ?

[*Hint :* Because it have polymeric structure consisting chains of P_4 tetrahedra, hence denser than white P while red P is not having angular strain as in white P, hence less reactive than white P.]

Q. 13. (i) The acidic character of hydrides of group 15 increases from NH_3 to BiH_3. Why ?

(ii) Phosphorus show marked tendency for catenation. Why ?

[*Hint :* (i) Because from NH_3 to BiH_3 thermal stability decreases hence acidic character increases from NH_3 to BiH_3.

(ii) Because phosphorus do not form pπ-pπ multiple bond due to its bigger size.]

Q. 14. Arrange the following trichlorides in decreasing order of bond angle :

NCl_3, PCl_3, $AsCl_3$, $SbCl_3$

[*Hint :* $NCl_3 < PCl_3 < AsCl_3 < SbCl_3$]

Q. 15. How many P – O – P bonds are there in (i) $H_4P_2O_7$ (ii) P_4O_{10} ?

[*Hint :* (i) $H_4P_2O_7 = 01$ (ii) $P_4O_{10} = 05$]

Q. 16. At low temperature, NO_2 becomes colourless. Why ?

[*Hint :* NO_2 gets condensed to N_2O_4.]

Q. 17. Give chemical reaction in support of the statement that all the bonds in PCl_5 molecule are not equivalent.

[*Hint :* PCl_5 dissociates into PCl_3 and Cl_2 on heating.]

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

Q. 18. (i) What is the covalency of N in N_2O_5 ?

(ii) Explain why phosphorus forms pentachloride whereas nitrogen and bismuth do not ?

[*Hint :* (i) 4

(ii) Because due to presence of vacant d-orbitals in the octet of 'p', it can expand its octet to form PCl_5, while N cannot expand its octet.]

Q. 19. Arrange the following in the decreasing order of their basicity. Assign the reason :

PH_3, NH_3, SbH_3, AsH_3, BiH_3.

[*Hint :* $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$]

Q. 20. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber's process.

[*Hint :* $N_2(g) + 3H_2(g) \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3(g)$

(i) High pressure (200 atm).

(ii) Moderate temperature (700 K).

(iii) Presence of catalyst Fe/FeO, with small amount of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.]

Q. 21. Explain the Ostwald's process to manufacture nitric acid. Give any two uses of HNO_3.

[*Hint :* $4NH_3\,(g) + 5O_2\,(g) \xrightarrow[9\text{ bar}]{\text{Pt, 500K}} 4NO\,(g) + 6H_2O\,(l)$

$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$

$3NO_2\,(g) + H_2O\,(l) \rightarrow 2HNO_3\,(aq) + NO\,(g)$

(68% by mass)

Uses :(i) Used in the manufacture of fertilizers, explosives.

(ii) Used as lab reagent.]

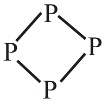
Q. 22. Why does PCl_3 fumes in moisture ? Give reaction also.

[*Hint :* PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

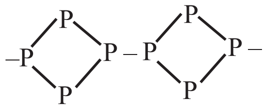
$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl \uparrow$]

Q. 23. Draw the structure of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why ?

[*Hint :* White phosphorus exists as discrete P_4 tetrahedral molecule, while red phosphorus is polymeric consisting of chains of P_4 tetrahedra linked together.



White P



Red P

White P is more reactive than red P, due to angular strain in it.]

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (i) How is HNO_3 prepared commercially ?

(ii) Write chemical equations of the reactions involved.

(iii) What concentration by mass of HNO_3 can be obtained ?

[*Hint :* Refer to Q. 21 SA-I type]

Q. 2. An unknown salt X reacts with hot conc. H_2SO_4 to produce a brown coloured gas which intensifies on addition on copper turnings. On adding dilute ferrous sulphate solution to an aqueous solution of X and then carefully adding conc. H_2SO_4 along the sides of the test tube, a brown complex Y is formed at the interface between the solution and H_2SO_4. Identify X and Y and write the chemical equation involved in the reaction.

[*Hint :* X = NO_3^- salt,] [Y = $[Fe(H_2O)_5(NO)]^{2+}$]

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

$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(Brown complex)}}{[Fe(H_2O)_5(NO)]^{2+}}] + H_2O$

Q. 3. Explain each of the following :

(i) The bond angles (O–N–O) are not of the same value in NO_2^- and NO_2^+.

(ii) BiH_3 is the strongest reducing agent amongst all the hydrides of group 15 elements.

(iii) Ammonia has greater affinity for protons than phosphine.

[*Hint :* (i) Due to presence of lone pair of electron on N in NO_2^-.

(ii) Bi–H bond dissociation enthalpy is least and releases hydrogen most easily.

(iii) NH_3 is stronger Lewis base than PH_3.]

Q. 4. Write balanced equation for the following reactions :

(i) Zn is treated with dilute HNO_3.

(ii) Copper metal with conc. HNO_3.

(iii) Iodine is treated with conc. HNO_3.

[*Hint :* (i) $4Zn + 10HNO_3 \text{ (dil.)} \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$

(ii) $3Cu + 8HNO_3 \text{ (dil.)} \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(iii) $I_2 + 10HNO_3 \text{ (conc.)} \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$]

Q. 5. A transluscent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous NaOH liberates a highly poisonous gas (C) having a rotten fish smell. (A) with excess of chlorine forms (D) which hydrolyses to form compound (E). Identify the compounds (A) to (E).

[*Hint :* A : White phosphorus, B : Red phosphorus, C : PH_3, D : PCl_5, E : H_3PO_4]

Q. 6. Assign the appropriate reason for the following :

(i) Nitrogen exists as diatomic molecule and phosphorus as P_4 at room temperature. Why ?

(ii) Why does $R_3P = O$ exist but $R_3N = O$ does not ? (R = an alkyl group).

(iii) Why is N_2 unreactive at room temperature ?

[*Hint :* (i) Due to its small size and high electronegativity, N forms $p\pi - p\pi$ multiple bond ($N \equiv N$) whereas P does not form $p\pi - p\pi$ bonds but forms P – P single bond.

(ii) In $R_3N = O$, N should have a covalence of 5 so the compound $R_3N = O$ does not exist since maximum covalence shown by N cannot exceed 4.]

GROUP 16 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis ?

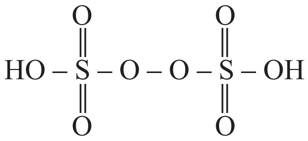
[*Hint :* Water molecule cannot attack 'S' atom due to steric hinderance and 'S' atom is also coordinately saturated in SF_6 molecule.]

Q. 2. In group 16, the stability of + 6 oxidation state decreases and that of + 4 oxidation state increases down the group. Why ?

[*Hint :* Due to inert pair effect.]

Q. 3. Draw the structure of $H_2S_2O_8$ and find the number of S – S bond, if any.

[*Hint :*



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Number of S – S bond ⇒ 0.]

Q. 4. What happens when sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt ?

[*Hint :* It converts Fe^{3+} ions to Fe^{2+} ions.

$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_2^{2-} + 4H^+$]

Q. 5. All the bonds in SF_4 are not equivalent. Why ?

[*Hint :* It is having see-saw shape. (4BP + 1LP)]

Q. 6. O_3 acts as a powerful oxidizing agent. Why ?

[*Hint :* Due to the ease with which it liberates atoms of nascent oxygen.]

$O_3 \rightarrow O_2 + [O]$

Q. 7. Which one of the following is not oxidized by O_3 ? State the reason :

KI, $FeSO_4$, K_2MnO_4, $KMnO_4$

[*Hint :* $KMnO_4$, since Mn is showing maximum oxidation state of + 7.]

Q. 8. Why does oxygen not show an oxidation state of + 4 and + 6 ?

[*Hint :* Due to absence of vacant d-orbitals in the octet of oxygen.]

Q. 9. Oxygen and sulphur in vapour phases are paramagnetic in nature. Explain why ?

[*Hint :* Due to presence of unpaired electrons in anti-bonding molecular orbitals in them.]

Q. 10. Thermal stability of hydrides of group 16 elements decreases down the group. Why ?

[*Hint :* Because down the group E – H bond dissociation enthalpy decreases.]

Q. 11. Why are the two S – O bonds in SO_2 molecule have equal strength ?

[*Hint :* Due to resonance, two S – O bonds have partial double bond character, hence have equal strength.]

Q. 12. $Ka_2 << Ka_1$ for H_2SO_4 in water, why ?

[*Hint :* $H_2SO_4\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + HSO_4^-\,(aq);\ Ka_1 > 10$

$HSO_4\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + SO_4^{-2}\,(aq);\ Ka_2 = 10^{-2}$

Ka_2 is less than Ka_1 because HSO_4^- ion has much less tendency to donate a proton.]

Q. 13. H_2O is a liquid while inspite of a higher molecular mass, H_2S is a gas. Explain.

[*Hint :* H_2O molecules are stabilized by intermolecular hydrogen bonding, while H_2S by weak van der Waal's forces.]

Q. 14. The electron gain enthalpy with negative sign for oxygen (– 141 KJ mol^{-1}) is numerically less than that for sulphur (– 200 KJ mol^{-1}). Give reason.

[*Hint :* Due to smaller size of oxygen than sulphur electron-electron repulsion is more in oxygen than sulphur.]

Q. 15. Dioxygen O_2 is a gas while sulphur (S_8) is a solid. Why ?

[*Hint :* Because oxygen is smaller in size hence have capacity to form pπ-pπ multiple bond, exists as dioxygen (O_2), whereas due to bigger size sulphur do not form multiple bond and exist as S_8.]

Q. 16. In the preparation of H_2SO_4 by contact process, why is SO_3 not absorbed directly in water to form H_2SO_4 ?

[*Hint :* Because it forms a dense fog of sulphuric acid which does not condense easily.]

SHORT ANWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Write the chemical equations of the following reactions :

(a) Glucose is heated with conc. H_2SO_4.

(b) Sodium nitrate is heated with conc. H_2SO_4.

[*Hint :* (a)

(b) $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$]

Q. 2. Mention the favourable conditions for the manufacture of sulphuric acid by contact process.

[*Hint :* (i) Low temperature (operating temperature is 720 K).

(ii) High pressure (2 bar).

(iii) Presence of catalyst (V_2O_5).

$2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)\ \Delta H^\theta = -\ 196.6\ KJ\ mol^{-1}$]

Q. 3. Complete the following reactions :

(a) $PbS + O_3 \rightarrow$

(b) $KI + H_2O + O_3 \rightarrow$

(c) $MnO_4^- + SO_2 + H_2O \rightarrow$

(d) $S_8 + H_2SO_4$ **(conc.)** $\rightarrow$

Q. 4. Explain why :

(a) **H_2S is more acidic than H_2O.**

(b) **Two S – O bonds in SO_2 are identical.**

(c) **SF_6 is inert and stable but SF_4 is reactive.**

(d) **Sulphur has greater tendency for catenation than oxygen.**

[*Hint :* (iii) Because six F atoms protect the sulphur atom from attack by any reagent due to steric hindrance but four F atoms in SF_4 cannot offer much steric hindrance, hence reactive.]

Q. 5. How is O_3 estimated quantitatively ?

[*Hint :* O_3 reacts with an excess of KI solution buffered with a borate buffer, I_2 is liberated which is titrated against standard solution of sodium thiosulphate.]

$2I^-\ (aq) + H_2O\ (l) + O_2\ (g) \rightarrow I_2\ (s) + O_2\ (g) + 2OH^-\ (aq)$

Q. 6. Explain why O_3 is thermodynamically less stable than O_2 ?

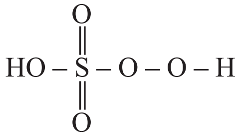
[*Hint :* Because O_3 is endothermic compound/decomposition of O_3 is exothermic and ΔG is negative/decomposition of O_3 is spontaneous.]

Q. 7. Draw the structure of :

(i) H_2SO_5

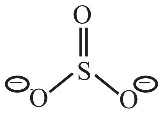
(ii) SO_3^{2-}

[*Hint :* (i)



$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-H$

(ii)



SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (i) How does O_3 react with lead sulphide ? Write chemical equation.

(ii) What happens when SO_2 is passed in acidified $KMnO_4$ solution ?

(iii) SO_2 behaves with lime water similar to CO_2. Explain why ?

[*Hint :* (i) $PbS\,(s) + 4O_3\,(g) \rightarrow PbSO_4\,(s) + 4O_2\,(g)$

(ii) It decolourises acidified $KMnO_4$ solution.

$$5O_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

(iii) It turns lime water milky due to the formation of insoluble $CaSO_3$.

$$Ca(OH)_2 + SO_2 \rightarrow \underset{\text{(milkiness)}}{CaSO_3} + H_2O$$

Q. 2. Complete the reactions :

(i) $CaF_2 + H_2SO_4$ (conc.) $\rightarrow$

(ii) $C_{12}H_{22}O_{11} + H_2SO_4$ (conc.) $\rightarrow$

(iii) $SO_2 + MnO_4^- + H_2O \rightarrow$

Q. 3. An amorphous solid 'A' burns in air to form a gas 'B' which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aq. $KMnO_4$ solution. Identify the solid 'A' and the gas 'B' and write the reaction involved.

[*Hint :* A = S_8; B = SO_2 (g)]

(i) How is SO_2 prepared in laboratory ?

(ii) What happens when SO_2 is passed through water and reacts with NaOH ? Write balanced equation.

(iii) Write its any two uses.

Hint :(i) $Na_2SO_3\,(s) + H_2SO_4\,(aq) \rightarrow SO_2\,(g) + Na_2SO_4\,(aq) + H_2O\,(l)$

(ii) $2NaOH + SO_2\,(g) \rightarrow Na_2SO_3\,(aq) + H_2O$

$Na_2SO_3\,(aq) + SO_2 + H_2O \rightarrow 2NaHSO_3\,(aq)$

(iii) It is used as bleaching agent and disinfectant.

Q. 4. Assign reason for the following :

(i) Sulphur in vapour state exhibits paramagnetism.

(ii) H_2O is less acidic than H_2Te.

(iii) In spite of having same electronegativity, oxygen forms hydrogen bond while chlorine does not.

[*Hint :* (iii) Due to bigger size of Cl.]

Q. 5. Write contact process for the manufacture of king of chemicals.

[*Hint :* (i) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

(ii) $2SO_2\,(g) + O_2\,(g) \;\; \frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{m_B \times 98} \;\; 2SO_3\,(g)$

(iii) $SO_3 + H_2SO_4$ (98%) $\rightarrow H_2S_2O_7$ (oleum)

(iv) $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$]

GROUP 17 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why fluorine forms only one oxoacid, HOF.

[*Hint :* Because of unavailability of d-orbitals in its valence shell.]

Q. 2. Why HF is the weakest acid and HI is the strongest ?

[*Hint :* $K_a\,(HF) = 7 \times 10^{-4}$ $K_a\,(HI) = 7 \times 10^{11}$

Intermolecular H-bonds in H – F and high bond dissociation enthalpy of H – F makes it weakest and weak bond in H – I makes it strongest.]

Q. 3. Explain why halogens are strong oxidizing agents.

[*Hint :* High electronegativity and more negative electron gain enthalpies of halogens.]

Q. 4. I_2 is more soluble in KI than in water. Why ?

[*Hint :* $KI + I_2 \rightarrow KI_3$]

Q. 5. What is cause of bleaching action of chlorine water ? Explain it with chemical equation.

[*Hint :* Formation of nascent oxygen.]

Q. 6. Electron gain enthalpy of fluorine (F) is less negative than that of chlorine (Cl). Why ?

[*Hint :* Due to small size of F atom and compact 2p orbitals there are strong interelectronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience more repulsion in F than in Cl.]

Q. 7. Why can't we prepare HBr by heating KBr with sulphuric acid ?

[*Hint :* As HBr readily reduces H_2SO_4 forming Br_2.]

Q. 8. Explain why : ICl is more reactive than I_2 ?

[*Hint :* Because I – Cl bond is weaker than I – I bond.]

Q. 9. Which oxide of iodine is used for the estimation of carbon mono oxide ?

[*Hint :* I_2O_5]

Q. 10. Arrange the following oxoacids of chlorine in increasing order of acid strength :

HOCl, HOClO, $HOClO_2$, $HOClO_3$

[*Hint :* HOCl < HOClO < $HOClO_2$ < $HOClO_3$]

Q. 11. Why does fluorine not play the role of a central atom in interhalogen compounds ?

[*Hint :* Due to smallest size of F.]

Q. 12. Fluorine exhibit only – 1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain why ?

[*Hint :* Due to absence of vacant d-orbitals in the octet of F.]

Q. 13. ClF_3 exists but FCl_3 does not. Why ?

[*Hint :* Because F does not show oxidation state other than – 1.]

Q. 14. Despite lower value of its electron enthalpy with negative sign, fluorine is a stronger oxidizing agent than chlorine. Explain.

[*Hint :* Due to its low bond dissociation enthalpy (F –F bond) and high hydration enthalpy of F^-.]

Q. 15. ClF_3 molecule has a bent T-shaped structure and not a trigonal planar structure. Explain.

[*Hint :* Due to presence of 2LP and 3BP.]

Q. 16. What happens when NaCl is heated with H_2SO_4 in the presence of MnO_2 ?

[*Hint :* $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$]

Q. 17. With what neutral molecule ClO^- is isoelectronic ?

[*Hint :* ClF or OF_2.]

Q. 18. Why HF acid is stored in wax coated glass bottle ?

[*Hint :* HF is corrosive, hence HF attacks glass surface.]

Q. 19. Bond dissociation enthalpy of F_2 is less than that of Cl_2. Explain why ?

[*Hint :* F_2 is having higher electron-electron repulsion due to its smaller size, as compared to Cl_2.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. (i) Interhalogen compounds are more reactive than halogens except F_2. Why ?

(ii) Give one important use of ClF_3.

[*Hint :* (i) Because X – X bond in interhalogens is weaker than X – X bond in halogens except F – F bond.

(ii) ClF_3 is used for the production of UF_6.]

Q. 2. (i) Write the composition of bleaching powder.

(ii) What happens when NaCl is heated with conc. H_2SO_4 in the presence of MnO_2. Write the chemical equation.

[*Hint :* (i) $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$]

Q. 3. A colourless pungent smelling gas, which easily liquefies to a colourless liquid and freezes to a white crystalline solid, gives dense white fumes with ammonia. Identify the gas and write the chemical equation for its laboratory preparation.

[*Hint :* $NaCl + H_2SO_4$ (conc.) $\rightarrow NaHSO_4 + HCl$]

Q. 4. NO_2 readily dimenise, whereas ClO_2 does not. Why ?

[*Hint :* Due to bigger size of Cl than N.]

Q. 5. Compare the oxidizing powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy, electron gain enthalpy of halogens and hydration enthalpy of halide ions.

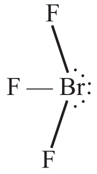
[*Hint :* It is due to low enthalpy of dissociation of F – F bond and high hydration enthalpy of F^-.]

Q. 6. Which fluorinating agent are oftenly used instead of F_2 ? Write chemical equation showing their use as flurorinating agents.

[*Hint :* $U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$]

Q. 7. Draw the structure of BrF_3.

Hint :



Bent T - shaped

Complete the following reactions :

8. (i) $Al_2O_3(s) + NaOH(aq) + H_2O(l) \rightarrow$

(ii) $HCl + O_2 \rightarrow$

9. (i) $Ca(OH)_2 + Cl_2 \rightarrow$

(ii) N_2 (excess) $+ Cl_2 \rightarrow$

10. (i) $Na_2SO_3 + Cl_2 + H_2O \rightarrow$

(ii) $N_2 + Cl_2$ (excess) $\rightarrow$

11. (i) $Cl_2 + NaOH$ (cold & dil.) →

(ii) $Cl_2 + NaOH$ (hot & conc.) →

12. (i) $Fe + HCl \rightarrow$

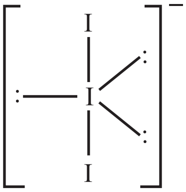
(ii) $Cl_2 + F_2$ (excess) →

13. (i) $U + ClF_3 \rightarrow$

(ii) $FeSO_4 + H_2SO_4 + Cl_2 \rightarrow$

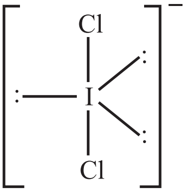
Q. 14. Draw the structure of : (a) I_3^- (b) ICl_2^-.

Hint :



Linear

$[I - I \leftarrow I^-]$



Linear

$[Cl - I \leftarrow Cl^-]$

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Give appropriate reason for each of the following :

(i) Metal fluorides are more ionic than metal chlorides.

(ii) Perchloric acid is stronger than sulphuric acid.

(iii) Addition of chlorine to KI solution gives it a brown colour but excess of Cl_2 makes it colourless.

[*Hint :* (i) According to Fajan's Rule, bigger ions are more polarized than the smaller ions by a particular cation.

(ii) ClO_4^- is more resonance stabilized than SO_4^{2-} since dispersal of negative charge is more effective in ClO_4^- as compared with SO_4^{2-}.

(iii) $2KI + Cl_2 \rightarrow 2KCl + I_2$

$$5Cl_2 \text{ (excess)} + I_2 + 6H_2O \rightarrow \underset{\text{(colourless)}}{2HIO_3} + 10HCl$$

Q. 2. X_2 is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in H_2O to give a solution which turns blue litmus red. When X_2 is passed through NaBr solution, Br_2 is obtained.

(i) Identify X_2, name the group to which it belongs.

(ii) What are the products obtained when X_2 reacts with H_2O ? Write chemical equation.

(iii) What happens when X_2 reacts with hot and conc. NaOH ? Give equation.

[*Hint :* (i) Cl_2, 17 group.

(ii) $Cl_2\,(g) + 2H_2O\,(l) \longrightarrow HCl\,(aq) + HOCl\,(aq)$

(iii) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

Q. 3. Arrange the following in the order of the property indicated for each set :

(i) F_2, Cl_2, Br_2, I_2 (Increasing bond dissocation energy)

(ii) HF, HCl, HBr, HI (decreasing acid strength)

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Decreasing base strength)

[*Hint :* (i) F_2 has exceptionally low bond dissociation enthalpy. Lone pairs in F_2 molecule are much closer to each other than in Cl_2 molecule. Stronger electron-electron repulsions among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low.

(ii) Acid strength depends upon H – X bond dissociation enthalpy. As the size of 'X' atom increases, bond dissociation enthalpy of H – X decreases.

(iii) Electron availability on the central atom 'E' in EH_3 decreases down the group.]

Q. 4. Draw the structure of :

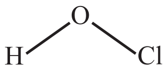
(i) Hypochlorous acid

(ii) Chlorous acid

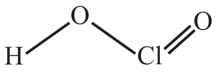
(iii) Perchloric acid

Hint :

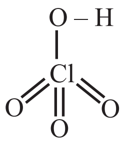
(a)



(b)



(c)



Q. 5. Which is more acidic among $HClO_4$ and HIO_4 ? Why ?

[*Hint :* $HClO_4$ is more acidic than HIO_4. Because Cl is more electronegative than Br, due to which ClO_3 group have more tendency to withdraw electrons of O – H bond towards itself as compared to BrO_3 group.]

GROUP 18 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What inspired N. Barlett for carrying out reaction between Xe and PtF_6 ?

[*Hint :* Almost same ionization enthalpy of oxygen and Xe.]

Q. 2. **Predict the shape and the asked angle (90° or more or less) in the following case :**

XeF_2 and the angle $F - \overset{\cdot\cdot\cdot\cdot}{\underset{\cdot\cdot}{Xe}} - F$

[*Hint :* Linear, 180°]

Q. 3. **Structure of Xenon fluoride cannot be explained by valence bond approach. Why ?**

[*Hint :* Due to fully filled octet of Xe.]

Q. 4. **Why do some noble gases form compounds with fluorine and oxygen only ?**

[*Hint :* Due to high electronegativity of F and oxygen.]

Q. 5. **XeF_2 has a straight linear structure and not a bent angular structure. Why ?**

[*Hint :* In XeF_2, 2 bond pairs and 3 lone pairs are present hence linear structure.]

Q. 6. **Why do noble gases have very low boiling point ?**

[*Hint :* Because noble gases are stabilized by weak van der Waal's forces.]

Q. 7. **Write the chemical equation involved in the preparation of XeF_4.**

[*Hint :* $Xe\,(g) + 2F_2\,(g) \rightarrow XeF_4\,(s)$]

Ratio 1 : 5

Q. 8. **Write IUPAC name of $O_2^+[PtF_6]$.**

[*Hint :* Dioxygenyl hexafluoroplatinate(iv).]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. **Suggest reason why only known binary compounds of noble gases are fluorides and oxides of Xenon and to a lesse extent of Kryton.**

[*Hint :* F and O are most electronegative elements Kr and Xe both have low ionization enthalpies as compared to He and Ne.]

Q. 2. **(i) Hydrolysis of XeF_6 is not regarded as a redox reaction. Why ?**

(ii) Write a chemical equation to represent the oxidizing nature of XeF_4.

[*Hint :* (i) Because oxidation number of Xe do not change during hydrolysis of XeF_6.

(ii) $XeF_4 + 2H_2 \rightarrow Xe + 4HF$]

Q. 3. **Write chemical equations when :**

(i) XeF_2 is hydrolysed.

(ii) PtF_6 and Xenon are mixed together.

[*Hint :* (i) $2XeF_2\,(s) + 2H_2O\,(l) \rightarrow 2Xe\,(g) + 4HF\,(aq) + O_2\,(g)$

(ii) $Xe + PtF_6 \rightarrow Xe^+[PtF_6]^-$]

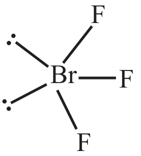
Q. 4. Complete the reactions :

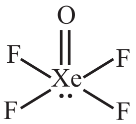
(i) $XeF_6 + H_2O \rightarrow$

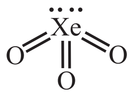
(ii) $XeF_6 + H_2O \rightarrow$

Q. 5. Draw the structure of BrF_3, $XeOF_4$, XeO_3 using VSEPR theory.

[*Hint :*







Q. 6. Account for the following :

(i) XeF_2 has linear structure and not a bent structure.

(ii) The majority of known noble gas compounds are those of Xenon. Why ?

[*Hint :* (ii) Xe has low ionization enthalpy as compared to other noble gases.]

Q. 7. Write the chemical reactions :

(i) $XeF_2\ (s) + H_2O\ (l) \rightarrow$

(ii) $XeF_4 + O_2F_2 \rightarrow$

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Assign reason to the following :

(i) Noble gases have large positive values of electron gain enthalpy.

(ii) Helium is used by scuba divers.

(iii) No chemical compound of helium is known.

[*Hint :* (i) Due to their electron configuration.

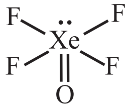
(ii) Due to its less solubility in blood.

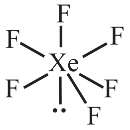
(iii) Due to its high ionization enthalpy.]

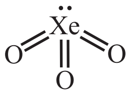
Q. 2. Draw the structure of :

(i) $XeOF_4$ (ii) XeF_6 (iii) XeO_3

[*Hint :*







Q. 3. **Complete the reactions :**

(i) $XeF_2 + NaF \rightarrow$

(ii) $XeF_4 + SbF_5 \rightarrow$

(iii) $XeF_4 + H_2O \rightarrow$

Q. 4. **(i)** **How is XeO_3 prepared from XeF_6 ? Write the chemical equation for the reaction.**

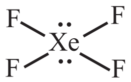
(ii) **Draw the structure of XeF_4.**

[*Hint :* (i) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

Or

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(ii)



LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. **How is PH_3 prepared in the laboratory ? How is it purified ? How does the solution of PH_3 in water react on irradiation with light and on adsorption in $CuSO_4$? How can you prove that PH_3 is basic in nature ?**

Write chemical equations for all the reactions involved.

[*Hint :* $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

It is purified by absorbing it in HI to form PH_4I which on treating with KOH gives off phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

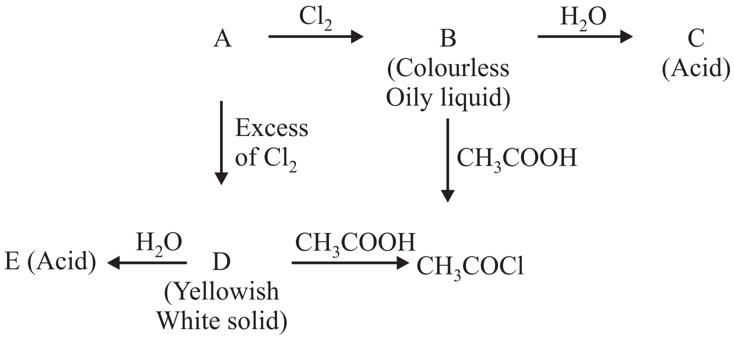
PH_3 in water decomposes into red phosphorus and hydrogen in presence of light.

$$4PH_3 \rightarrow P_4 + 6H_2$$

Reaction with $CuSO_4$:

$$3CuSO_4 + 3PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4]$$

Q. 2. **Identify A, B, C, D and E in the following sequence of reactions :**



Complete the reactions of the above mentioned sequence.

[*Hint :* A is P_4, B is PCl_3.

$$\underset{}{PCl_3} + 3H_2O \rightarrow \underset{(C)}{H_3PO_3} + 3HCl$$

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$P_4 + 10Cl_2 \rightarrow \underset{(D)}{4PCl_5}, \ PCl_5 + 4H_2O \rightarrow \underset{(E)}{H_3PO_4} + 3HCl$$

Q. 3. Write the structure of A, B, C, D and E in the following sequence of reactions :

$$\mathbf{NH_3 + O_2 \rightarrow A + H_2O}$$

$$\mathbf{A + O_2 \rightarrow B} \text{ (Brown fumes)}$$

$$\mathbf{B + H_2O \rightarrow C + A} \text{ (C is an oxoacid)}$$

$$\mathbf{C + I^- \rightarrow D} \text{ (Violet vapours)}$$

Complete the reactions of the above mentioned sequence and name the process by which 'C' is obtained.

[*Hint :* A is NO and Ostwald process for the manufacture of HNO_3.

$$\underset{(A)}{2NO} + O_2 \rightarrow 2NO_2$$

$$\underset{(B)}{3NO_2} + H_2O \rightarrow \underset{(C)}{2HNO_3} + NO$$

$$6I^- + 2NO_3^- + 8H^+ \rightarrow 3I_2 + 2NO + 4H_2O$$

Q. 4. A waxy transluscent solid, M, insoluble in water but soluble in CS_2 glows in dark. M dissolves in NaOH in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of Q.

(a) Identify M, N and Q and write the chemical equations of the reactions involved.

(b) 'M' exists in the form of discrete tetrahedral molecules. Draw its structure.

(c) 'M' on heating at 573K is changed into other less reactive form, R, which is non-poisonous, insoluble in water as well as in CS_2 and does not glow in dark. Identify R and draw its structure.

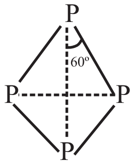
[*Hint :* (a) M is white phosphorus.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{(N)}{PH_3} + 3NaH_2PO_2$$

$P_4 + 5O_2 \rightarrow P_4O_{10}$

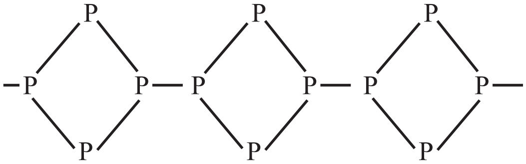
white fumes (Q)

(b)



(c) White phosphorus $\xrightarrow{573K}$ Red phosphorus

(R)



Q. 5. Assign a possible reason for the following :

(a) Stability of + 5 oxidation state decreased and that of + 3 oxidation state increases down the group 15 elements.

(b) H_2O is less acidic than H_2S.

(c) SF_6 is inert while SF_4 is highly reactive towards hydrolysis.

(d) H_3PO_2 and H_3PO_3 act as reducing agents while H_3PO_4 does not.

(e) Helium gas is used by scuba divers.

[*Hint :* (a) Due to inert pair effect.

(b) Due to more bond dissociation enthalpy of O – H as compared to S – H bond.

(c) Due to more steric hindrance offered by six F in SF_6 as compared to SF_4.

(d) Due to presence of P – H bond in them.

(e) He is very less soluble in blood.]

Q. 6. (a) How is XeF_6 prepared from the XeF_4 ? Write the chemical equation for the reaction.

(b) Deduce the structure of XeF_6 using VSEPR theory.

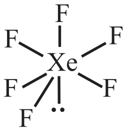
(c) How does XeF_2 reacts with PF_5 ?

(d) Give one use each of helium and neon.

(e) Write the chemical equation for the hydrolysis of XeF_4.

[*Hint :* (a) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

(b) Distorted octahedral (6BP + 1LP)



(c) $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$

(d) He is used in filling balloons/used by scuba divers.

Ne is used in discharge tubes, advertisement display purposes.

(e) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2]$

MATCHING TYPE QUESTIONS

Q. 1. Match the compounds given in Column I with the hybridisation ans shape given in Column II and mark the correct option :

	Column I		Column II
(A)	XeF_6	(1)	sp^3d^3 – distorted octahedral
(B)	XeO_3	(2)	sp^3d^2 – square planar
(C)	$XeOF_4$	(3)	sp^3 – pyramidal
(D)	XeF_4	(4)	sp^3d^2 – square pyramidal

Q. 2. Match the formula of oxides given in Column I with the type of oxide given in Column II and mark the correct option :

	Column I		Column II
(A)	Pb_3O_4	(1)	Neutral oxide
(B)	N_2O	(2)	Acidic oxide
(C)	Mn_2O_7	(3)	Basic oxide
(D)	Bi_2O_3	(4)	Mixed oxide

Q. 3. Match the items of Columns I and II and mark the correct option :

	Column I		Column II
(A)	H_2SO_4	(1)	Highest electron gain enthalpy
(B)	CCl_3NO_2	(2)	Chalcogen
(C)	Cl_2	(3)	Tear gas
(D)	Sulphur	(4)	Storage batteries

Q. 4. Match the species given in Column I with the shape given in Column II and mark the correct option :

	Column I		Column II
(A)	SF_4	(1)	Tetrahedral
(B)	BrF_3	(2)	Pyramidal
(C)	BrO_3^-	(3)	Sea-saw shaped
(D)	NH_4^+	(4)	Bent T-shaped

Q. 5. Match the items of Columns I and II and mark the correct option :

	Column I		Column II
(A)	Its partial hydrolysis does not change oxidation state of central atom	(1)	He
(B)	It is used in modern diving apparatus	(2)	XeF_6
(C)	It is used to provide inert atmosphere for filling electrical bulbs	(3)	XeF_4
(D)	Its central atom is in sp^3d^2 hybridisation	(4)	Ar

ANSWERS

1.	(A) – (1)	(B) – (3)	(C) – (4)	(D) – (2)
2.	(A) – (4)	(B) – (1)	(C) – (2)	(D) – (3)
3.	(A) – (4)	(B) – (3)	(C) – (1)	(D) – (2)
4.	(A) – (3)	(B) – (2)	(C) – (1)	(D) – (4)
5.	(A) – (2)	(B) – (3)	(C) – (2)	(D) – (4)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Chlorofluorocarbons (CFCs) and gas emitted from the exhaust system of supersonic aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

(i) Name the gas emitted from the exhaust of supersonic aeroplanes.

(ii) Name the element of CFCs which depletes ozone.

(iii) Write the chemical reactions involved in the ozone layer depletion.

(iv) Mention the values that are learnt by the students in the depletion of ozone layer.

Q. 2. A student accidently spills concentrated H_2SO_4 on his hand. Before the teacher gets to know, his friend washed his hands with water and also with soap but the burning sensation on hand was still going on. The friend then rubs the paste of sodium bicarbonate on his hand and then washed with water, finally the burning sensation is relieved.

(i) Mention the values shown by student's friend.

(ii) Can you recommend another substance available in the laboratory which can be used instead of sodium bicarbonate ?

(iii) Write the chemical reaction involved in the treatment of acid burn with sodium bicarbonate.

(iv) Can we use NaOH solution in place of $NaHCO_3$? If not, why ?

Q. 3. Ramu, a caretaker of swimming pool was using chlorine for disinfecting swimming pool water. His friend Jagat, also a swimming pool caretaker, was using ozone in place of chlorine.

(i) How do chlorine and ozone disinfect water ?

(ii) In your opinion, which is better way of disinfecting water in a swimming pool ?

(iii) Mention the values associated with your reply.

UNIT 8

THE *d*- AND *f*-BLOCK ELEMENTS

1. Introduction

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals – 3*d* series (Sc to Zn), 4*d* series (Y to Cd) and 5*d* series (La to Hg, omitting Ce to Lu).

d-block elements are known as transition elements because their position in the periodic table is between the s-block and p-block elements. Electronic configuration of the *d*-block elements is $(n-1)d^{1\text{-}10}ns^{o-2}$ but Cu^+, Zn, Cd, Hg etc. $[(n-1)d^{10}]$ are *d*-block elements, but not transition metals because these have completely filled *d*-orbitals.

Transition Metals of *d*-block Elements

3rd group ns^2	**4th group** $d^1\ ns^2d^2$	**5th group** ns^2d^3	**6th group** ns^2d^5	**7th group** ns^2d^5	**8th group** ns^2d^6	**9th group** ns^2d^7	**10th group** ns^2d^8	**11th group** ns^2d^{10}	**12th group** ns^2d^{10}
$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

2. General Properties of the Transition Elements

(i) Atomic and Ionic Radii

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements of the series.

(ii) Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms. They have stronger interatomic interaction and hence, stronger bond.

(iii) Ionisation Enthalpies

- In a series from left to right, ionization enthalpy increases due to increase in nuclear charge.

- The irregular trend in the first ionization enthalpy of the 3*d* metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals.

(iv) Oxidation States

- Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are

Sc(+ 3), Ti(+ 4), V(+ 5), Cr(+ 3, + 6), Mn(+ 2, + 7), Fe(+ 2, + 3), Co(+ 2, + 3), Ni(+ 2), Cu)+ 2), Zn(+ 2)

- The transition elements in their lower oxidation states (+ 2 and + 3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.
- Only Os and Ru show + 8 oxidation states in their compounds.
- Ni and Fe in $Ni(CO)_4$ and $Fe(CO)_5$ show zero oxidation state.

(v) Trends in the Standard Electrode Potentials

- Transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials.
- If sum of the first and second ionization enthalpies is greater than hydration enthalpy standard potential ($E^{o}_{M^{2+}/M}$) will be positive and reactivity will be lower and vice-versa.

(vi) Trends in Stability of Higher Oxidation States

The higher oxidation numbers are achieved in TiX_4, VF_5 and CrF_6. The + 7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3 and increasing order of oxidizing power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO^{4-}$.

(vii) Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.
- The magnetic moment is determined by the number of unpaired electrons.

$$\text{Magnetic moment} = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

(viii) Formation of Coloured Ions

- The *d*-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.

- In V_2O_5, V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.

(ix) Formation of Complex Compounds

- Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of electron from ligands.

- They have vacant *d*-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

(x) Catalytic Properties

- Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.

- Transition metals also provide larger surface area for the reactant to be adsorbed.

(xi) Formation of Interstitial Compounds

- Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.

- The principal physical and chemical characteristics of these compounds are as follows :

  (i) They have high melting points, higher than those of pure metals.
  (ii) They are very hard, some borides approach diamond in hardness.
  (iii) They retain metallic conductivity.
  (iv) They are chemically inert.

(xii) Alloy Formation

Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogeneous mixture and form the alloy.

E.g., Brass (copper-zinc) and bronze (copper-tin) etc.

3. Some Important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

(i) Ore

Ferrochrome or chromate ($FeO.Cr_2O_3$) or ($FeCr_2O_4$)

(ii) Preparation

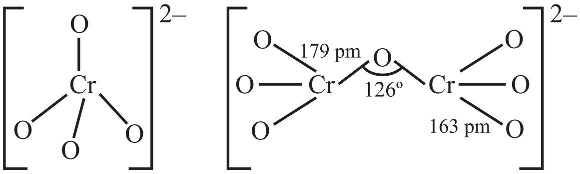
$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow \underset{\text{(yellow)}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \rightarrow \underset{\text{(orange)}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.



chromate ion sp^3 dichromate ion sp^3

(iii) Properties

Sodium and potassium dichromates are strong oxidizing agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$

$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

(iv) Uses

(a) $K_2Cr_2O_7$ is used as oxidizing agent in volumetric analysis.

(b) It is used in mordant dyes, leather industry, photography (for hardening of film).

(c) It is used in chromyl chloride test.

(d) It is used in cleaning glassware.

Potassium Permanganate ($KMnO_4$)

(i) Ore

Pyrolusite (MnO_2)

(ii) Preparation

$2MnO_2 + 4KOH + O_2 \rightarrow \underset{\text{(green)}}{2K_2MnO_4} + 2H_2O$

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

(iii) Commercial preparation

$$\underset{}{MnO_2} \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH oxidised}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} \underset{\substack{\text{Permanganate ion} \\ \text{(purple)}}}{MnO_4^{-}}$$

(iv) Properties

$KMnO_4$ acts as strong oxidizing agent.

(a) In presence of dilute H_2SO_4, $KMnO_4$ is reduced to manganous salt.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Acidic $KMnO_4$ solution oxidizes oxalates to CO_2, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

$$C_2O_4^{2-} \rightarrow CO_2 + 2e^-$$

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

$$NO_2^- \rightarrow NO_3^- + 2e^-$$

$$2I^- \rightarrow I_2 + 2e^-$$

To acidify $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as oxidizing agent.

(b) In alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2.

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

Alkaline or neutral $KMnO_4$ solution oxidizes I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.

(v) Uses

(a) In laboratory preparation of Cl_2.

(b) $KMnO_4$ is used as an oxidizing agent, disinfectant.

(c) In making Baeyer's reagent.

4. The Inner Transition Elements (*f*-Block)

The *f*-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

Lanthanoids

General characteristics

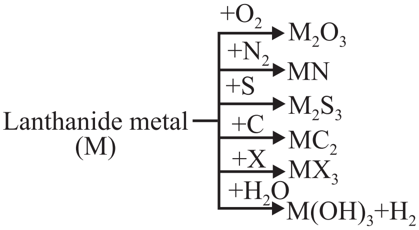
- General configuration [Xe] $4f^{1\text{-}14}$, $5d^{0\text{-}1}$, $6s^2$.
- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.

- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.

- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodymium.

- Oxidation states → Ce^{4+}; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common + 3 state. The E^o_{value} for Ce^{4+}/Ce^{3+} is + 1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu^{2+} is formed by losing the two s-electrons and its f^7 configuration accounts for the formation of this ion. However, Eu2+ is a strong reducing agent changing to the common + 3 state. Similarly, Yb^{2+} which has f^{14} configuration is a reductant, Tb^{4+} has half-filled *f*-orbitals and is an oxidant.

- Lanthanoid are very reactive metals like alkaline earth metals.



- Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon about 10.5% are used in cigarette and gas lighters, toys, tank and tracer bullets.

Actinoids

- Genral configuration [Rn] $5f^{1\text{-}14}$, $6d^{0\text{-}2}$, $7s^2$.

- Actinoids exhibit a range of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* orbitals. The genral oxidation state of actinoids is + 3.

- All the actinoids are strong reducing agents and very reactive.

- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc. like lanthanoids.

- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain $CuSO_4.5H_2O$ is blue while $CuSO_4$ is colourless ?

Ans. Because water molecules act as ligands and results in crystal field splitting of *d*-orbitals of Cu^{2+} ion.

Q. 2. Which element among 3*d* series exhibit highest oxidation state ?

Ans.	Mn
Q. 3.	**In 3*d* series (Sc to Zn), the enthalpy of atomization of Zn is low. Why ?**
Ans.	Due to absence of unpaired electrons.
Q. 4.	**Which element among 3*d* series exhibit only one oxidation state ?**
Ans.	Sc
Q. 5.	**Why is the 3rd ionization energy of Mn (Z = 25) is unexpectedly high ?**
Ans.	Due to half-filled electronic configuration.
Q. 6.	**Define alloy.**
Ans.	Alloys are homogeneous solid solutions of two or more metals.
Q. 7.	**Transition metals show zero oxidation state with ligands like CO. Explain.**
Ans.	Co form synergic bonding with metal ion.
Q. 8.	**Why can't HCl acid be used to acidify $KMnO_4$ solution ?**
Ans.	Because $KMnO_4$ oxidize HCl into Cl_2.
Q. 9.	**Name one ore of Mn and Cr.**
Ans.	Mn : MnO_2 Cr : $FeCr_2O_4$
Q. 10.	**Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their + 3 state ?**
Ans.	Mn^{+2} has half-filled electronic configuration.
Q. 11.	**Why do transition metal (elements) show variable oxidation states ?**
Ans.	Due to presence of vacant *d*-orbitals.
Q. 12.	**Write any uses of pyrophoric alloy.**
Ans.	Making bullets, shells and ligher flints.
Q. 13.	**Which is more basic – $La(OH)_3$ or $Lu(OH)_3$? Why ?**
Ans.	$La(OH)_3$, due to lanthanide contraction, lower size, more covalent character, least basic.
Q. 14.	**Find out number of Cr – O – Cr bond/bonds in $Cr_2O_7^{2-}$ ion.**
Ans.	1
Q. 15.	**What is effect of increasing pH on $K_2Cr_2O_7$ solution ?**
Ans.	It changes into K_2CrO_4 solution/orange colour change into yellow colour.
Q. 16.	**Why is Ce^{4+} in aqueous solution a good oxidizing agent ?**

Ans. Because Ce^{4+} is most stable in Ce^{+3} state in aqueous solution.

Q. 17. Why do Zr and Hf exhibit similar properties ?

Ans. Due to lanthanide contraction.

Q. 18. What is lanthanoid contraction ?

Ans. The regular slow decrease in the atomic or ionic radii of lanthanoids with increasing atomic number.

Q. 19. Why is Cu (Z = 29) considered a transition metal ?

Ans. Due to its partially filled *d*-orbital in Cu^{2+} state.

Q. 20. Arrange the given in increasing order of acidic character :

CrO_3, CrO, Cr_2O_3.

Ans. $CrO < Cr_2O_3 < CrO_3$

Q. 21. Why $KMnO_4$ or MnO_4^- ion is coloured ?

Ans. Due to charge transfer complex formation.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Chromium is typical hard metal while mercury is a liquid. Explain why ?

Ans. Cr has five unpaired *d*-electrons. Hence metallic bonds are strong. In Hg, there is absence of unpaired electrons and size is larger.

Q. 2. Why $KMnO_4$ is used in cleaning surgical instruments in hospitals ?

Ans. This is because $KMnO_4$ has a germicidal action.

Q. 3. Most of the transition metals do not displace hydrogen from dilute acids, why ?

Ans. Due to their –ve reduction potential.

Q. 4. Explain why Cu^+ is not stable in aqueous solution ?

Ans. Due to less –ve $\Delta_{hyd}H^{\theta}$ of Cu^+/it cannot compensate 2nd ionization potential of Cu.

Q. 5. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

Ans. Oxygen and fluoride have small size and high electronegativity. They can oxidise the metal.

Q. 6. Write electronic configuration of Cu^{+2} and Co^{+2}.

Ans. $Cu^{+2} = [Ar]\ 3d^9\ 4s^0$

$Co^{+2} = [Ar]\ 3d^7$

Q. 7. Balance the following equations :

(a) $\mathbf{MnO_4^- + Fe^{2+} + H^+ \rightarrow}$

(b) $\mathbf{Cr_2O_7^{2-} + Sn^{2+} + H^+ \rightarrow}$

Ans. (a) $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{+2} + Fe^{+3}$

(b) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \rightarrow Cr^{+3} + Sn^{+4}$

Q. 8. Briefly explain why electronic configuration of lanthanoids are not known with certainty ?

Ans. 4*f*/5*d* subshells are very close in energy. +ve electrons can jump from 4*f* to 5*d* or vice-versa.

Q. 9. Why Zn, Cd, Hg are soft and have low melting point ?

Ans. Due to weak interatomic attraction/absence of unpaired electrons.

Q. 10. What is the effect of pH on the solution of $\mathbf{K_2Cr_2O_4}$ solution ?

Ans. $K_2Cr_2O_4$ solution changes into $K_2Cr_2O_7$/yellow colour changes into orange colour.

Q. 11. Which of the following is/are transition element and why ?

Zn, Cd, Ag, Fe, Ni

Ans. Fe, Ni, Ag

Q. 12. What are interstitial compounds ? Give example.

Ans. When small atoms like C, H, B and N occupy interstitial site in their lattice. Example, TiC, Fe_3H,

Q. 13. Why are Zn, Cd, Hg volatile metals ? Explain.

Ans. Due to weak interatomic attraction/low boiling point.

Q. 14. Why is first ionization energy of 5*d* elements higher than those of 3*d* and 4*d* elements ?

Q. 15. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% lanthanoid and 5% iron and traces of S, C, Ca and Al. Used in lighter flint, bullet tips etc.

Q. 16. The following two reactions of $\mathbf{HNO_3}$ with Zn are given :

(a) $\mathbf{Zn + conc.\ HNO_3 \rightarrow Zn(NO_3)_2 + X + H_2O}$

(b) $\mathbf{Zn + dil.\ HNO_3 \rightarrow Zn(NO_3)_2 + Y + H_2O}$

Identify X and Y.

Ans. $X = NO_2$

$Y = N_2O$

Q. 17. Complete the equations :

(a) $\mathbf{KMnO_4 \xrightarrow{\Delta}}$

(b) $\mathbf{3K_2MnO_4 \xrightarrow[\text{for long time acidic medium}]{\text{on standing}}}$

Ans. (a) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(b) $3K_2MnO_4 \rightarrow MnO_4^- + MnO_2 + 2H_2O$

Q. 18. Out of Fe and Cu, which one would exhibit higher melting point ?

Ans. Fe, due to large number of unpaired *d*-electrons/more interatomic attraction.

Q. 19. Sc, the first member of first transition series does not exhibit variable oxidation state. Why ?

Ans. Due to noble gas electronic configuration in + 3 oxidation state no other oxidation state is stable.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (a) Deduce the number of 3*d* electrons in the following ions :

$\mathbf{Cu^{2+}, Sc^{+3}}$

(b) Why do transition metals form alloy ?

(c) Why $\mathbf{Zn^{+2}}$ salts are white ?

Ans. (a) Cu^{+2} : 9 electrons

Sc^{+3} : 0 electron

(b) Transition metals have similar atomic radii.

(c) Absence of unpaired electron.

Q. 2. Complete and balance the following equations :

(a) $\mathbf{MnO_4^{2-} + H^+ \rightarrow}$

(b) $\mathbf{KMnO_4 \xrightarrow{heat}}$

(c) $\mathbf{MnO_4^- + FeC_2O_4 \xrightarrow{H^+}}$

Ans. (a) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(b) $2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$

(c) $MnO_4^- + FeC_2O_4 + H^+ \rightarrow Mn^{+2} + Fe^{+3} + CO_2$

Q. 3. Describe the oxidizing action of $\mathbf{K_2Cr_2O_7}$ with the following. Write ionic equations for its reaction (acidic medium) with :

(a) $\mathbf{I^-}$ **(b) Iron(II)** **(c)** $\mathbf{H_2S}$

Ans. (a) It liberates I_2 form I^-.

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{+3} + 7H_2O + 3I_2$

(b) It oxidizes Fe^{+2} to Fe^{+3}.

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

(b) It oxidizes H_2S to sulphur.

$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3S$

Q. 4. Write any four differences between lanthanoids and actinoids.

Ans.

	Lanthanoids	**Actinoids**
(a)	They are generally non-radioactive.	They are radioactive.
(b)	Most of their ions are colourless.	Coloured ions.
(c)	Show + 3, + 4 and + 2 oxidation state.	Beside + 3, show higher oxidation state.
(d)	Less tendency of complex formation.	Higher tendency.

Q. 5. (a) Why is separation of lanthanoid elements difficult ?

(b) Transition metal exhibit higher enthalpies of atomization. Explain why ?

(c) Why have the transition metal high enthalpy of hydration ?

Ans. (a) Due to lanthanide contraction, the size of these elements is nearly same.

(b) Transition metal contain large number of unpaired electrons, and they have strong interatomic attractions.

(c) Due to their small size and large nuclear charge.

Q. 6. (a) Use Hund's rule to derive the electronic configuration of Ce^{+3} ions and calculate its magnitude moment.

(b) Is lanthanum a *f*-block element ?

Ans. (a) $_{58}Ce = [Xe]\ 4f^1\ 5d^1\ 6s^2$

$Ce^{+3} = 4f^1$ one unpaired electron

$$\mu = \sqrt{n(n+2)} = 1.73\ \text{BH}$$

(b) No, it is a *d*-block element.

Q. 7. Account for the following :

(a) Silver chloride dissolves in excess of NH_3.

(b) Cuprous chloride is diamagnetic while cupric chloride is paramagnetic.

(c) In CrO_4^{2-} ion, all the Cr – O bond length are equal.

Ans. (a) AgCl forms a soluble complex with NH_3.

$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

(b) $Cu^+ : 3d^{10}\, 4s^0$ – All electrons are paired.

$Cu^{+2} : 3d^9$ – Here, one unpaired electron is present.

(c) Due to resonance.

Q. 8. The E° values in respect of electrodes of Cr, Mn and iron are :

$Cr^{+3}/Cr^{+2} = -0.4$ V

$Mn^{+3}/Mn^{+2} = +1.5$ V

$Fe^{+3}/Fe^{+2} = +0.8$ V

Compare the feasibilities of further oxidation of these ions.

Ans. Cr^{+3} is more stable than Cr^{2+}.

Mn^{+2} is more stable than Mn^{+3}.

Fe^{3+} is more stable than Fe^{2+}.

Order of feasibility of + 2 oxidation state is :

$Mn^{+2} > Fe^{+2} > Cr^{+2}$

Q. 9. Write any three properties of interstitial compounds.

Ans. (a) They are chemically inert.

(b) They retain metallic conductivity.

(c) They have high melting point than their pure metals.

(d) These are harder and more corrosion resistant.

Q. 10. Account for the following :

(a) All Scandium salts are white.

(b) The Ist ionization energy of the 5*d* series are higher than 3*d* and 4*d* transition elements in respective groups.

(c) Ce^{+3} can be easily oxidized to Ce^{+4}.

Ans. (a) Sc has only + 3 oxidation state, there is no unpaired electron.

(b) Due to lanthanide contraction, effective nuclear charge increase.

(c) Due to gain noble gas electron configuration.

Q. 11. A green chromium compound (A) on fusion with alkali gives a yellow compound (B) which on acidification gives a orange coloured compound (C). Identify A, B, C. Write equations for reactions.

Ans. A : $FeCr_2O_4$ B : Na_2CrO_4 C. $Na_2Cr_2O_7$

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

(A) (B)

$Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

(C)

Q. 12. **When an oxide of Mn (A) is fused with KOH in the presence of an oxidizing agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionate in neutral or acidic solution to give purple compound (C). Identify A, B, C.**

Ans. A : MnO_2 B : K_2MnO_4 C : $KMnO_4$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. **A violet compound of manganes (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of KNO_3 to give compound (B). On heating compound (C) with conc. H_2SO_4 and NaCl, Cl_2 gas is liberated and compound (D) of manganese is formed. Identify A, B, C, D alongwith reactions involved.**

Ans. A : $KMnO_4$ B : K_2MnO_4 C : MnO_2 D : $MnCl_2$

$$\underset{(A)}{KMnO_4} \xrightarrow{\Delta} \underset{(B)}{K_2MnO_4} + MnO_2 + O_2$$

$$\underset{(C)}{MnO_2} + KOH + KNO_3 \rightarrow \underset{(B)}{K_2MnO_4}$$

$$\underset{(C)}{MnO_2} + NaCl + \text{conc. } H_2SO_4 \rightarrow \underset{(D)}{MnCl_2}$$

Q. 2. **(a)** **What is meant by disproportionation of an oxidation state ? Give one example.**

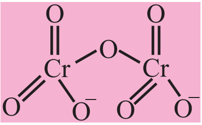
(b) **Draw the structures of $Cr_2O_7^{2-}$, CrO_4^{-2}, MnO_4^{-}.**

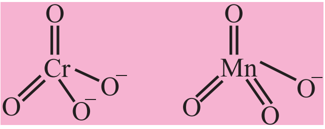
(c) **What is the effect of lanthoids contraction beyond lanthanoid ?**

Ans. (a) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.

$$2Cu^{+} \rightarrow Cu^{+2} + Cu$$

(b)





(c) Size of respective 4*d* and 5*d* series elements becomes comparable from fourth group onwards (*e.g.*, Zr and Hf).

VALUE BASED QUESTIONS (4 Marks)

Q. 1. A group of students was smoking cigarettes in college premises. A social activist noticed and advised them not to smoke.

(a) By forbidding them not to smoke, which value of social activity wants to be inculcated among the youth ?

(b) As a chemistry student, write the name of 'alloy' used in lighter's flint.

(c) Mention diseases caused by smoking.

(d) Name the chemical present in the smoke which is habit forming.

Q. 2. It is a general myth that we should not come out of the house to see solar eclipse because it can have evil impact on life but nowadays educated people allow their children to see solar eclipse, treating them as a natural science phenomenon, but children are advised to see them by uv protected sun glasses (crooke's lenses) to avoid harmful impact of uv light on eyes.

(a) Write the name of *d*-block metal oxide used in making uv protected lens.

(b) By allowing the children to see solar eclipse using uv protected lens, which value the educated people are trying to inculcate in the children ?

(c) Which rays are present in the light which can damage the eye while viewing solar eclipse with naked eye ?

(d) Name the oxide of a lanthanoid also present in uv protected lenses.

Q. 3. In Chemistry lab, Lalit used $Na_2Cr_2O_7$ for the estimation of Fe^{2+} and I^- in redox reactions while Sahil uses $K_2Cr_2O_7$ for the same estimation of ions.

(a) Out of these two, who is performing correct estimation of ions ?

(b) Draw the structure of $Cr_2O_7^{2-}$ ion.

(c) Explain why CrO_4^{2-} and $Cr_2O_7^{2-}$ are interconvertible by the change in pH of the medium.

(d) Name the value learnt by the use of $K_2Cr_2O_7$ in the estimation of ions.

Q. 4. For automotive catalytic converters, transition metals like Pt, Pd, Rd, Fe, Cr etc. used in industry are expensive while ceramic cores are inexpensive.

(a) Which property of transition metal makes them useful as catalyst ?

(b) What is the function of catalytic convertor ?

(c) As a student of chemistry, would you suggest the use of explosive metals like Pt, Pd and Rh ? Give reasons.

(d) Which value is promoted through the use of catalytic convertors in industry ?

Q. 5. Due to scarcity to water, the resident of a colony decided to refuse their well which was not used for the past six months. The secretary of RWA decided to clean the well by adding small amount of potassium permanganate in the well and then loaded the well water with alum crystals.

(a) Why did the secretary of RWA add potassium permanganate in well ?

(b) Draw the structure of permanganate ion, MnO_4^-.

(c) Why did secretary of RWA add alum to the well ?

(d) What values are associated with the use of $KMnO_4$ and alum ?

UNIT 9

COORDINATION COMPOUNDS

1. Introduction

Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in solution are known as complex compounds. In these compounds metal atoms are bound to a number of anions.

Example,

$$K_4\ [Fe(CN)_6] + H_2O \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

2. Types of Complex

(i) Anionic complex

$$K_3[Fe(C_2O_4)_3] \rightarrow 3K^+ + \underset{\text{anionic complex}}{[Fe(C_2O_4)_3]^{3-}}$$

(ii) Cationic complex

$$[CoCl_2(en)_2]Cl \rightarrow \underset{\text{cationic complex}}{[CoCl_2(en)_2]^+} + Cl^-$$

(iii) Neutral complex

$[Ni(CO)_4]$

neutral complex

3. Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Types of Ligands

(i) Unidentate, a ligand which is bound to a metal ion through a single donor atom.

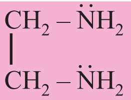
e.g., H_2O, NH_3, CO, Cl^-, NH_2^- etc.

(ii) Didentate, a ligand which is bound to a metal ion through a two donor atoms.

e.g.,

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array}$$

Oxalate ion



$$\begin{array}{l} CH_2 - \ddot{N}H_2 \\ | \\ CH_2 - \ddot{N}H_2 \end{array}$$

ethylene diamine

(iii) Polydentate, a ligand which is bound to a metal ion through a several donor atoms.

e.g., ethylene diamine tetraacetate ion $[EDTA]^{4-}$.

(iv) Ambidentate ligands, which can ligate through two different atoms.

e.g., $-NO_2$ – ONO, – SCN – NCS etc.

(v) Chelate ligands, these may be a di- or polydentate ligand which form closed ring with central metal ion. Closed ring is known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

4. Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups *e.g.,* $Co(NH_3)_6]^{3+}$ are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups *e.g.,* $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

5. Nomenclature of Coordination Compounds

Cationic Complex

$[Cr(NH_3)_3(H_2O)_3]Cl_2$

triamminetriaquachromium (III) chloride

(i) Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.

(ii) Central metal atom and oxidation state indicated by Roman numeral in parenthesis.

(iii) Name of ionisable anion.

Anionic Complex

$K_3[Fe(CN)_6]$

Potassium hexacyanoferrate (III)

(i) Name of ionisable metal and oxidation state

(ii) Name of ligand in an alphabetical order

(iii) Central metal atom + ate and oxidation state

Neutral Complex

$[Pt(NH_3)_2Cl(NO_2)]$

Diammine chloronitrito-N-platinum (II)

(i) Name of ligands in an alphabetical order

(ii) Central metal atom and oxidation state

6. Isomerism in Coordination Compounds

Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types : geometrical isomerism and optical isomerism.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

(i) **Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate),** the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer.

e.g., $[Pt(NH_3)_2Cl_2]$

(ii) **Square planar complex of the type $[MABXL]$ (where A, B, X, L are unidentates)** shows three isomers – **two *cis* and one *trans*.** Such isomerism is not possible for tetrahedral geometry.

e.g., $[Pt(NH_3)(Br)(Cl)(Py)]$

(iii) **Octahedral complexes of formula $[MX_2L_4]_1$** in which the two ligands X may be oriented *cis* or *trans* to each other.

e.g., $[Co(NH_3)_4Cl_2]^+$

(iv) **Octahedral complexes of formula $[MX_2A_2]$** where X are unidentates and A are didentate and form *cis* and *trans* isomers.

e.g., $[CoCl_2(en)_2]$

(v) **Octahedral coordination entities of the type $[Ma_3b_3]$** like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meriodional (mer) isomer.

Optical Isomerism

- It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called *dextro* (*d*) and *laevo* (*l*).
- Optical isomerism is common in octahedral complexes but at least one didentate ligand should be present.

  e.g., $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$ etc.

Structural Isomerism

In structural isomerism, isomers have different bonding pattern. Different types of structural isomerism is as follows :

(i) Linkage isomerism, arises in a coordination compound containing ambidentate ligand.

e.g., $[Co(NH_3)_5(NO_2)]Cl_2$

$[Co(NH_3)_5(ONO)]Cl_2$

(ii) Coordination isomerism, arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

e.g., $[Co(NH_3)_6][Cr(CN)_6]$

$[Cr(NH_3)_6][Co(CN)_6]$

(iii) Ionisation isomerism, when the ionisable anion exchange with anion ligand.

e.g., $[CO(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

(iv) Solvate isomerism, is also known as 'hydrate isomerism'. In this case water is involved as a solvent.

e.g., $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl_2.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

7. Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies – primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

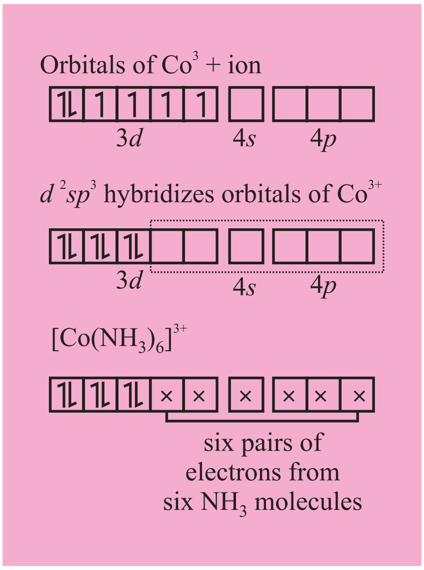
According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

(i) Six ligands (unidentate) (octahedral entity) Generally central atom belongs 3*d* series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

(a) Inner orbital complexes, which are formed due to participation of (n –1)d orbitals in hybridisation is (d^2sp^3) and shape of complex will be octahedral.

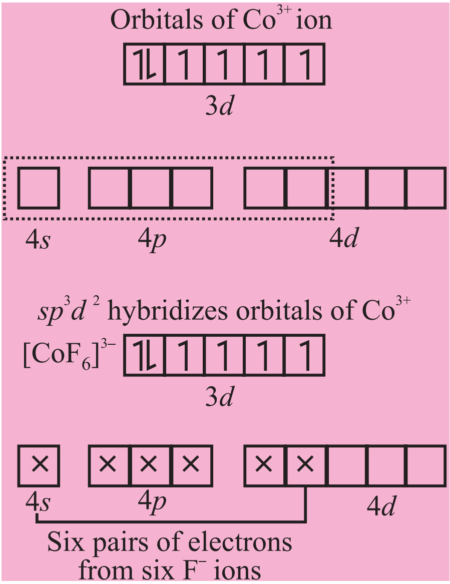
(b) Outer orbital complexes, which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2). Generally halides (F^-, Cl^-, Br^-, I^-), SCN^-, S^{2-} form outer orbital complexes and other ligands form inner orbital complexes.

e.g., **Inner orbital complex,** $[Co(NH_3)_6]^{3+}$



All electrons are paired therefore, complex will be diamagnetic in nature.

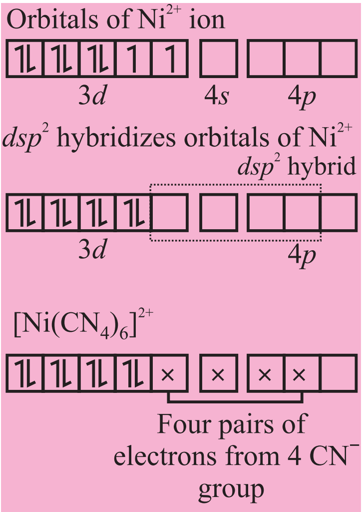
e.g., **Outer orbital complex,** $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

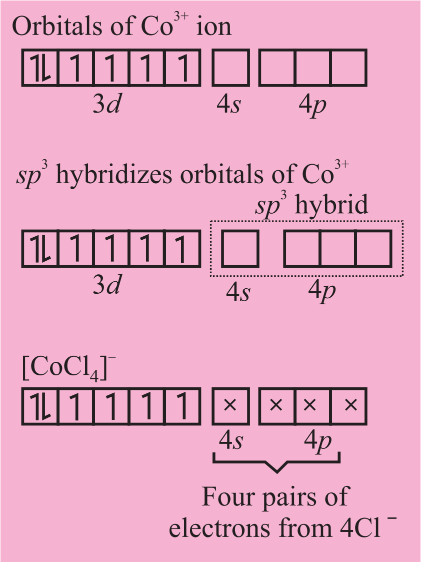
Complexes with coordination number : 4

1. $[Ni(CN)_4]^{2-}$



All electrons are paired. Complex will be diamagnetic in nature.

2. $[CoCl_4]^-$

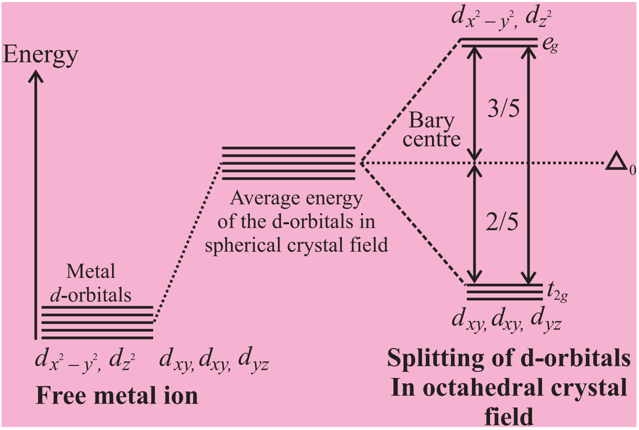


Complex has unpaired electrons. Complex will be paramagnetic in nature.

Crystal Field Theory

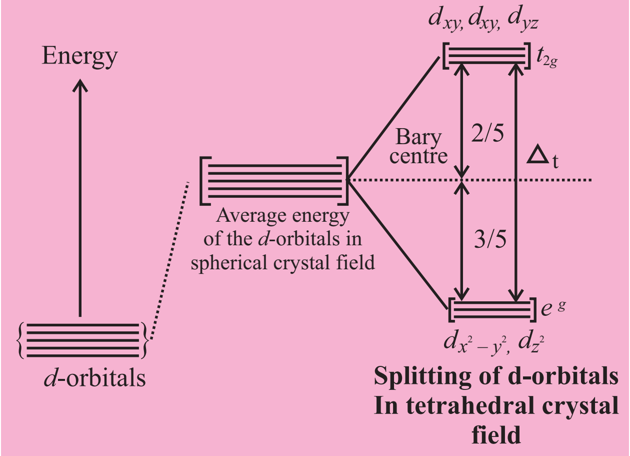
The five *d*-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory. The five *d*-orbitals in a gaseous metal atom/ion have same energy.

(i) Crystal field splitting in octahedral coordination entities.



- Energy separation is denoted by Δ_o (the subscript o is for octahedral).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by $(3/5)\Delta_o$ and that of the three t_{2g} (lower energy orbitals) will decrease by $(2/5)\Delta_o$.
- If $\Delta_o < p$, the fourth electron enters one of the e_g, orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < p$ are known as weak field ligands and form high spin complexes.
- If $\Delta_o > p$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes, where p represents the energy required for electron pairing in a single orbital.

(ii) Crystal field splitting in tetrahedral coordination entities.



- In tetrahedral coordination entities, $\Delta_t = (4/9)\Delta_o$. Consequently the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

- Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

- In complex compounds *d*-orbitals split in two sets t_{2g} and e_g. These have different energies. The difference in energies lies in visible region and electron jump from ground state t_{2g} level to higher state e_g level. This is known as *d-d* transition and it is responsible for colour of coordination compounds.

- *d-d* transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured. On the other hand, the ions d^0 and d^{10} configuration do not show *d-d* transition.

9. Importance and Applications of Coordination Compounds

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

- Some important extraction processes of metals, like those of silver and gold make use of complex formation.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(PH_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

Supplementary List of Ligands

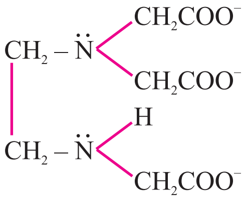
Ligand	F^-	Cl^-	Br^-	I^-	OH^-	CN^-	O^{2-}	O_2^{2-}	O_2^-	CO_3^{2-}	PH_3
Name	fluoro	chloro	bromo	iodo	hydroxo	cyano	oxo		super-oxo	carbonato	phosphine
Ligand	SO_4^{2-}	NO_2^-	ONO^-	SCN^{-1}	NCS	CH_3COO^-	C_5H_5N	S^{2-}	$S_2O_3^{2-}$	NO_3^-	SO_3^{2-}
Name	sulphato	nitro	nitrito	thiocyanato	isothiocyanato	acetate	pyridine (Py)	sulphido	thiosulphato	nitrato	sulphito
Ligand	NC^-	$(C_6H_5)_3P$	CS	NH_2^-	NH^{2-}	H_2NCSNH_2	$C_2O_4^{2-}$	H_2O	NH_3	CO	NO
Name	isocyano	triphenyl phosphine	thiocarbonyl	amido	imido	thiourea (tu)	oxalate (ox)	aqua	ammine	carbonyl	nitrosyl

$H_2N{-}CH_2{-}CH_2{-}NH_2$

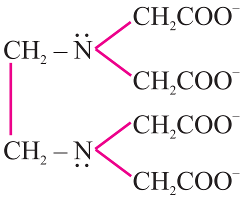
Ethylene diamine (en)

$H_2NCH_2CH_2NHCH_2CH_2NH_2$

Diethylenetriamine (diene)



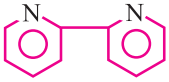
Ethylene diamine triacetate ion $EDTA^{3-}$



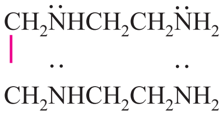
Ethylene diamine triacetate ion $EDTA^{3-}$

$H_2\ddot{N} - CH_2 - COO^-$

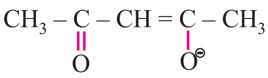
Glycinato (gly)



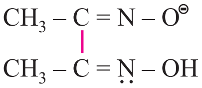
2,2' Bipyridyl



$$\begin{array}{l} CH_2\ddot{N}HCH_2CH_2\ddot{N}H_2 \\ | \\ CH_2\ddot{N}HCH_2CH_2\ddot{N}H_2 \end{array}$$



$$CH_3 - \underset{\underset{O}{\|}}{C} - CH = \underset{\underset{O^{\ominus}}{|}}{C} - CH_3$$



$$\begin{array}{l} CH_3 - C = N - O^{\ominus} \\ \qquad\ \ | \\ CH_3 - C = \ddot{N} - OH \end{array}$$

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Write the oxidation state of Nickel in $[Ni(CO)_4]$.

Ans. Zero

Q. 2. What is ambidentate ligand ? Give one example.

Ans. Monodentate ligands contain more than one coordinating atoms. Example, CN^-.

Q. 3. Write the IUPAC name of $[PtCl_2(en)_2(NO_3)_2]$.

Ans. Dichloridobis(ethylenediammine)nitratoplatinum(IV)

Q. 4. Write the name of a complex compound used in chemotherapy.

Ans. Cis-platin.

Q. 5. What is a chelate ligand ? Give one example.

Ans. The ligand which contain from two or more donar sites simutaneously to form cyclic complaces. Example, ethane-1-2 diammine.

Q. 6. Name one homogeneous catalyst used in hydrogenation of alkenes.

Ans. Wilkinson's catalyst.

Q. 7. How many geometrical isomers are possible for the $[Ni(NH_3)_4]^{+2}$?

Ans. Not possible because all 4 ligands are same.

Q. 8. Write IUPAC name of $[Co(C_2O_4)_3]^{-3}$.

Ans. Trioxalatocobalate(III) ion.

Q. 9. Give an example of coordination isomerism.

Ans. $[Co(NH_3)_6][Cr(CN)_6]$

Q. 10. Name an ionization isomer of $[Cr(H_2O)_5Br]SO_4$.

Ans. Pentaaquasulphatochromium (III) bromide.

Q. 11. Define coordination polyhedron.

Ans. The spatial arrangement of the ligand with the central metal ion.

Q. 12. Give the chemical formula of potassium hexacyano ferrate (II).

Ans. $K_4[Fe(CN)_6]$

Q. 13. Which of these cannot act as a ligand ?

NH_3, H_2O, CO, NH_4^+

Ans. NH_4^+ does not have lone pair of electron.

Q. 14. Give one use of Ziegler Natta catalyst.

Ans. Heterogeneous catalysis or in high density polymerisation.

Q. 15. Name the metal present in :

(i) Chlorophyll (ii) Haemoglobin (iii) Vit. B-12
(iv) cis platin

Ans. (i) Mg (ii) Fe (iii) Co (iv) Pt

Q. 16. The chemical formula of Wilkinson's catalyst is :

Ans. $(C_6H_5)_3P.RhCl$

Q. 17. Which of the two is more stable – $K_4[Fe(CN)_6]$ Or $K_3[Fe(CN)_6]$?

Ans. $K_4[Fe(CN)_6]$ because Fe has d^6 configuration in this case.

Q. 18. How many moles of AgCl will be precipitated when an excess of $AgNO_3$ is added to a molar solution of $[CrCl(H_2O)_5]Cl_2$?

Ans. 2 moles because 2 Cl^- ions are present as counter ion in the complex.

Q. 19. Which type of ligands form chelates ?

Ans. Polydentate ligand.

Q. 20. Arrange the following complexes in order of increasing electrical conductivity :

$[CO(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4]Cl_3$

Ans. $[CO(NH_3)_3Cl_3] < [Co(NH_3)_4]Cl_3 < [Co(NH_3)_5Cl]Cl_2$

More number of ions < more electrical conductivity

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Calculate the magnetic moments of the following complexes :

(i) $[Fe(CN)_6]^{-4}$ (ii) $[FeF_6]^{-3}$

Ans. (i) $Fe^{+2} \rightarrow 3d^6$. CN^- is a strong ligand so e^- pair 4p, no unpaired e^- then magnetic moment

$$\mu_{BH} = \sqrt{n(n+2)}$$

$n = 5$, So

$$\mu = \sqrt{n(n+2)}$$

$$\mu = \sqrt{5(5+2)}$$

$$\mu = \sqrt{35} = 5.96 \text{ BM}$$

Q. 2. Explain the following :

(i) NH_3 act as a ligand but NH_4^+ does not.

(ii) CN^- is a ambidentate ligand.

Ans. (i) NH_3 has one lone pair while NH_4^+ does not.

(ii) Because it has two donor atoms in a monodentate ligand.

Q. 3. **Mention the main postulates of Werner theory.**

Ans. (i) Metal ion has two types of valency.

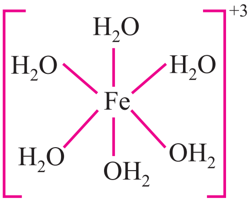
(ii) Primary valency and secondary valency.

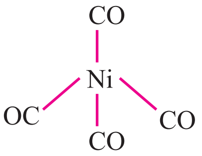
(iii) Secondary valency is equal to coordination number.

Q. 4. **Draw the structure of :**

(i) $[Ni(CO)_4]$ **(ii) $[Fe(H_2O)_6]^{+3}$**

Ans.





Q. 5. **How does EDTA help as a cure for lead poisoning ?**

Ans. Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble compled lead-EDTA is eliminated in urine.

Q. 6. **Define homoleptic and heteroleptic complexes.**

Ans. **Homoleptic :** When metal atom/ion is linked with one type of ligands. Example, $[Ni(CO)_4]$.

Heteroleptic : With the more than one kind of ligands. Example, $[Co(NH_3)_4Cl_2]^+$.

Q. 7. **$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why ?**

Ans. In $[NiCl_4]^{-2}$, Ni has $3d^8 4s^0$ configuration, Cl^- can't pair up while in $[Ni(CO)_4]$, Ni has $3d^8 4s^2$ configuration, CO pair up electrons

Q. 8. **The oxidation number of cobalt in the complex :**

(i) $K[Co(CO)_4]$ **(ii) $[Co(C_2O_4)_3]^{-3}$**

Ans. (i) -1 (ii) $+3$

Q. 9. **What are t_{2g} and e_g orbitals ?**

Ans. In a free transition metal ion, the *d*-orbitals are degenerate. When it form complex, the degeneracy is split and *d*-orbitals split into t_{2g} and e_g orbitals.

Q. 10. **What is the solution in which photographic film is washed ? What reaction takes place ?**

Ans. Hypo solution.

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Q. 11. **What is spectrochemical series ?**

Ans. The arrangement of ligands in order of their increasing crystal field splitting field strength.

Q. 12. What are the assumptions of Crystal Field theory.

Ans. (i) Ligand act as a point charge.

(ii) Metal ion has electrostatic attraction force with the ligand.

(Or any other)

Q. 13. $CuSO_4$ is colourless while $CuSO_4.5H_2O$ is coloured. Why ?

Ans. $CuSO_4$ does not has any ligand, so splitting of *d*-orbital take place while $CuSO_4.5H_2O$ has water ligand.

Q. 14. What is the difference between inner and outer orbital complexes ?

Ans. **Inner sphere complex :** When *d*-orbital of inner shell take part in hybridisation.

Outer sphere complex : When *d*-orbital of outermost shell take part in hybridisation.

Q. 15. How is stability of coordination compound determined in aqueous solution ?

Ans. By using stability constant.

More stability constant, more stability.

Q. 16. In a complex ion $[Co(NH_3)_5NO_2]Cl_2$,

(i) Identify the ligand.

(ii) Oxidation number of metal ion.

Ans. (i) NH_3, NO_2.

(ii) + 3

Q. 17. Explain how the nature of ligand affects the stability of complex ion.

Ans. Strong ligand : More stability

Weak ligand : Less stability

Q. 18. What is meant by denticity of a ligand ? Find out denticity of :

(i) $C_2O_4^{-2}$ (ii) EDTA

Ans. The number of ligand group/coordinating group.

(i) 2 (ii) 6

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. A coordination compound has the formula $CoCl_3.4NH_3$. It does not liberate NH_3 but forms a precipitate with $AgNO_3$. Write the structure and IUPAC name of the complex compound. Does it show geometrical isomerism ?

Ans. Formula : $[Co(NH_3)_4Cl_2]Cl$

Name : Tetraaminedichloridocobalt(III) chloride

Yes, it show geometrical isomerism.

Q. 2. Why does a tetrahedral complex of the type $[MA_2B_2]$ not show geometrical isomerism ?

Ans. Because all position of tetrahedral is same in orientation.

Q. 3. **The molar conductivity of the complex $CoCl_3.4NH_3.2H_2O$ is found to be same as that of 3 : 1 electrolyte. What is the structural formula. Name and number of geometrical isomer of the complex.**

Ans. As coordination number of Co is 6 and complex should be A_3B or AB_3 type, formula is $[Co(NH_3)_4(H_2O)_2]Cl_3$.

Name : Tetraaminediaqua cobalt (III) chloride

Geometrical isomer : 2 (cis and trans)

Q. 4. **$[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. Why ?**

Ans. $[Ti(H_2O)_6]^{3+}$: In this core Ti^{+3} has one unpaired e^- while Sc^{+3} does not has any unpaired electron.

Q. 5. **Describe with an example of each, the role of coordination compounds in :**

(i) Biological system

(ii) Analytical chemistry

(iii) Medicinal chemistry

Ans. (i) Vit. B-12, it is a antipernicious anemia factor.

(ii) Determining and estimation of metal.

(iii) EDTA is used in lead poisoning.

Q. 6. **Write the type of isomerism exhibited by the following complexes :**

(i) $[Co(NH_3)_5Cl]SO_4$

(ii) $[Co(en)_3]^{+3}$

(iii) $[Co(NH_3)_6][Cr(CN)_6]$

Ans. (i) Ionization

(ii) Optical

(iii) Coordination isomerism

Q. 7. **Explain the following :**

(i) CO is stronger ligand than NH_3.

(ii) Low spin octahedral complexes of nickel are not known.

(iii) Aqueous solution of $[Ti(H_2O)_6]^{+3}$ is coloured.

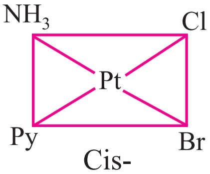
Ans. (i) CO has high value of crystal field splitting energy than Cl.

(ii) Ni has d^8 configuration which does not affect by field strength of ligand.

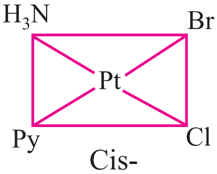
(iii) In this case, Ti^{+3} has $t_{2g}^{\ 1}\ e_g^{\ 0}$ configuration. It can perform *d-d* transition.

Q. 8. **Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(Py)]$ and how many of these will exhibit optical isomerism ? Here, Py = Pyridine.**

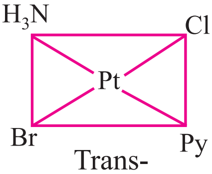
Ans. 3 isomers are possible.



Cis-



Cis-



Trans-

Monodentate ligand in square planar complex do not show optical isomerism.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_o > p$:

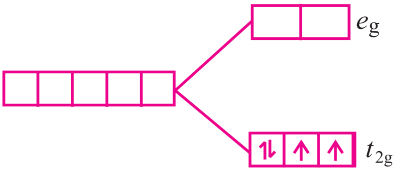
(i) Draw the diagram showing *d*-orbital splitting during this complex formation.

(ii) What type of hybridisation will M^{n+} have ?

(iii) Name the type of isomerism exhibited by this complex.

(iv) Write the electronic configuration of metal M^{n+}.

Ans. (i) If $\Delta_o > p$ then



(ii) d^2sp^3

(iii) $[M(AA)_3]$ type complex show optical isomerism.

(iv) $t_{2g}^{\ 4}\ e_g^{\ 0}$

Q. 2. (i) Discuss the nature of bonding in metal carbonyls.

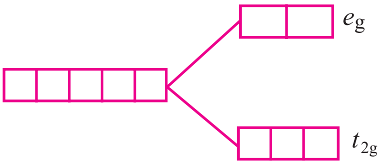
(ii) Draw figure to show the splitting of *d*-orbitals in an octahedral crystal field and write electronic configuration of M^{s+} ion when :

(a) $p > \Delta_o$

(b) $\Delta_o > p$

Ans. (i) The metal carbon bond in metal carbonyls possess both σ and π character. The M – C σ bond if formed by the M ← C ≡ O while M – C π bond if formed by the donation of a pair of electron from filled *d*-orbital of metal to antibonding π* orbital of CO.

(ii)



(a) $t_{2g}^{\ 3}\ e_g^{\ 2}$ (b) $t_{2g}^{\ 5}\ e_g^{\ 0}$

Q. 3. **(i)** **$[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution. Why ?**

(ii) **A complex is prepared by mixing $CoCl_3$ and NH_3 in the molar ratio of 1 : 4. 0.1M solution of this complex was found to be freeze at – 0.372º C. What is the formula of the complex ? $K_f = 1.86^{\circ}C/M$**

Ans. (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN^- and H_2O has different crystal field splitting energy.

(ii) $\Delta T_f = i.K_f.m$

i = 2 means complex dissociate into two ions.

Hence the formula is $[Co(NH_3)_4Cl_2]Cl$

VALUE BASED QUESTIONS (4 Marks)

Q. 1. A lots of children, working in a lead industry were rescued by NGO's activists. The children were sent to the hospital and found to be excess exposure to lead so called lead poisoning. Lead is very poisonous.

(i) Name the ligand (compound) used for treatment of lead poisoning.

(ii) Name the cell wherein lead is used.

(iii) Write the reaction involved for removal of lead from living organism.

(iv) During this rescue operation, which values are shown by NGO's activists ?

Q. 2. Cancer is not a communicable disease. It occurs due to unlimited growth of body cells leading to tumours. We should shake hands, eat together with people suffering from cancer. These activities boost up the confidence in them for living.

(i) Write the name of coordination compound used as a chemotherapeutic agent to curb the growth of tumours.

(ii) Draw the structure of this coordination compound.

(iii) How is copper poisoning treated by the use of Ca-EDTA complex ?

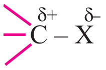
(iv) By showing such attitude to cancer patients, mention the values reflected by us.

UNIT 10

HALOALKANES AND HALOARENES

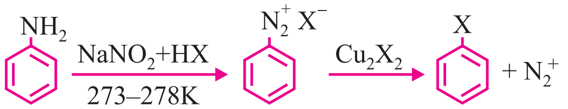
Points to Remember

1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I)
2. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula Ar – X.
3. Since halogen is more electronegative than C, hence C – X bond is polar.



4. **Named Reactions :**

(a) Sandmeyer Reaction :



(X = Cl, Br)

(b) Finkelstein Reaction :

$$R-X+NaI\xrightarrow{\text{dry acetone}}R-I+NaX\quad(X=Cl,\ Br)$$

(c) Swartz Reaction :

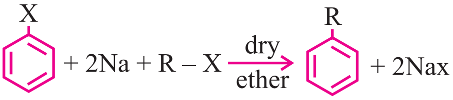
$$CH_3-Br+AgF\rightarrow CH_3-F+AgBr$$

Instead of Ag – F, other metallic fluoride like Hg_2F_2, CoF_2 or SbF_3 can also be used.

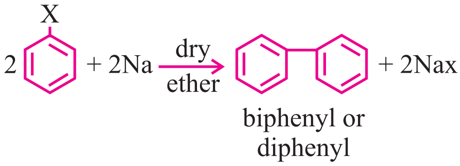
(d) Wurtz Reaction :

$$2R-X+2Na\xrightarrow{\text{dry ether}}R-R+2NaX$$

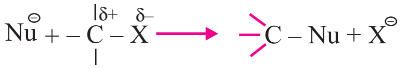
(e) Wurtz-Fittig Reaction :



(f) Fittig Reaction :



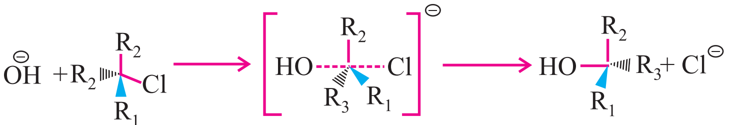
5. Nucleophilic Substitution Reactions :



$$\overset{\ominus}{Nu} + -\overset{|\delta+}{\underset{|}{C}}-\overset{\delta-}{X} \longrightarrow \rangle C-Nu + X^{\ominus}$$

haloalkane

(a) Substitution nucleophilic bimolecular ($S_N{}^2$) :



Reactants

Unstable transition state

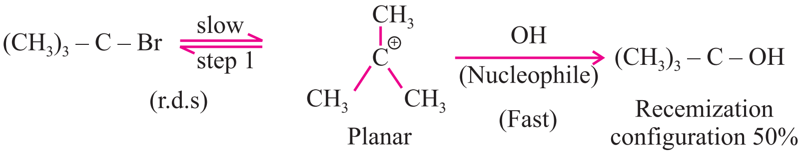
Inversion of configuration

1. 1° haloalkane
2. Bimolecular, 2nd order
3. One step

Order of reactivity : 1° > 2° > 3°

Deciding factor : Steric hindrance

(a) Substitution nucleophilic unimolecular ($S_N{}^1$) :



Planar carbo cation

Recemization configuration 50% relation (Racemic mixture is formed) & 50% inversion

1. 3° haloalkane
2. Unimolecular, 1st order
3. Two steps

Order of reactivity : 3° > 2° > 1°

Deciding factor : Stability of carbo cation

* Allylic $\left[CH_2=CH-\overset{\oplus}{C}H_2\right]$ and benzylic $\left[C_6H_5\overset{\oplus}{C}H_2\right]$ halides undergo reaction via SN^1 mechanism as the corresponding carbo cations are resonance stabilized.

6. Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

7. Halogen is deactivating but *o, p*-directing in electrophilic substitution reaction of haloarenes.

8. $CHCl_3$ is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

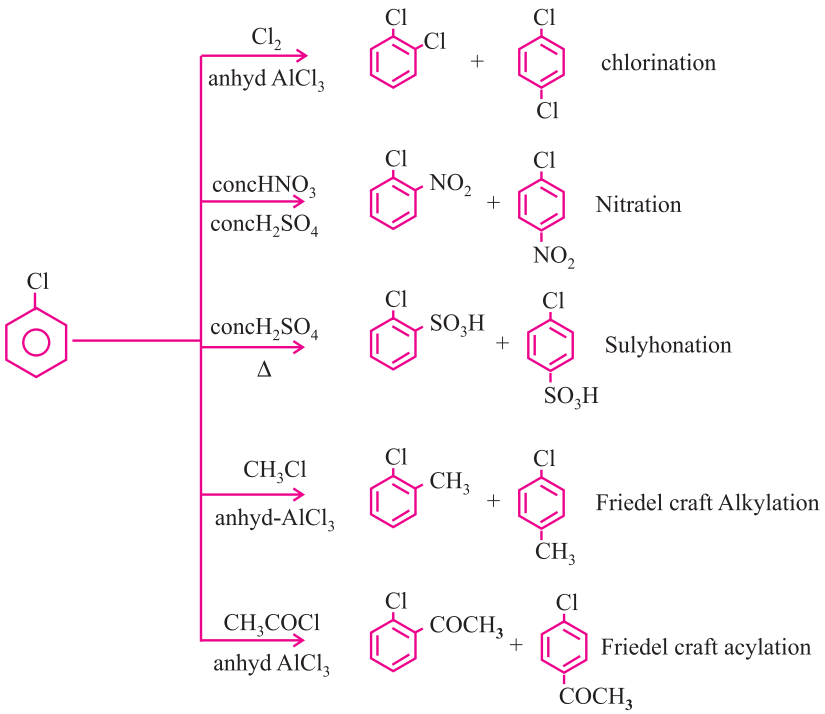
$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Chloroform — Carbonyl chloride (phosgene)

9. Reaction of Haloalkanes :

$$R{-}X \xrightarrow[\text{or KOH}]{\text{NaOH}} R{-}OH$$
$$R{-}X \xrightarrow{\text{NaI}} R{-}I$$
$$R{-}X \xrightarrow{\text{KCN}} RCN$$
$$R{-}X \xrightarrow{\text{AgCN}} RNC$$
$$R{-}X \xrightarrow{\text{KNO}_2} R{-}O{-}N = O$$
$$R{-}X \xrightarrow{\text{AgNO}_2} R{-}NO_2$$
$$R{-}X \xrightarrow{\text{LAH}} RH$$
$$R{-}X \xrightarrow{\text{NH}_3} R{-}NH_2$$
$$R{-}X \xrightarrow{\text{Mg}} R{-}MgX$$
$$R{-}X \xrightarrow{\text{Na, D.E.}} R{-}R$$
$$R{-}X \xrightarrow{\text{NaOR}} R{-}O{-}R'$$
$$R{-}X \xrightarrow{\text{R'COOAg}} R'COOR$$

10. Electrophilic Substitution Reaction of Haloarenes :

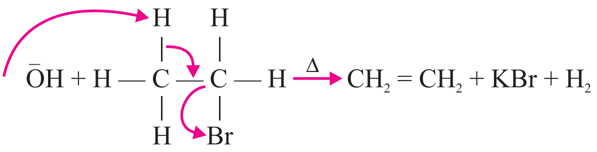


11. Elimination reaction: Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atom. [Reverse of addition]

Two types (*i*) β-Elimination ⟶ (E_1 → Two step eliminate; E_2 → One step eliminate)

(*ii*) α-elimination

Saytzaff's Rule



$$\bar{O}H + H - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{Br}{C}} - H \xrightarrow{\Delta} CH_2 = CH_2 + KBr + H_2$$

$$CH_3 - CH_2 - \underset{Br}{CH} - CH_3 \xrightarrow{Aloc.KOH} CH_2 = CH_2 + KBr + H_2$$

(81% More highly substituted Alkenes, More stable)

12. Distinguishing test for alkyl chlorides, bromides and iodide : Alkyl chlorides react with $AgNO_3$ to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with $AgNO_3$ to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with $AgNO_3$ to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.

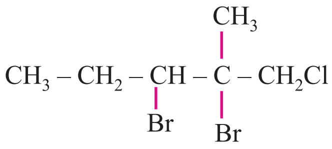
E.g., $CH_3 - Cl \xrightarrow[AgNO_3]{HNO_3} AgCl \downarrow$

White ppt.

Vinyl and aryl halides do not yield silver halide under these conditions.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Give IUPAC name of :



$$CH_3 - CH_2 - \underset{Br}{CH} - \overset{CH_3}{\underset{Br}{C}} - CH_2Cl$$

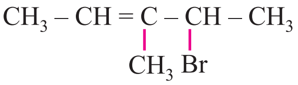
[*Hint :* 1-chloro-2, 3-dibromo-2-methyl pentane]

Q. 2. Identify A and B in each of the following processes :

$$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{Reduction} B$$

[*Hint :* A : $CH_3 - CH_2 - CN$; B : $CH_3CH_2CH_2NH_2$]

Q. 3. Draw the structure of 4-bromo-3-methylpent-2-ene.

[*Hint :* 
$CH_3 - CH = C(CH_3) - CH(Br) - CH_3$

Q. 4. Why Grignard reagent should be prepared under anhydrous conditions ?

Q. 5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Q. 6. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure ?

[*Hint* 
$CH_3 - CH(Cl) - CH_2 - CH_3$

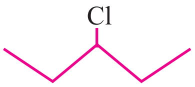
Q.7. An organic compound 'A' on treatment with KCN gave B which on hydrolysis with dil. HCl gave acetic acid. Identify A.

[*Hint :* A : CH_3Cl]

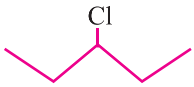
Q. 8. Write IUPAC name of iodoform.

[*Hint :* Triiodomethane]

Q. 9. Which one of the following two substances undergo SN^1 reaction faster and why ?



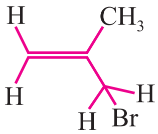
Or

(Hint : 

(2°)

Q. 10. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanides as the chief product. Explain.

Q. 11. Write the IUPAC name of the following compound :



[*Hint :* 3-bromo-2-methylprop-1-ene]

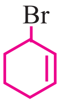
Q. 12. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions :

$CH_3F, CH_3I, CH_3Br, CH_3Cl$

[*Hint :* $CH_3F < CH_3Cl < CH_3Br < CH_3I$]

Q. 13. Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why ?

Q. 14. Complete the reaction :

(Hint : 

)

Q. 15. How will you convert 2-bromo propane into 1-bromo propane ?

Q. 16. Give one chemical test to distinguish between chlorobenzene and benzyl chloride ?

[*Hint :* $AgNO_3$ test]

Q. 17. Why iodoform show antiseptic properties ?

[*Hint :* Due to free liberated iodine.]

Q. 18. The presence of nitro group (– NO_2) at ortho or para positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. Explain.

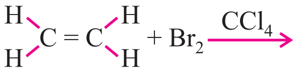
Q. 19. For the preparation of alkyl chlorides from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following reactions :

(i) $C_6H_5N_2Cl + KI \rightarrow$

(ii)



Q. 2. Carry out the following conversions in not more than two steps :

(i) Toluene to benzyl alcohol

(ii) Benzyl alcohol to phenylethanenitrile

Q. 3. Give reasons :

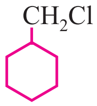
(i) Boiling point of alkyl bromide is higher than alkyl chloride.

(ii) Alkyl halides are better solvents than aryl halides.

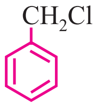
[*Hint :* (i) High magnitude of van der Waal's forces in alkyl bromides.

(ii) C – X is more polar in haloalkanes.]

Q. 4. Which of the following compounds would undergo $S_N{}^1$ reaction faster and why ?



(A)



(B)

Hint : (A)

Q. 5. Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre :

(i) 1, 2-dichloropropane

(ii) 3-bromopent-1-ene

Q. 6. Convert :

(i) Benzene to m-nitrochlorobenzene

(ii) Benzene to diphenyl

Q. 7. What happens when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

Q. 8. (i) An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure ?

(ii) Alkyl iodides develop colouration on long standing particularly in light. Explain.

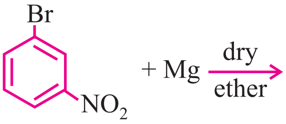
[*Hint :* (i) $CH_3 - CH(Cl) - CH_2 - CH_3$

(ii) Due to decomposition by light and produce I_2.]

Q. 9. Tert-butyl bromide reacts with aq. NaOH by $S_N{}^1$ mechanism while n-butylbromide reacts with $S_N{}^2$ mechanism. Why ?

Q. 10. Although chlorine is an electron withdrawing group, yet it is o, p-directing in electrophilic aromatic substitution reactions. Explain, why is it so ?

Q. 11. Identify the products :

(i) 

(ii) 

$$CH_3 - \underset{\displaystyle Br}{\underset{|}{C}H} - CH_3 \xrightarrow{\text{alc.KOH}} A \xrightarrow[H_2O_2]{HBr} B$$

Q. 12. (i) Arrange the following halides in order of increasing $S_N{}^1$ reactivity :

CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

(ii) Which out of 1-bromobutane & 2-bromobutane would react faster by $S_N{}^2$ pathway and why ?

Q. 13. Identify the products :

$$C_6H_6 \xrightarrow[\text{anhy.}AlCl_3]{CH_3Cl} A \xrightarrow[hv]{Cl_2\,(1\text{ mole})} B \xrightarrow{\text{aq.KOH}} C \xrightarrow{HBr} D$$

Q. 14. Carry out the following conversions :

(i) But-1-ene to n-butyliodide

(ii) Isopropyl alcohol to iodoform

Q. 15. An organic compound A reacts with PCl_5 to give compound B. Compound B reacts with Na/ether to give n-butane. What are compounds A and B ?

[*Hint :* A = C_2H_5OH, B = C_2H_5Cl]

Q. 16. Write short note on :

(i) Sandmeyer reaction

(ii) Finkelstein reaction

Q. 17. Name the reagents used to convert :

(i) 2-chloropropane to 2-nitropropane

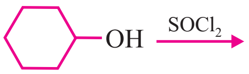
(ii) Chloroethane to n-butane

[*Hint :* (i) $AgNO_2$

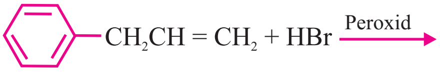
(ii) Na/dry ether]

Q. 18. Draw structure of monohalo product in each of the following :

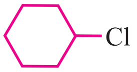
(i)



(ii)



Ans. (i)



(ii)

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement :

(i) 2-bromo-2-methyl butane, 1-bromopentane, 2-bromopentane

(ii) 1-bromo-3-methylbutane, 2-bromo-2-methyl butane, 2-bromo-3-methyl butane

(iii) 1-bromobutane, 1-bromo-2, 2-dimethyl propane, 1-bromo-2-methyl butane

Q. 2. Answer the following :

(i) Haloalkanes easily dissolve in organic solvents, why ?

(ii) What is known as racemic mixture ? Give example.

(iii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why ?

Q. 3. Answer the following :

(i) What is meant by chirality of a compound ? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why ?

$$CH_3CHClCH_2CH_3 \text{ or } CH_3CH_2CH_2Cl$$

(iii) Which one undergo S_N^2 substitution reaction faster and why ?

Q. 4. Complete the following reactions :

(i) $CH_3CH_2OH \xrightarrow{SOCl_2} A \xrightarrow{KCN} B$

(ii) $(CH_3)_2CHBr + Na \rightarrow$

(iii) $CH_3CH_2Cl \xrightarrow{AgNO_3}$

Q. 5. How the following conversions can be carried out ?

(i) But-1-ene to n-butyl iodide

(ii) Tert-butyl bromide to isobutyl bromide

(iii) Ethanol to but-1-yne

Q. 6. Write short notes on :

(i) Wurtz-Fittig reaction

(ii) Fittig reaction

(iii) Dehydrohalogenation reaction

Q. 7. An organic compound 'A' having molecular formula C_4H_8 on treatment with dil. H_2SO_4 give another compound 'B'. B on treatment with conc. HCl and anhy. $ZnCl_2$ gives 'C'. C on treatment with sodium ethoxide gives back 'A'. Identify the compound. Write the equations involved.

Q. 8. What happens when :

(i) 1-bromopropane reacts with metallic sodium.

(ii) Bromoethane is treated with caustic potash.

(iii) Iodomethane is treated with ammonia.

Q. 9. Identify A, B and C :

$$\text{2-propanol} \xrightarrow{SOCl_2} A \xrightarrow{Mg} B \xrightarrow{H_2O} C$$

Q. 10. Account for the following :

(i) A small amount of ethyl alcohol is added to $CHCl_3$ stored for use as an anaesthetic.

(ii) After using CCl_4 as a fire extinguisher inside a closed space, the space is thoroughly ventilated.

(iii) When 2-chloro-3-methylbutane is treated with alcoholic potash, 2-methyl-2-butene is the main product.

[*Hint :* (i) To convert harmful $COCl_2$ to ethyl carbonate.

(ii) To sweep out $COCl_2$ formed by CCl_4 vapour and H_2O vapour.

(iii) Saytzeff rule.

Q. 11. How will you distinguish between :

(i) Vinyl chloride and ethyl chloride

(ii) Chlorobenzene and cyclohexyl chloride

(iii) Ethyl chloride and ethyl bromide

Q. 12. Explain the following :

(i) The dipole moment of chloroethane is higher than that of chlorobenzene.

(ii) Although haloalkane are polar in character yet they are insoluble in water.

(iii) Vinyl chloride is unreactive in nucleophilic substitution reactions.

Q. 13. (i) Which will have a higher boiling point ?

1-chloroethane or 2-chloro-2-methyl butane. Give reason.

(ii) p-chloronitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving resonating structure as well.

Q. 14. (i) What are ambident nucleophiles ? Explain with an example.

(ii) Convert ethyl bromide to diethyl ether.

(iii) What are freons ?

Q. 15. A hydrocarbon 'A' (C_4H_8) is added with HBr in accordance with Markonikov's rule to give compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ($C_4H_{10}O$). Identify A, B and C.

Q. 16. (i) Which isomer of C_4H_9Cl will have the lowest boiling point ?

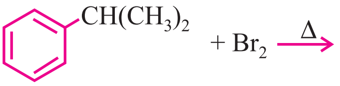
(ii) Predict the alkenes that would be formed by dehydrohalogenation with sodium ethoxide and ethanol. Predict major alkenes :

(a) 2-chloro-2-methylbutane

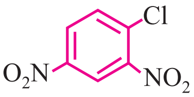
(b) 3-bromo-2, 2, 3-trimethylpentane

Q. 17. Write the structure of major product in each of the following :

(i)



(ii)

(iii)  $+ C_2H_5ONa \xrightarrow[\Delta]{\text{Ethanol}}$

Q. 18. Write the main products when :

(i) n-butyl chloride is treated with alcoholic KOH

(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.

(iii) Methyl chloride is treated with AgCN.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How would you bring about the following conversions :

(i) Propene to 2-bromopropane

(ii) Bromoethane to propanoic acid

(iii) 1-chloropropane to 1-propanol

(iv) Ethanol to chloroethane

(v) 1-iodopropane to propene

Q. 2. What happens when : (Give chemical reactions)

(i) Cyclohexanol is treated with thionyl chloride

(ii) p-hydroxybenzyl alcohol is heated with HCl.

(iii) Ethyl bromide is refluxed with NaI in acetone.

(iv) Ethyl bromide is treated with mercurous fluoride.

(v) Chlorobenzene is subjected to hydrolysis.

Q. 3. Complete the following reactions :

(i) $C_6H_6 \xrightarrow{Cl_2/Fe} X \xrightarrow[\text{Pyridine}]{\text{CuCN}} Y \xrightarrow{H^+, H_2O}$

(ii) $C_2H_4 \xrightarrow{\text{HBr}} X \xrightarrow{\text{aq. KOH}} Y \xrightarrow{I_2, \text{NaOH}} Z$

(iii) $CH_3CH_2Br \xrightarrow{\text{AgCN}} A$

(iv) 3-ethylpent-2-ene $\xrightarrow{Br_2/H_2O} B$

Q. 4. Account for the following :

(i) Sulphuric acid is not used during the reaction of alcohols with KI.

(ii) p-methoxybenzyl bromide reacts faster than p-nitrobenzyl bromide with sodium ethoxide to form an ether product.

(iii) Organic halogen compounds used as solvents in industry are chlorides rather than bromides and iodides.

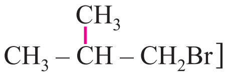
(iv) Wurtz reaction fails in case of tert-alkyl halides.

(v) Alkyl halides are insoluble in water though they contain a polar C – X bond.

(vi) Use of $CHCl_3$ as anaesthetic is not preferred.

Q. 5. (i) A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

(ii) Iodoform gives a precipitate with $AgNO_3$ on heating while $CHCl_3$ does not. Why ?

[*Hint :* A : ⇒ 
$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2Br$]

CONCEPTUAL QUESTIONS

Q. 1. Why haloalkanes are more reactive than haloarenes?

Ans. In haloarenes, there is partial double bond character b/w carbon and halogen due to resonance effect which makes him less reactive.

(ii) In benzene, carbon being sp^2 hybridised which is smaller in size than sp^3 present in haloalkanes. So C–Cl bond in aryl halides is shorter and stronger.

Q. 2. Why do haloalkenes under go nucleophillic substitution whereas haloarenes under go electophillic substitution?

Ans. Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophillic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophillic reagents.

Q. 3. When an alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide where as if alkyl halide is treated with AgCN,the major product is alkyl isocyanide?

Ans. Refer NCERT

Q. 4 The treatment of alkyl chlorides with aqueous KOH lead to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain?

Ans. In aqueous KOH,OH^- is nucleophile which replaces another nucleophile.

$$R\text{-}X + KOH \longrightarrow R\text{-}OH + KX$$

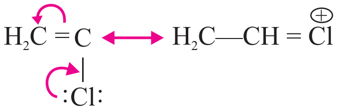
Where as in alcoholic KOH, $C_2H_5O^-$ ion is produced which is a strong base hence β-elimination took place to form alkane

$C_2H_5OH + KOH \longrightarrow C_2H_5O- + K^+$

$CH_3CH_2\text{-}Cl + \text{alcoholic KOH} \longrightarrow CH_2 = CH_2 + C_2H_5OH$

Q. 5 Explain why vinyl chloride is unreactive in nucleophillic substitution reaction?

Ans. Vinyl chloride is unreactive in nucleophillic substitution reaction because of double bond character between C–Cl bond which is difficult to break.



Q. 6 Arrange the following compounds according to reactivity towards nucleophillic substitution reaction with reagents mentioned :-

(i) 4-nitrochlorobenzene> 2,4 dinitrochlorobemzene > 2,4,6, trinitrochlorobenzene with CH_3ONa

Ans. 2,4,6, trinitrochlorobenzene > 2,4 dinitrochlorobemzene > 4- nitrochlorobenzene

Q. 7 Why Grignard reagent should be prepared under an hydrous conditions?

Ans. Grignard reagent react with H_2O to form alkanes, therefore they are prepared under anhydrous condition.

Q. 8 Why is Sulphuric acid not used during the reaction of alcohols wiht KI?

Ans. It is because HI formed will get oxidized to I_2 by concentrated Sulphuric acid which is an oxidizing agent.

Q. 9 p-dichlorobenzene has highest m.p. than those of ortho and m-isomers?

Ans. p-dichlorobenzene is symmetrical, fits into crystal lattice more readily and has higher melting point.

Q. 10. Give reasons:

(i) C–Cl bond length in chlorobenzene is shorter than C–Cl bond in CH_3Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_N1 reactions are accompained by racemization in optically active alkyl halides.

Ans. (i) In chlorobenzene, each carbon atom is sp^2 hybridised/ resonating structures / partial donable bond character.

(ii) Due to + R effect in chlorobenzene / difference in hybridization i.e., sp^2 and sp^3 respectively.

(iii) Due to formation of planer carbocation.

HOTS

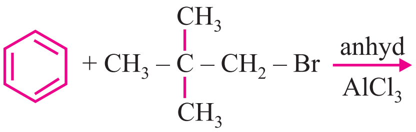
Q. 1. Why alkyl halides are generally not prepared in laboratory by free radical halogenations of alkanes ?

Q. 2. Hydrolysis of 2-bromo-3-methylbutane (2°) gives only α-methyl-2-butanol (3°). Explain.

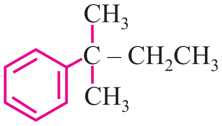
Q. 3. Write major product of the following reactions :

(i) $CH_2 = CH - Br \xrightarrow[\text{ethanol}]{\text{AgCN}}$

(ii)



[*Hint :* (i) No reaction (ii)



Q. 4. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium ? Give reason for your answer.

MULTIPLE CHOICE QUESTIONS

Q. 1. The chiral compound is :

(a) 3-chloropentane (b) Propene

(c) 2-chloropropane (d) 2-chlorobutane

Ans. (d)

Q. 2. Chloroethane on heating with alcoholic KOH gives :

(a) Ethane (b) Ethene

(c) Ethyne (d) Ethyl alcohol

Ans. (b)

Q. 3. Phosgene is a common name for :

(a) Phosphoryl chloride (b) Carbonyl chloride

(c) Carbon dioxide & phosphine (d) Carbon tetrachloride

Ans. (b)

Q. 4. Which of the following possesses highest melting point ?

(a) Chlorobenzene (b) m-dichlorobenzene

(c) o-dichlorobenzene (d) p-dichlorobenzene

Ans. (d)

Q. 5. KCN reacts readily to form a cyanide with :

(a) Ethyl alcohol (b) Ethyl bromide

(c) Bromobenzene (d) Chlorobenzene

Ans. (b)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Chlorofom is a colourless oily liquid with a peculiar smell. It is sparingly soluble in water. The vapour when enhaled cause unconsciousness and therefore, it is used as anaesthetic.

Answer the following questions :

(i) What happens when $CHCl_3$ is not protected from O_2 during its storage ?

(ii) Why is the use of $CHCl_3$ as an anaesthetic has been reduced ?

Q. 2. DDT is one of the most powerful insecticide which is effective against the mosquitoes that spread malaria. Mukesh's mother wanted to buy DDT from the market to use at night but Mukesh stopped her.

(i) Why did Mukesh stopped her mother for using DDT at night ?

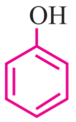
(ii) What values are attached to Mukesh's suggestion ?

UNIT-11

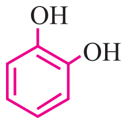
ALCOHOLS, PHENOLS AND ETHERS

Quick Concepts to Remember

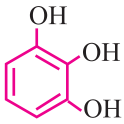
1. Hydroxyl (– OH) derivatives of alkane are called alcohols.
2. Alcohols are classified as 1°, 2° and 3°.
3. –OH group is attached to sp^3 hybridized carbon. Alcohols further may be monohydric, dihydric and polyhydric on the basis of OH group.
4. **Phenols :** Compounds containing – OH group bound directly to benzene ring.



Phenol

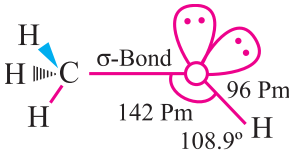


Catechol



Pyrogallol

5. **Structure :** Oxygen atom is sp^3 hybridised and tetrahedral geometry of hybrid atomic orbitals ROH bond angle depends upon the R group. R – O – H angle for $CH_3 – OH$ is 108.9°.



6. **Isomerism :**
   - (i) Functional isomerism
   - (ii) Chain isomerism
   - (iii) Positional isomerism
7. **General Methods of Preparation :**
   - **(i) Acid catalysed hydration of alkenes :**

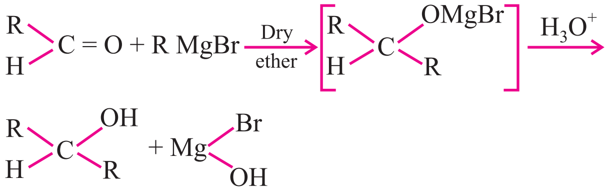
$$CH_3 – CH = CH_2 + H_2O \xrightarrow{\text{dil.}H_2SO_4} CH_3 – \overset{\overset{\displaystyle OH}{|}}{C}H – CH_3$$

   - **(ii) Hydroboration oxidation :**

$$3CH_3 – CH = CH_2 + ½B_2H_6 \xrightarrow{D.E} (CH_3 – CH_2 – CH_2)_3B \xrightarrow[H_2O_2]{OH^-}$$

$$CH_3 – CH_2 – CH_2OH + H_3BO_3$$

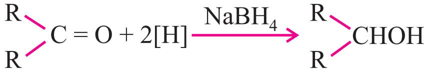
(iii) From carbonyl compounds with Grignard's reagent :



Formaldehyde gives 1° alcohol and ketones gives tertiary alcohol.

(iv) By reduction of carbonyl compounds :

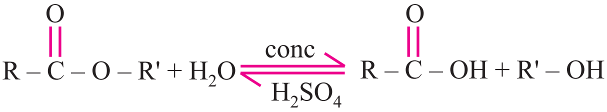
$$RCHO + 2[H] \xrightarrow{Pd} RCH_2OH$$



(v) By reduction of esters with $LiAlH_4$ or Na/C_2H_5OH :

$$R-\overset{\overset{\displaystyle O}{||}}{C}-OR' + 4[H] \xrightarrow{LiAlH_4} R-CH_2OH + R'-OH$$

(vi) By hydrolysis of esters :



$$R-\overset{\overset{\displaystyle O}{||}}{C}-O-R' + H_2O \underset{H_2SO_4}{\overset{conc}{\rightleftharpoons}} R-\overset{\overset{\displaystyle O}{||}}{C}-OH + R'-OH$$

(vii) From alkyl halides :

$$R-X + KOH\ (aq) \rightarrow R-OH + KX$$

(viii) By reduction of acids and their derivatives :

$$R-COOH \xrightarrow{LiAlH_4} RCH_2OH$$

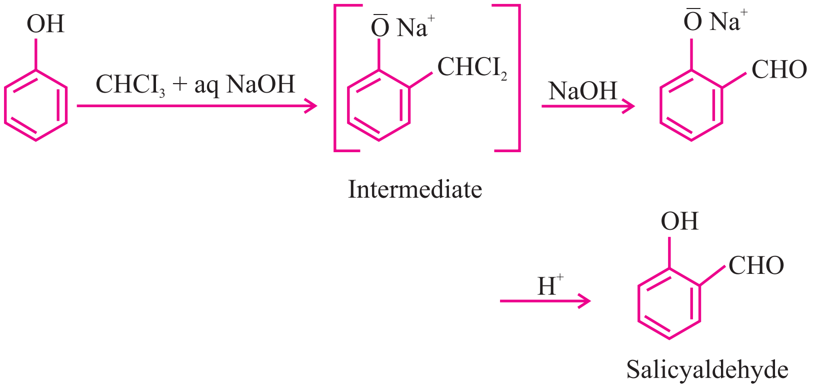
$$R-COCl + 2H_2 \xrightarrow{Ni} R.CH_2OH + HCl$$

(ix) From 1° amines :

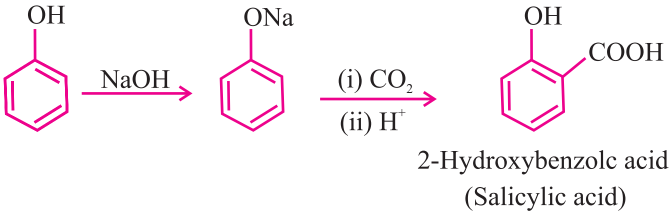
$$R-NH_2 \xrightarrow{NaNO_2+HCl} ROH + H_2O + N_2$$

NAME REACTIONS

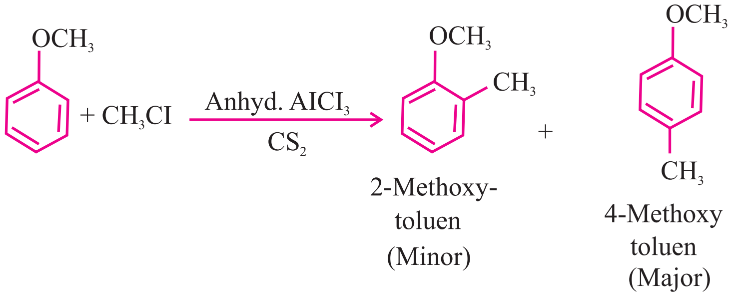
1. Reimer Tiemann Reaction x

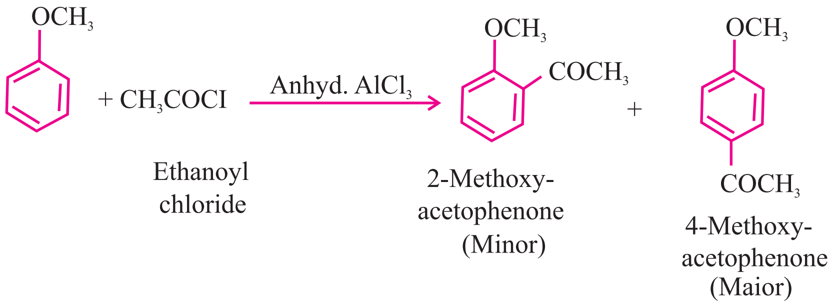


2. Kolbe reaction



3. Friedel craft reaction

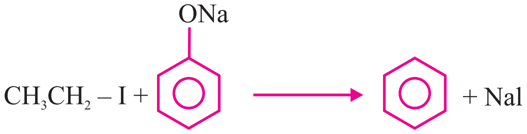




4. Williamson synthesis: Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide is called Williamson synthesis.

$$R-X+R^1-O-Na \longrightarrow R-O-R^1+NaX$$

$$CH_3I+CH_3CH_2ONa \longrightarrow CH_3O.CH_2-CH_3+Nal$$

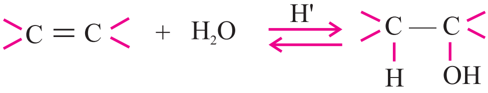


Both simple and mixed ether can be produced.

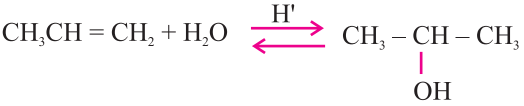
Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN^2 or SN^1 mechanism.

MECHANISMS

1. Hydration of Alkene :



$$>C=C< + H_2O \underset{}{\overset{H'}{\rightleftharpoons}} >\underset{H}{C}-\underset{OH}{C}<$$



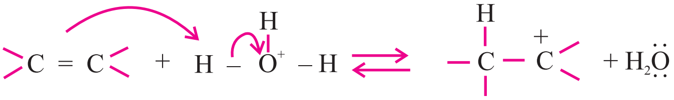
$$CH_3CH=CH_2+H_2O \overset{H'}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

Mechanism

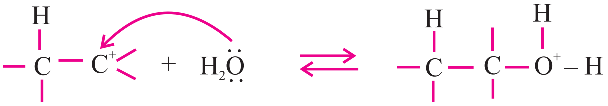
The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

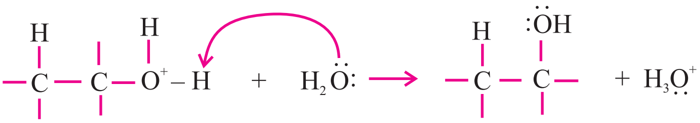
$$H_2O+H^+ \rightarrow H_3O^+$$



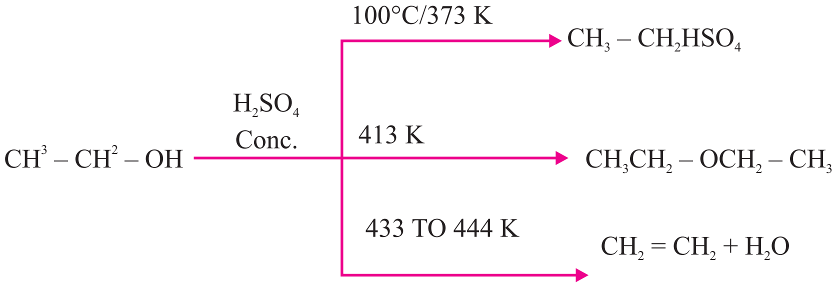
Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.

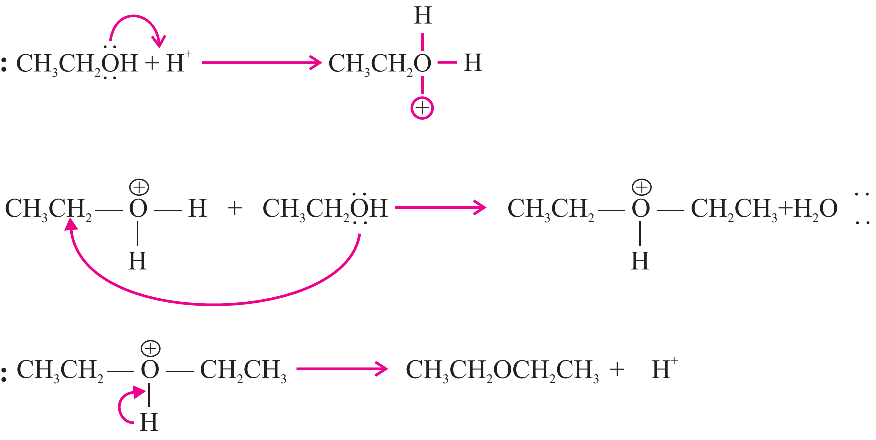


2. Dehydration Reaction



(1) $2CH_3CH_2OH \xrightarrow[H_2SO_4 \; 413\ k]{Conc.} CH_3CH_2OCH_2CH_3$

Mechanism:

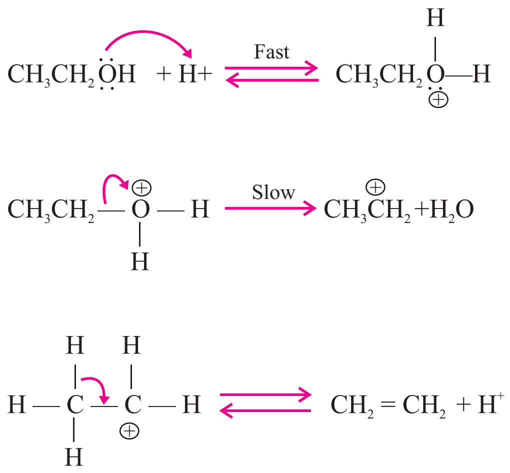


Step 1: $CH_3CH_2\ddot{\underset{..}{O}}H + H^+ \longrightarrow CH_3CH_2\overset{H}{\underset{\oplus}{O}} - H$

Step2: $CH_3CH_2 - \overset{\oplus}{\underset{H}{O}} - H + CH_3CH_2\ddot{\underset{..}{O}}H \longrightarrow CH_3CH_2 - \overset{\oplus}{\underset{H}{O}} - CH_2CH_3 + H_2\ddot{\underset{..}{O}}$

Step 3: $CH_3CH_2 - \overset{\oplus}{\underset{H}{O}} - CH_2CH_3 \longrightarrow CH_3CH_2OCH_2CH_3 + H^+$

(2) $CH_3CH_2OH \xrightarrow[443\ K]{Conc.\ H_2SO_4} H_2C = CH_2 + H_2O$



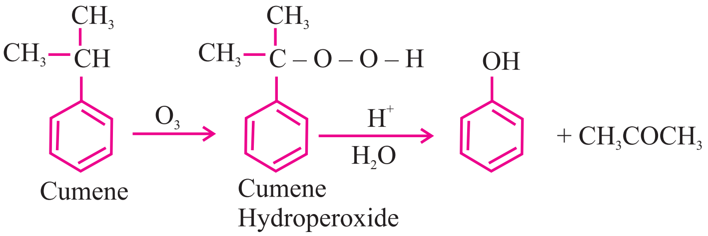
Step 1: $CH_3CH_2\ddot{\underset{..}{O}}H + H+ \underset{}{\overset{Fast}{\rightleftharpoons}} CH_3CH_2\overset{H}{\underset{\oplus}{\underset{..}{O}}} - H$

Step 2: $CH_3CH_2 - \overset{\oplus}{\underset{H}{O}} - H \xrightarrow{Slow} CH_3\overset{\oplus}{C}H_2 + H_2O$

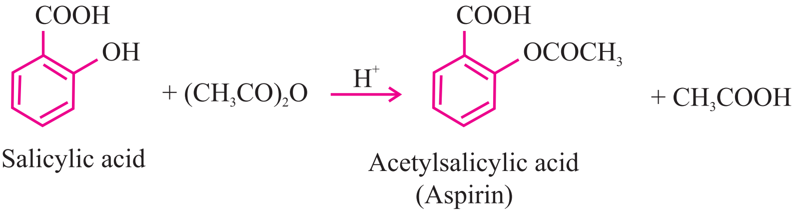
Step 3: $H - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{\oplus}{C}} - H \rightleftharpoons CH_2 = CH_2 + H^+$

IMPORTANT PREPARATIONS

(1) Preparation of phenol from Cumene



(2) Prepation os spirin



8. Ethers are dialkyl derivatives of water or monoalkyl derivatives of alcohols with formula R – O – R'

9. Lucas test can be used to distinguish primary, secondary and tertiary alcohols ($ZnCl_2$ + HCl).

   (3° turbidity – instant, 2° - 5 minutes, 1° - heating for 60 minutes)

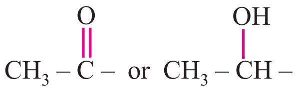
10. Ethers are relatively inert and hence are used as solvents.

11. 100% ethanol is known as absolute alcohol.

12. 95% ethanol is called rectified spirit.

13. A mixture of 20% ethanol and 80% gasoline is known as power alcohol.

14. Iodoform test is used for distinguishing compounds having the groups



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}- \quad \text{or} \quad CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-$$

15. Presence of EWGs increase the acid strength of phenols while EDG decrease the acid strength.

    EWG : $-NO_2$, – X, – CN, – COOH etc.

    EDG : – R, – OR, – OH, $-NH_2$ etc.

16. 3° alcohols are resistant to oxidation due to lack of α-hydrogen.

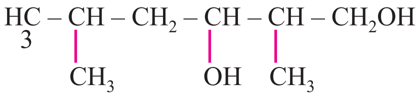
17. Intermolecular H-bonds of *p*- and *m*-nitrophenol increases water solubility/acid strength while intramolecular H-bonds in *o*-nitrophenol decreases these properties.

18. In the reaction of alkyl aryl ether (anisole) with HI, the products are always alkyl halide and phenol because O – R bond is weak than O – Ar bond which has partial double character due to resonance.

19. C – O – C bond in ether is bent and hence the ether is always polar molecule even if both alkyl groups are identical.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Write IUPAC name of the following compound :

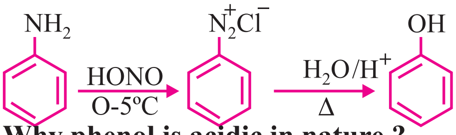


$$H_3C-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2OH$$

Ans. 2,5-Dimethylhexane-1, 3 diol.

Q. 2. How is phenol obtained from aniline ?

Ans.



Q. 3. Why phenol is acidic in nature ?

Ans. Due to stability of phenoxide ion by resonance.

Q. 4. Arrange the following in decreasing order of their acidic character :

(i)

(ii) C_6H_5OH

(iii)

Ans. (iii) > (ii) > (i)

Q. 5. Among HI, HBr and HCl, HI is most reactive towards alcohols. Why ?

Ans. Due to lowest bond dissociation energy of HI.

Q. 6. Name a compound which is used as antiseptic as well as disinfectant.

Ans. Solution of phenol : 0.2% antiseptic, 2% disinfectant.

Q. 7. What is nitrating mixture ?

Ans. Conc. $(H_2SO_4 + HNO_3)$

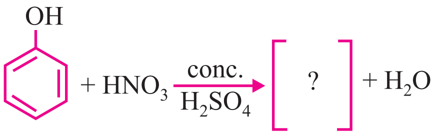
Q. 8. Lower alcohols are soluble in water, higher alcohols are not. Why ?

Ans. Due to formation of hydrogen bonds.

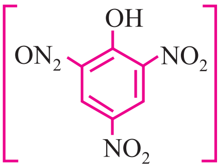
Q. 9. What happens when CH_3CH_2OH heated with red P and HI ?

Ans. $C_2H_5OH + 2HI \xrightarrow{\text{Red P}} C_2H_6 + I_2 + H_2O$

Q. 10. Complete the following reaction :



Ans.



2, 4, 6- rinitro phenol (Picric acid)

Q. 11. Ethanol has higher boiling point than methoxy methane. Give reason.

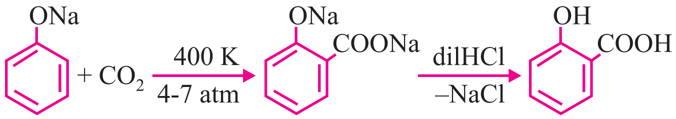
Ans. Because of H-bonds.

Q. 12. How could you convert ethanol to ethane ?

Ans. $C_2H_5OH \xrightarrow[443\ K]{Conc.\ H_2SO_4} CH_2 = CH_2 + H_2O$

Q. 13. Explain Kolbe's reaction with example.

Ans.



Q. 14. Which of the following isomer is more volatile :

o-nitrophenol or p-nitrophenol

Ans. o-nitrophenol.

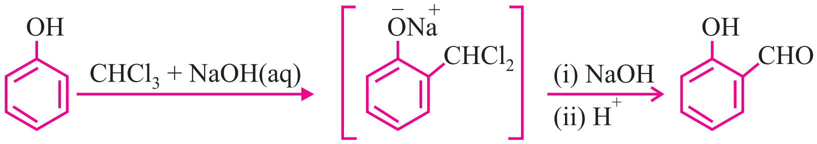
SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Write one chemical reaction to illustrate the following :

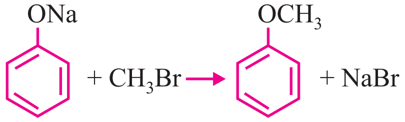
(i) Reimer-Teimann reaction

(ii) Williamson's synthesis

Ans. (i)



(ii)



Q. 2. Account for the following :

(i) Phenol has a smaller dipole moment than methanol.

(ii) Phenol goes electrophilic substitution reactions.

Ans. (i) Due to – ve charge on oxygen in delocalized by resonance.

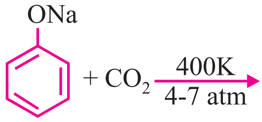
(ii) Due to greater electron density than benzene.

Q. 3. **Complete the following equations and name the products :**

(i) **Phenol + $FeCl_3 \rightarrow$**

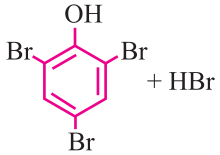
(ii) **$C_6H_5OH + CHCl_3 + NaOH \xrightarrow{340\ K}$**

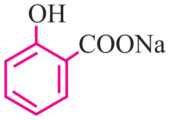
(iii) **$C_6H_5OH + Br_2$ (aq) $\rightarrow$**

(iv) 

Ans. (i) $[(C_6H_5O)_3Fe] + 3HCl$

(ii) 

(iii) 

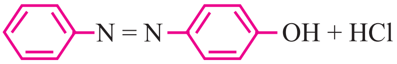
(iv) 

Q. 4. **Write :**

(i) **Friedel-Crafts reaction**

(ii) **Coupling reaction**

Ans. (i) 

(ii) $C_6H_5N_2Cl + C_6H_5OH \xrightarrow{pH=9-10}$ 

Q. 5. **Give one reaction of alcohol involving cleavage of :**

(i) **C – O bond**

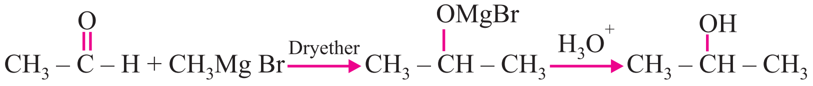
(ii) **O – H bond**

Ans. (i) $CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$

(ii) $CH_3CH_2OH + Na \rightarrow CH_3CH_2ONa + H_2$

Q. 6. **Etherial solution of an organic compound 'X' when heated with Mg gave 'Y'. 'Y' on treatment with CH_3CHO followed by acid hydrolysis gave 2-propanol. Identify the compound 'X'. What is 'Y' known as ?**

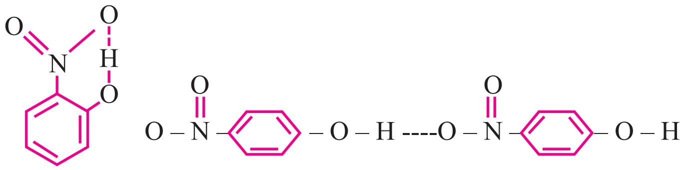
Ans. $\underset{x}{CH_3Br} + Mg \xrightarrow{\text{Dryether}} \underset{(y)}{CH_3MgBr}$



$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3MgBr \xrightarrow{\text{Dryether}} CH_3-\overset{\overset{OMgBr}{|}}{CH}-CH_3 \xrightarrow{H_3O^+} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

Q. 7. **While separating a mixture of *o*- and *p*-nitrophenols by steam distillation name the isomer which is steam volatile. Give reason.**

Ans.



H-bonding and association of molecules.

Q. 8. **Account for the following :**

(i) **Phenol has a smaller dipole moment than CH_3OH.**

(ii) **Phenol do not give protonation reactions readily.**

Ans. (i) Because phenol has electron attracting benzene ring.

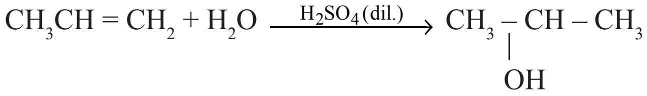
(ii) Resonance and +ve charge oxygen does not have tendency to accept a proton.

Q. 9. **Write the reactions and conditions involved in the conversion of :**

(i) **Propene to propan-2-ol.**

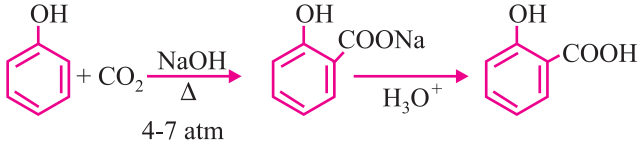
(ii) **Phenol to salicylic acid.**

Ans. (i)



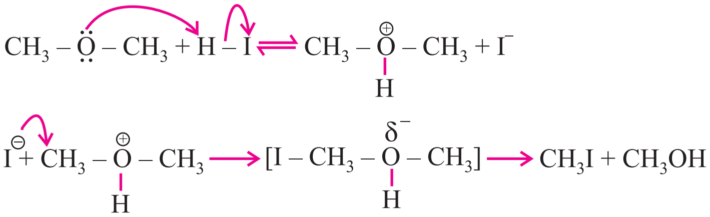
$$CH_3CH=CH_2 + H_2O \xrightarrow{H_2SO_4\text{(dil.)}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

(ii)



Q. 10. **Write mechanism of reaction of HI with methoxymethane.**

Ans.



$$CH_3-\ddot{\underset{..}{O}}-CH_3 + H-I \rightleftharpoons CH_3-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-CH_3 + I^-$$

$$\overset{\ominus}{I} + CH_3-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-CH_3 \longrightarrow [I-CH_3-\underset{\underset{H}{|}}{\overset{\delta^-}{O}}-CH_3] \longrightarrow CH_3I + CH_3OH$$

Q. 11. **Arrange in order of boiling points :**

(i) $C_2H_5 - O - C_2H_5$, C_4H_9COOH, C_4H_9OH

(ii) C_3H_7CHO, $CH_3COC_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

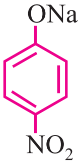
Ans. (i) $C_4H_9COOH > C_4H_9OH > C_2H_5 - O - C_2H_5$

(ii) $(CH_3CO)_2O > C_2H_5COOCH_3 > CH_3COC_2H_5 > C_3H_7CHO$

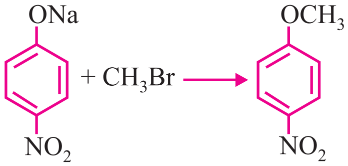
Q. 12. **Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?**

(i) 

+ CH_3ONa

(ii) 

+ CH_3Br

Ans. (ii) 

It is because of double bond character, (C – Br) bond in 

due to resonance it is less reactive towards SN, RXN.

Q. 13. **Ethers are relatively inert. Justify.**

Ans. Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides $\left(C - \underset{\cdot\cdot}{\ddot{O}} - C\right)$.

Q. 14. **How will you distinguish between CH_3OH and C_2H_5OH ?**

Ans. $C_2H_5OH + 4I_2 + 3Na_2CO_3 \xrightarrow[\text{Iodoform (yellow)}]{\text{warm}} CHI_3 + HCOONa + 5NaI + 2H_2O + 3CO_2$

CH_3OH does not give this test.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. **Name the reagents which are used in the following conversions :**

(i) **1° alcohol to an aldehyde**

(ii) **Butan-2-one to butan-2-ol**

(iii) **Phenol to 2, 4, 6 tribromophenol**

Ans. (i) PCC, a complex of chromium trioxide with pyridine and HCl.

(ii) $NaBH_4$, sodium borohydride.

(iii) Br_2 (water)

Q. 2. Write structures of the major products of the following :

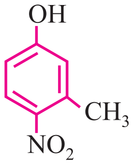
(i) Mononitration of 3-methylphenol

(ii) Dinitration of 3-methylphenol

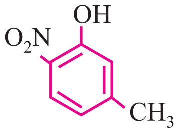
(iii) Mononitration of phenyl ethanoate

Ans. – OH and – CH_3 are *o*- and *p*-directing groups. The products are :

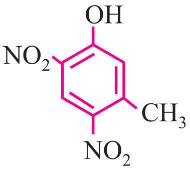
(i)



and



(ii)



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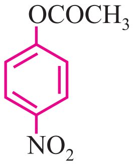


Q. 3. Complete the following reactions :

(i) $CH_3CH_2CH_2CHO \xrightarrow{Pd/H_2/Ni}$

(ii) $CH_3CH = CHCH_2OH \xrightarrow{PCC}$

(iii) $CH_3CH = CH_2 \xrightarrow[(2)\ 3H_2O_2/OH^-]{(1)\ B_2H_6}$

(iv) $C_6H_5OH \xrightarrow[(2)\ CO_2,H^+]{(1)\ Aq.NaOH}$

(v) $CH_2Br - CH_2Br \xrightarrow{KOH}$

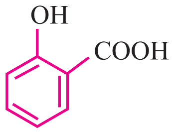
(vi) $C_2H_5NH_2 \xrightarrow{HNO_2}$

Ans. (i) $CH_3CH_2CH_2CH_2OH$

(ii)

(iii) $CH_3CH_2CH_2OH$

(iv)



(v) $CH_2OH - CH_2OH$

(vi) CH_3CH_2OH

Q. 4. Give equations of the following reactions :

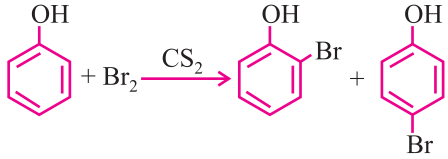
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(ii) Bromine in CS_2 with phenol.

(iii) Treating phenol with chloroform in presence of aqueous NaOH.

Ans. (i) $CH_3 - CH_2 - CH_2OH + 2[O] \xrightarrow[KMnO_4]{alkaline} CH_3CH_2COO^- K^+$

(ii)



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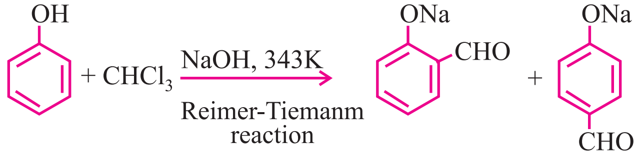


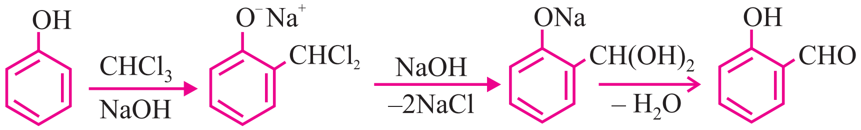
Q. 5. Describe the following reactions with examples :

(i) Reimer-Teimann reaction

(ii) Kolbe's reaction

(iii) Friedel Crafts acylation of anisole

Ans. (i)



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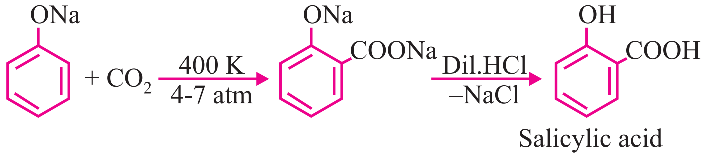

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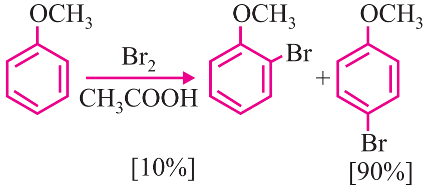


Q. 6. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3. Explain.

Ans. In acidic medium alcohols protonated then loses H_2O to form a carbo cation. If HCl Cl^- strong nucleophile cause nucleophilic substitution, HNO_3 causes oxidation.

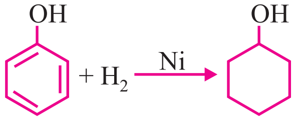
Q. 7. How will you convert :

(i) Phenol to cyclohexanol

(ii) Benzyl chloride to benzyl alcohol

(iii) Anisole to phenol

Ans. (i)



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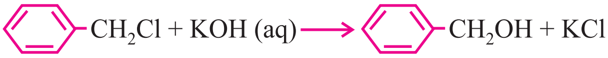

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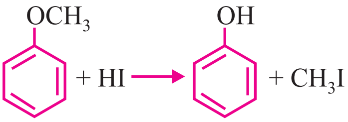


LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. An alcohol A ($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives carboxylic acid 'B' ($C_4H_8O_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443 K gives compound 'C' with aqueous H_2SO_4. 'C' gives compound 'D' ($C_4H_{10}O$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidized. Identify A, B, C and D and write their structure.

Ans.

A : $(CH_3)_2CHCH_2OH$

B : $CH_3CH(CH_3)COOH$

C : $(CH_3)_2C = CH_2$

D : $(CH_3)_3 - C - OH$

Q. 2. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

Ans. A :

$\mathrm{CH_3CH_2OCH}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}$

B : CH_3CH_2OH

C : $CH_3CHOHCH_3$

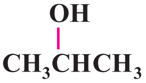
D : CH_3COOH

E : CH_3COCH_3

Q. 3. Which of the following compounds gives fastest reaction with HBr and why ?

(i) $(CH_3)_3COH$

(ii) $CH_3CH_2CH_2OH$

(iii)

$\overset{OH}{|}$ $CH_3\overset{|}{C}HCH_3$

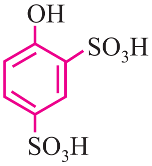
(iv)

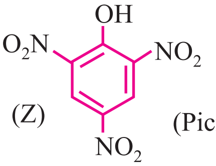
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2OH$

Ans. (i) $(CH_3)_3C-OH$

Due to formation of EDG and formation of cation.

Q. 4. Phenol, C_6H_5OH when it first reacts with concentrated sulphuric acid, forms Y. The compound, Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted commercially to Z by reacting it with conc. HNO_3.

Ans. (Y)


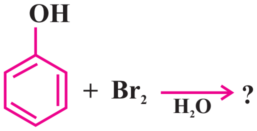
(Z)


(Picric acid)

Phenol is not reacted directly with conc. HNO_3 because the yield of picric acid is very poor.

Q. 5. Fill in the blanks :

(i) Glucose $\xrightarrow{\text{Zymase}}$

(ii)


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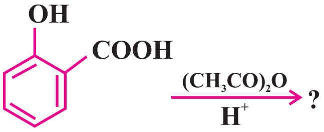


(iv)

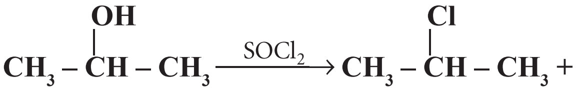
$CH_3\overset{\overset{CH_3}{|}}{C}HOCH_2CH_3 \xrightarrow{HI} ?$

(v) Phenol + Zn (dust) →

(vi) Phenol + Na →

(vii) $R_2CHOH + HCl + \underset{\text{(anhydrous)}}{ZnCl_2} \rightarrow R_2CHCl +$ ....

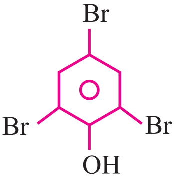
(viii) $R-CHOH-R \xrightarrow{[O]}$

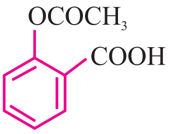
(ix) 

$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow{SOCl_2} CH_3-\overset{\overset{Cl}{|}}{C}H-CH_3 +$$

(x) $CH_3-CH_2-OH \xrightarrow{\text{Bleaching powder}}$

Ans. (i) C_2H_5OH

(ii) 

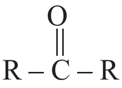
(iii) 

(iv) $(CH_3)_2CHOH$ and CH_3CH_2I

(v) C_6H_6

(vi) C_6H_5ONa

(vii) H_2O

(viii) 

$$R-\overset{\overset{O}{||}}{C}-R$$

(ix) SO_2

(x) $CHCl_3$

VALUE BASED QUESTIONS (4 Marks)

Q. 1. An owner of a paint company who was using ethanol as solvent noted that his stock of ethanol was misued by his employees. To prevent this, he decided to add small amount of blue coloured compound (A) and another nitrogen containing heterocyclic base (B) which gives a foul smell to alcohol.

(i) Do you think that he took right decision and mention the values with this decision.

(ii) Write the names of compound A and B.

(iii) Consumption of methylated ethanol by person can cause blindness and even death. How is methanol poisoning treated ?

(iv) Mention values associated with the above decision.

Q. 2. Recently Delhi Police launched a special drive to curb the crimes and accidents related to 'Drunken Driving'. An instrument known as alcometer is used to test whether a driver has consumed alcohol or not beyond a certain limit.

(i) Write the name and chemical formula of the compound used in alcometer.

(ii) Write the chemistry involved in above test.

(iii) Write the ionic equation involved in the chemistry of the test.

(iv) Mention the value shown by Delhi Police.

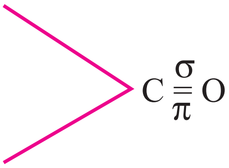
UNIT 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Points to Remember

1. Aldehydes, ketones, carboxylic acids and their derivatives are commonly called as carbonyl compounds.
2. In Rosenmund's reduction, poisoning of Pd with $BaSO_4$ prevent reduction of R – CHO to R – CH_2OH.
3. In the reaction of toluene with CrO_3, acetic anhydride is used to protect benzaldehyde by forming benzylidenediacetate to avoid its oxidation to benzoic acid.
4. Order of reactivity of aldehydes and ketones towards nucleophilic addition is :
   (i) $HCHO > CH_3CHO > CH_3CH_2CHO$.
   (ii) HCHO > RCHO > R CO R.
   (iii) ArCHO > Ar COR > Ar CO Ar.
5. Benzaldehyde does not reduce Fehling's reagent.
6. Aldehydes and ketones with atleast one α–H atom get condensed in presence of a base. This is known as Aldol condensation.
7. Aldol condensation involves carbanion as intermediate.
8. Aldehydes with no α–H atoms under Cannizzaro's reaction.
9. Ketones react with dihydric alcohols to form cyclic ketals.
10. Monocarboxylic acids having (C_{12}–C_{18}) carbon atoms, are called fatty acids.
11. Boiling points of carboxylic acids is greater than corresponding alcohols.
12. Presence of EWGs enhances the acidic character of carboxylic acids.
13. –COOH group is *m*-directing in electrophilic substitution reactions.
14. Compounds containing – CHO group are named as carbaldehydes if – CHO groups are three or more.
15. Isomerism : Chain, position and functional.

16. Structure of –CHO group *sp*^{2} hybridised.



17. General Methods of Preparation :

(i) Controlled oxidation of 1° alcohols :

$$RCH_2OH \xrightarrow{PCC/CrO_3} RCHO$$

(Collin's reagent)

(ii) Dehydrogenation of 1° alcohols :

$$RCH_2OH \xrightarrow{Cu/573\ K} RCHO + H_2$$

(iii) From Rosenmund reaction/reduction :

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

(iv) Hydration of alkynes :

$$CH \equiv CH \xrightarrow[40\%\ H_2SO_4]{1\%\ HgSO_4} [CH_2 = CHOH] \xrightarrow{Tautomerism} CH_3CHO$$

(v) Reductive ozonolysis of alkenes :

$$R - CH = CH - R \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} 2RCHO + H_2O_2$$

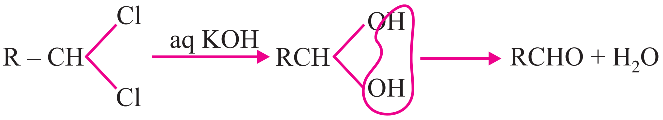
(vi) From salts of fatty acids :

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{D\ Dist.} 2RCHO + 2CaCO_3$$

(vii) Stephen's reduction of nitrile compounds :

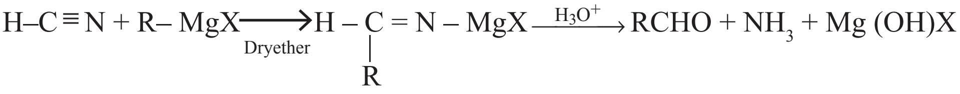
$$R - C \equiv N \xrightarrow{SnCl_2/HCl} [R - CH = NH.HCl] \xrightarrow[H_2O + H^+]{H_3{}^+O} RCHO + NH_4Cl$$

(viii) Hydrolysis of germinal halides :



$$R - CH\begin{matrix} Cl \\ Cl \end{matrix} \xrightarrow{aq\ KOH} RCH\begin{matrix} OH \\ OH \end{matrix} \longrightarrow RCHO + H_2O$$

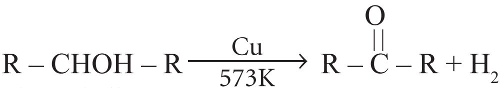
(ix) From Grignard's reagent :



$$H{-}C \equiv N + R{-}\,MgX \xrightarrow[Dryether]{} \underset{\displaystyle R}{\underset{|}{H - C}} = N - MgX \xrightarrow{H_3O^+} RCHO + NH_3 + Mg\,(OH)X$$

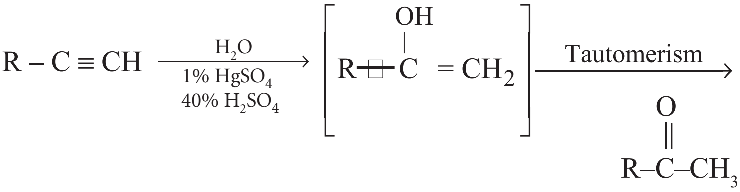
General Methods of Preparation of Ketones only

(i) Dehydrogenation of 2° alcohols :



$$R-CHOH-R \xrightarrow[573K]{Cu} R-\overset{O}{\overset{||}{C}}-R+H_2$$

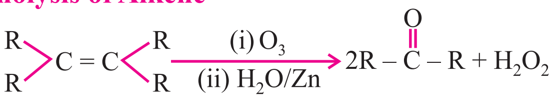
(ii) Hydration of alkynes :



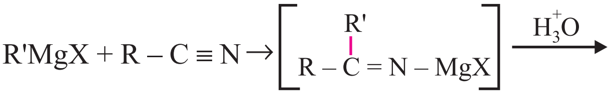
$$R-C\equiv CH \xrightarrow[\substack{1\%\ HgSO_4\\ 40\%\ H_2SO_4}]{H_2O} \left[R-\overset{OH}{\overset{|}{C}}=CH_2\right] \xrightarrow{\text{Tautomerism}} R-\overset{O}{\overset{||}{C}}-CH_3$$

Ozonolysis of Alkene

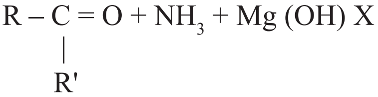
(iii)



(iv) From Grignard's reagents :

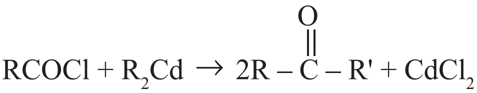


$$R'MgX+R-C\equiv N \rightarrow \left[R-\overset{R'}{\overset{|}{C}}=N-MgX\right] \xrightarrow{H_3\overset{+}{O}}$$



$$R-\underset{R'}{\underset{|}{C}}=O+NH_3+Mg\,(OH)\,X$$

(iv) From acid chlorides :



$$RCOCl+R_2Cd \rightarrow 2R-\overset{O}{\overset{||}{C}}-R'+CdCl_2$$

Physical Properties :

HCHO is a gas at normal temperature. Formalin is 40% as solution of HCHO. Due to polarity they have high values of boiling point. Solubility in water is only for lower members.

Reactivity :

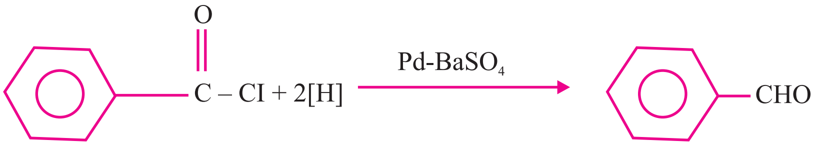
(i) + I effect of alkyl groups decreases the +ve charge on carbonyl carbon.

(ii) Steric hindrance : Bulky group hinder approach of nucleophile.

(iii) α-hydrogen atom is acidic due to resonance.

1. ROSENMUND REDUCTION:

Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes



Benzoyl chloride Benzaldehyde

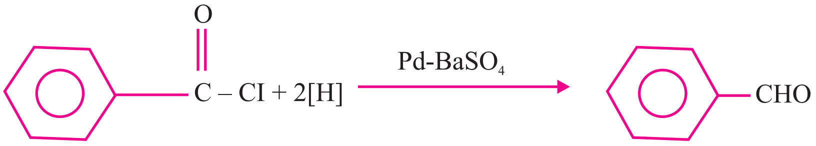
2. STEPHEN REACTION

Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCI_2 + HCI \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

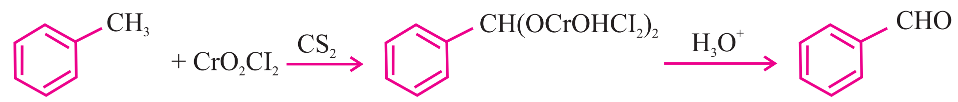
3. ETARD REACTION

On treating toluene with chromyl chloride CrO_2Cl_2, the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



Benzoyl chloride Benzaldehyde

OR



Toluene Chromium complex Benzaldehyde

This reaction is called Etard reaction

4. CLEMMENSEN REDUCTION

The carbonyl group of aldehydes and ketone is reduced to -CH2 group on treatment with zinc amalgam and cone. Hydrochloric acid.

$$> C{=}O \xrightarrow[\text{CHI}]{\text{Zn - Hg}} > CH_2 + H_2O$$

Alkanes -

5. WOLFF- KISHNER REDUCTION

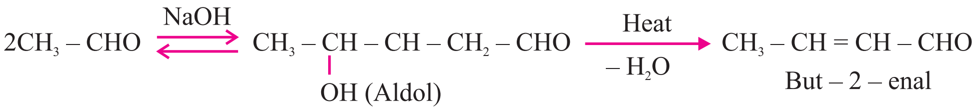
On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol

$$> C{=}O \xrightarrow[\text{CHI}]{\text{Zn - Hg}} > CH_2 + H_2O$$

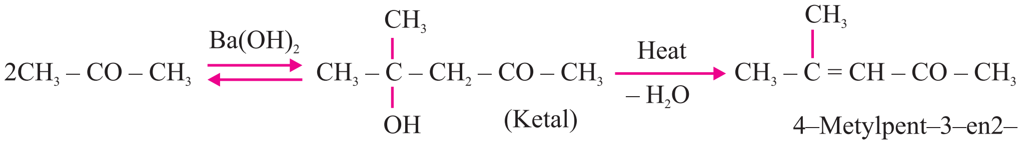
Alkanes -

6. ALDOL CONDENSATION

Aldehydes and ketones having at least one a-hydrogen condense in the presence of dilute alkali as catalyst to form p-hydroxy ehydes (aldol) or β-hydroxy ketones (ketol).



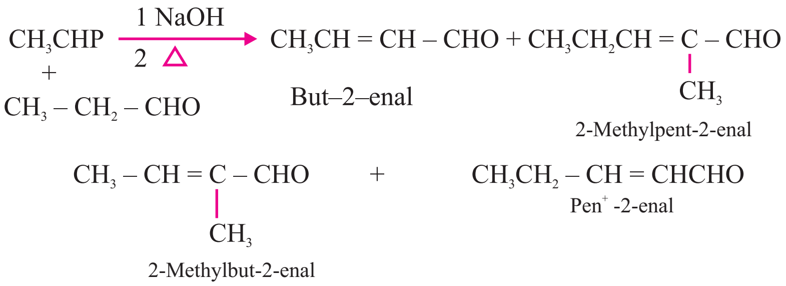
$$2CH_3-CHO \underset{}{\overset{\text{NaOH}}{\rightleftharpoons}} CH_3-\underset{\text{OH (Aldol)}}{\underset{|}{CH}}-CH-CH_2-CHO \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{But}-2-\text{enal}}{CH_3-CH=CH-CHO}$$



$$2CH_3-CO-CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3-\overset{CH_3}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2-CO-CH_3 \;\text{(Ketal)} \xrightarrow[-H_2O]{\text{Heat}} \underset{4\text{–Metylpent–3–en2–}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CO-CH_3}$$

7. CROSS- ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.



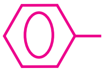
$$\begin{matrix} CH_3CHP \\ + \\ CH_3-CH_2-CHO \end{matrix} \xrightarrow[2\ \triangle]{1\ \text{NaOH}} \underset{\text{But–2–enal}}{CH_3CH=CH-CHO} + \underset{\text{2-Methylpent-2-enal}}{CH_3CH_2CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

$$\underset{\text{2-Methylbut-2-enal}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO} \quad + \quad \underset{Pen^{+}\text{ -2-enal}}{CH_3CH_2-CH=CHCHO}$$

8. CANNIZARO REACTION

Aldehydes which do not have an a-hydrogen atom, undergo self oxidation and reduction (dispropotionation) reaction on treatment with concentrated alkali, to yield carboxylic acid salt and an alcohol respectively.

$$\text{H-CHO} + \text{H-CHO} + \text{Conc.KOH} \longrightarrow CH_3OH + HCOOK$$



$$\text{—CHO} + \text{NaOH (con.)} \xrightarrow{\text{Methanol}} C_6H_5CH_2OH + C_6H_5\,COONa^+$$

Benzaldehyde

Benzyl alcoho Sodium benzoate

CARBOXYLIC ACID

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)

Carboxylic acids having an a - hydrogen are halogenated at the a -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give a -halocarboxylic acids.

$$RCH_2 - COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/ Red phosphorus}}$$

$$\underset{\displaystyle X}{R - \overset{}{CH} - COOH}$$

X = CI, Br

α – halocarboxylic acids

2. ESTERIFICATION

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc.H_2SO_4 as catalyst to form esters.

$$RCOOH + R'OH \xrightleftharpoons{H^+} RCOOR' + H_2O$$

18. Vinegar is 8 to 10% solution of CH_3COOH.

19. α-hydrogen atoms in carboxylic acid are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction.

21. Relative acid strength of $RCOOH > HOH > ROH > HC \equiv CH > NH_3$. It is because a strong acid has weak conjugate base.

22. Some dicarboxylic acids bearing general formula $HOOC - (CH_2)_n - COOH$ where $n - 0, 1, 2,$ ....etc.

$HOOC - COOH$	Oxalic acid	1, 2 ethanedioic acid
$HOOC - CH_2 - COOH$	Malonic acid	1, 3 propanedioic acid
$HOOC - (CH_2)_2 - COOH$	Succinic acid	1, 4 butanedioic acid
$HOOC - (CH_2)_3 - COOH$	Glutonic acid	1, 5 pentamdioic acid
$HOOC - (CH_2)_4 - COOH$	Adipic acid	1, 6 hexanedioic acid

23. Melting points : Higher : Even carbon atoms than next lower or higher homologues containing even number of carbon atoms due to symmetry and closer packing of molecules in the crystal lattice.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

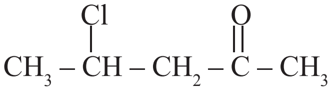
Q. 1. Arrange the following compounds in increasing order of their acid strengths :

$(CH_3)_2CHCOOH, CH_3CH_2CH(Br)COOH, CH_3CH(Br)CH_2COOH$

Ans. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

Q. 2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.

Ans.



$$CH_3-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Q. 3. Which type of aldehyde can go Cannizzaro reaction ?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogen.

Q. 4. Name the aldehyde which does not give Fehling's solution test.

Ans. Benzaldehyde.

Q. 5. Arrange the following in order of their increasing reactivity towards HCN :

$CH_3CHO, CH_3COCH_3, HCHO, C_2H_5COCH_3$

Ans. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

Q. 6. Mention industrial product obtained from HCHO.

Ans. Bakelite

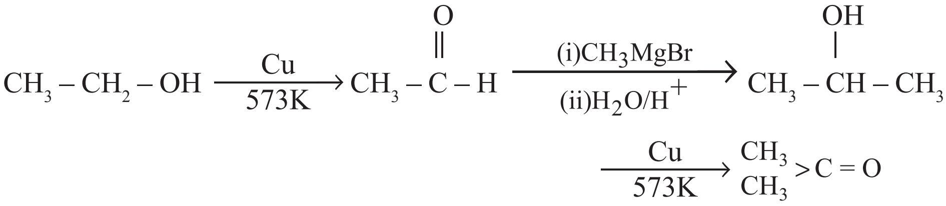
Q. 7. Arrange the following compounds in increasing order of their boiling point :

$CH_3CHO, CH_3CH_2OH, CH_3-O-CH_3, CH_3-CH_2-CH_3$

Ans. $CH_3-CH_2-CH_3 < CH_3-O-CH_3 < CH_3CHO < CH_3CH_2OH$

Q. 8. How is acetone obtained from ethanol ?

Ans.



$$CH_3-CH_2-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[(ii)H_2O/H^+]{(i)CH_3MgBr} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3$$

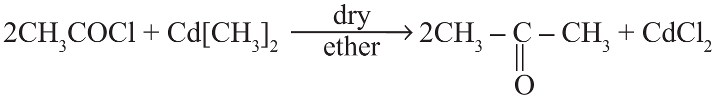
$$\xrightarrow[573K]{Cu} \begin{matrix}CH_3\\CH_3\end{matrix}>C=O$$

Q. 9. Why do aldehydes and ketones have lower boiling point than alcohols ?

Ans. Due to presence of associated molecules with H-bonding in alcohols.

Q. 10. Write reaction between acetyl chloride and dimethyl cadmium.

Ans.

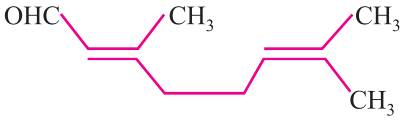


$$2CH_3COCl + Cd[CH_3]_2 \xrightarrow[\text{ether}]{\text{dry}} 2CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CdCl_2$$

Q. 11. What happens when CH_3CHO is treated with $K_2Cr_2O_7$ in presence of H_2SO_4 ?

Ans. $CH_3CHO + [O] \xrightarrow{K_2Cr_2O_7+H_2SO_4} CH_3COOH$

Q. 12. Write the IUPAC name of



Ans. 3, 7-Dimethylocta-2, 6 dien-1-al

Q. 13. Give balanced equation and name of products when CH_3COOH is treated with PCl_5 ?

Ans. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

Q. 14. What product is obtained when ethyl benzene is oxidized with alkaline $KMnO_4$?

Ans. Benzoic acid (C_6H_5COOH) is obtained.

Q. 15. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Give reason.

Ans. Because the positive charge on carbonyl carbon of CH_3CHO decreases to lesser extent due to one ERG –CH_3) andhence more reaction.

Q. 16. What is RDX ?

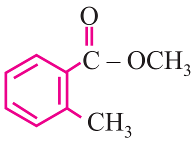
Ans. RDX is Research and Development Explosive which is prepared by the nitration of hexamethylene under controlled conditions.

Q. 17. Write IUPAC names of the following compound :

HOOC – CH = CH - COOH

Ans. But-2-ene-1, 4-dioic acid

Q. 18. Write the IUPAC name of



Ans. Methyl-2-methylbenzoate.

Q. 19. Why does benzoic acid not undergo Friedel-Craft reaction ?

Ans. – COOH group in C_6H_5COOH is an E. W. G. which deactivates the benzene ring. Hence electrophilic substitution becomes difficult.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. How will you convert :

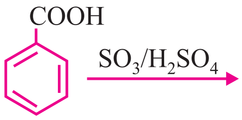
(i) $C_2H_2 \rightarrow CH_3COOH$

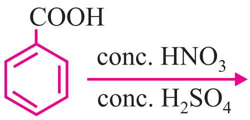
(ii) $C_6H_5CONH_2 \rightarrow C_6H_5COOH$

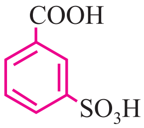
Ans. (i) $$\begin{array}{c}CH\\|||\\CH\end{array} \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[\text{dil } H_2SO_4]{KMnO_4} CH_3COOH$$

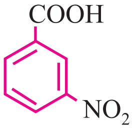
(ii) $C_6H_5CONH_2 + HNO_2 \rightarrow C_6H_5COOH + N_2 + H_2O$

Q. 2. Complete the following :

(i) 

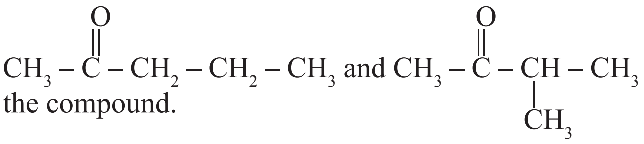
(ii) 

Ans. (i) 

(ii) 

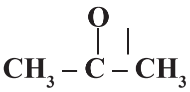
Q. 3. An organic compound X has molecular formula $C_5H_{10}O$. It does not reduce Fehling's solution but forms a bisulphate compound. It also gives positive Iodoform test. What are possible structures of X ? Explain your reasoning relating structure.

Ans. Ketone give +ve test with Iodoform. It is methyl-ketone.



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$ and $CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ are possible structures of the compound.

Q. 4. Give the chemical test to distinguish between :



(i) CH_3CHO and $CH_3-\overset{\overset{O}{|}}{C}-CH_3$

(ii) CH_3CHO and C_6H_5CHO

Ans. (i) CH_3CHO gives Tollen's reagent test.

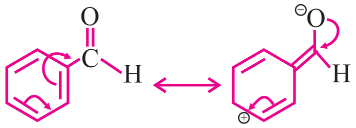
$$CH_3CHO + 2AgNO_3 + 2NH_4OH \rightarrow CH_3COOH + \underset{\text{Silver mirror}}{2Ag} + 2NH_4NO_3 + 2H_2O$$

(ii) CH_3CHO gives brick red ppt.

$$CH_3CHO + 2CuSO_4 + 4NaOH \rightarrow CH_3COOH + \underset{\text{Brick red ppt.}}{Cu_2O} + Na_2SO_4 + 2H_2O$$

Q. 5. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal ? Explain your answer.

Ans. Carbon atom of carbonyl is C_6H_5CHO is less reactive than that of propanal. C_6H_5CHO less polar due to resonance.

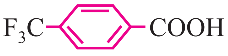


Q. 6. Which acid of each pair shown here would you expect to be stronger ?

(i) CH_3CO_2H or CH_2FCO_2H

(ii) CH_2FCO_2H or CH_2ClCO_2H

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

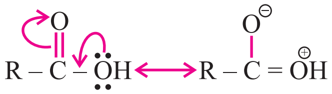
(iv)  **or** 

Ans. (i) FCH_2COOH (ii) CH_2FCOOH

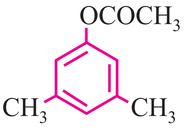
(iii) $CH_3-\overset{\overset{F}{|}}{CH}-CH_2COOH$

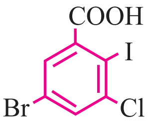
(iv) 

Q. 7. Carboxylic acids do not give reactions of aldehydes and ketones why ?

Ans. It is due to resonance  Position of $> C = O$ group keep changing.

Q. 8. Write IUPAC name of the following :

(i) 

(ii) 

Ans. (i) 3, 5 Dimethylphenylethanoate

(ii) 5 bromo 3-chloro-2-iodobenzoic acid

Q. 9. Account for the following :

(i) Oxidation of toluene to C_6H_5CHO with CrO_3 is carried out in presence of acetic anhydride.

(ii) Melting point of an acid with even number is higher than those of its neighbours with odd number of carbon atoms.

Ans. (i) It is used to prevent oxidation to benzoic acid.

(ii) Acids with even number of carbon atoms fit into crystal lattice.

Q. 10. Distinguish between :

(i) C_2H_5OH and CH_3CHO

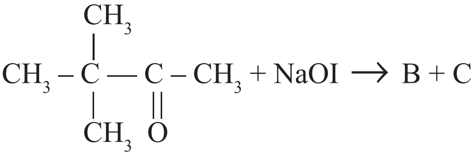
(ii) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$

Ans. (i) C_2H_5OH evolves H_2 gas with Na, CH_3CHO not.

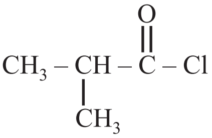
(ii) Acetophenone will give yellow ppt. of iodoform while $C_6H_5CH_2CHO$ will not.

Q. 11. Complete the following reactions by identifying A, B and C :

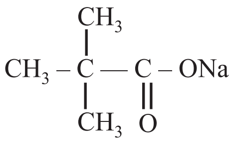
(i) $\mathbf{A + Hydrogen\ (g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CH - CHO}$

(ii) 

$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} — \underset{\underset{O}{||}}{C} - CH_3 + NaOI \longrightarrow B + C$$

Ans. (i) 'A' is 

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - \overset{\overset{O}{||}}{C} - Cl$$

(ii) 'B' is CHI_3 and 'C' is 

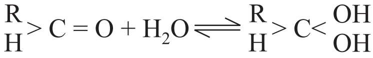
$CH_3-C(CH_3)_2-C(=O)-ONa$

Q. 12. Benzaldehyde gives a positive test with Tollen's reagent but not with Fehling's and Benedict solutions. Why ?

Ans. It is due to stronger oxidizing nature of Tollen's reagent as compared to Fehling and Benedict's solution and cannot oxidise benzaldehyde to benzoic acid. In general, all these three can oxidise aliphatic aldehydes.

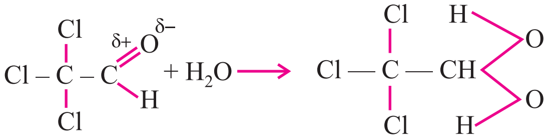
Q. 13. Aldehydes usually do not form stable hydrates but chloral normally exists as chloral hydrate. Give reason.

Ans. In case of aldehyde reaction is reversible.



$$\begin{matrix}R\\H\end{matrix}\!>C=O+H_2O \rightleftharpoons \begin{matrix}R\\H\end{matrix}\!>C<\!\begin{matrix}OH\\OH\end{matrix}$$

In case of CCl_3CHO, Cl atoms increases +ve charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.



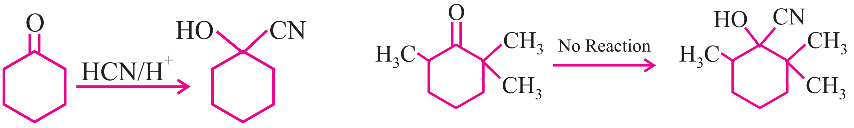
Chloralhydrate

Q. 14. Give possible explanation for the following :

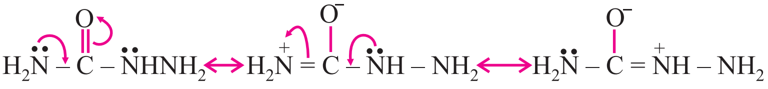
(i) Cyclohexanone forms cyanohydrins in good yield but 2, 2, 6 trimethyl-cyclohexanone does not.

(ii) There are two – NH_2 groups in semicarbazide. However, only one is involved in formation of semi carbozone.

Ans. (i) Due to steric hindrance for CN^- at C = O and not of 3-methyl groups at α-position but in case of



(ii) Only one – NH_2 group attached to C = O is involved in resonance. As result electron density on these NH_2 group decreases and hence does not act as nucleophile.



Q. 15. Aldehydes are easily oxidisable yet propanal can conveniently be prepared by the oxidation of propanol by acidic $K_2Cr_2O_7$.

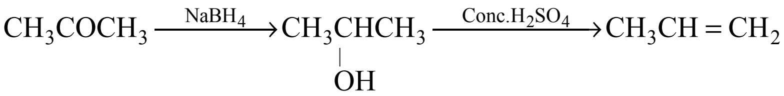
Ans. Aldehydes having boiling points less than 373 K can be removed by distillation therefore propanal 323 can easily be prepared from propanol-1 by distillation from the alcohol acid dichromate solution.

Q. 16. Do the following conversions in not more than two steps

(i) Benzoic acid to Benzalolehyde (ii) Propanone to propene

Ans. (i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[H_2]{Pol-BaSO_4} C_6H_5CHO$

(ii)

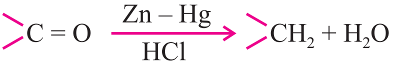


$$CH_3COCH_3 \xrightarrow{NaBH_4} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{Conc.H_2SO_4} CH_3CH=CH_2$$

Q. 17. Write the reactions involved in the following reactions:

(i) Clemmensen reduction (ii) Cannizzoro reaction

Ans. (i)



$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$

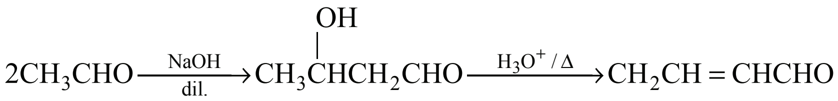
(ii)

$$\begin{matrix}H\\H\end{matrix}>C=O + \begin{matrix}H\\H\end{matrix}>C=O \xrightarrow[KOH]{Conc.} CH_3OH + HCOO^-K^+$$

Q. 18. Convert the following (i) Ethyl benzene to benzoic acid (ii) Ethanal to but-2-enal

Ans. (i) $C_6H_5C_2H_5 \xrightarrow{K_2Cr_2O_7/H^+} C_6H_5COOH$

(ii)



$$2CH_3CHO \xrightarrow[dil.]{NaOH} CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2CHO \xrightarrow{H_3O^+/\Delta} CH_2CH=CHCHO$$

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

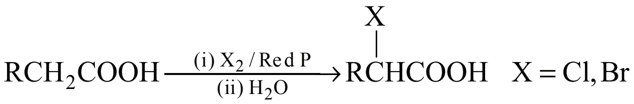
Q. 1. Illustrate the following name reactions :

(i) Hell-Volhard Zelinsky reaction

(ii) Wolff kishner reduction

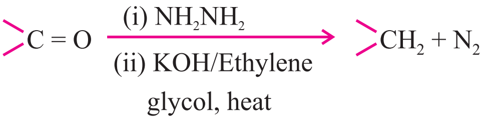
(iii) Etard reaction

Ans. (i)



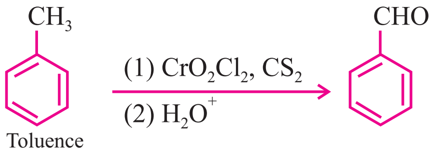
$$RCH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/Red\ P} R\overset{\displaystyle X}{\overset{|}{C}}HCOOH \quad X = Cl, Br$$

(ii)



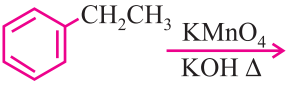
$$>C=O \xrightarrow[(ii)\ KOH/Ethylene\ glycol,\ heat]{(i)\ NH_2NH_2} >CH_2 + N_2$$

(iii)



Q. 2. Predict the organic products of the following reactions :

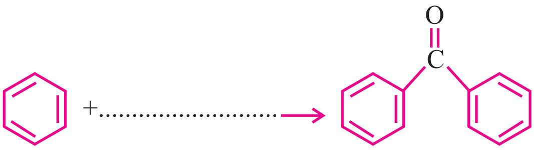
(i)



(ii)

(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iv)



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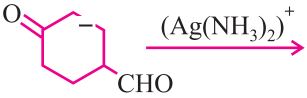

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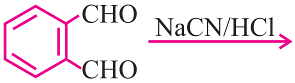
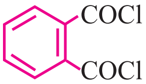


Ans. (i) $C_6H_5 - COOK$

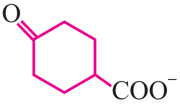
(ii)



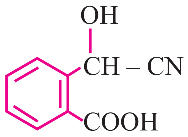
(iii) $C_6H_5CH = N - NHCONH_2$

(iv) $C_6H_5COCl/AlCl_3$

(v)



(vi)



Q. 3. Write chemical reaction to affect the following transformations :

(i) Butan-1-ol → Butanoic acid

(ii) Benzyl alcohol to pheynylethanoic acid

(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid

(iv) 4-methylacetophenone to Terephthalic acid

(v) Cyclohexene → Hexane-1, 6 dioic acid

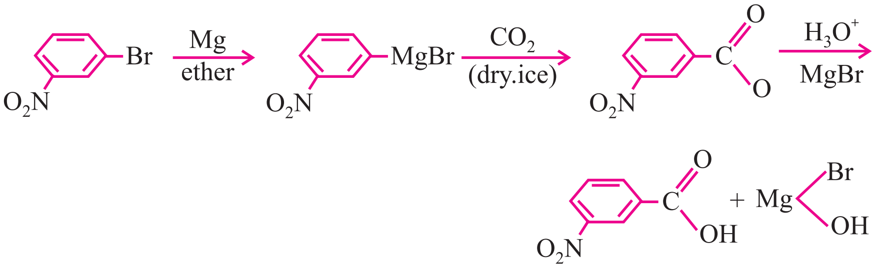
(vi) Butanal → Butanoic acid

Ans. (i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3+H_2SO_4} CH_3CH_2CH_2COOH$

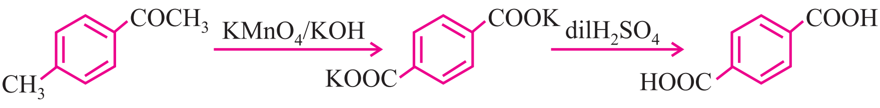
(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN$

$\xrightarrow[H_3O]{\Delta} C_6H_5CH_2COOH$

(iii)



(iv)



(v)

(vi) $CH_3CH_2CH_2CHO \xrightarrow[\text{Tollen's reagent}]{\text{Amm. } AgNO_3} CH_3CH_2CH_2COOH$

Q. 4. Draw the structure of the following derivatives :

(i) 2, 4-dinitrophenylhydrazone of C_6H_5CHO

(ii) Cyclopropanone oxime

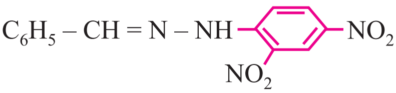
(iii) Acetaldehydedimethylacetal

(iv) Semicarbazone to cyclobutanone

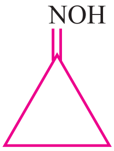
(v) Ethylene ketal of hexan-3-one

(vi) Methylhemiacetal of formaldehyde

Ans. (i)



(ii)



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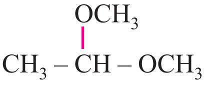
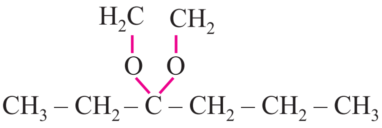


$$CH_3 - \overset{\overset{\displaystyle OCH_3}{|}}{C}H - OCH_3$$

(iv)

(v)



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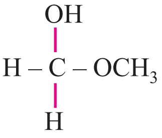


$$H - \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}} - OCH_3$$

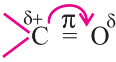
Q. 5. Draw the structure of a carbonyl group and indicate :

(i) hybridized state of carbon

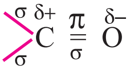
(ii) the σ and π bonds

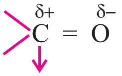
(iii) the electrophilic and nucleophilic centres

Ans. (i)



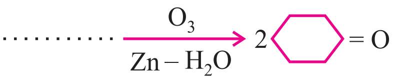
hybridized state of 'C' is sp^2

(ii) 

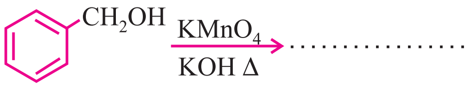
(iii) 

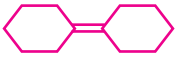
Nucleophilic centre

Q. 6. Complete the following as missing starting material, reagent or products :

(i) 

(ii) 

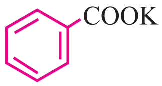
(iii) 

Ans. (i) 

(Ozonolysis)

1, 2 Dicyclohexylethene

(ii) B_2H_6/THF, H_2O_2/OH^-, PCC (Hydroboration)

(iii) 

(Oxidation)

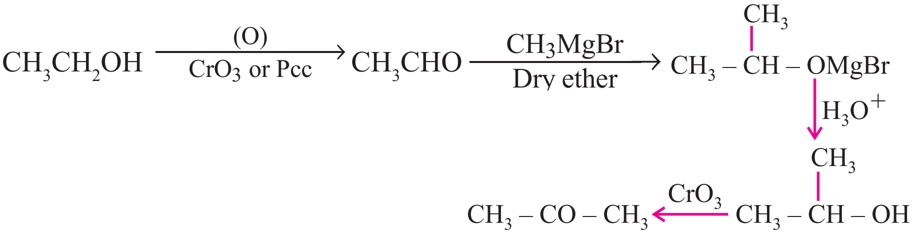
Potassium benzoate

Q. 7. How can the following converted :

(i) Ethanol → Acetone

(ii) Benzene → Acetophenone

(iii) Benzoic acid → Benzaldehyde

Ans. 

$$\text{(i) } CH_3CH_2OH \xrightarrow[CrO_3 \text{ or Pcc}]{(O)} CH_3CHO \xrightarrow[\text{Dry ether}]{CH_3MgBr} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-OH \xrightarrow{CrO_3} CH_3-CO-CH_3$$

(ii) 

$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Anhydrous} C_6H_5COCH_3$$

(iii) $C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$

Q. 8. Give reasons for the following :

(i) Carboxylic acids do not give characteristic reactions of carbonyl group.

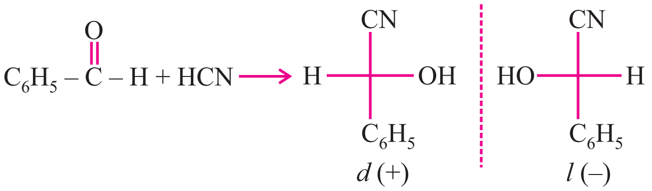
(ii) Treatment of C_6H_5CHO with HCN gives a mixture of two isomers which cannot be separated even by fractional distillation.

(iii) Sodium bisulphate is used for purification of ketones and aldehydes.

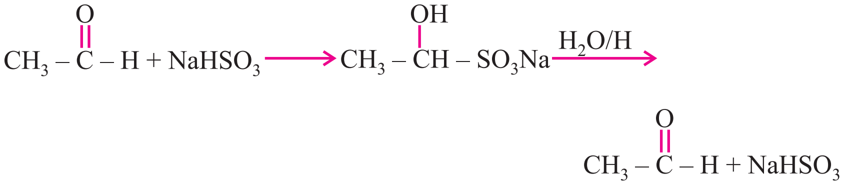
Ans. (i) 

$R-\overset{\overset{O}{\|}}{C}-\ddot{O}H \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=\overset{\oplus}{O}H$ Because of resonance, the position of $>C=O$ group is changing.

(ii) Due to two optical isomers fractional distillation is not possible.



(iii) Due to formation of additional compound with $NaHCO_3$ whereas impurities do not.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + NaHSO_3 \longrightarrow CH_3-\overset{\overset{OH}{|}}{C}H-SO_3Na \xrightarrow{H_2O/H} CH_3-\overset{\overset{O}{\|}}{C}-H + NaHSO_3$$

Q. 9. Write tests to distinguish between :

(i) CH_3CHO and C_6H_5CHO

(ii) C_6H_5-OH and CH_3COOH

(iii) Pentanal and Pentan-2-one

Ans. (i) CH_3CHO gives brick red ppt. with Fehling, C_6H_5CHO not.

(ii) Phenol does not give brisk effervescence but CH_3COOH gives this test with $NaHCO_3$.

(iii) Pentanal forms silver mirror but pentan-2-one does not.

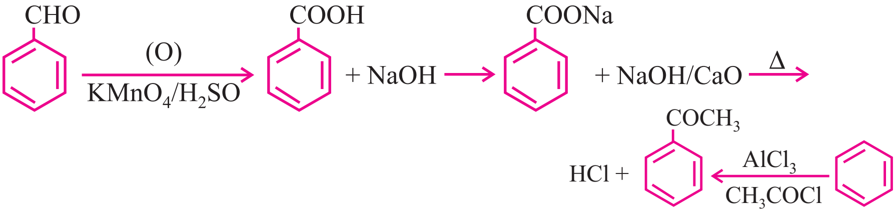
Q. 10. Convert :

(i) Benzaldehyde to acetophenone

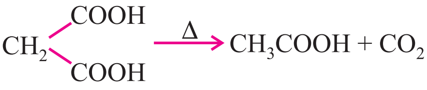
(ii) Malonic acid to acetic acid

(iii) Acetaldehyde to 2-butanol

Ans. (i)



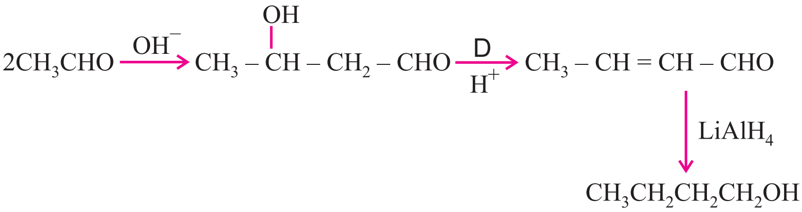
(ii)



$$CH_2\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow{\Delta} CH_3COOH + CO_2$$

Malonic acid

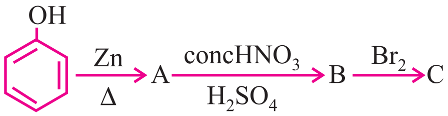
(iii)



$$2CH_3CHO \xrightarrow{OH^-} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CHO \xrightarrow[H^+]{D} CH_3-CH=CH-CHO \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

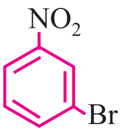
2-Butanol

Q. 11. Write the structures of organic compound A to F in the following sequence of reactions :

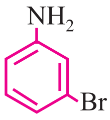


$$C \xrightarrow{H_2/pt\text{-}v} D \xrightarrow[HCl]{HNO_2} E \xrightarrow{H_3O^+} F$$

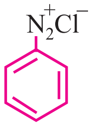
Ans. A = C_6H_6 B = $C_6H_5NO_2$ C =



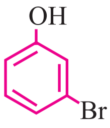
D =



E =



F =

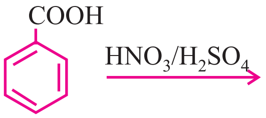


Q. 12. Complete the following :

(i) $CH_3CONH_2 + HNO_2 \rightarrow$

(ii) $CH_3CONH_2 + NaOH + Br_2 \rightarrow$

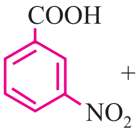
(iii)



Ans. (i) $CH_3COOH + N_2 + H_2O$

(ii) $CH_3NH_2 + Na_2CO_3 + NaBr + H_2O$

(iii)



$+ H_2O$

Q. 13. Write the structures of A, B, C, D and E in the following reactions:

$$\begin{tikzcd}
C_6H_6 \arrow[r, "CH_3COCl", "\text{anhyd. } AlCl_3"'] & A \arrow[r, "Zn\text{–}Hg", "HCl"'] \arrow[d, "NaOI"] & B \arrow[r, "(1)\ KMnO_4 - KOH", "(2)\ H_3O"'] & C \\
 & D + E & &
\end{tikzcd}$$

Ans. $A = CH_5COCH_3$

$B = C_6H_5CH_2CH_3$

$C = C_6H_5COOH$

$D = C_6H_5COONa$

$E = CHI_3$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Which of the following compounds would undergo Aldol condensation, which the Cannizzaro reaction and which neither ? Write the structures of the expected products of aldol condensation and Cannizzaro reaction :

(i) Methanal	**(ii) 2-Methylpentanal**
(iii) Benzaldehyde	**(iv) Benzophenone**
(v) Cyclohexanone	**(vi) 1-Phenylpropanone**
(vii) Phenylacetaldehyde	**(viii) Butan-1-ol**
(ix) 2, 2 Dimethylbutanal	

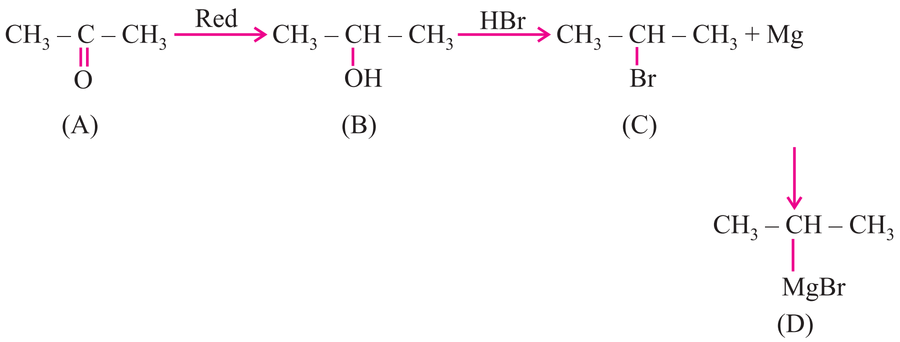
Ans. (i), (iii) and (ix) will give Cannizzaro reaction due to absence of α-hydrogen.

(ii), (v), (vi) and (vii) will give aldol condensation due to presence of α-hydrogen.

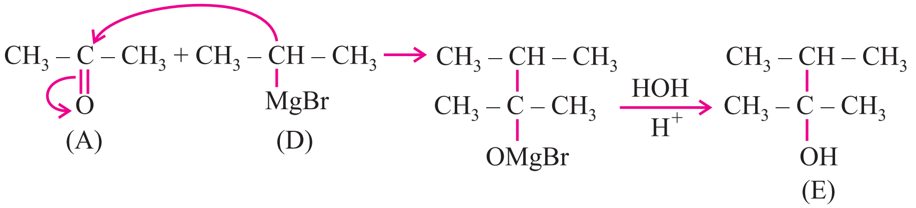
(iv) and (viii) will neither undergo Cannizzaro's reaction nor Aldol condensation because benzophenone does not give α-hydrogen and butanol is alcohol, not aldehyde which cannot undergo aldol condensation.

Q. 2. An organic compound 'A' (C_3H_6O) is resistant to oxidation but forms compound 'B' (C_3H_8O) on reduction. 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D' which reacts with 'A' to form a product which on hydrolysis gives 'E'. Identify 'A' to 'E'.

Ans. 'A' must be ketone.



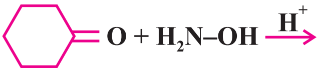
$$\underset{(A)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{\text{Red}} \underset{(B)}{CH_3-\underset{OH}{CH}-CH_3} \xrightarrow{\text{HBr}} \underset{(C)}{CH_3-\underset{Br}{CH}-CH_3} + Mg \longrightarrow \underset{(D)}{CH_3-\underset{MgBr}{CH}-CH_3}$$



$$\underset{(A)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{(D)}{CH_3-\underset{MgBr}{CH}-CH_3} \longrightarrow CH_3-\underset{OMgBr}{\overset{CH_3-CH-CH_3}{C}}-CH_3 \xrightarrow[H^+]{HOH} \underset{(E)}{CH_3-\underset{OH}{\overset{CH_3-CH-CH_3}{C}}-CH_3}$$

2, 3 Dimethylbutan-2-ol

Q. 3. (a) Write the products of the following reactions:

(i) 

$=O + H_2N{-}OH \xrightarrow{H^+}$

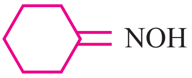
(ii) $2C_6H_5CHO + \underset{\text{Conc.}}{NaOH} \longrightarrow$

(iii) $CH_3COOH \xrightarrow{Cl_2/P}$

(b) Give simple tests to distinguish between the following pairs of compounds.

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and propanone

Ans. **(a)** (i) 

(ii) 

(ii) Cl–CH$_2$COOH

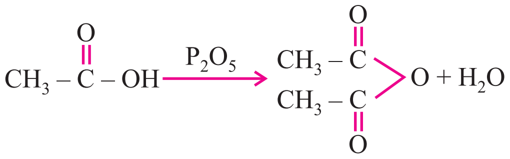
(b) (i) Add $NaHCO_3$, benzoic acid will give brisk ettervscence whereas benzaldehyde will not give this test.

(ii) Refer Q.7(e) of long answer type questions.

Q. 4. (i) How will you prepare (a) acetic anhydride and (b) acetyl chloride from CH_3COOH ? Write the equation involved in each case.

(ii) Why is the boiling point of acid anhydride higher than the acid from which it is obtained ?

Ans. (i) (a)



$$CH_3-\overset{\overset{\large O}{||}}{C}-OH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$$

(b)

$$CH_3-\overset{\overset{\large O}{||}}{C}-OH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

(ii) Acid anhydride bigger size than corresponding acids and stronger van der Waal's forces of attraction than their corresponding acids.

Q. 5. Complete the following reactions and write main products :

(i) $CH_3CONH_2 + HNO_2 \rightarrow$

(ii) $CH_3COCl + H_2O$ (steam) $\rightarrow$

(iii) $CH_3MgBr \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CO_2/H^+}$

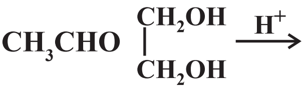
(iv) $CH_3COOH + NH_3 \xrightarrow{\Delta}$

(v) $CH_3COOH + C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4}$

(vi) $HCHO + NH_3 \rightarrow$

(vii) $CH_3CHO \xrightarrow{LiAlH_4}$

(viii)



$$CH_3CHO \; \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{H^+}$$

(ix) $CH_3COR + NaOI \rightarrow$

(x) $C_6H_5CHO + NH_2-NH_2 \rightarrow$

Ans. (i) CH_3COOH

(ii) CH_3COOH

(iii) CH_3COOH

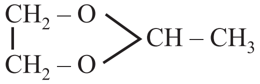
(iv) CH_3CONH_2

(v) $CH_3COOC_2H_5$

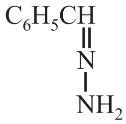
(vi) $(CH_2)_6N_4$ (Urotropine)

(vii) CH_3CH_2OH

(viii)



(ix) CHI_3

(x) 
$C_6H_5CH{=}N{-}NH_2$

Q. 6. Give reasons for the following :

(i) C_6H_5COOH is weaker than formic acid.

(ii) HCOOH and CH_3COOH differentiated by Tollen's reagent.

(iii) R – COOH do not give characteristic reaction with > C = O.

(iv) Carboxylic acids are stronger acids than phenols.

(v) Acid amides are weakly basic in nature.

Ans. (i) Due to unstability of carboxylate anion due to conjugation.

(ii) HCOOH acid is a stronger acid than CH_3COOH.

(iii) > C = O group is sterically hindered in carboxylic acid.

(iv) Dispersal of –ve charge on carboxylate ions than phenate ion.

(v) Acid amides are basic due to lone pair of electrons on nitrogen atom.

Q. 6. (a) Write the chemical equation for the reaction involved in cannizzaro reaction.

(b) Draw the structure of semicarbazone of ethanal

(c) Why pka of F-CH2COOH is lower than that of Cl–CH_2COOH

(d) Write the product in the following reaction

$$\mathbf{CH_3CH = CHCH_2CN \xrightarrow[(2)\ H_2O]{(1)\ DIBAL\text{ - }H}}$$

(e) How can you distinguish between propanal and propanone?

Ans. (a) $$HCHO + HCHO \xrightarrow{\text{Conc. NaOH}} HCOONa + CH_3OH$$

(b) $CH_3CH = N{-}NHCONH_2$

(c) Stronger –I effect of fluorine makes F-CH_2COOH to be stronger acid than Cl–CH_2COOH and less pka

(d) $CH_3CH = CHCH_2CHO$

(e) Silver mirror formed on adding ammonical silver nitrate to propanal and not with propanone.

UNIT 13

AMINES

Points to Remember

1. Amines are alkyl and/or aryl derivatives of $\ddot{N}H_3$.

2. Functional groups of 1°, 2° and 3° amines are respectively as given below :

$$-\ddot{N}H_2, -\ddot{N}H- \text{ and } -\underset{|}{\ddot{N}}-$$

3. Gabriel phthalimide synthesis can't be used for the preparation of 2° and 3° amines. It gives aliphatic primary amine only.

4. Hoffmann's bromamide reaction gives 1° amines having one carbon atom less than parent primary amide.

5. The order of basic strength of aliphatic amines is :

   (i) Aliphatic amines are more basic than $\ddot{N}H_3$.

   (ii) In aqueous solution medium, the order is 2° > 1° > 3° (for–CH_3 group) and 2° > 3° > 1° for – C_2H_5 group.

   (iii) In non-aqueous medium or gaseous phase, the order is 3° > 2° > 1°.

6. Basic strength of aromatic amines :

   (i) Aromatic amines are weaker bases than $\ddot{N}H_3$.

   (ii) ERGs like – CH_3, – OR, – NH_2 etc. increase basic strength while EWGs like – NO_2, – CN etc. decrease the basic strength. The effect of substituents is more at para positions and less at meta position.

7. Basic strength of amines is expressed in terms of K_b or pK_b.

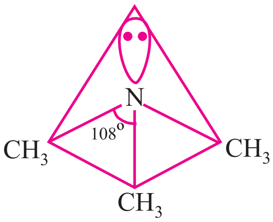
8. 1°, 2° and 3° amines can be distinguished by Hinsberg's test.

9. Hinsberg's reagent is benzenesulphonyl chloride ($C_6H_5SO_2Cl$).

10. 3° amines like trimethylamine are used as insect attractants.

11. Diazonium salts are represented by the general formula $[Ar\,N \equiv N]^+ X^-$.

12. **Structure of amines :** Pyramidal for trimethyl amine $(CH_3)_3-\ddot{N}$. They are Lewis bases.



13. Carbylamine test only given by 1° amines.

14. Manich reaction involves the reaction of ketones with HCHO and NH_3 (or amine) in acidic medium to form Manich bases.

15. 1° amines give effervescence with HNO_2.

16. $-NH_2$ group in aniline is *o*- and *p*- directing and is highly activating in nature.

17. Acylation of aniline is done before subjecting it to nitration or halogenation.

18. Aliphatic diazonium salts are very unstable and do not exist while aromatic salts are relatively stable.

19. These salts are prepared from 1° aryl amines by diazotization reactions.

20. Diazotised salts (diazonium salts) are used to prepare a variety of aromatic compounds.

21. $R-C\equiv N$ have generally pleasant odours but alkyl isocyanides have highly unpleasant odours.

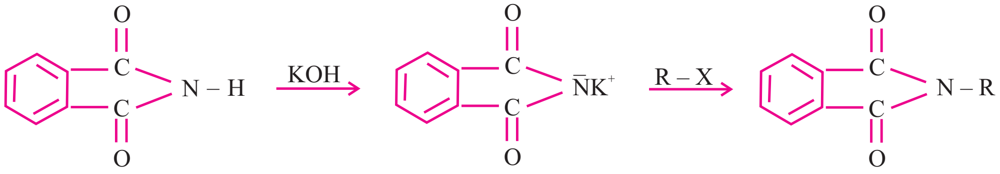
22. Alkyl isocyanides have lower boiling points than that of isomeric alkyl cyanides due to lower dipole moments.

23. Arenediazonium salts are highly reactive compounds and reactivity is due to excellent leaving ability of diazo group as N_2 gas.

NAME REACTIONS

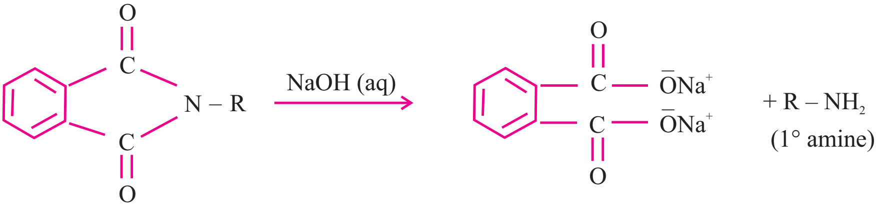
1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment wi ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



Phthalimide

N–Alkylphthalimide



2. **Hoffmann bromamide degradation reaction**

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than mat present in the amide.

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

3. **Carbylamine reaction**

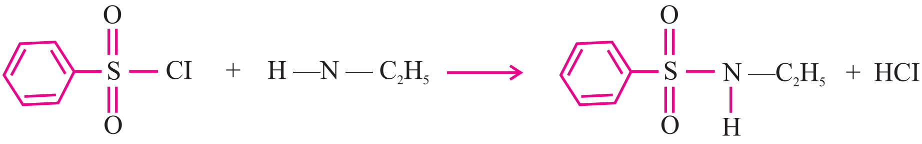
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2O$$

4. **Hinsberg Test:**

Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

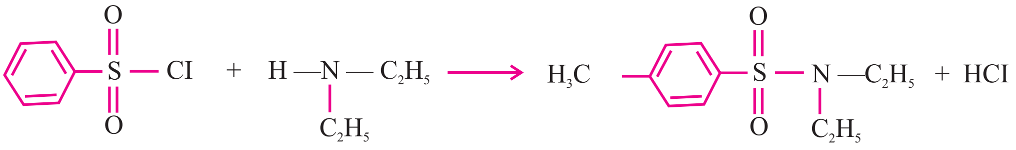
(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



N-Ethylbenzenesulphonamide
(soluble in alkali)

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

(b) In the reaction with secondary amine, N, N-diethylbenzenesuIphonamide is formed.



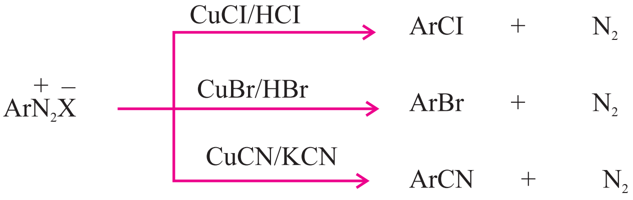
N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

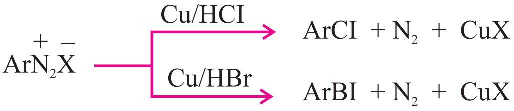
5. Sandmeyer Reaction

The C1-, Br- and CN- nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



6. Gatterman Reaction

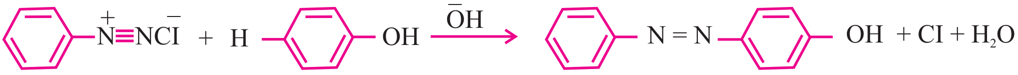
Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



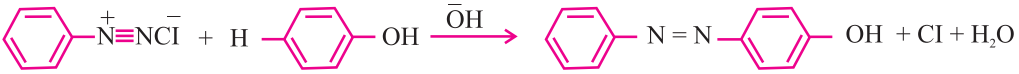
7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the -N=N- bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



P-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine

(ii) Secondary and tertiary amines

(iii) Ethylamine and aniline

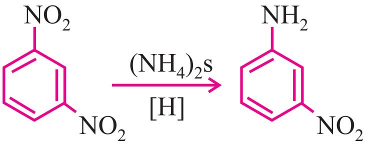
VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Write IUPAC name of CH_3NC.

Ans. Methane carbylamine.

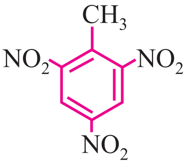
Q. 2. Convert m-dinitrobenzene to m-nitro aniline.

Ans.

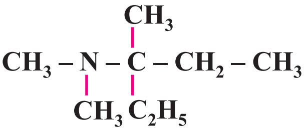


Q. 3. Draw structure of TNT, an explosive.

Ans.



Q. 4. Write IUPAC name of



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-\underset{\displaystyle C_2H_5}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_3$$

Ans. 3-Methyl-N,N-dimethyl pentanamine

Q. 5. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., $[CH_3(CH_2)_{15}N(CH_3)_2]^+Cl^-$.

Q. 6. What is Hinsberg's reagent ?

Ans. Benzene sulphonyl chloride, 

Q. 7. Why aniline dissolves in HCl ?

Ans. $C_6H_5NH_2 + HCl \rightarrow [C_6H_5NH_3]^+Cl^-$.

It dissolves due to its basic nature.

Q. 8. How will you test the presence of primary amine ?

Ans. By carbyl amine test.

$RNH_2 + CHCl_3 + 3KOH \rightarrow RN \equiv C + 3KCl + 3H_2O$

Q. 9. What is vapour phase nitration ?

Ans. $CH_4 + HNO_3 \xrightarrow{623\ K} CH_3NO_2$

(High temperature and nitration in vapour phase only)

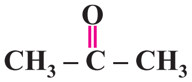
Q. 10. Write one use of dopamine and atropine alkaloid.

Ans. Dopamine : Neurotransmitter

Atropine alkaloid : 0.5-1.0% solution ophthalmic examination.

Q. 11. Direct nitration of aniline is not carried out. Explain.

Ans. ($H_2SO_4 + HNO_3$) easily oxidized aniline into tarry complex product due to high e^- density on the benzene ring of aniline.

Q. 12. Among the compounds as following which will react with  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ **to give product containing $>C=N-$?**

(i) $C_6H_5NH_2$ **(ii)** $(CH_3)_3N$

(iii) $C_6H_5NHC_6H_5$ **(iv)** $C_6H_5NHNH_2$

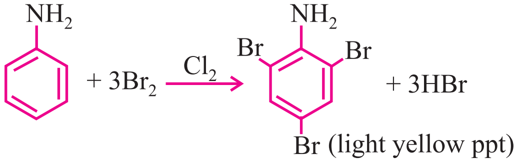
Ans. $C_6H_5NH_2$ and $C_6H_5NHNH_2$.

Q. 13. How will you give expression for K_b to indicate its basic strength ?

Ans.
$$K_b = \frac{\left[RNH_3^+\right]\left[OH^-\right]}{\left[R-NH_2\right]}$$

Q. 14. What happens when aniline is treated with bromine ?

Ans.



Q. 15. Write a chemical equation to illustrate the ammonolysis.

Ans. For alcohols :

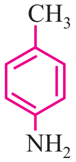
$$C_2H_5OH \xrightarrow[Al_2O_3/620K]{NH_3} C_2H_5\ddot{N}H_2 \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_2\,\ddot{N}H \xrightarrow{C_2H_5OH} (C_2H_5)_3\,\ddot{N}$$

For alkyl halides :

$$C_2H_5I \xrightarrow[-HI]{NH_3/373\,K} C_2H_5\ddot{N}H_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2\,\ddot{N}H \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3\,\ddot{N} \xrightarrow[-HI]{C_2H_5I} \left[(C_2H_5)_3\,\ddot{N}\right]^+ I^-$$

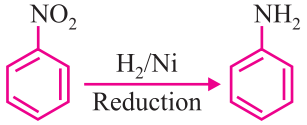
Q. 16. Write the structure of p-toluidine.

Ans.



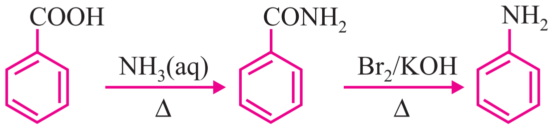
Q. 17. Prepare/convert nitrobenzene into aniline.

Ans.



Q. 18. Convert C_6H_5COOH to $C_6H_5NH_2$.

Ans.



Q. 19. Write isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

Q. 20. Arrange the following compounds in increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

SHORT AN SWER TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following acid-base reactions and name the products :

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$

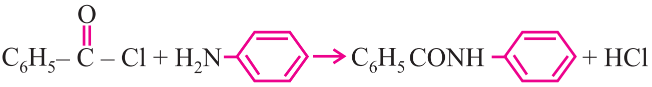
(ii) $(CH_3CH_2)_3N + HCl \rightarrow$

Ans. (i) $CH_3CH_2CH_2N^+H_3Cl^-$ (n-propyl ammonium chloride)

(ii) $(CH_3CH_2)_3 - N^+HCl^-$ (Triethyl ammonium chloride)

Q. 2. Write chemical reaction of $C_6H_5NH_2 + C_6H_5COCl$ and name product obtained.

Ans.



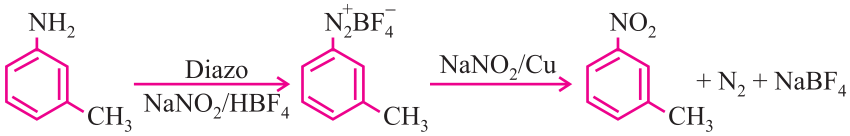
N-phenyl benzamide

Q. 3. How will you convert :

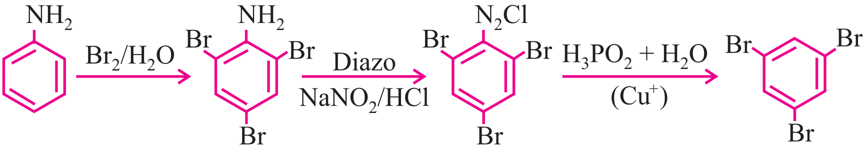
(i) **3-methylaniline → 3-nitrotoluene**

(ii) **Aniline → 1, 3, 5-tribromobenzene**

Ans. (i)



(ii)



Q. 4. How will you convert :

(i) **Propanoic acid → Ethanoic acid**

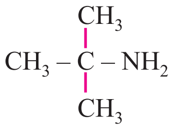
(ii) **Nitromethane → Dimethylamine**

Ans. (i) $C_2H_5COOH \xrightarrow[\Delta]{NH_3} C_2H_5CONH_2 \xrightarrow{Br_2/KOH} C_2H_5NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$

(ii) $CH_3NO_2 \xrightarrow{H_2/Ni} CH_3NH_2 \xrightarrow{CH_3Cl/KOH} CH_3N \equiv C \xrightarrow{H_2/Ni} CH_3 - NH - CH_3$

Q. 5. Draw the structures of the following compounds :

(i) **N-isopropylaniline** **(ii)** **t-butylamine**

Ans. (i)  (ii) 

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-NH_2$

Q. 6. **Why $C_6H_5N^+(CH_3)_3OH^-$ a stronger base than NH_4OH ?**

Ans. Due to – I effect of phenyl group, it decreases e^- density on nitrogen atom but no such group in NH_4OH.

Q. 7. **Explain Kb order : $Et_2NH > Et_3N > EtNH_2$ in aqueous solution.**

Ans. Basicity of amines in aqueous solution depends upon :

(i) + I effect of an alkyl group.

(ii) Extent of hydrogen bonding with H_2O.

(iii) Steric effects of alkyl groups.

Q. 8. **Distinguish between** 1°, 2° and 3° amines by HNO_2 **acid test.**

Ans. 1° gives N_2 gas. 2° gives yellow oily compound. 3° form water soluble salts.

$$CH_3CH_2NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$$

$$R_2NH + HNO_2 \rightarrow R_2N - N = O + H_2O$$

$$(CH_3CH_2)_3N + HNO_2 \longrightarrow [(CH_3CH_2)_3\overset{\oplus}{N}H]\,NO_2^-$$

Soluble in water

Q. 9. **A compound 'A' having molecular formula C_3H_7ON reacts with Br_2 in presence of NaOH to give compound 'B'. This compound 'B' reacts with HNO_2 to form alcohol and N_2 gas. Identify compound 'A' and 'B' and write the reaction involved.**

Ans. 'A' is $CH_3CH_2CONH_2 \xrightarrow[NaOH]{Br_2} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow{HNO_2} C_2H_5OH + N_2 + H_2$

Q. 10. **Write chemical equation for the following conversions :**

(i) $\mathbf{CH_3 - CH_2 - Cl \rightarrow CH_2 - CH_2 - CH_2 - NH_2}$

(ii) $\mathbf{C_6H_5 - CH_2 - Cl \rightarrow C_6H_5CH_2CH_2 - NH_2}$

Ans. (i) With NaCN and reduction.

i.e., $C_2H_5Cl \xrightarrow[NaCN]{Ethanol} C_2H_5 - C \equiv N \xrightarrow{red\ n} CH_3 - CH_2 - CH_2 - NH_2$

(ii) $C_6H_5CH_2Cl \xrightarrow[\text{NaCN}]{\text{Ethanol}} C_6H_5-C\equiv N \xrightarrow{H_2/Ni} C_6H_5CH_2CH_2-NH_2$

Q. 11. Account for :

(i) Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions. Aniline on nitration gives a substantial amount of m-nitroaniline.

(ii) Aniline does not go Friedel Crafts reaction.

Ans. (i) It is because aniline is formed by protonation with $\overset{\oplus}{N}H_3$ *i.e.,* EWG hence it is m-directing *i.e.,* 47%.

(ii) It is because aniline is basic, can form adduct with $AlCl_3$, electrophile cannot be generated.

Q. 12. Account for the following :

(i) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(ii) Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

Ans. (i) $-NH_2$ is ERG, electrophilic substitution takes place faster.

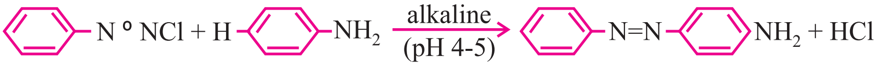
(ii) Nitro compounds are more polar than hydrocarbons therefore have more van der Waal's forces of attraction.

Q. 13. Write short notes on :

(i) Coupling reaction

(ii) Ammonolysis

Ans. (i)



(ii) Ammonolysis : $R-X+NH_3 \rightarrow R-NH_2+HX$

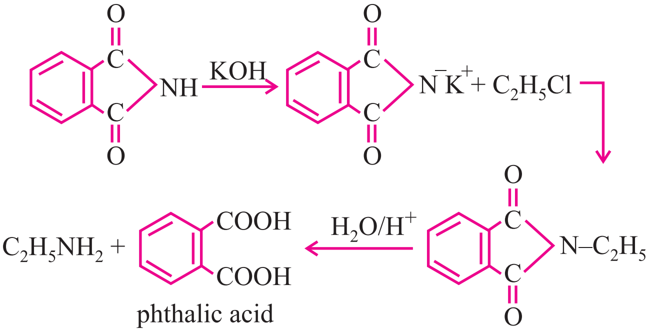
$RNH_2+R-X \rightarrow (R)_2N+HX$

$(R)_2NH+R-X \rightarrow (R)_3N+HX$

$(R)_3N+R-X \rightarrow [R_4N]^{\oplus}X^{-}$

Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.

Ans. By Gabriel Phthalimide Reaction



ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. What happens when :

- **(i) An alkyl halide reacts with $AgNO_2$ and product is reduced.**
- **(ii) An alkyl halide is treated with AgCN and product is hydrolysed.**
- **(iii) Methyl magnesium is treated with cyanogens chloride.**

Ans. (i) $R-X+AgNO_2 \xrightarrow[-AgX]{} R-NO_2 \xrightarrow[{[H]}]{Sn/HCl} R-NH_2$

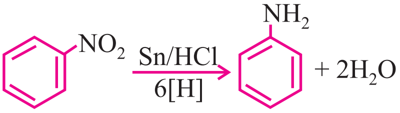
(ii) $R-X+AgCN \xrightarrow[-AgX]{} RNC \xrightarrow{H_2O/H^+} RNH_2+HCOOH$

(iii) $CH_3MgBr+CN-Cl \rightarrow CH_3CN+Mg<^{Cl}_{Br}$

Q. 2. How would you prepare :

- **(i) $C_6H_5NH_2$ from $C_6H_5NO_2$**
- **(ii) CH_3NH_2 from $C_2H_5NH_2$**
- **(iii) $C_2H_5NH_2$ from CH_3NH_2**

Ans. (i)



(ii) $C_2H_5NH_2 \xrightarrow{HNO_2} C_2H_5OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{(O)} CH_3COOH \xrightarrow{NH_3}$

$CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$

(iii) $CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{KCN} CH_3CN$

$\xrightarrow{[H]} CH_3CH_2NH_2$

Q. 3. Write the structure of the products in each case :

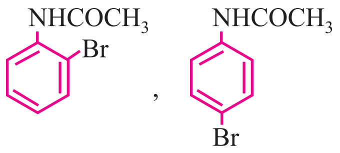
(i) $CH_3CH_2NH_2 \xrightarrow[\Delta]{(CH_3CO)_2O}$

(ii) $CH_3CONHC_6H_5 \xrightarrow{Br_2/Fe}$

(iii) $CH_3CH_2CN \xrightarrow{H_2O/H^+}$

Ans. (i) $CH_3CH_2NHCOCH_3$, CH_3COOH

(ii)



(iii) $CH_3CH_2COOH + NH_4^+$

Q. 4. Write the structures of A, B and C in following

(i) $C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} A \xrightarrow[0\text{-}5°C]{NaNO_2+HCl} B \xrightarrow{KI} C$

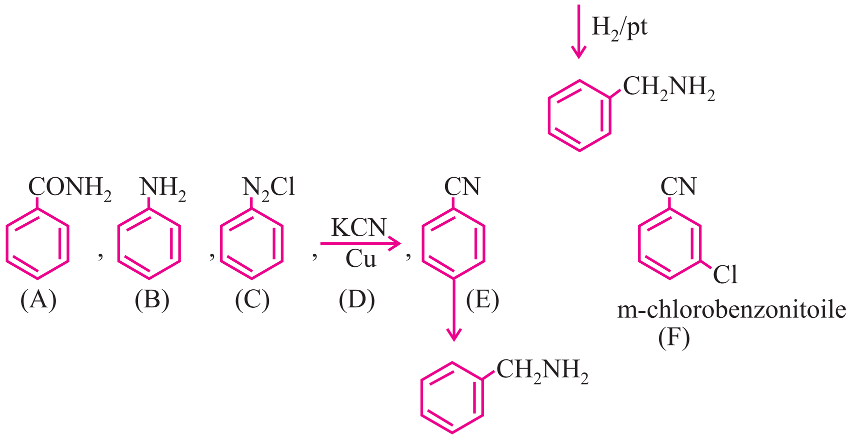
(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{CHCl_3+AlCKOH} C$

Ans. (i) $C_6H_5NH_2, C_6H_5N_2^+Cl^-, C_6H_5I$

(ii) CH_3CN, $CH_3CH_2NH_2$, CH_3CH_2NC

Q. 5. Write the structure of reagents/organic compounds 'A' to 'F' :

Ans. $A \xrightarrow[H_2O]{NaOH/Br_2} B \xrightarrow[O'C]{NaNO_2/HCl} C \xrightarrow{D} E \xrightarrow{Cl_2/Fe} F$



m-chlorobenzonitoile
(F)

Benzylamine

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Arrange the following :

(i) In decreasing order of pKb 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 :

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(iii) In decreasing order of basic strength :

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$, CH_3NH_2

(iv) Decreasing order of basic strength in gas phase :

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) Increasing order of boiling point :

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Ans. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) (a) p-nitroaniline < aniline < p-toluidine

(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(iii) $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$

(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

Q. 2. How will you convert :

(i) Ethanoic acid into methanamine

(ii) Hexane nitrile into 1-aminopentane

(iii) Methanol into ethanoic acid

(iv) Ethanamine into methanamine

Ans. (i)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Hydrazoic acid}}{HN_3} \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} \underset{\text{Methylamine}}{CH_3NH_2} + N_2 + CO_2$$

(ii) $\underset{\text{Hexane nitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{partial hydrolysis}]{\text{Conc. HCl}} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{1-Aminopentane}}{CH_3(CH_2)_4NH_2}$

(iii) $\underset{\text{Methanol}}{CH_3OH} \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{\text{KCN (alc)}} CH_3CN \xrightarrow{H^+/H_2O} \underset{\text{Ethanoic acid}}{CH_3COOH}$

(iv) $\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[(NaNO_2+HCl)]{HNO_3} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3COOH \xrightarrow{NH_4OH} CH_3COONH_4$

$\xrightarrow{\text{heat}} CH_3CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

Q. 3. Write short note on the following :

(i) Carbylamine reaction

(ii) Diazotization

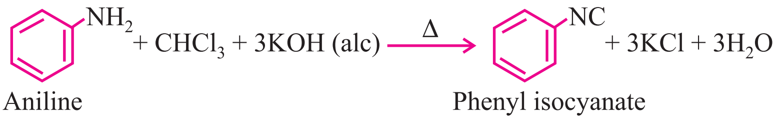
(iii) Hoffmann's bromide reaction

(iv) Coupling reaction

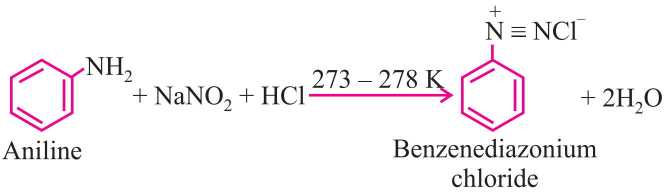
(v) Ammonolysis

Ans. (i) **Carbylamine reaction :** When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identify the presence of primary amine or chloroform.

$$RCH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} RCH_2NC + 3KCl + 3H_2O$$



(b) **Diazotization :** When primary aromatic amine is treated with $NaNO_2$ and HCl at 273-278 K, diazonium salt is obtained. This reaction is known as diazotization.



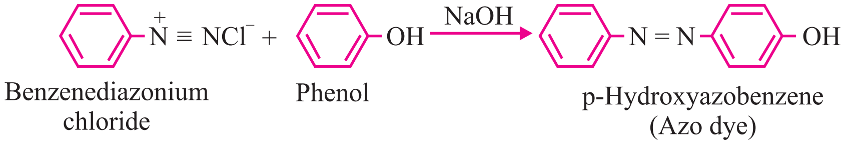
Benzenediazonium chloride is a very important synthetic compound, which can be changed into heloarenes, phenol, cyanobenzene, benzene etc.

(c) **Hoffmann's bromide reaction :** When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

This reaction is used to reduce one carbon atom from a compound.

(d) **Coupling reaction :** When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes are produced in which diazo (– N = N –) group is retained. Coupling reactions generally take place at p-position of phenol or aromatic amines.



(e) **Ammonolysis :** Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.

$$\begin{tikzcd} RCH_2Cl + NH_3 \arrow[r, "-HCl"'] & RCH_2NH_2 \arrow[r, "RCH_2Cl", "-HCl"'] & (RCH_2)NH \arrow[r, "-HCl"'] & (RCH_2)_3N \arrow[d, "-HCl"', "RCH_2Cl"] \\ & & & (RCH_2)_3\overset{+}{N}\overset{-}{Cl} \end{tikzcd}$$

Q. 4. Complete the following reactions :

(i) $C_6H_5NH_2 + H_2SO_4$ (conc.) →

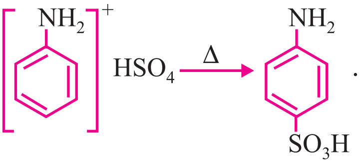
(ii) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(iii) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(iv) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(v) $C_6H_5NH_2 + CHCl_3 + 3KOH$ (alc.) →

Ans. (i)



(ii) $C_6H_6 + N_2 + HCl + CH_3CHO$

(iii) $C_6H_5NHCOCH_3 + CH_3COOH$

(iv) $C_6H_6 + H_3PO_3 + HCl + N_2$

(v) $C_6H_5NC + 3KCl + 3H_2O$

Q. 5. Write A, B and C in the given reactions :

(i) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$

(iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{HNO_2} B \xrightarrow[2\Delta]{H_2O/H^+} C$

(iv) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(v) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{partial hydrolysis}]{OH^-} B \xrightarrow{NaOH/Br_2} C$

Ans. (i) $C_6H_5CN, C_6H_5COOH, C_6H_5CONH_2$

(ii) $CH_3CH_2CN, CH_3CH_2NH_2, CH_3CH_2OH$

(iii) $C_6H_5NH_2, C_6H_5N_2Cl, C_6H_5OH$

(iv) $CH_3CONH_2, CH_3NH_2, CH_3OH$

(v) $CH_3CH_2CN, CH_3CH_2CONH_2, CH_3CH_2NH_2$

Q. 6. Accomplish the following conversions :

(i) $C_6H_5NO_2 \rightarrow C_6H_5 - COOH$

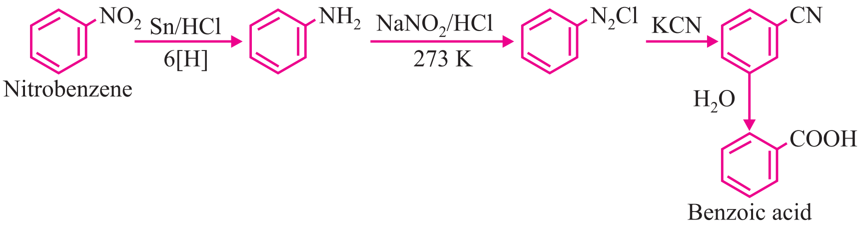
(ii) Benzene → m-bromophenol

(iii) $C_6H_5COOH \rightarrow C_6H_5NH_2$

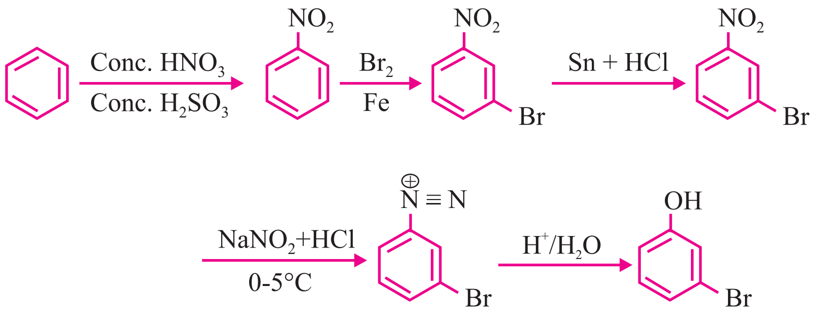
(iv) Aniline → 2, 4, 6 tribromoaniline

(v) Benzylchloride → 2-phenyl ethanamine

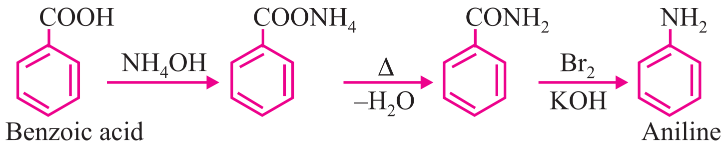
Ans. (i)



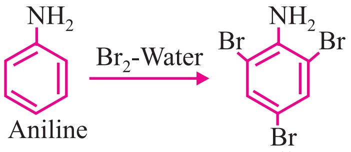
(ii)



(iii)

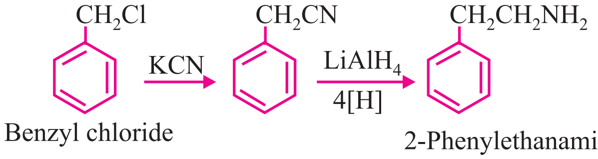


(iv)



2, 4, 6-Tribromoaniline

(v)



2-Phenylethanamine

Q. 7. Given reasons : (i) Acetylation of aniline reduces its activatino effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$

(iii) Although $–NH_2$ group is o/p directing , yet aniline on nitration gives a significant amount of m-nitroaniline

(ii) Benzene → m-bromophenol

Ans. (i) Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group/resonating structures.

(ii) Because of +I effect in methylamine electron density at nitrogen increases whereas in aniline resonance takes place and electron density on nitrogen decreases / resonating structures.

(iii) Due to protonation of aniline / formation of anilinium ion

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Sushil's friend want to play Holi with synthetic colours. Ramesh persuades his friends to play Holi with natural colours as synthetic colours may cause skin allergy. Sushil's friends agreed and prepared natural colours using flowers and leaves.

How are following dyes prepared from phenol :

(i) p-hydroxyazobenzene

(ii) p-aminoazobenzene

(iii) Write the name of one pigment present in natural colours. (Hint : Cartenoids)

(iv) Mention the values shown by Sushil.

Q. 2. Neetu and Asha took organic compound synthesis as their chemistry project. They prepared benzene diazonium chloride and stored it at room temperature. Due to holiday, they start preparing azo dye but it cannot be prepared. Then, their friend Reena told them to prepare benzene diazonium chloride again and to use it immediately to prepare azo dye and they proceeds accordingly and prepared azo dye successfully.

(i) Write the chemical reaction involved in azo dye formation.

(ii) Write the values associated with the suggestion given by Reena.

How is diazonium salt used in the preparation of following dyes :

(iii) p-hydroxyazobenzene

(iv) p-aminoazobenzene

UNIT 14

BIOMOLECULES

1. **Carbohydrates :** These are optically active polyhydroxy aldehydes or ketones or the compounds which produce these on hydrolysis.

2. **Classification :**

   (i) **Monosaccharides :** Those carbohydrates which cannot be hydrolysed into further simpler carbohydrates. *E.g.,* glucose, fructose, galactose etc.

   (ii) **Disaccharides :** Those carbohydrates which produces two monosaccharides on hydrolysis. *E.g.,* sucrose, maltose and lactose.

   (iii) **Oligosaccharides :** Those carbohydrates which give two to ten monosaccharides on hydrolysis.

   (iv) **Polysaccharides :** Those carbohydrates which on hydrolysis give large number of monosaccharides hydrolysis. *E.g.,* starch, cellulose, glycogen.

3. **Sugar :** Carbohydrates which are sweet in taste.

   (i) **Reducing sugars :** Those which reduce Fehling's or Tollen's reagent due to availability of free aldehydic groups. *E.g.,* glucose, fructose, galactose.

   (ii) **Non-reducing sugars :** Those which do not reduce Fehling's or Tollen's reagent. They do not have free aldehydic group. *E.g.,* sucrose.

4. **Glucose :** It is a monosaccharide with molecular formula $C_6H_{12}O_6$.

5. **Preparation :**

   (i) **From sucrose :**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad \text{(only from sucrose)}$$

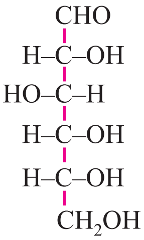
   (ii) **From starch :**

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

6. **Structure :**

   Fischer structure :

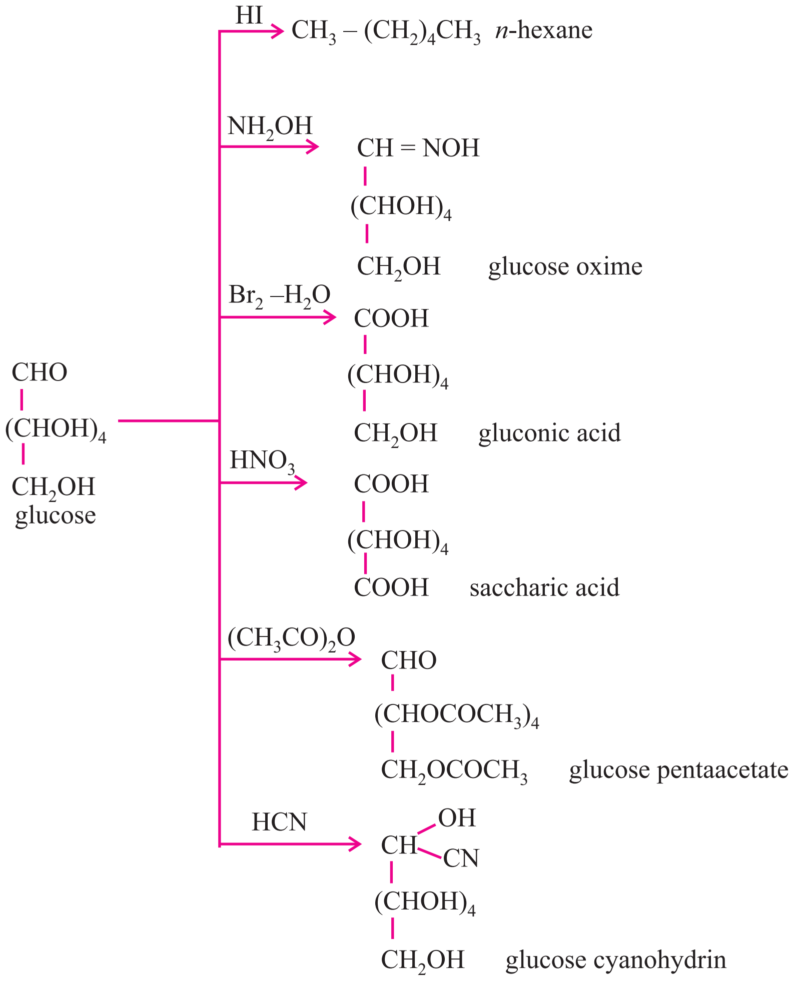
   (+) glucose has 'D' configuration as shown :



D-(+)-glucose

'D'- means – OH group on first chiral 'C' from the bottom is on right hand and (+) means it is dextrorotatory *i.e.,* it rotates plane polarized light towards right.

Reactions of glucose :



Objections against open chain structure of glucose

The open chain structure was unable to explain the following reactions :

(a) It does not give the 2, 4-DNP test, Schiff's test and does not form the hydrogensulphite product with $NaHSO_3$.

(b) The pentacetate of glucose does not react with NH_2OH, indicating the absence of free aldehydic group.

(c) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

After which a close chain (cyclic) structure of glucose was proposed by Haworth.

* Anomers are isomers which have a different configuration at C-1 functional group c-atom

7. **Glycosidic linkage :** The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

8. **Proteins :** These are macro molecules made up of amino acids joined by amide linkage [– (– CONH –) –] is here called as peptide linkage. These are required for growth and development of the body.

9. **Amino acids :** These contain an amino (- NH_2) and an acidic (- COOH) group and are therefore amphoteric in nature. In solution they exist in the form of zwitter ion (a dipolar ion).

10. **Classification**

Fibrous Protein	Glubular Protein
(i) Polypeptide chains run par`allel or anti-parallel and held together by hydrogen and disulphide bonds.	(i) Chains of polypeptide coil around to give a spherical shape.
(ii) Generally insoluble in water *e.g.,* keratin, collagen, myosin, fibroin.	(ii) Usually soluble in water, *e.g.,* insulin, thyroglobin, albumin, haemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.

11. **Structure and shape of protein (Ref. page no. 416 NCERT Book)**

Primary structure	Secondary structure	Tertiary structure	Quaternary structure
The specific sequence of amino acids in the polypepide chain. Change in amino acids sequence changes the protein completely. They have covalent bonds.	It is the shape in which the long polypeptide chain can exist. It is of two types : α-helix and β-pleated. These structures arise due to regular folding of the backbone of the polypeptide chain due to H-bonding between the C = O and – NH – groups of the peptide bond.	Represents overall folding of the polypeptide chain. It gives rise to the fibrous or globular molecular shapes. Forces stabilizing the 2° and 3° structures are hydrogen bonds, disulphide linkages, van der Waal's and electrostatic forces of attraction.	Protein can be composed of two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units with respect to each other is quaternary structure of the protein.

12. **Native state of protein :** The parental state or the natural state in which the protein is found.

13. **Denaturation of protein :** Destruction of the native state of protein is denaturation. It can be brought by physical and chemical methods. The 2° and 3° structures are destroyed, only 1° structure is retained.

    Enzymes : These are biocatalyst and generally globular proteins *e.g.,* invertase, zymase, phenylalanine hydroxylase, urease etc.

    Main characteristics of enzymes :

    (i) It speed up the biological reaction upto million times.

    (ii) It is highly specific and work on lock and key theory.

    (iii) It is highly sensitive to pH and temperature.

14. **Vitamins :** They are organic compounds required in the diet in small amounts to perform specific biological functions for maintenance of optimum growth and health of the organism. They are classified as follows :

    (i) Fat soluble vitamins : Vitamin A, D, E and K. They are stored in liver and adipose tissues.

(ii) Water soluble vitamins : B group vitamins and vitamin C. They need to supplied regularly in diet as they are excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Their deficiency causes diseases. (Ref. table in page no. 418 of NCERT Book)

Biotin (Vit H) is however neither fat nor water soluble. Its deficiency leads to loss of hair.

15. **Nucleic acids :** These are biomolecules which are long chain polymers of nucleotides. They are of two types :

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

16.

Vitamin	**Deficiency disease**
A	Xerophthalmia, night blindness
B_1	Beri-beri
B_2	Ariboflavinosis, cheilosis, burning sensation of skin
B_{12}	Pernicious anaemia, inflammation of tongue and mouth
C	Scurvy
D	Rickets & osteomalacia
E	Increased fragility of RBC and muscular weakness
K	Increased blood clotting time
H	Loss of hair

17. Hormones are chemical substances which are produced in ductless glands in the body.

18. Nuceloside = Base + Sugar

Nucleotide = Base + Sugar + Phosphate

19.

DNA	**RNA**
(i) Double helical.	(i) Single stranded.
(ii) Sugar is 2-deoxyribose.	(ii) Sugar is ribose.
(iii) Bases : A, T, G, C.	(iii) Bases : A, U, G, C.
(iv) Property of replication.	(iv) Do not replicate.
(v) It is responsible for transmission of heredity character.	(v) Helps in protein biosynthesis.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Name polysaccharides which is stored in the liver of animals.

Ans. Glycogen.

Q. 2. What structural feature is required for a carbohydrate to behave as reducing sugar ?

Ans. The carbonyl group of any one monosaccharide present in carbohydrate should be free.

Q. 3. Give the significance of (+) sign in the name D-(+)-glucose.

Ans. (+) sign indicates dextro-rotatory nature of glucose.

Q. 4. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give reason.

Ans. The – CHO group reacts with – OH group at C-5 to form a cyclic hemiacetal.

Q. 5. Why is sucrose called invert sugar ?

Ans. When sucrose is hydrolysed by water, the optical rotation of solution changes from positive to negative.

Q. 6. Name the amino acid which is not optically active.

Ans. Glycine.

Q. 7. Give reason :

Amylase present in the saliva becomes inactive in the stomach.

Ans. HCl present in stomach decreases the pH.

Q. 8. Which forces are responsible for the stability of α-helical structure of proteins ?

Ans. Hydrogen bonding.

Q. 9. Which nucleic acid is responsible for carrying out protein synthesis in the cell ?

Ans. RNA (Ribonucleic acid)

Q. 10. When RNA is hydrolysed, there is no relationship among quantities of different bases obtained. What does this fact suggest about structures of RNA ?

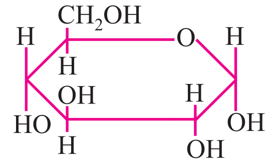
Ans. RNA is single stranded.

Q. 11. What type of linkage holds together the monomers of DNA and RNA ?

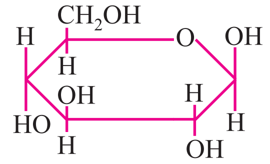
Ans. Phosphodiester linkage.

Q. 12. Give the Howarth projection of D-glucopyranose.

Ans.



α-D(+) Glucopyranose



β-D(+) Glucopyranose

Q. 13. Name the vitamin responsible for coagulation of blood.

Ans. Vitamin K.

Q. 14. Where does the water present in the egg go after boiling the egg ?

Ans. On boiling, during denaturation process water gets absorbed in denaturated proteins.

Q. 15. What is native state of protein ?

Ans. The energetically most stable shape of the protein at normal pH and temperature is called native state.

Q. 16. Why is cellulose not digested in human body ?

Ans. It is due to the fact that human beings do not have enzyme to digest cellulose.

Q. 17. Name the enzyme that is used to dissolve blood clots ?

Ans. Streptokinase.

Q. 18. Name two diseases caused due to deficiency of enzymes.

Ans. Albinism and phenyl keto urea.

Q. 19. Give one example of : (a) water soluble, (b) fat soluble vitamins.

Ans. (a) Vitamin C (b) Vitamin D

Q. 20. Name a protein which is insoluble in water.

Ans. Keratin.

Q. 21. Name the deficiency disease resulting from lack of Vitamin 'A' in the diet.

Ans. Night blindness, Xerophthalmia.

Q. 22. Mention two important functions of carbohydrates in plants.

Ans. Major energy source, storage molecules like starch in plants.

Q. 23. Name two of the different types of RNA molecules found in cells of organisms.

Ans. tRNA, mRNA, rRNA.

Q. 24. The deficiency of which vitamin causes the disease pernicious anaemia ?

Ans. Vitamin B_{12}.

Q. 25. Why are carbohydrates generally optically active ?

Ans. Because they contain one or more chiral atom.

Q. 26. During curdling of milk, what happens to sugar present in it ?

Ans. Lactose changes to lactic acid.

Q. 27. What are the products of hydrolysis of lactose ?

Ans. β-D-galactose and β-D-glucose.

Q. 28. The two strands in DNA are not identical but complementary. Explain.

Ans. Base pairing rule is followed; A = T and G ≡ C.

Q. 29. If one strand of DNA has the sequence 5’-G-G-A-C-T-A-C-T-3’, what is the sequence of bases in the complementary strand ?

Ans. 3’-C-C-T-G-A-T-G-A-5’

Q. 30. What are monosaccharides ?

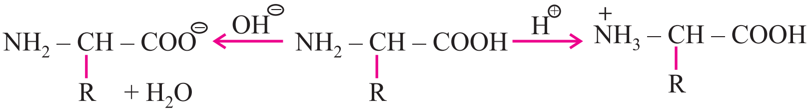
Ans. Sugars which cannot be hydrolysed to give simpler units or compounds.

Q. 31. What is the difference between native protein and denatured protein ?

Ans. Proteins found in a biological system with unique 3D-structure and biological activity is called native protein. When native protein is subjected to physical and chemical change, protein loses its biological activity and is called denatured protein.

Q. 32. Amino acids are amphoteric in nature. Explain.

Ans. It can react with acid and base both as per the following reaction :



$$NH_2-\underset{\underset{R}{|}}{CH}-COO^{\ominus} + H_2O \xleftarrow{OH^{\ominus}} NH_2-\underset{\underset{R}{|}}{CH}-COOH \xrightarrow{H^{\oplus}} \overset{+}{N}H_3-\underset{\underset{R}{|}}{CH}-COOH$$

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Define the following terms in relation to proteins :

(i) Peptide linkage **(ii) Denaturation**

Ans. (i) **Peptide linkage :** A link between two amino acids with loss of water /– CO – NH – peptide linkage.

(ii) A process that changes the three dimensional structure of native protein is called denaturation of protein. It results into breaking of hydrogen bonds and disulphide linkages. Thus, a completely denatured protein has a shape of random coil.

Q. 2. List the reactions of glucose which cannot be explained by its open chain structure.

Ans. (i) Despite having the aldehyde group, glucose does not give 2, 4 DNP test or Schiff's test.

(ii) It does not form hydrogensulphite addition product with $NaHSO_3$.

(iii) The penta acetate of glucose does not react with hydroxylamine indicating the absence of free – CHO group.

Q. 3. Explain what is meant by :

(i) Biocatalyst **(ii) Peptide linkage**

Ans. (i) Biocatalysts are the catalysts which increases the rate of metabolism/ biochemical reactions.

(ii) **Peptide linkage :** A link between two amino acids with loss of water/– CO – NH – peptide linkage.

Q. 4. Explain the following terms :

(i) Invert sugar **(ii) Polypeptides**

Ans. (i) An equimolar mixture of glucose and fructose produced on hydrolysis of sucrose is called invert sugar. It is called so because sucrose is dextro rotatory whereas its hydrolysis product is laevo rotatory.

(ii) Polypeptides are polymers of amino acids containing less than 100 amino acids. For example, oxytocin, vasopressin, etc.

Q. 5. Explain what is meant by :

(i) Peptide linkage **(ii) Glycosidic linkage**

Ans. (i) Refer Q1 of SA-I type question

(ii) The linkage between the monosaccharide units through oxygen is called glycosidic linkage.

Q. 6. Name the product of hydrolysis of sucrose. Why is sucrose not a reducing sugar ?

Ans. On hydrolysis, sucrose gives equimolar mixture of D-(+)-glucose and D-(−)-fructose. Sucrose is not a reducing sugar as glucose and fructose are linked through their reducing centres in structure of sucrose.

Q. 7. State clearly what are known as nucleotides and nucleosides.

Ans. A nucleoside contain only two basic components of nucleic acids *i.e.,* pentose sugar and nitrogenous base.

A nucleotide contains all the three basic components of nucleic acids *i.e.,* a phosphoric acid group, pentose sugar and nitrogenous base.

Q. 8. Describe what do you understand by primary structure and secondary structure of proteins.

Ans. **Primary structure of proteins :** The protein in which amino acids linked with each other in a specific sequence is said to be the primary structure of that protein.

Secondary structure of proteins : It refers to the shape in which a long polypeptide chain can exist *i.e.,* α-helix and β-pleated structure.

Q. 9. What is essentially the difference between α-form of glucose and β-form of glucose ? Explain.

Ans. α-form of glucose and β-form of glucose differ only in the configuration of the hydroxyl group at C_1 in cyclic structure of glucose/hemiacetal form of glucose.

Q. 10. Explain :

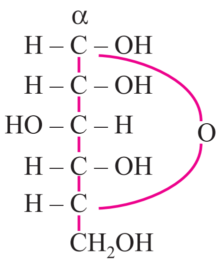
(i) Mutarotation **(ii) Avitaminosis**

Ans. (i) Mutarotation : Spontaneous change in specific rotation of an optically active compound with time, to an equilibrium value is called mutarotation.

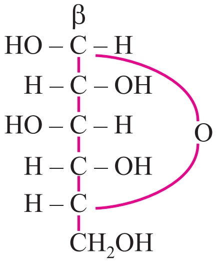
(ii) Avitaminosis : Multiple deficiencies caused by lack of more than one vitamin is called avitamineosis.

Q. 11. What are anomers ? Give the structures of two anomers of glucose.

Ans. Monosaccharides which differs in configuration at functional *gp-c*-atom (C_1 and C_2), *e.g.,* α-glucose and β-glucose.



α-Glucose



β-Glucose

Q. 12. Write the hydrolysed product of :

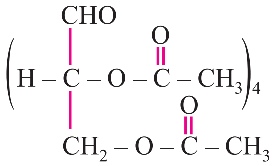
(i) Maltose **(ii) Cellulose**

Ans. (i) α-D-glucose (ii) β-D-glucose

Q. 13. (i) Acetylation of glucose with acetic anhydride gives glucose penta-acetate. Write the structure of penta acetate.

(ii) Explain why glucose penta acetate does not react with hydroxylamine ?

Ans. (i)



$$\begin{array}{c} CHO \\ | \\ \left(H-C-O-\overset{\overset{O}{\|}}{C}-CH_3 \right)_4 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3 \end{array}$$

Glucose pentaacetate

(ii) The molecule of glucose penta acetate has a cyclic structure in which – CHO is involved in ring formation.

Q. 14. What are vitamins ? How are they classified ?

Ans. Vitamins are a group of biomolecules (other than carbohydrates, fats and proteins) most of which cannot be produced by body but must be supplied in small amount to perform specific biological functions of the body.

Types :

(i) Water soluble vitamins : Vitamin B and C.

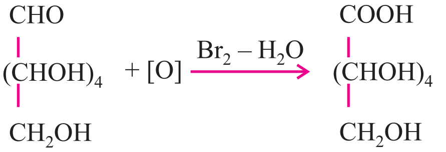
(ii) Fat soluble vitamins : Vitamin A, D, E and K.

Q. 15. Write the products of oxidation of glucose with :

(i) Bromine water

(ii) Nitric acid

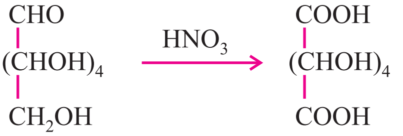
Ans. (i)



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} + [O] \xrightarrow{Br_2 - H_2O} \begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}$$

Glucose Gluconic acid

(ii)



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array} \xrightarrow{HNO_3} \begin{array}{c}COOH\\|\\(CHOH)_4\\|\\COOH\end{array}$$

Glucose Saccharic acid

Q. 16. State two main differences between globular and fibrous proteins.

Ans.

	Globular protein		**Fibrous protein**
(i)	They form a α-helix structure.	(i)	They have β-pleated structure.
(ii)	They are water soluble.	(ii)	They are water insoluble.

Q. 17. (i) Name the disease caused by deficiency of vitamin D.

(ii) Why cannot vitamin C be stored in our body ?

Ans. (i) Rickets.

(ii) Vitamin C is a water soluble vitamin which is excreted in urine and cannot be stored in our body.

Q. 18. Name the constituents of starch and what is the difference between them ?

Ans. Amylase : A linear polymer of α-glucose, water soluble.

Amylopectin : Branched polymer of α-glucose, water insoluble.

Q. 19. What are essential and non-essential amino acid ? Give two examples of each type.

Ans. Essential amino acids are those which are not produced in our body and required to be supplied from outside, *e.g.,* valine, leucine.

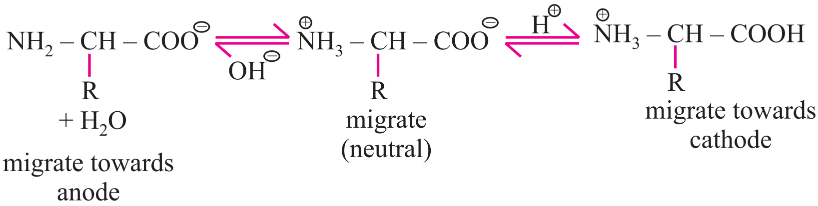
Non-essential amino acids are those which are produced by our body, *e.g.,* glycine, alanine.

Q. 20. Give reasons :

(i) On electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution these migrate towards anode.

(ii) The monoamino monocarboxylic acids have two pk values.

Ans. (i)



$$\underset{\underset{R}{|}}{NH_2-CH}-COO^{\ominus} + H_2O \underset{OH^{\ominus}}{\rightleftharpoons} \overset{\oplus}{N}H_3-\underset{\underset{R}{|}}{CH}-COO^{\ominus} \overset{H^{\oplus}}{\rightleftharpoons} \overset{\oplus}{N}H_3-\underset{\underset{R}{|}}{CH}-COOH$$

(ii) Due to zwitter ion formation.

Q. 21. Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

Ans. Protein albumin present in egg white gets denatured *i.e.,* 2° & 3° structures are destroyed and 1° structure is retained.

Q. 22. Describe two important functions of nucleic acids.

Ans. (i) DNA is responsible for transfer of heredity information from one generation to another.

(ii) RNA is responsible for protein synthesis.

Q. 23. Hormones are called chemical messengers. Explain.

Ans. Hormones are molecules that act as intercellular messengers. These are produced by endocrine glands in the body and are poured directly in the blood stream which transports them to the site of action.

For example,

(i) Glucocorticoids control carbohydrate metabolism.

(ii) Testosterone is responsible for development of 2° male characteristics like deep voice, facial hair or general physical constitution.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (i) Deficiency of which vitamin causes scurvy ?

(ii) What type of linkage is responsible for the formation of proteins ?

(iii) Write the product formed when glucose is treated with HI.

Ans. (i) Vitamin C.

(ii) Peptide linkage.

(iii) n-hexane.

Q. 2. (i) Write the name of two monosaccharides obtained by hydrolysis of lactose sugar.

(ii) Why vitamin C cannot be stored in our body ?

(iii) What is the difference between nucleotide and nucleoside ?

Ans. (i) β-D-glucose and β-D-galatose.

(ii) Water soluble, excreted out of body.

(iii) In nucleotide, phosphoric acid/phosphate group attached to the nucleoside/ nucleotide = base + sugar + phosphate group, nucleoside = base + sugar.

Q. 3. (i) Deficiency of which vitamin causes night blindness ?

(ii) Name the base that is found in nucleotide of RNA only.

(iii) Glucose on reaction with HI gives n-hexane. What does it suggest about structure of glucose ?

Ans. (i) Vitamin A.

(ii) Uracil.

(iii) This reaction suggests that all six carbon atoms in glucose are arranged in a straight chain.

Q. 4. Differentiate between the following :

(i) Secondary and tertiary structure of protein

(ii) α-helix and β-pleated sheet structure of protein

(iii) Fibrous and globular protein

Ans. (i) **Secondary structure** is responsible for the shape of protein α-helix and β-pleated sheets in which polypeptide chains have peptide bonds.

Tertiary structure represents overall folding of polypeptide chain and give rise to the fibrous or globular molecular shape.

(ii) **α-helix structure :** The peptide chains coiled up to form right handed helix involving H-bonding (Intramolecular).

β-pleated sheets : The peptide chains lie side by side together by intermolecular hydrogen bonding.

(iii) Same as Q. 16 (Two marks questions)

Q. 5. (i) Name the four bases present in DNA.

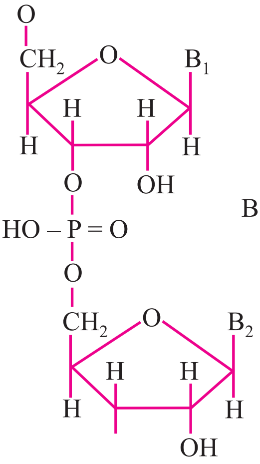
(ii) Which of them is not present in RNA ?

(iii) Give the structure of a nucleotide of DNA.

Ans. (i) Adenine, Guanine, Thymine, Cytosine.

(ii) Thymine.

(iii)



B_1 & B_2 = Nitrogeneous bone
(Adeninine, guanine,
Cytasine or thymine)

Q. 6. Define with example :

(i) Isoelectric point **(ii) Mutarotation** **(iii) Transcription**

Ans. (i) Isoelectric point : The pH at which there is no net migration of any ion towards electrode *e.g.,* amino acids have isoelectric point at pH = 5.5-6.3.

(ii) Mutarotation : It is spontaneous change in optical rotation when an optically active substance is dissolved in water *e.g.,* α-glucose when dissolved in water changes its optical rotation from 111° to 52.5°.

(iii) Transcription : It is process by which m-RNA is generated from DNA *e.g.,* if DNA has base sequence ATACA then m-RNA has base sequence UAUGU

Q. 7. Glucose or sucrose are soluble in water but cyclohexane and benzene are insoluble in water. Explain.

Ans. Glucose contain 5 – OH groups and sucrose contain eight – OH groups, because of this they form intermolecular hydrogen bonding, so they are soluble in water.

But benzene and cyclohexane doesn't contain – OH groups hence doesn't form intermolecular hydrogen bonding, so they are not soluble in water.

Q. 8.(i) Fructose contains a keto group but still it reduces Tollen's reagent. Explain.

(ii) Give the chemical name and sources of :

(a) Vitamin C **(b) Vitamin B_1**

Q.9.Name the components of starch. How do they differ from each other structurally ?

Ans. Amylose and Amylopectin.

Amylose is long unbranched chain with α-D-glucose units held by C1-C4 glycosidic linkage.

Amylopectin is branched chain polymer of α-D-glucose formed by C1-C4 glycosidic linkage and branching occurs by C1-C6 glycosidic linkage.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (i) Give one example each of fibrous protein and globular protein.

(ii) What happens when D-glucose reacts with Br_2 water ?

(iii) What type of linkage is responsible for the formation of protein ?

(iv) Explain mutarotation with suitable example.

Ans. (i) Fibrous protein : Keratin

Globular protein : Hormone

(ii) $C_6H_{12}O_6 + Br_2$ water → gluconic acid

(iii) Peptide bond

(iv) Spontaneous change in specific rotation of an optically active compound with time, to an equilibrium value is called mutarotation. For example,

$$\alpha\text{-D glucose} \rightleftharpoons \text{Equilibrium mixture} \rightleftharpoons \beta(\text{D})\text{glucose}$$

$$[\alpha]_D = +111^\circ \qquad [\alpha]_D = +52.5^\circ \qquad [\alpha]_D = +19.2^\circ$$

Q. 2. (i) Name the three major classes of carbohydrates and give an example of each of these classes.

(ii) Answer the following :

(a) What type of linkage is responsible for primary structure of proteins ?

(b) Name the location where protein synthesis occurs in our body

Ans. (i) Carbohydrates are classified as :

(a) Monosaccharides *e.g.,* Glucose.

(b) Oligosaccharides *e.g.,* Sucrose

(c) Polysaccharides *e.g.,* Starch

(ii) (a) Peptide bond

(b) Protein synthesis occurs in cytoplasm of cell by mRNA with the help of rRNA and tRNA.

HOTS

Q. 1. An optically active compound having molecular formula $C_6H_{12}O_6$ is found in two isomeric forms [A] and [B] in nature. When [A] and [B] are dissolved in water, they show the following equilibrium :

$$\textbf{A} \rightleftharpoons \textbf{Equilibrium mixture} \rightleftharpoons \textbf{B}$$

$$[\alpha]_D = 111^\circ \qquad 52.2^\circ \qquad (19.2^\circ)$$

(i) What are such isomer called ?

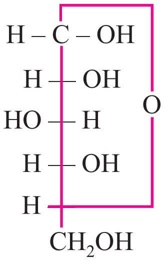
(ii) Can they be called enantiomers ? Justify your answer.

(iii) Draw cyclic structure of isomer (A).

Ans. (i) Such isomers are called **anomers.**

(ii) These anomers cannot be called enantiomers because they are not mirror images of each other (or they do not rotate the plane polarized light equally but in opposite directions).

(iii) Cyclic structure of A [α-D(+)-glycopyranose] is given as :



α-D(+)–Glucopyranose

Q. 2. Name the vitamins whose deficiency is responsible for :

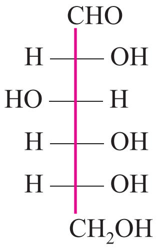
(i) Night blindness **(ii) Poor coagulation of blood**

(iii) Sterility

Ans. (i) Vitamin A (ii) Vitamin K

(iii) Vitamin E

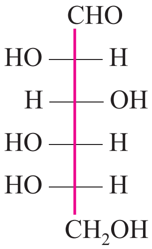
Q. 3. The Fischer projection of D-glucose is :



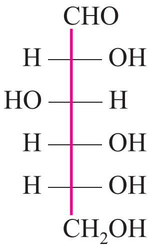
(i) Give the Fischer projection of L-glucose.

(ii) What happens when L-glucose is treated with Tollen's reagent ?

Ans. (i) The Fischer projection of L-glucose is the mirror image of D-glucose.

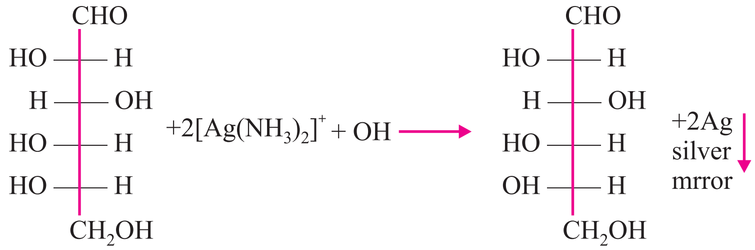


L-Glucose



D-Glucose

(ii) L-glucose reduces Tollen's reagent to silver mirror.



L-Glucose L-Glucose acid

Q. 4. An optically active amino acid (A) can exist in three forms depending on the pH of the medium. The molecular formula of (A) is $C_3H_7NO_2$.

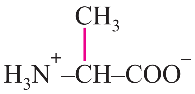
(i) Write the structure of compound (A) in aqueous medium. What are such ions called ?

(ii) In which medium will the cationic form of compound (A) exist ?

(iii) In alkaline medium, towards which electrode will the compound (A) migrate in electric field ?

Ans. A = Alanine.

(i) An aqueous medium alanine exists as Zwitter ion.



$$H_3\overset{+}{N}-\overset{CH_3}{\overset{|}{CH}}-COO^-$$

Alanine

(ii) In acidic medium.

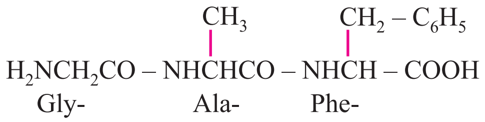
(iii) In alkaline medium, it will exist in anionic form and will migrate towards anode in electric field.

Q. 5. If three amino acids viz., glycine, alanine and phenyl alanine react together, how many possible tripeptides can be formed ? Write down the structures and names of each one. Also write their names using three and one letter abbreviations for each amino acid.

Ans. If each of the amino acids is used only once, then six tripeptides are possible :

(i) Glycylalanyl phenylalanine.

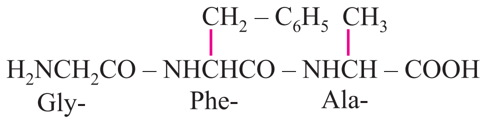
(Gly-Ala-Phe) (G–A–F).



$$\underset{\text{Gly-}}{H_2NCH_2CO} - \underset{\text{Ala-}}{NH\overset{\overset{CH_3}{|}}{C}HCO} - \underset{\text{Phe-}}{NH\overset{\overset{CH_2 - C_6H_5}{|}}{C}H} - COOH$$

(ii) **Glycylphenylalanyl alanine.**

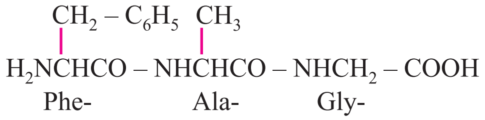
(Gly-Phe-Ala) (G–F–A).



$$\underset{\text{Gly-}}{H_2NCH_2CO} - \underset{\text{Phe-}}{NH\overset{\overset{CH_2 - C_6H_5}{|}}{C}HCO} - \underset{\text{Ala-}}{NH\overset{\overset{CH_3}{|}}{C}H} - COOH$$

(iii) **Phenylalanylalanyl glycine.**

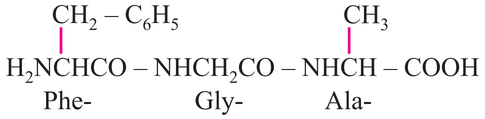
(Phe-Ala-Gly) (F–A–G).



$$\underset{\text{Phe-}}{H_2N\overset{\overset{CH_2 - C_6H_5}{|}}{C}HCO} - \underset{\text{Ala-}}{NH\overset{\overset{CH_3}{|}}{C}HCO} - \underset{\text{Gly-}}{NHCH_2} - COOH$$

(iv) **Phenylalanylglycyl alanine.**

(Phe-Gly-Ala) (F–G–A).



$$\underset{\text{Phe-}}{H_2N\overset{\overset{CH_2 - C_6H_5}{|}}{C}HCO} - \underset{\text{Gly-}}{NHCH_2CO} - \underset{\text{Ala-}}{NH\overset{\overset{CH_3}{|}}{C}H} - COOH$$

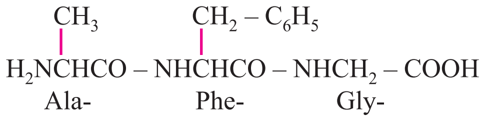
(v) **Alanylglycyl phenylalanine.**

(Ala-Gly-Phe) (A–G–F).

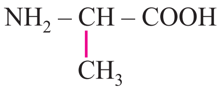
$$\underset{\text{Ala-}}{H_2N\overset{\overset{CH_3}{|}}{C}HCO} - \underset{\text{Gly-}}{NHCH_2CO} - \underset{\text{Phe-}}{NH\overset{\overset{CH_2 - C_6H_5}{|}}{C}H_2} - COOH$$

(vi) **Alanylphenylalanyl glycine.**

(Ala-Phe-Gly) (A–F–G).



$$\underset{\text{Ala-}}{H_2N\overset{\overset{CH_3}{|}}{C}HCO} - \underset{\text{Phe-}}{NH\overset{\overset{CH_2 - C_6H_5}{|}}{C}HCO} - \underset{\text{Gly-}}{NHCH_2} - COOH$$

Q. 6. Alanine has the structure  $NH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$ Write its structure at pH = 2 & pH = 10.

Q. 7. What forces are responsible for the stability of α-helix ? Why is it also known as 3.6_{13} helix ?

Q. 8. Activation energy for the acid catalysed hydrolysis of sucrose is 6.22 kJ/mol, while the activation energy is only 2.15 kJ/mol when hydrolysis is catalysed by enzyme sucrose. Explain.

Q. 9. Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in dinucleotides ? What does the word ‘diester’ in the name of linkage indicate ? Which acid is involved in the formation of this linkage ?

Q. 10. What is the smallest aldose which can form a cyclic hemiacetal ? Which functional groups are involved in its formation ?

MULTIPLE CHOICE QUESTIONS

Q. 1. Which one is the complementary base in RNA strand to the thymine base in DNA during protein synthesis ?

(a) Adenine (b) Uracil

(c) Cytosine (d) Guanine

Ans. (a)

Q. 2. Which of the vitamin deficiency causes Xerophthalmia ?

(a) A (b) B

(c) E (d) K

Ans. (a)

Q. 3. Which one is not present in RNA ?

(a) Uracil (b) Thymine

(c) Ribose (d) Phosphate

Ans. (b)

Q. 4. Which of the following is a disaccharide ?

(a) Fructose (b) Glucose

(c) Sucrose (d) Xylose

Ans. (c)

Q. 5. Fructose is a :

(a)	Aldose	(b)	Ketose
(c)	Both aldose and ketose	(d)	None of these

Ans (b)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. After watching a programme on TV about the adverse effects of junk food and soft drinks on the health of school children, Sonali, a student of class XII, discussed the issue with principal. They instructed canteen person to replace fast food with fibre & vitamin rich food like salad, fruits, sprouts etc. This decision was welcomed by the parents and students.

After reading above passage, answer the following :

(i) What values are expressed by Sonali & Principal of school ?

(ii) Give two examples of water soluble vitamins. *(DSB, 2013; CBSE, 2013)*

Ans. (i) Sonali : Concerned for society, socially active and helpful to others.

Principal : Caring, commanding and serious about the welfare of students.

(ii) Vitamin B and C.

UNIT 15

POLYMERS

1. **Polymer :** It is a very large molecule having molecular mass 10^3-10^7 g mol^{-1}. They are formed by joining together repeating structural units, called monomers.

2. **Classification of Polymers :**

(a) Based on Source :

(i) **Natural :** Found in plants and animals, e.g., Proteins, cellulose, natural rubber, silk, wool.

(ii) **Synthetic :** Man-made, e.g., Nylon, polyster, neoprene, bakelite, teflon, PVC, polystyrene.

(iii) **Semisynthetic :** Natural but modified by man e.g. cellulose nitrate.

(b) Based on Structure :

(i) **Linear polymers :** This consist of long and straight chain repeating units, e.g., Polythene (HDPE), PVC, nylon, polyester.

(ii) **Branched polymers :** This contain linear chains having some branches, e.g., amylopectin, glycogen etc.

(iii) **Cross-linked polymers :** Strong covalent bonds are present between various linear polymer chains, e.g., Bakelite, urea-formaldehyde polymer, melamine, formaldehyde polymer etc.

(c) Based on mode of polymerization :

(i) **Addition polymers :** These are formed by the repeated addition of monomer molecules possessing multiple bonds, e.g., polythene, polypropene, polystyrene, PMMA (polymethyl metha crylate).

(ii) **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, polyster, urea-formaldehyde resin.

(d) Based on molecular forces :

(i) **Elastomers :** Forces of interaction between polymer chains is weakest, e.g., natural rubber, neoprene, vulcanized rubber.

(ii) **Fibers :** Strong hydrogen bonds are present between the polymer chains. They have high tensie strength, e.g., Nylon, polyster, silk, wool, orlon, rayon etc.

(iii) **Thermoplastics :** They are linear/slightly branched chains molecules capable of repeated softening on heating and hardening on cooling, e.g., Polythene, PVC, polystyrene, polypropene.

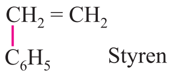
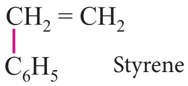
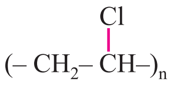
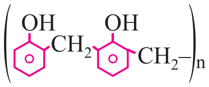
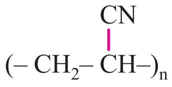
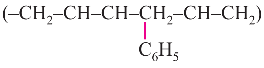
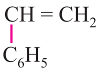
(iv) **Thermosetting plastics :** They are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g., Bakelite, urea-formaldehyde resin.

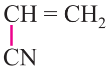
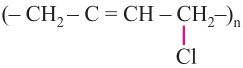
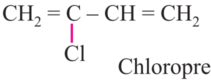
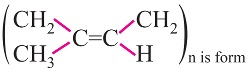
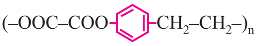
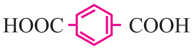
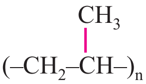
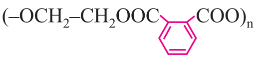
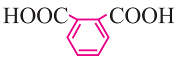
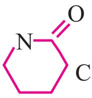
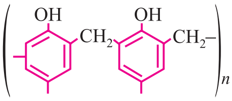
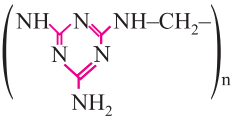
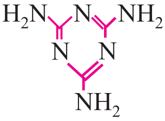
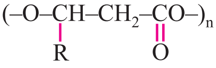
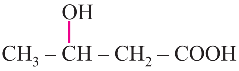
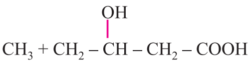
(e) **Based on growth of polymerization :** Depending upon the mechanism of polymerization, polymers are classified as :

(i) **Addition polymers or Chain growth polymers :** They follow mostly free radical mechanism.

(ii) **Condensation polymers or Step growth polymers :** Because they are formed in gradual steps.

Polymers and Their Monomers

S. No.	Name of Polymer	Structure	Monomer	Uses
1.	Polythene	$(-CH_2-CH_2-)_n$	$CH_2=CH_2$	As insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	 $\underset{C_6H_5}{CH_2}=CH_2$ Styren	 $\underset{C_6H_5}{CH_2}=CH_2$ Styrene	As insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	 $(-CH_2-\overset{Cl}{CH}-)_n$	$CH_2=CHCl$ Vinyl chloride	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Teflon	$(-CF_2-CF_2-)_n$	$CF_2=CF_2$ TFE	As lubricant, insulator and making cooking wares.
5.	NOVOLAC		(a) HCHO (b) C_6H_5OH	In making bonding give varnishes, lacquers etc.
6.	Polyacrylonitrile (Orion) (Acrilian)	 $(-CH_2-\overset{CN}{CH}-)_n$	$CH_2=CHCN$ Acrylonitrile	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or Buna-S)	 $(-CH_2-CH-CH-CH_2-\underset{C_6H_5}{CH}-CH_2)$	(a) $CH_2=CH-CH=CH_2$ (b)  $\underset{C_6H_5}{CH}=CH_2$	In making automobile tyres and footwear.

8.	Nitrile rubber (Buna-N)	 $(-CH_2-CH-CH-CH_2-CH-CH_2)$, CN on CH	(a) $CH_2 = CH - CH = CH_2$ (b)  $CH = CH_2$, CN	In making oil seals, manufacture of hoses and tank linings.
9.	Neoprene	 $(-CH_2-C=CH-CH_2-)_n$, Cl	 $CH_2 = C - CH = CH_2$, Cl Chloroprene	As insulator, making conveyor belts and printing rollers.
10.	Natural rubber (NR)		 $CH_2 = C - CH = CH_2$, CH_3 Isoprene	In making erasers, tyres, tubes, valcanised rubber etc.
11.	Terylene (Dacron)		(a)  (b) $HO - CH_2 - CH_2 - OH$	For making fibres, safety belts, tyre cords, tents etc.
12	Polypropene = P Propene	 $(-CH_2-CH-)_n$, CH_3	Propen $H_3 - CH = CH_2$	Ropes, toys, pipes, fibre etc. strings.
13.	Glyptal			As binding material in preparation of mixed plastics and plants.
14.	Nylon 6	 $(NH - [CH_2]_5 - \overset{O}{\overset{\parallel}{C}} -)_n$	 Capralactum	In making fibres, plastics, tyre cords and ropes.
15.	Nylon 66	$(NH - [CH_2]_4NHCO[CH_2]_4CO-)_n$	(a) $HOOC - (CH_2)_4 - COOH$ (b) $H_2N - (CH_2)_6 - NH_2$	In making brushes, synthetic fibres, parachutes, ropes and carpets.
16.	Bakellite		(a) HCHO (b) C_6H_5OH	For making gears, protective coating and electrical fittings.
17.	Urea formaldehyde resin	$(- NH - CO - NH - CH_2 -)_n$	(a) HCHO (b) NH_2CONH_2	For making unbreakable cups and laminated sheets.
18.	Melamine formaldehyde resin		(a)  (b) HCHO	In making plastic crockery, unbreakable cups and plates.
19.	Poly-β-hydroxy butyrate-co-β-hydroxy valerate [PHBV]	 $(-O-\underset{R}{CH}-CH_2-\underset{O}{\overset{\parallel}{CO}}-)_n$ $R = CH_3C_2H_5$	 $CH_3 - \overset{OH}{CH} - CH_2 - COOH$  $CH_3 + CH_2 - \overset{OH}{CH} - CH_2 - COOH$	As packaging, orthopaedic devices and in controlled drug release.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Define the term 'homopolymerisation' giving an example.

Ans. The polymer formed by the polymerization of single/same monomeric species is known as homopolymerisation. E.g., Polythene/PVC/Polypropene.

Q. 2. Give an example of elastomer.

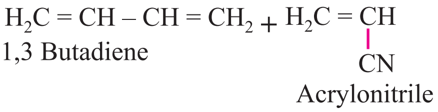
Ans. Natural rubber or Buna-S or Buna-N or Neoprene.

Q. 3. Why is bakelite a thermosetting polymer ?

Ans. Because bakelite have three dimensional network of covalent bonds with cross-linking between chains.

Q. 4. Write the monomers of Buna-N.

Ans.



$$H_2C = CH - CH = CH_2 + H_2C = \underset{\displaystyle CN}{\underset{|}{CH}}$$

1,3 Butadiene

Acrylonitrile

Q. 5. Is $\text{-[}H_2C\,CH(C_6H_5)\text{]-}_n$ a homopolymer or copolymer ? Why ?

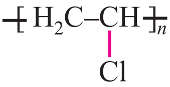
Ans. Homopolymer, because it is formed by polymerization of one kind of monomer species.

Q. 6. Write the structure and one use of urea formaldehyde resin.

Ans. $\text{-[}HNCONHCH_2\text{]-}_n$

It is used in unbreakable crockery.

Q. 7. Is



$\text{-[}H_2C{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{]-}_n$ **a homopolymer or a copolymer ?**

Ans. Homopolymer.

Q. 8. Which of the following is natural polymer ?

Buna-S, Proteins, PVC

Ans. Proteins.

Q. 9. Based on molecular forces what type of polymer is neoprene ?

Ans. Elastomer.

Q. 10. Which of the following is a fibre ?

Nylon, Neoprene, PVC

Ans. Nylon

Q. 11. Name a natural elastomer.

Ans. Natural rubber.

Q. 12. Write name of a synthetic polymer which is an ester.

Ans. Terylene.

Q. 13. Name of monomer of Nylon 6.

Ans. Caprolactum

Q. 14. Write the monomer units of bakelite.

Ans. Phenol and formaldehyde.

Q. 15. Define a copolymer.

Ans. The polymers made by addition polymerisation from two different monomers are termed as copolymers. E.g., Buna-S, Buna-N etc.

Q. 16. Write one use of PVC.

Ans. In manufacture of raincoats and vinyl flooring.

Q. 17. Define polymer.

Ans. Polymer is defined as very large molecules having molecular mass (10^3-10^7 u). These are also referred to as macromolecules.

Q. 18. Give an example of thermoplastics.

Ans. Thermoplastics are polythene, polystyrene, polyvinyls etc.

Q. 19. To which class of polymers does Nylon-66 belong ?

Ans. Polyamides.

Q. 20. Name the type of monomers in terylene.

Ans. Ethylene glycol and terephthalic acid.

Q. 21. How do you explain the functionality of a monomer ?

Ans. Functionality means the number of bonding sites in a molecule. E.g.,

$\curvearrowleft CH_2 \div CH_2 \curvearrowright$

Q. 22. Give chemical name of teflon.

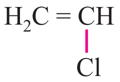
Ans. Polytetrafluoroethene.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Draw the structure of monomers of each of the polymers :

(i) PVC **(ii) Nylon-6**

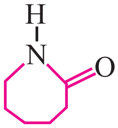
Ans. (i)



$H_2C = CH-Cl$

Vinyl chloride

(ii)



Caprolactum

Q. 2. What is the repeating unit in the condensation polymer obtained by combining HOOCCH$_2$CH$_2$COOH (succinic acid) and H$_2$NCH$_2$CH$_2$NH$_2$ (ethylene diamine) ?

Ans.

$$nHOOC-CH_2CH_2COOH + nH_2NCH_2CH_2NH_2 \longrightarrow \left(\overset{O}{\overset{\|}{C}} - CH_2CH_2\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - CH_2CH_2\overset{H}{\overset{|}{N}} \right)_n$$

Q. 3. Draw the structure of monomers of the following polymers :

(i) Teflon **(ii) Polythene**

Ans. (i) $F_2C = CF_2$ Tetrafluoroethene

(ii) $H_2C = CH_2$ Ethene

Q. 4. Name the two groups into which polymers are classified on the basis of magnitude of intermolecular forces.

Ans. (i) Elastomers

(ii) Fibres

(iii) Thermoplastic polymers

(iv) Thermosetting polymers

Q. 5. Mention two important uses of each of the following :

(i) Bakelite **(ii) Nylon-6**

Ans. (i) Bakelite : For making combs, electrical switches, handles of utensils, computer disc etc.

(ii) Nylon-6 : For making tyre cords, fabrics, ropes etc.

Q. 6. Distinguish between homopolymers and copolymers with an example of each.

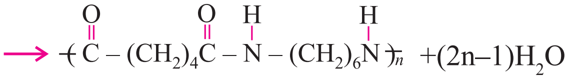
Ans. **Homopolymers :** Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers. For example, Polythene.

Copolymers : Polymers whose repeating structural units are derived from two or more types of monomer units are called copolymers. For example, Nylon-6, 6.

Q. 7. What is step growth polymerisation ? Explain with an example.

Ans. Step growth polymerisation involves condensation between monomers having multifunctional groups. It is also known as condensation polymerisation. E.g.,

$$nHOOC{-}(CH_2)_4{-}COOH + nH_2N{-}(CH_2)_6NH_2$$



$$\longrightarrow \left[\overset{O}{\overset{\|}{C}} - (CH_2)_4\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6\overset{H}{\overset{|}{N}} \right]_n + (2n-1)H_2O$$

Nylon 6, 6

Q. 8. What is the difference between elastomers and fibres ? Give one example of each.

Ans. **Elastomers :** Polymers in which the intermolecular forces of attraction between the polymer chains are weakest are called elastomers. E.g., Natural rubber.

Fibres : Polymers in which intermolecular forces of attraction are the strongest are called fibres. E.g., Nylon-6, 6.

Q. 9. Mention the important uses of each :

(i) Nylon-6, 6 **(ii) PVC**

Ans. (i) Uses of Nylon-6, 6 :

(a) It is used in making carpets, textile fibres etc.

(b) It is used for making elastic hosiery.

(ii) Uses of PVC :

(a) It is used for making raincoats, hand bags etc.

(b) It is used in making water pipes.

Q. 10. Arrange the following polymers in the order of increasing intermolecular forces :

(i) Nylon-6, Buna-S, Polythene

(ii) Nylon-6, Neoprene, Polyvinyl chloride

Ans. (i) Buna-S < Polythene < Nylon-6

(ii) Neoprene < Polyvinyl chloride < Nylon-6

Q. 11.Define thermoplastic and thermosetting polymers. Give one example of each.

Ans. **Thermoplastics :** Polymers in which the intermolecular forces of attraction are in between those of elastomers and fibres are called thermoplastics. E.g., Nylon-6, PVC, etc.

Thermosetting polymers : These are semi-fluid substances with low molecular masses which when heated in a mould undergo a permanent change in chemical composition to give hard, infusible and insoluble mass. E.g., Bakelite.

Q. 12.What is biodegradable polymer ? Give an example of a biodegradable polymer.

Ans. Biodegradable polymers are those which are decomposed by micro organisms. E.g., PHBV (Poly-B-hydroxybutyrate – Co – B – hydroxyl valerate).

Q. 13.How does vulcanization change the character of natural rubber ?

Ans. It introduce sulphur bridge or cross-link between polymer chain.

Q. 14.Name a polymer each for the following applications :

(i) Insulation of electrical switches

(ii) Making laminated sheets

Ans. (i) Bakelite (ii) Urea formaldehyde resin

Q. 15. How does the presence of double bonds in rubber influence their structure and reactivity ?

Ans. Natural rubber is a cis-polyisoprene. These cis- double bonds do not allow to polymer unit to come close for effective interaction. Hence rubber show elasticity.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Write the names and structure of the monomers of the following polymers :

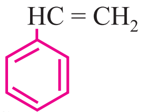
(i) Buna-S **(ii) Neoprene** **(iii) Nylon-6**

Ans. (i) Buna-S :

$H_2C = CH - CH - CH_2$

1, 3-Butadiene

and



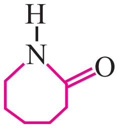
Styrene

(ii) Neoprene :

$$H_2C = \overset{\overset{Cl}{|}}{C} - CH = CH_2$$

Chloroprene

(iii) Nylon-6 :



Caprolactum

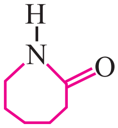
Q. 2. Write names and structure of monomers of following polymers :

(i) Bakelite (ii) Nylon-6 (iii) Polythene

Ans. (i) Phenol and formaldehyde

$C_6H_5OH + HCHO$

(ii) Caprolactum



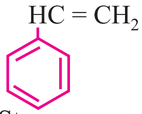
(iii) Ethene

$H_2C = CH_2$

Q. 3. Write names and structure of monomers of following polymers :

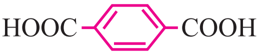
(i) Polystyrene (ii) Dacron (iii) Teflon

Ans. (i) Styrene



Styrene

(ii) Ethylene glycol + Terephthalic acid

$HOH_2C - CH_2OH$ + 

(iii) Tetrafluoroethene

$F_2C = CF_2$

Q. 4. (i) What is the role of t-butyl peroxide in the polymerisation of ethane ?

(ii) Identify the monomers in the following polymer :

$$\mathbf{+\ HN(CH_2)_6NHCO(CH_2)_4CO\ +}$$

(iii) Arrange the following polymers in the increasing order of their intermolecular forces :

Polystyrene, Terylene, Buna-S

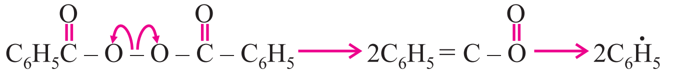
Ans. (i) Catalyst/initiator of free radical

(ii) Hexamethylenediamine and adipic acid

(iii) Buna-S < Polystyrene < Terylene

Q. 5. Write the mechanism of free radical polymerisation of ethane.

Ans. (i) Chain initiation step



$$C_6H_5\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \longrightarrow 2C_6H_5=C-\overset{\overset{O}{\|}}{O} \longrightarrow 2C_6\dot{H}_5$$

Benzoyl peroxide

Phenylradical

$C_6\dot{H}_5 + H_2C = C_2 \rightarrow C_6H_5CH_2\dot{C}H_2$

(ii) Chain propagating step

$$C_6H_5CH_2\dot{C}H_2 + H_2C = CH_2 \longrightarrow C_6H_5CH_2CH_2\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5(CH_2CH_2)_nCH_2\dot{C}H_2$$

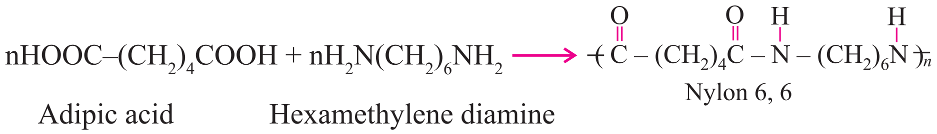
(iii) Chain terminating step

$$\begin{array}{c} C_6H_5(CH_2CH_2)_nCH_2\dot{C}H_2 \\ + \\ C_6H_5(CH_2CH_2)_nCH_2\dot{C}H_2 \end{array} \longrightarrow C_6H_5(CH_2CH_2)_nCH_2CH_2CH_2(CH_2CH_2)_nC_6H_5$$

Q. 6. Write chemical equation for the synthesis of :

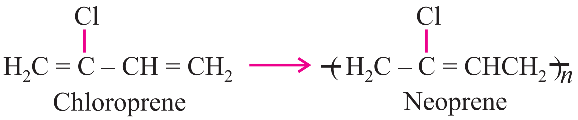
(i) Nylon-6, 6 (ii) Neoprene (iii) Terylene

Ans. (i) Nylon-6, 6 :



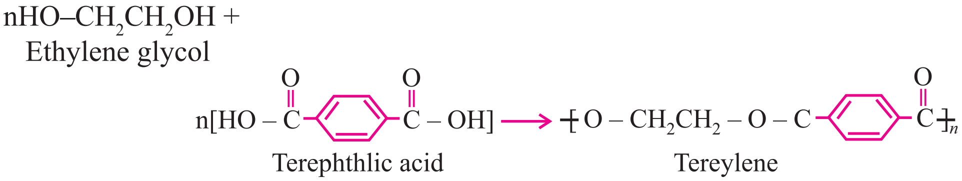
$$\underset{\text{Adipic acid}}{nHOOC{-}(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{nH_2N(CH_2)_6NH_2} \longrightarrow \underset{\text{Nylon 6, 6}}{\left(\overset{O}{\overset{\|}{C}} - (CH_2)_4\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6\overset{H}{\overset{|}{N}}\right)_n}$$

(ii) Neoprene :



$$\underset{\text{Chloroprene}}{H_2C = \overset{Cl}{\overset{|}{C}} - CH = CH_2} \longrightarrow \underset{\text{Neoprene}}{\left(H_2C - \overset{Cl}{\overset{|}{C}} = CHCH_2\right)_n}$$

(iii) Terylene :



nHO–CH$_2$CH$_2$OH +
Ethylene glycol

Terephthlic acid

Tereylene

Q. 7. Write the monomers which are used for the synthesis of following polymers :

(i) Terylene (ii) Polythene (iii) Bakelite

Indicate the type of polymerisation for each which forms polymers.

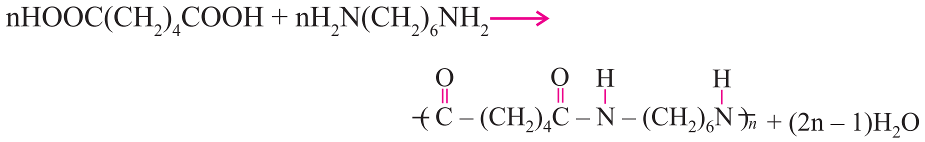
Ans.	**Monomers**	**Type of polymerisation**
(i)	Ethylene glycol + Terephthalic acid	Condensation
(ii)	Ethene	Addition
(iii)	Phenol + Formaldehyde	Condensation

Q. 8. How are polymers classified on the basis of mode of polymerisation ? Explain with examples.

Ans. Addition polymers : Are formed by repeated addition of a large number of same or different monomers possessing double or triple bonds. E.g., Polythene.

$$\underset{\text{Ethene}}{nH_2C = CH_2} \rightarrow \underset{\text{Polythene}}{\left(H_2C - CH_2\right)_n}$$

Condensation polymers : Are formed by repeated condensation reaction between two bifunctional or trifunctional monomer units usually with the elimination of small molecules like water, alcohol, ammonia, etc. E.g., Nylon-6, 6.



$$nHOOC(CH_2)_4COOH + nH_2N(CH_2)_6NH_2 \longrightarrow \left[\overset{O}{\overset{\|}{C}} - (CH_2)_4\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6\overset{H}{\overset{|}{N}} \right]_n + (2n-1)H_2O$$

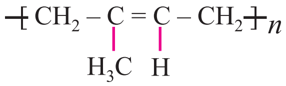
Nylon 6, 6

Q. 9.A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mol of $CH_3{-}\overset{O}{\overset{\|}{C}}{-}CHO$. Write the structure of monomer and polymer and each step of reaction.

Ans. Structure of monomer :

$$CH_2O + O = \overset{CH_3}{\overset{|}{C}} - CH_3 + OCH_2 \longrightarrow CH_2 = \overset{CH_3}{\overset{|}{C}} - CH = CH_2$$

Structure of polymer :



$$\left[CH_2 - \underset{H_3C}{\underset{|}{C}} = \underset{H}{\underset{|}{C}} - CH_2 \right]_n$$

Q. 10.Can a copolymer be formed in both addition and condensation polymerisation ? Explain with examples.

Ans. Yes. Buna-S, Buna-N : Addition polymer

Nylon-6, 6, terylene : Condensation

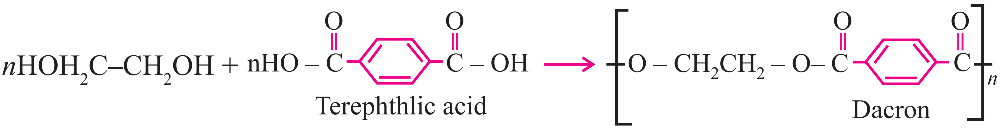
LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How are following polymers obtained ? Write the names and structures of monomers and structure of respective polymers :

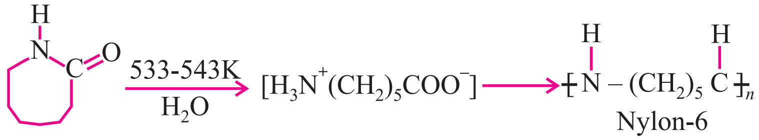
(i) Dacron **(ii) Nylon-6** **(iii) Buna-N**

(iv) Glyptal **(v) PHBV**

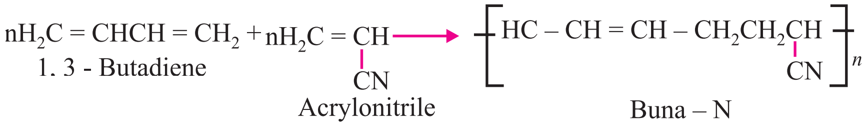
Ans. (i) Dacron : By condensation polymerisation.



(ii) Nylon-6 : By condensation polymerisation.

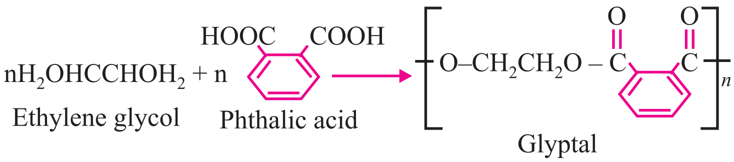


(iii) Buna-N : By addition polymerisation.

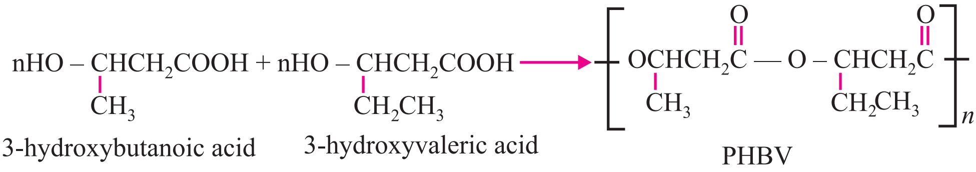


$$nH_2C=CHCH=CH_2 + nH_2C=\underset{CN}{\underset{|}{CH}} \longrightarrow \left[HC-CH=CH-CH_2CH_2\underset{CN}{\underset{|}{CH}} \right]_n$$

(iv) Glyptal : By condensation polymerisation.



(v) PHBV : By condensation polymerisation.



$$nHO-\underset{CH_3}{\underset{|}{CH}}CH_2COOH + nHO-\underset{CH_2CH_3}{\underset{|}{CH}}CH_2COOH \longrightarrow \left[O\underset{CH_3}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}} \right]_n$$

VALUE BASED QUESTIONS (4 Marks)

Q. 1. In school, lot of emphasis is given to 3R principle to Reduce, Refuse and Recycle. Two shopkeepers, Naresh Jain is using bags made up of jute, a polymer of cellulose while Rakesh Gupta using polythene as packing material. Abdul Kadir, a science student told Rakesh Gupta not to use polythene bags for packing but to use jute bags.

(i) Why is jute preferred over polythene as packing material by Abdul Kadir ?

(ii) Give monomers of jute and polythene.

(iii) Is polythene an addition polymer or a condensation polymer ?

(iv) Mention the values associated with the use of jute.

Q. 2. During war or accidents people get deep injuries which require stitching of wounds. Rohit told his friend, Avi, that earlier these wounds were used to be stitched by nylon-6 thread but nowadays instead of it Nylon-2-Nylon-6 fibre is used.

(i) Why should Nylon-2-Nylon-6 be used for stitching of wounds instead of Nylon-6 thread ?

(ii) Give monomers of Nylon-6 and Nylon-2-Nylon-6.

(iii) Is this polymer an addition polymer or a condensation polymer ?

(iv) Mention the values associated with use of Nylon-2-Nylon-6.

Q. 3. Two shopkeepers are using LDP (low density polythene) and HDP (high density polythene) polymers for packing of materials.

(i) Name the polyethene preferred for packaging.

(ii) Name the catalyst used in synthesis of HDP.

(iii) HDP has high density. Why ?

(iv) Mention the value associated with the use of a specific polymer.

Q. 4. PHBV (poly-β-hydroxybutyrate-co-β-hydroxyvalerate) is a iodegradable polymer. It is a co-polymer of 3-hydroxybutanoic acid and 3-hydroxy pentanoic acid.

(i) How has PHBV found utility in medicines as capsule ?

(ii) Write the name of polymer used in artificial limb popularly known as Jaipur foot.

(iii) Is this polymer an addition polymer or condensation polymer ?

(iv) Write the values associated with the use of PHBV.

Q. 5. Vidhi's mother followed a very traditional way of cooking using earthenwares, copper utensils etc. Her daughter replaced all the kitchen steel utensils with teflon coated ones.

(i) In your opinion, who is correct in present situation ?

(ii) Give monomer of teflon. Is it an addition or a condensation polymer ?

(iii) Write the structure of teflon.

(iv) Mention the values shown by Vidhi.

UNIT 16

CHEMISTRY IN EVERYDAY LIFE

Points to Remember

1. **Drugs :** Drugs are chemical of low molecular masses, which interact with macromolecular targets and produce a biological response.

2. **Chemotherapy :** The use of chemicals for therapeutic effect is called chemotherapy.

3. **Classification of Drugs :**

   (i) **On the basis of pharmacological effect :** Drugs for a particular type of problem as analgesics for pain relieving.

   (ii) **On the basis of drug action :** Action of drug on a particular biochemical process.

   (iii) **On the basis of chemical action :** Drugs having similar structure, *e.g.,* sulpha drugs.

   (iv) **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, van der Waal or dipole-dipole interactions.

   (ii) **Drug-enzyme interactions :**

      (a) Drug complete with natural substrate for their attachments on the active sites of enzymes. They are called competitive inhibitors.

      (b) 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. *E.g.,* Aluminium hydroxide, magnesium hydroxide.

8. **Anti Histamines :** The drugs which interfare with the natural action of histamines and prevent the allergic reaction. *E.g.,* Rantidine, tegarnet, avil.

9. **Tranquilizers :** The class of chemical compounds used for the treatment of stress, mild or even severe mental diseases. *E.g.,* Idardil, iproniagid, luminal, seconil equanil.

10. **Analgesics :** They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system. *E.g.,* Aspirin, seridon, 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 substances which are produced by micro-organisms. *E.g.,* Penicillin, Ofloxacin.

    Narrow spectrum antibiotics : These are effective mainly against gram positive or gram negative bacteria. *E.g.,* Penicillin, streptomycin.

    Broad spectrum antibiotics : They kill or inhibit a wide range of micro-organisms. *E.g.,* Chloramphenicol, tetracydine.

    (ii) **Antiseptics or Disinfectant :** These are which either kill/inhibit the growth of micro-organisms.

    Antiseptics are applied to the living tissues such as wounds, cuts, ulcers etc. *E.g.,* Furacine, chloroxylenol and terpinol (dettol). Disinfectant are applied to inanimate objects such as floors, drainage system.

    E.g., 0.2% solution of phenol is an antiseptic while 1% solution is an disinfectant.

12. **Antifertility drugs :** These are the chemical substances used to control the pregnancy. They are also called oral contraceptives or birth control pills. *E.g.,* Mifepristone, norethindrone.

13. **Artificial Sweetening Agents :** These are the chemical compounds which give sweetening effect to the food without adding calorie. They are good for diabetic people. *E.g.,* Aspartame, saccharin, alitame, sucrolose.

14. **Food Preservatives :** They prevents spoilage of food to microbial growth. *E.g.,* Salt, sugar and sodium benzoate.

15. Cleansing Agents :

(i) **Soaps :** They are sodium or potassium salts of long chain fatty acids. They are obtained by the saponification reaction, when fatty acids are heated with aqueous sodium hydroxide. They do not work well in hard water.

(ii) **Toilet soaps :** That are prepared by using better grade of fatty acids and excess of alkali needs to be removed. Colour and perfumes are added to make them attractive.

(iii) **Medicated soaps :** Substances or medicinal value are added. *E.g.,* Bithional, dettol.

16. **Synthetic Detergents :** They are cleaning agents having properties of soaps, but actually contain no soap. They can be used in both soft and hard water. They are :

(i) **Anionic detergents :** They are sodium salts of sulphonated long chain alcohols or hydrocarbons. *E.g.,* Sodium lauryl sulphonate. They are effective in acidic solution.

$$CH_3(CH_2)CH_2OH \rightarrow CH_3(CH_2)_{10}CH_2OSO_3H \text{ (lauryl alcohol)} \rightarrow$$

$$CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$$

(sodium lauryl sulphonate)

(ii) **Cationic detergents :** They are quarternary ammonium salts of amines with acetates, chlorides or bromides. They are expensive used to limited extent. *E.g.,* cetyltrimethylammonium bromide.

(iii) **Non-ionic detergents :** They do not contain any ions. Some liquid dishwashing detergents are of non-ionic type.

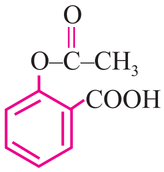
17. **Biodegradable Detergents :** The detergents which are linear and can be attacked by micro-organisms are biodegradable. *E.g.,* Sodium 4-(1-dodecyl) benzene/ sulphonate.

18. **Non-biodegradable Detergents :** The detergents which are branched and cannot be decomposed by micro-organisms are called non-biodegradable. *E.g.,* Sodium 4-(1, 3, 5, 7 tetramethyloctl)-benzene sulphonate. It creates water pollution.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

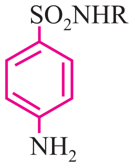
Q. 1. Write the formula and IUPAC name of aspirin.

[*Hint :*



[IUPAC name : 2-Acetoxybenzoic acid]

Q. 2. Name the type of drugs having following structural formula :



[*Hint :* Sulpha drugs]

Q. 3. Name two types of the drugs classified on the basis of pharmacological effect.

[*Hint :* Analgesics, Antiseptics.]

Q. 4. What is the role of Bithional in toilet soaps ?

[*Hint :* To impart antiseptic properties to soaps.]

Q. 5. Why is sodium benzoate added to packed containers of jams and pickles ?

[*Hint :* It prevents spoilage of jams and pickles due to microbial growth. It is a food preservative.]

Q. 6. Why the receptors embedded in cell membranes show selectivity for one chemical messenger over the other ?

[*Hint :* The active site of receptor has specific shape and specific functional groups which can bind only specific messenger which fits in.]

Q.7. With reference to which classification has the statement 'Ranitidine is an antacid' been given ?

[*Hint :* Classification based on pharmacological effect.]

Q.8. Give the name of medicine used for the treatment of syphilis.

[*Hint :* Salvarsan.]

Q.9. Give the composition of tincture of iodine.

[*Hint :* 2-3% solution of iodine in alcohol-water mixture.]

Q.10. How does aspirin act as analgesic ?

[*Hint :* Aspirin inhibits the synthesis of prostaglandins which cause pain.]

Q.11. Name the antiseptic agents present in dettol.

[*Hint :* Chloroxylenol and Terpinol.]

Q.12. What precaution should be taken before administrating penicillin to a patient ?

[*Hint :* To confirm beforehand that the patient is not allergic to penicillin.]

Q.13.Explain why aspirin finds use in prevention of heart attacks ?

[*Hint :* Due to anti blood clotting activity.]

Q.14.Mention one use of drug meprobamate.

[*Hint :* Antidepressant drug.]

Q.15.Name the derivative of sucrose which tastes like sugar and can be safely used by weight conscious people.

[*Hint :* Sucrolose.]

Q.16.Why synthetic detergents are preferred over soaps for use in washing machines ?

[*Hint :* They work well even with hard water and not form any scum.]

Q.17.How is acidity cured with cimetidine ?

[*Hint :* Cimetidine prevents the interaction of histamines with the receptors present in stomach wall.]

Q.18.While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other ?

[*Hint :* Antacids and antiallergic drugs bind to the different receptor sites. Therefore, they do not interfere with the function of each other.]

Q.19.Which of the following two compounds can be used as a surface agent and why ?

[*Hint :* Compound (i) acts as a surface agent because its one end is hydrophobic while the other end is hydrophilic in nature.]

Q.20.What type of drug is chloramphenicol ?

[*Hint :* Bacteriostatic broad spectrum antibiotic.]

Q.21.Name a chemical used as an antiseptic as well as disinfectant.

[*Hint :* Phenol. (0.2% solution antiseptic and 1% solution disinfectant)]

Q.22.Give two examples of antidepressants.

[*Hint :* Iproniazid, Phenelzine.]

Q.23.Name the antioxidants commonly used to increase the storage of butter.

[*Hint :* BHA (Butylated Hydroxy anisole).]

Q.24. Give the name of medicine having – As = As – linkage.

[*Hint :* Arsphenamine.]

Q.25.Which antibiotic is supposed to be toxic towards certain strains of cancer cells ?

[*Hint :* Dysidazirine.]

Q.26.Name one antioxidant used in wine, butter and beers.

[*Hint :* BHA, BHT.]

Q.27.Hair shampoos belong to which class of synthetic detergent ?

[*Hint :* They belong to cationic detergents. E.g., Cetyltrimethyl-ammonium bromide.]

Q.28.Dishwashing soaps are synthetic detergents. What is their chemical nature ?

[*Hint :* They are non-ionic detergents. *E.g.,* Polyethylene glycol-stearate.]

Q.29.What is the cause of a feeling of depression in human beings ? Name a drug which can be useful in treating depression.

[*Hint :* Low level of noradrenaline, a neurotransmitter causes depression in human beings. Antidepressant drugs are Iprniazid, Phenelzine.]

Q.30.Mention one use of drug Meprobamate.

[*Hint :* Antidepressant drug.]

Q.31.How is acidity cured with cimetidine or ranitidine ?

[*Hint :* Cimetidine or Ranitidine prevents the interaction of histamine with the receptors present in stomach walls and therefore, secretion of acid is prevented.]

Q.32.While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other ?

[*Hint :* Antacids and antiallergic drugs bind to the different receptor sites. Therefore, they do not interfere with the function of each other.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. What are antihistamines ? Give two examples.

[*Hint :* The group of compounds which destroy histamine produced in the body by allergens. *E.g.,* Bromopheniramine, seldane.]

Q. 2. What are narcotic and non-narcotic analgesics ? Give one example of each.

[*Hint :* Non-narcotics are the drugs which relieve or decrease pain without causing unconsciousness. Example, Aspirin.

Nartotics analgesics are those drugs which relieve pain, but produce sleep and unconsciousness. Example, Morphine.]

Q. 3. Explain the following terms as used in medicinal chemistry :

(i) Target molecules **(ii) Enzyme inhibitors**

[*Hint :* (i) Drugs that interact with biomolecules such as lipids, carbohydrates, proteins and nucleic acids, are called target molecules.

(ii) They inhibit the catalytic activity of the enzyme.]

Q. 4. Give one important use of each of the following :

(i) Equanil **(ii) Morphine**

[*Hint :* (i) Tranquilizer (antidepressant).

(ii) Narcotic analgesics]

Q. 5. What are neurologically active drugs ? Give two examples.

[*Hint :* Tranquilizers and analgesics are neurologically active drugs. Example : Equanil, morphine.]

Q. 6. (i) What are antibiotics ?

(ii) What is meant by the term broad spectrum antibiotic ?

[*Hint :* (i) A substance produced wholly or partly by chemical synthesis which in low concentration inhibits the growth or destroys microorganism by interfering with their metabolic processes.

(ii) Antibiotics which kills or inhibits wide range of bacteria.]

Q. 7. From the given examples – ciprofloxacin, phenelzine, morphine, ranitidine – choose the drug used for :

(i) treating allergic conditions (ii) to get relief from pain

[*Hint :* (i) Ranitidine (ii) Morphine]

Q. 8. Why a drug should not be taken without consulting a doctor ? Give two reasons.

[*Hint :* (i) To avoid side effects caused by drug.

(ii) To have the advice for proper dose of drug.]

Q. 9. State the main difference between bacteriostatic and bactericidal antibiotics. Give one example of each.

[*Hint :* Bacteriostatic antibiotics have inhibitory effect while bactericidal antibiotics have killing effect on microbes.

Example : Bacteriostatic antibiotic : Tetracycline

Bactericidal antibiotic : Ofloxacin]

Q.10. What are antifertility drugs ? Name the constituents of an oral contraceptive.

[*Hint :* Drugs used to check pregnancy in women to control birth rate. Oral contraceptives contains a mixture of synthetic estrogen and progesterone derivatives.]

Q.11. What do you mean by non-biodegradable detergents ? How can we make biodegradable detergents ?

[*Hint :* Detergents which cannot be degraded by nature. Biodegradable detergents can be prepared by minimazing the branching of the hydrocarbon chain, as unbranched chains can be biodegraded.]

Q.12. If water contains dissolved calcium hydrogencarbonate, which out of soap and detergent, will you prefer to use ? Why ?

[*Hint :* We will use detergent because it will not form insoluble precipitate with Ca^{2+}.]

Q.13. What are barbiturates ? What is the action of barbiturates on human body ?

[*Hint :* Barbaturic acid derivatives are called barbiturates. They are highly effective pain relieving agents.]

Q.14.Write the structures of soaps obtained by the hydrolysis of the following fats :

(i) $(C_{15}H_{31}COO)_3C_3H_5$ Glyceryl palmitate

(ii) $(C_{17}H_{33}COO)_3C_3H_5$ Glyceryl oleate

[*Hint :* (i) $C_{15}H_{31}COO^{-}Na^{+}$ (ii) $C_{17}H_{33}COO^{-}Na^{+}$]

Q. 15. What are antagonists and agonists ?

[*Hint :* Drugs which bind to the receptor site and inhibits its natural function. They are useful when blocking of message is required.

Agonists are the drugs which imitate (mimic) the natural messenger by switching on the receptor. They are useful when there is lack of natural chemical messenger.]

Q. 16. What is the advantage of using antihistamines over antacids in the treatment of acidity ?

[*Hint :* Antihistamines prevent the interaction of histamine with the receptors present in stomach wall and thus lesser amount of HCl is released.]

Q. 17. From the given examples – Promethazine, phenelzine, morphine, ranitidine – choose the drug used for :

(i) treating allergic conditions **(ii) to get relief from pain**

[*Hint :* (i) Ranitidine (ii) Morphine]

Q. 18. Write two side effects of Aspirin.

[*Hint :* (i) It is toxic to liver.

(ii) It also causes bleeding from stomach sometimes, thus it is a gastric irritant.]

Q. 19.What are sulpha drugs ? Give two examples.

[*Hint :* A group of drugs which are derivatives of sulphanilamide and are used in place of antibiotics is called sulpha drugs. E.g., sulphadiazine, sulphanilamide.]

Q. 20.What forces are involved in holding the active sites of enzymes ?

[*Hint :* The forces involved in holding the active sites of enzymes are hydrogen bonding, ionic bonding, dipole-dipole attractions or van der Waal's forces of attraction.]

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (i) Why are artificial sweetening agents harmless when taken ?

(ii) Name one such artificial sweeting agent.

(iii) Why is the use of aspartame as an artificial sweetener limited to cold foods ?

[*Hint :* (i) Because they are not metabolized by body and excreted from the body in urine unchanged.

(ii) Aspartame.

(iii) Because it is unstable at cooking temperature.]

Q. 2. Pick out the odd one amongst the following on the basis of their medicinal properties. Give suitable reason :

(i) Luminal, seconal, terfenadine, equanil.

(ii) Chloroxylenol, phenol, chloamphenicol, bithional.

(iii) Sucralose, aspartame, alitame, sodium benzoate.

[*Hint :* (i) Terfenadine is antihistamine other three are used as tranquilizers.

(ii) Chloramphenicol is a broad spectrum antibiotic. Other three have antiseptic properties.

(iii) Sodium benzoate is a food preservative. Other three are artificial sweetners.]

Q. 3. Give the main function of following in the body of human beings :

(i) Enzymes

(ii) Receptor proteins

(iii) Neurotransmitter

[*Hint :* (i) Catalyse biochemical reactions.

(ii) Important for the communication system of the body.

(iii) They control mood changes in organisms.]

Q. 4. Identify the class of drug :

(i) Phenelzine (Nardin)

(ii) Aspirin

(iii) Cimetidine

[*Hint :* (i) Antidepressant drug (ii) Analgesics and antipyretic

(iii) Antihistamine]

Q. 5. Give the pharmacological function of the following type of drugs :

(i) Analgesics (ii) Tranquilizers (iii) Antifertility drugs

[*Hint :* (i) Which reduce or abolish pain.

(ii) They are neurologically active drugs used to treat mental diseases.

(iii) Drugs used to check pregnancy in women to control birth rate.]

Q. 6. Give the name of medicine used in the treatment of following diseases :

(i) Typhoid

(ii) Join pain (in Arthritis)

(iii) Hypertension

[*Hint :* (i) Antibiotics (ii) Non-narcotic analgesics (iii) Tranquilizers]

Q. 7. Give the class of drugs to which these substances belong :

(i) Bithional (ii) Amoxycillin (iii) Salvarsan

[*Hint :* (i) Antiseptic (ii) Broad spectrum antibiotic

(iii) Antimicrobial (antibacterial)]

Q. 8. How are antiseptics different from disinfectants ? How does an antibiotic different from these two ? Give one example of each of them.

[*Hint :* Antiseptics may kill or stop the growth of microbes and safe for living tissues, where an disinfectants kill microbes but not safe for living tissues. While antibiotic are produced by micro-organism, can inhibit the growth of other micro-organism.

Example : Antiseptic : 0.2% phenol, Disinfectant : 1% phenol, Antibiotic : Penicillin]

Q. 9. Explain the following terms with suitable examples :

(i) Cationic detergents

(ii) Anionic detergents

(iii) Non-ionic detergents

[*Hint :* (i) Those in which cationic part of the molecule is involved in cleansing action. E.g., cetyltrimethyl ammonium bromide.

(ii) Those in which anionic part of the molecule is involved in cleansing action. *E.g.,* sodium laurylsulphate.

(iii) Which do not contain any ion in their constitution. *E.g.,* Lauryl alcohol ethoxylate.]

Q.10.Classify the following as cationic detergents, anionic detergents or non-ionic detergents :

(i) $CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$

(ii) $[CH_3-(CH_2)_{15}N(CH_3)_3]^+Br^-$

(iii)

Where (n = 5 – 10)

[*Hint :* (i) Anionic detergent (ii) Cationic detergent

(iii) Non-ionic detergent]

Q. 11. How do enzyme inhibitors work ? Distinguish between competitive and non-competitive enzyme inhibitors.

[*Hint :* An enzyme inhibitor either blocks the active site of enzyme or changes the shape of the active site by binding at an allosteric site. They are of two types :

(i) Competitive enzyme inhibitor competes with natural substance for their attachment on the active sites of enzymes.

(ii) Non-competitive enzyme inhibitor binds at allosteric site and changes the shape of the active site in such a way that the substrate cannot recognize it.]

Q. 12.(i) What class of drug is Ranitidine ?

(ii) If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergents, which will you use for cleaning clothes ?

(iii) Which of the following is an antiseptic :

0.2% phenol or 1% phenol

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (i) Discuss two ways in which drugs prevent the attachment of native substrate on active site of an enzyme.

(ii) What are antibiotics ? Distinguish between narrow spectrum and broad spectrum antibiotics. Classify the following into bactericidal bacteriostatic antibiotics :

Tetracycline, Penicillin, Ofloxacin and Chloramphenicol.

Q. 2. What are detergents ? How are they classified ? Why are detergents usually preferred to soaps for washing clothes ? Give an example of detergents.

HOTS

Q. 1. Name two drugs which inhibit the action of enzyme which metabolise noradrenaline.

[*Hint :* Iproniazid and phenelzine.]

Q. 2. Which type of detergents will you use to formulate a toilet cleaner ? Explain why ?

[*Hint :* Cationic detergent, due to its germicidal properties.]

Q. 3. Name the antiseptic you will add to soap to make it useful for control of pimples.

[*Hint :* Bithional]

Q. 4. Name the chemical responsible for nasal congestion with common cold and allergic response to pollen.

[*Hint :* Histamine]

Q. 5. Name the important by-product of soap industry.

[*Hint :* Glycerol]

MATCHING TYPE QUESTIONS

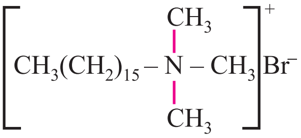
Q. 1. Match the medicines given in Column I with their use given in Column II :

	Column I		Column II
(i)	Ranitidine	(a)	Tranquilizer
(ii)	Furacine	(b)	Antibiotic
(iii)	Phenelzine	(c)	Antihistamine
(iv)	Chloramphenicol	(d)	Antiseptic
		(e)	Antifertility drug

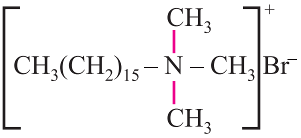
Q. 2. Match the soaps given in Column I with items given in Column II :

	Column I		Column II
(i)	Soap chips	(a)	dried miniature soap bubbles
(ii)	Soap granules	(b)	small broken pieces of soap formed from melted soaps
(iii)	Soap powder	(c)	soap powder + abrasives + builders (Na_2CO_3, Na_3PO_4)
(iv)	Scouring soap	(d)	soap powder + builders like Na_2CO_3 and Na_3PO_4)

Q. 3. Match structures given in Column I with the type of detergents given in Column II :

Column I	Column II
(i) $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$	(a) Cationic detergent
(ii) $C_{17}H_{35}COO^-Na^+$	(b) Anionic detergent
(iii) $CH_3-(CH_2)_{10}CH_2SO_3^-Na^+$	(c) Non-ionic detergent
(iv)  $\left[CH_3(CH_2)_{15}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}-CH_3\right]^+Br^-$	(d) Soap

Q. 4. Match the detergents given in Column I with their uses given in Column II :

	Column I	Column II
(i)	 $\left[CH_3(CH_2)_{15}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{N}}-CH_3\right]^+Br^-$	(a) Dishwashing powder
(ii)		(b) Laundry soap
(iii)	$C_{17}H_{35}COO^-Na^+ + Na_2CO_3$ + Rosin	(c) Hair conditioners
(iv)	$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$	(d) Toothpaste

Q. 5. Match the class of compounds given in Column I with their functions given in Column II :

	Column I		Column II
(i)	Antagonists	(a)	Communicate message between two neurons and that between neurons to muscles
(ii)	Agonists	(b)	Bind to the receptor site and inhibit its natural function
(iii)	Chemical messenger	(c)	Crucial to body's communication process
(iv)	Inhibitors	(d)	Mimic the natural messenger
(v)	Receptors	(e)	Inhibit activities of enzymes

Q. 6. Match the classes of drugs given in Column I with their action given in Column II :

	Column I		Column II
(i)	Analgesics	(a)	Inhibit the growth of micro-organisms, can be given orally
(ii)	Antiseptics	(b)	Treatment of stress
(iii)	Antihistamines	(c)	Applied to inanimate objects
(iv)	Antacids	(d)	Prevents the interaction of histamine with its receptor
(v)	Tranquilisers	(e)	Pain killing effect
(vi)	Antibiotics	(f)	Applied to diseased skin surfaces
(vii)	Disinfectants	(g)	Treatment of acidity

ANSWERS

1.	(i) – (c)	(ii) – (d)	(iii) – (a)	(iv) – (b)		
2.	(i) – (b)	(ii) – (a)	(iii) – (d)	(iv) – (c)		
3.	(i) – (c)	(ii) – (d)	(iii) – (b)	(iv) – (a)		
4.	(i) – (c)	(ii) – (d)	(iii) – (b)	(iv) – (a)		
5.	(i) – (b)	(ii) – (d)	(iii) – (a)	(iv) – (e)	(v) – (c)	
6.	(i) – (e)	(ii) – (f)	(iii) – (d)	(iv) – (g)	(v) – (b)	
					(vi) – (a)	(vii) – (c)

MULTIPLE CHOICE QUESTIONS

1. Which is the correct statement about birth and control pills ?

(a) Contain estrogen only (b) Contain progesterone only

(c) Progesterone increases ovulation (d) Contains a mixture of estrogen & progesterone derivatives

Ans. (d)

2. Which of the following is used for the treatment of tuberculosis ?

(a) Penicillin (b) Aspirin

(c) Chloamphenicol (d) Streptomycin

Ans. (d)

3. Glycerol is added to soap. Its function is :

(a) As a filler (b) To increase lathering

(c) To prevent rapid drying (d) To make soap granules

Ans. (c)

4. Which of the following is not a target molecule for drug function in body ?

(a) Vitamins (b) Lipids

(c) Carbohydrates (d) Proteins

Ans. (a)

5. Which of the following can act as an antiseptic as well as disinfectant ?

(a) Aspirin (b) Chlorine

(c) Phenol (d) Dettol

Ans. (b)

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Ram's father recovered from a heart attack. The doctor gave him Aspirin.

(i) Why was Aspirin prescribed by the doctor ?

(ii) What is the IUPAC name of Aspirin ?

(iii) After some time, he started to develop some ache in stomach. Then his wife gave him some butter milk. Why ?

(iv) What values do you get from this ?

Q. 2. Harish was feeling headache. His friend, Vikram observed that Harish had fever. He advised him to take two tablets of oflaxin 200 mg but his sister, a XII class Chemistry student, advised her brother to go to family doctor.

(i) Is it right to take medicine as per you friend's advice ?

(ii) Write the values shown by his sister.

(iii) The doctor prescribed Harish to take paracetamol tablets for three days after taking food and advised rest.

(iv) Is this medicine an antibiotic or antipyretic ?

SOLVED SAMPLE PAPER

Chemistry-XII (Theory)

Time allowed **Max. Marks = 70**

(i) All questions are compulsory.

(ii) Questions number 1 to 5 are urey short-answer questions and carry 1 mark each.

(iii) Questions number 6 to 10 are short-answer questions and carry 2 marks eack.

(iv) Questions number 11 to 22 are also short-answer questions and carry 3 marke each.

(v) Question number 23 is a value based question and carries 4 marks.

(vi) Questions number 24 to 26 are long-answer questions and carry 5 marks each.

(vii) Ues log tables, if necessary. Use of calculators is not allowed.

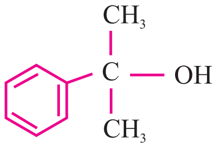
---

1. Arrange the following hydrides of Group-16 elements in the decreasing order of their reducing charcter:

   H_2O, H_2S, H_2Se H_2Te 1

2. What is the role of desorption in the process of catalysis? 1

3. Write the IUPAC name of the following compound: 1



4 Among the isomers of pentane (C_5H_{12}), write the. one which on photochemical chlorination yields a single monochloride.1

5 What is the formula of a compound in which the element P forms ccp lattice and atoms of Q occupy l/3rd of tetrahedral voids?1

6. In a galvanic cell, the following cell reaction occurs :

   $Zn\ (s) + 2\ Ag^+\ (aq)$ ® $Zn^{2+}\ (aq) + 2\ Ag\ (s)\ E°_{cell} = +\ 1.56V$

   (b) Is the direction of flow of electrons from zinc to silver or silver to zinc ?

   (b) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions ? 3

7 In the following ions :

Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}

(Atomic no : Mn = 25, V = 23, Cr = 24, Ti = 22)

(a) Which ion is most stable in an aqueous solution ?

(b) Which ion is the strongest oxidizing agent ?

(c) Which ion is colourless ? .

(d) Which ion has the highest number of unpaired electrons?

8 Do the following conversions in not more than two steps :

(a) Propene to Acetone

(b) Propanoic acid to 2-hydroxypropanoic acid

OR

Write the reaction involved in the following :

(a) Etard reaction (b) Wolff-Kishner reduction

9 What is meant by elevation in boiling point ? Why is it a colligative property ?

10 (a) Write the IUPAC name of the following complex :

$[Co(NH_3)_4 CI (NO_2)]CI$

(b) Write the formula for the following :

Dichloridobis (ethane-l,2-chainine)cobalt(III) chloride

11. Account for the following :

(a) $CuCl_2$ is more stable than CU_2CI_2.

(b) Atomic radii of 4d and 5d series elements are nearly same.

(c) Hydrochloric acid is not used in permanganate titrations.

12. Define the following terms :

(a) Analgesic (b) Anionic detergent

(c) Antacid

13 The electrical resistance of a column of 0.05 M KOH solution of diameter 1 cm and length 45.5 cm is 4.55×10^3 ohm. Calculate its molar conductivity.

14. Define the following terms with an example in each :

(a) Lyophobic colloids (b) Homogeneous catalysis

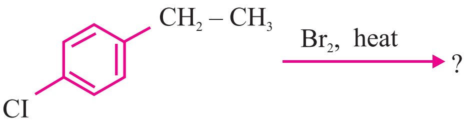
(c) O/W emulsion

OR

Write three differences between Physisorption and Chemisorption.

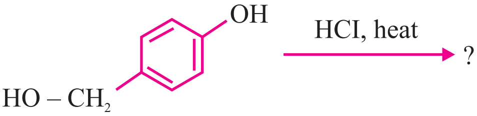
15. Draw the structures of the major monohalo product for each of the following reactions:

(a)



(b)

(c)



16. A solution of glucose (Molar mass = 180 g mol^{-1}) in water has a boiling point of 100.20°C. Calculate the freezing point of the same solution. Molal constants for water Kf and Kb are 1.86 K kg mol^{-1} and 0.512 K kg mol^{-1} respectively.

17. (a) Write the name of the method used for the refining of the following metals:

(i) Titanium (ii) Germanium (iii) Copper

(b) Write the name of the method of concentration applied for the following ores:

(i) Zinc blende (ii) Haematite (iii) Bauxite

18. (a) What is the radius of sodium atom if it crystallizes in bcc structure with the cell edge of 400 pm?

(b) Examine the given detective crystal:

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

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

(ii) What is the result when XY crystal is doped with divalent (Z^{2+}) impurity?

19. Give reasons:

    (a) Propanone is less reactive than ethanal towards nucleophilic addition reactions.

    (b) $O_2N - CH_2 - COOH$ has lower pKa value than CH_3COOH.

    (c) $(CH_2)_3CH - CHO$ undergoes aldol condenstion whereas $(CH_3)_3C - CHO$ does not.

20. Write the names and structures of the monomers of the following polymers:

    (a) Neoprene

    (b) Buna-N .

    (c) PHBV

21. (a) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta > P$.

    (b) Write the hybridization and magnetic character of $[CoF_6]^{3-}$ (At. no. of Co = 27)

22. What happens when

    (a) $(CH_3)_3C - O - CH_3$ is treated with HI,

    (b) Anisole is treated with CH_3COCl / anhydrous $A1C1_3$,

    (c) Phenol is treated with Br_2 / CS_2?

    Write chemical equations in support of your answer.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Veena, a class XII student, decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins-rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and students.

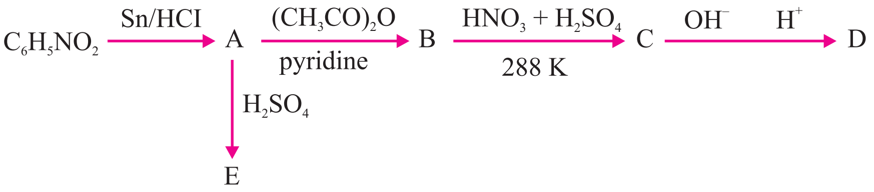
    (a) What are the values (at least two) displayed by Veena?

    (b) Which polysaccharide component of carbohydrates is commonly present is bread?

    (c) Write the two types of secondary structures of proteins.

    (d) Give two examples of water soluble vitamines.

24. Write the structures of A, B, C, D and E in the following reactions:



(a) Write the structures of the main products when benzene diazonium chloride reacts witht he following reagents:

(i) CuCN (ii) CH_3CH_2OH

(iii) Cu / HCl

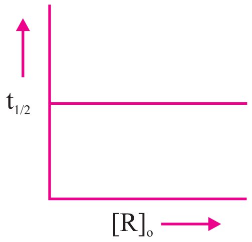
(b) Arrange the follownig in the increasing order of their basic strength:

CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

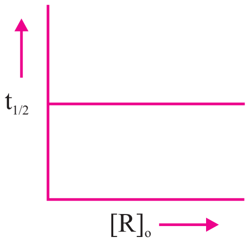
25. (a) A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

(b) Predict the order of the reaction in the given plots:

(i)



(ii)



Where $[R]_0$ is the initial concentration of reactant.

(Given : log 2 = 0.3010, log 4 = 0.6021)

OR

The following data were obtained for the reaction:

$2NO + O_2 \longrightarrow 2NO_2$

Experiment	[NO]/M	$[O_2]$/M	Initial rate of formation of NO_2/M min–1
1	0.3	0.2	7.2 × 10–2
2	0.1	0.1	6.0 × 10–3
3	0.3	0.4	2.88 × 10–1
4	0.4	0.1	2.40 × 10–2

(a) Find the order of reaction with respect to NO and O_2.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k).

26. (a) Account for the following :

    (i) BiH_3 is the strongest reducing agent in Group 15 elements hydrides.

    (ii) CI_2 acts as a bleaching agent.

    (iii) Noble gases have very low boiling points.

    (b) Draw the structures of the following :

    (i) H_4P_2O7

    (ii) $XeOF_4$

OR

(a) Although nitrogen and chlorine have nearly same electronegativity yet nitrogen forms hydrogen bonding while chlorine does not. Why ?

(b) What happens when F_2 reacts with water ?

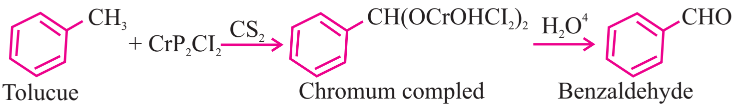
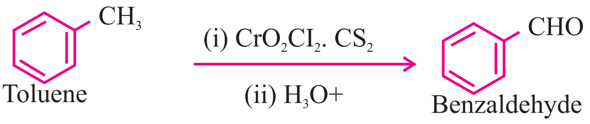
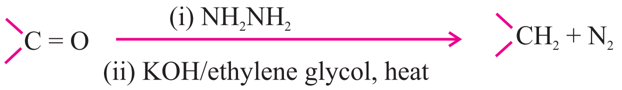
(c) Write the name of the gas evolved when Ca_3P_2 is dissolved in water.

(d) Write the formula of a noble gas species which is isostructural with IBr^-.

(e) Complete the equation :

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow$$

MARKING SCHEME

Q.NO	VALUE POINTS	MARKS
1	$H_2Te > H_2Se > H_2S > H_2O$	1
2	To make the surface avalable again for more reaction to occur/ To remove the product formed from the surface of the catalyst.	
3	2- Phenylpropan-2-ol	1
4	Neopentane, $C(CH_3)_4$	1
5	P_3Q_2	1
6	a. Zine to silver	1
	b. Concentration of Zn^{2+} ions will increase and Ag^+ lions will decrease.	
7	a. Cr^{3+}	
	b. Mn^{3+}	
	c. Ti^{4+}	
	d. Mn^{3+}	
8	a. 	
8	a. Etard reaction  b. Wolff-Kishner reduction:  or 	

9.	The increase in boiling point of the solvent in a solution when a non-volatile solute is added.	1
	Becaues it depends upon molality / the number of solute particales rather than-their nature/$\Delta T_b \propto m$	1
10.	a. Tetraamminechloridonitrito-N-cobalt (lll) chloride	1
	b. $[COCI_2(en)_2]CI$	1
11	a. In $CuCI_2$, Cu is in +2 oxidation state which is more stable due to high hydration enthalpy as compared to Cu_2Cl_2 in which Cu is in +1 oxidation state	1
	b. Due to lanthanoid conraction	1
	c. Because HCI is oxidised to chlorine.	1
12	a. Drugs that reduce or abolish pain without causing impairment of consciousnes, mental confusion or paralysis.	1
	b. Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons/alkylbenzene sulphonate of detergents whose anionic part is involved in cleansing action.	1
	c. Anacids are chemical compounds which are used for the treatment of excess acid produced in the stumach.	1
13	$A = \pi r^2$ $= 3.14 \times 0.5 \times 0.5\ cm^2$ $= 0.785\ cm^2$ $l = 45.5\ cm$ $\rho = R \times A/1$ $\rho = 4.55 \times 10^3\ \Omega \times 0.785\ cm^2 / 45.5\ cm$ $\rho = 78.5\ \Omega\ cm$ conductivity, $k = 1/p$ $= 1/78.5\ S\ cm^{-1} = 0.0127\ S\ cm^{-1}$ Molar conductivity $Am = k \times 1000/C$ $= 0.0127\ S\ cm^{-1} \times 1000/0.05\ mol/xm^3$ $= 254.77\ S\ cm^2\ mol^{-1}$	

or

$A = \pi r^2$

$= 3.14 \times 0.5 \times 0.5\ \text{cm}^2$

$= 0.785\ \text{cm}^2$

$l = 45.5\ \text{cm}$

$= G^* = l/A = 4.45 \times 10^3\ \Omega\ \ = 1.27 \times 10^{-2}\ \text{S cm}^{-1}$

$= 57.96\ \text{cm}^{-1}$

$l = G^*/R$

$= 57.96\ \text{cm}^{-1}/4.55 \times 10^3\ \Omega = 1.27 \times 10^{-2}\ \text{S cm}^{-1}$

$\text{Am} = K \times 1000/C$

$= [1.27 \times 10^{-2}\ \text{S cm}^{-1}] \times 1000\ /\ 0.05\ \text{mol/cm}^3$

$= 254.77\ \text{S cm}^2\ \text{mol}^{-1}$

14 a. The particles of the dispersed phase have no affinity for the dispersion medium/solvent repelling (hating) colloidal sols.

Example: metal and their sulphides

b. The reactant and the catalyst are in the same phase.

$CH_3COOCH_3(l) + H_2O(l)\quad CH_3COOH(aq) + CH_3OH(aq)$

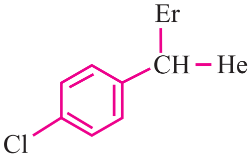
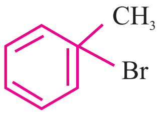
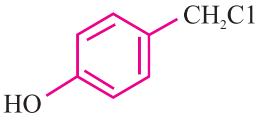
c. oil is dispersed in water/Oil is dispersed phase and water is dispersion medium.

Ex- milk (or any other correct example)

14

	Physisorption	**Chemisorption**
1	Because of van der Waals forces	Caused by chemical bond formation
2	Reversible	Irreversible
3	Enthalpy of adsorption is low(20-40 kJ/mol)	Enthalpy of adsorption is high(80-240)kJ/mol

(Or any other correct difference)

15	   	
16	Given : T_b of glucose solution = 100.20°C $\Delta T_b = K_b.m$ $m = 0.20/\ 0.512$ $m = 0.390$ mol/kg $\Delta T_f = K_f.\ m$ $\Delta T_f = 1.86$ K kg/mol × 0.390 mol/kg $\Delta T_f = 0.725$ K Freezing point of solution = 273.15 k – 0.725 = 272.425 K	
17	a. (i) Vapour phase refining/ van Arkel method76. (ii) Zone refining77. (iii) Electrolytic refiningb. b. (i) Froth floation process (ii) Magnetic separation (iii) Leaching	
18	a. For bcc structure $a = 4r/$ or $r = a/4$ $r = \times 400$ pm /4 $= 1.732 \times 400$ pm/4 = 173.2 pm h (i) Impurity defect (ii) Cationic vacancies are created.	
19	a. Due to steric hindrance and +1 effect caused by two alkylgroups in propanone. b. Due to electron withdrawing nature of $-NO_2$ group whichincreases the acidic strength and decreases the pKa value.	

c. $(CH_3)_2CH-CHO$ has one a -H atom whereas a- H atom isabsent in $(CH_3)_3C-CHO$.

20 a. Chloroprene, $CH_2=C(Cl)-CH=CH_2$

b. 1,3-Butadiene & Acrylonitrile

$CH_2 = CH - CH = CH_2$ & $CH_2= CHCN$

c. 3-Hydroxybutanoic acid & 3-Hydroxypentanoic acid

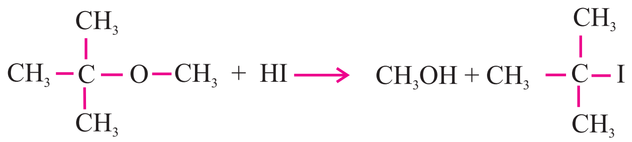
$CH_3CH(OH)CH_2COOH$ & $CH_3CH_2CH(OH)CH_2COQH$

21 a. It is the magnitude of difference in energy between thetwo sets of d orbital i.e. t_{2g} and e_g

$t^4_{2g}eg^{\circ}$

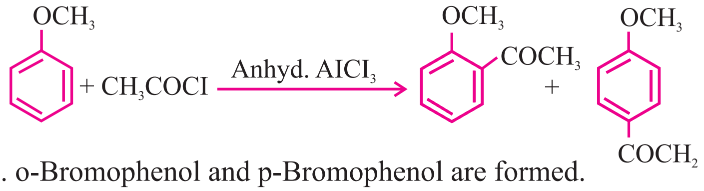
b. sp^3d^2, paramagnetic

22 a. Methanol and 2-methyl-2-iodopropane are formed.

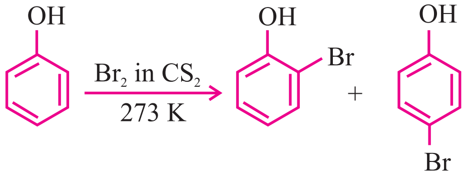


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

b. 2-Methoxy acetophenone and 4-Methoxy acetophenone are formed



c. o-Bromophenol and p-Bromophenol are formed.



(Award full marks if the student writes only equation)

23 (i) Concerned , caring, socially alert, leadership (or any other 2 values)

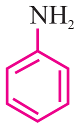
(ii) starch

(iii) α -Helix and β -pleated sheets

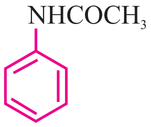
(iv) Vitamin B / B_1 / B_2 / B_6 / C (any two)

24

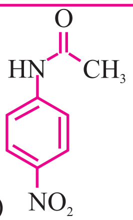
(A)



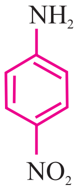
(B)



(C)



(D)



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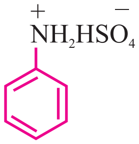
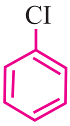


24

a. (i)

(ii)

(iii)



b. $C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH$

c. Add $NaNO_2$ + HCI to both the compounds at 273K followed by addition of phenaol. Aniline gives orange dye (or any other correct test)

25.

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

$$= \frac{2.303}{40}\log\frac{100}{25}$$

$$= \frac{2.303}{40}\log 4$$

$$= \frac{2.303}{40}\times 0.6021$$

$$= 0.0347\ \text{min}^{-1}$$

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

$$= t_{1/2} = \frac{0.693}{0.0347\ \text{min}^{-1}} = 19.98\ \text{, min} = 20\ \text{min}$$

b. (i) first order reaction

(ii) Zero order reaction

OR

25 (a) Rate = k $[NO]^x [O2]^y$

$7.2 \times 10^{-2} = k [0.3]^x [0.2]^y$ --------- Eqn (1)

$6.0 \times 10^{-3} = k [0.1]^x [0.1]^y$ ---------- Equ (2)

$2.88 \times 10^{-1} = k [0.3]^x [0.4]^y$ ---------Equ (3)

$2.40 \times 10^{-2} = k [0.4]^x[0.1]^y$ --------- Equ (4)

Dividing equ 4 by eqn 2

$$\frac{2.40\times10^{-2}}{6.0\times10^{-3}}=\frac{k[0.4]\times[0.1]^y}{K[0.1]\times[0.1]^y}$$

$x = 1$

Dividing equ 3 by equ 1

$$\frac{2.88\times10^{-1}}{7.2\times10^{-2}}=\frac{k[0.3]\times[0.4]^y}{k[0.3]\times[0.2]^y}$$

$y = 2$

order w.r.t. NO = 1, order w.r.t. O_2 is 2

(b) Rate law

Rate = k $[NO]^1 [O_2]^2$, The overal order of the reaction is 3.

c. rate constant $k = \dfrac{\text{rate}}{[NO]^1[O_2]^2} = \dfrac{7.2\times10^{-2}}{0.3\times(0.2)^2}$

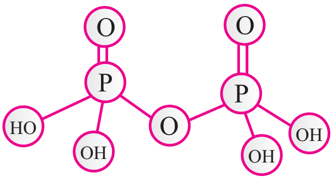
$k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

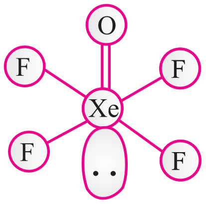
26. a. (i) Thermal stability of hydrides decreases down the group/

Bond dissociation enthalpy decreases down the group.

(ii) Because Cl_2 in presence of moisture liberates nascent oxygen.

(iii) Interatomic interactions are weak





b. (i) (ii)

26	(a) Size of nitrogen is smaller than Chlorine. (b) $2F_2 + 2H_2O + \longrightarrow 4HF + O_2$ / HF and O_2 are produced (c) PH_3 Phosphine (d) XeF_2 (e) $[Fe(H_2O)_6]^{2+}$ NO $\longrightarrow$ $[Fe(H_2O)_5(NO)]^{2+}$ H_2O	1 1 1 1 1

UNSOLVED SAMPLE PAPER-1

Chemistry-XII (Theory)

Time: 3 ***M.M: 70***

General Instructions:

(i) *All questions are compulsory.118.*

(ii) *Questions number **1** to **5** are very short-answer questionsand 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 questionsand carry **3** marks each.*

(v) *Question number **23** is a value based question and carries**4** marks.*

(vi) *Questions number **24** to **26** are long-answer questions andcarry **5** marks each.*

(vii) *Use Log Tables, if necessary. Use of calculators is **not***

---

1. Why are solids containing F-centres paramagnetic? 1

2. Write the formulae of two oxo acids of chlorine. 1

3. On heating zinc granules with concentrated HNO_3, a brown gas is evolved which undergoes dimerization. Identify the gas. 1

4. Write the IUPAC name of $[[Co\text{-}(NH_3)_5\ NO_2]\ (NO_3)]$ 1

5. Arrange the following in increasing order of basic strength : Aniline, p-methylaniline, p-nitroaniline. 1

6. Why does a solution containing non-volatile solute have higher boiling point than pure solvent? Why is the elevation of boiling point a colligative property? 2

7. For a reaction A + B ® P, the rate is given by 2

   Rate = k $[A]^2$ [B]

   (a) How is the rate of reaction affected, if the concentration of A is doubled?

   (b) What is the overall order of reaction, if B is present in large excess?

8. Write the balanced chemical equations for the following reactions: 2

   (a) $XeF_4 + SbF_5 \rightarrow$

   (b) $XeF_2 + H_2O\ (l) \rightarrow$

OR

Give reasons for the following :

(a) Xenon does not form fluorides such as XeF_3 and XeF_5.

(b) Out of noble gases, only Xenon is known to form real chemical compounds.17.

9. (a) Name the oil soluble vitamin which is a powerful antioxidant. 2

(b) Name the product of hydrolysis of sucrose.

10. (a) What change occurs in the nature of egg protein on boiling ? 2

(b) What is the difference between the structure of starch and cellulose?

11. Determine the type of cubic lattice to which iron crystal belongs if its unit cell has an edge length of 300 pm and density of iron is 7.2 g cm^{-3}. 3

[Atomic mass of Fe = 56 g mol^{-1} $N_A = 6.02 \times 10^{23}$ mol^{-1}

12. 3.9 gbenzoic acid dissolved in 49 g of water shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated/ dissociated). 3

[Given : Molar mass of

Benzoic Acid = 122 g mol^{-1}, K_f (H_2O) = 1.86 K kg mol^{-1}]

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

OR

The rate constant of a first order reaction increases from 4×10^{-2} to 24×10^{-2}, when the temperature changes from 300 K to 350 K. Calculate the energy of activation (E_a).

[Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021,

log 6 = 0.7782; R = 8.314 J K^{-1} mol^{-1}]

14. (a) Indicate the principle behind the method for the refining of zinc. 3

(b) Account for the following :

(i) It is advantageous to roast sulphide ore to oxidebefore reduction.

(ii) Zinc oxide can be reduced to metal by heating with carbon but not Cr_2O_3.

15. Account for the following: 3

    (a) Interhalogen compounds are more reactive than pure halogens.

    (b) Nitrogen is less reactive at room temperature.

    (c) Reducing character increases from NH_3 to BiH_3.

16. For the complex $[CoF_6]^{3-}$ write the hybridization type, magnetic character and spin nature of the complex. 3

    (Atomic number of Co = 27)

17. How do you convert the following? 3

    (a) Properness to propan-2-ol

    (b) Bromobenzene to 2-bromoacetophenone

    (c) Alkyl halides though polar, are immiscible with water. Why?

18. Write the reactions involved in the following: 3

    (a) Aldol condensation

    (b) Cannizzaro's reaction1

    (c) Rosenmund reduction

19. Give reasons for the following: 3

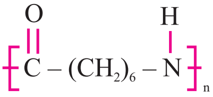
    (a) Aldehydes and Ketones have lower boiling points than corresponding alcohols.

    (b) Chloroacetic acid is stronger than acetic acid.

    (c) Formaldehyde does not take part in aldol condensation.

20. An aromatic compound A on tratment with ammonia followed by heating forms compound B which on heating with Br_2 and KOH forms compound C having molecular formula C_6H_7N. Give the structures of A, B and C. 3

21. (a) Identify the monomers in the following polymeric structure: 3



$$\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}\right]_n$$

    (b) Which one of the following is an Elastomer?

    Urea-formaldehyde, Resin, Buna-S, PVC

    (b) On the basis of forces between their molecules in apolymer, to which class does polyester belong?

22. Give one example for each of the following: 3

(a) An artificial sweetener whose use is limited to cold drinks.

(b) A non-ionic detergent.

(c) A pain reliever used for relief from severe pain like post-operative pain.

23. Aadik Behl was playing in the park with his friends. While running to catch a ball, one of his friends, Saurish fell down and he had a cut on his hand due to which lot of blood was coming out. Aadik took him to his house and applied alum on the cut due to which the blood stopped. 4

Answer the following questions:

(a) Why did the blood stop after applying alum on the cut ?

(b) Alum is used for the purification of water. Why?

(c) Artificial rain is caused by spraying silver iodide on the clouds. Give reason.

(d) What are the values (any two) displayed by Aadik?

24. Calculate the emf and ΔG for the following cell at 298 K : 5

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

[Given: $E^0_{Mg2+/Mg} = -2.34$ V; $E^0_{Ag^+/Ag} = 0.80$ V]

OR

(a) Give reasons for the following:

(i) Iron does not rust even if zinc coating is broken in agalvanized pipe.

(ii) Copper sulphate solution cannot be stored in zinc container.

(b) The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}.

Calculate its degree of dissociation and dissociation constant.

[Gvien : $\lambda^0_{H+} = 349.6$ S cm^2 mol^{-1} and

$\lambda^0_{HCOO-} = 54.6$ S cm^2 mol^{-1}]

25. (a) Why do actinoids show a wide range of oxidation states? Write one similarity between the chemistry of lanthanoids and actinoids.

(b) Second I.E. of chromium and copper are exceptionally higher than that of their neighbouring elements. Explain.

(c) Zinc has lowest enthalpy of atomization in 3d-series. Why? 5

OR

(a) Give reasons for the following:

(i) Transition metals are paramagnetic.

(ii) Transition metals show variable oxidation states.

(iii) Zr and Hfhave nearly similar atomic radii.

(b) Write the preparation of $KMnO_4$ from pyrolusite ore(MnO_2).

26. (a) How do you convert the following? 5

(i) Phenol to Benzene

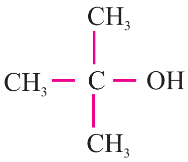
(ii) Ethanol to Ethene

(b) Give the chemical tests to distinguish between the following pairs of compounds:

(i) Ethanol and Phenol

(ii) Butan-2-ol and 2- methylpropan-2-ol

(c) Write the IUPAC name of



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

OR

(a) Write the mechanism for the preparation of alcohols from alkenes (acid catalyzed hydration).

(b) Gvie reasons for the following:

(i) Phenols do not undergo sudergo substitution of the –OH group like alcohols.

(ii) p-nitrophenol is more acidic than p-methylphenol.

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UNSOLVED SAMPLE PAPER

Chemistry-XII (Theory)

Time allowed **Max. Marks = 70**

(i) All questions are compulsory.

(ii) Questions number 1 to 5 are urey short-answer questions and carry 1 mark each.

(iii) Questions number 6 to 10 are short-answer questions and carry 2 marks eack.

(iv) Questions number 11 to 22 are also short-answer questions and carry 3 marke each.

(v) Question number 23 is a value based question and carries 4 marks.

(vi) Questions number 24 to 26 are long-answer questions and carry 5 marks each.

(vii) Ues log tables, if necessary. Use of calculators is not allowed.

---

1. What is the effect of catalyst on: 1

   (i) Gibbs energy (ΔG) and

   (ii) Activation energy of a reaction?

2. Write one similarity between Physisorption and Chemisorption. 1

3. White the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number. 1

4. Write the structure of 3-Bromo-2-methylprop-1-ene. 1

5. Write IUPAC name of the following compound. 1

   $(CH_3)_2N - CH_2CH_3$

6. Write the reactions involved in the following reactions: 1+1=2

   (i) Clemmensen reduction

   (ii) Cannizzaro reaction

7. Draw the structures of the following: 1+1=2

   (i) $H_4P_2O_7$

   (ii) $XeOF_4$

8. Define the following terms: 1+1=2

   (i) Abnormal molar mass

   (ii) Van't Hoff factor (i)

9. Calculate the degree of dissociation α of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^{2}mol^{-1}. 2

Given $\lambda°$ (H^+) = 349.6 S cm^2 mol^{-1} and $\lambda°$ (CH_3COO^-) = 40.9 S cm^2 mol^{-1}

10. Complete the following chemical equations: 1+1=2

(i) $F_2 + 2Cl^- \longrightarrow$

(ii) $2XeF_2 + 2H_2O \longrightarrow$

OR

What happens when

(i) $\mathrm{HC}l$ is added to MnO_2?

(ii) $\mathrm{PC}l_5$ is heated?

White the equations involved.

11. Given reasons: 1×3=3

(i) Acetylation of aniline reduces is its sctivation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although $-NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

12. Give reasons: 1×3=3

(i) Thermal stability decreases from H_2O to H_2Te.

(ii) Fluoride ion has higher hydration enthalpy than chloride ion.

(iii) Nitrogen does not form pentahalide.

13. Define the following: 1×3=3

(i) Anionic detergents

(ii) Limited spectrum antibiotics

(iii) Tranquilizers

14. Write the structures of the monomers used for getting the following polymers: 1×3=3

(i) Nylon-6

(ii) Melamine-formaldehyde polymer

(iii) Teflon

15. Write structures of compounds A, B and C in each of the following reactions:

(i) $C_6H_5Br \xrightarrow{\text{Mg/dry ether}} A \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } CO_{2(g)}} B \xrightarrow{\mathrm{PC}l_5} C$

(ii) $CH_3CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a)} SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$

OR

Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic aicd

(iii) Prapanone to Propene

16. (a) Write the principle of method used for the refining of germanium.

1×3=3

(b) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably?

(c) What is the significance of leaching in the extraction of aluminium?

17. Following compounds are given to you: 1×3=3

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards $S_N2$reaction.

(ii) Write the compound which is optically active.

(iv) White the compound which is most reactive towards β-elimination reaction.

18. Following data are obtained for the reaction: 3

$N_2O_5 \rightarrow 2NO_2 + ½O_2$

t/s	0	300	600
$[N_2O_5]$/mol L–1	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows order reaction.

(b) Calculate the half-life.

(Given log 2 = 0.3010 log 4 = 0.6021)

19. Write one difference between each of the following: 1×3=3

(i) Multimolecular colloid and Macromolecular colloid

(ii) Sol and Gel

(iii) O/W emulsion and W/O emulsion

20. (i) What type of isomerism is shown by the complex $[Co(en)_3]\ Cl_3$? 3

(iii) Write the hybridization and magnetic character $[Co(C_2O_4)_3Cl_3]$ (At. No. of Co = 27)

(iv) Write IUPAC name of the following Complex $[Co(NH_3)_3\ Cl_3]$

21. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes. 2+1=3

(Given : Molar mass of Ag = 108 g mol^{-1} 1F = 96500 C mol^{-1})

(b) Define fuel cell.

22. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K. 3

Given: (Molar mass of sucrose = 342 g mol^{-1})

(Molar mass of glucose = 180 g mol^{-1})

23. After watching a programme on TV about the presence of crainogens (cancer causing agents) Potassium bromate and Patassium iodate in bread and other bakery products, Ritu a class XII student to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. Principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins rich food like fruits, salads, sprouts etc. The decision was welcomed by the parents and students.

After reading the above passage, answer the following questions:

(i) What are the values (at least two) displayed by Ritu?

(ii) Which polysaccharide component of carbohydrates is commonly present in bread?

(iii) Write the two types of secondary structure of proteins.

(iv) Give two examples of water soluble vitamins. 4

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

(b) Write any two differences between amorphous solids and crystalline solids.

Or

(a) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a f.c.c. structure. (Atomic mass of A*l* = 27 g mol^{-1})

(b) Give reasons:

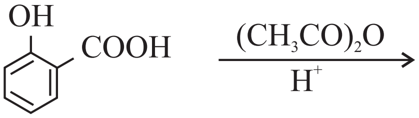
(i) In stoichiometric defects, NaC*l* exhibits Schottky defect and not Frenkel defect.

(ii) Silicon on doping with Phosphorus forms n-type semiconductor.

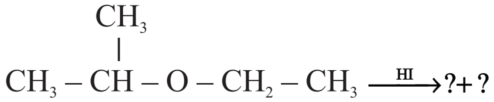
(iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances. 2+3=5

25. (a) Write the product(s) in the following reactions: 2+2+1=5

(i)



(ii)



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-O-CH_2-CH_3 \xrightarrow{HI} ?+?$$

(iii) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC}$

(*b*) Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol

Or

(a) White the formula of reagents used in the following reactios:

(i) Broination of phenol to 2, 4, 6-tribromophenol

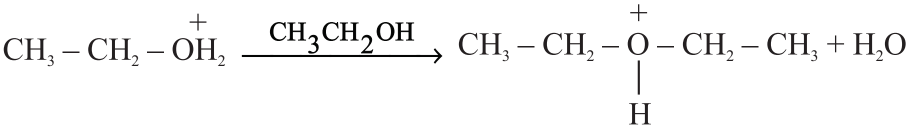
(ii) Hydroboration of propene and then oxidation to propanol.

(b) Arrange the following compound groups in the increasing order of their property indicated:

(i) P-nitrophenol, ethanol, phenol (acidic character)

(ii) Propanol, Propane, Propanal, (boiling point)

(c) Write the mechanism (using curved arrow notation) of the following reaction:



$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3+H_2O$$

26. (a) Account for the following: 3+2=5

(i) Transtiton metals form large number of complex compounds.

(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(iii) E° value for the Mn^{3+}/Mn^{2+}, couple is highly positive (+1.57 V) as compare to Cr^{3+}/Cr^{2+}.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

OR

(a) (i) How is the variability in oxidation states of transition metals different from that of the p-block elements?

(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali, Why?

(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give tow reasons.

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