DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL
(2018-2019)

Class: XII
CHEMISTRY

Under the Guidance of

Mr. Sandeep Kumar
Secretary (Education)

Mr. Sanjay Goel
Director (Education)

Dr. Saroj Bala Sain
Addl. DE (School & Exam.)

Coordinators

Mrs. Mukta Soni
DDE (Exam)

Mr. U.D. Ojha
DEO (Exam)

Mr. Raj Kumar
OSD (Exam)

Mr. Krishan Kumar
OSD (Exam)
PREFACE

It gives me immense pleasure to present the Support Material for various subjects. The material prepared for students of classes IX to XII has been conceived and developed by a team comprising of the Subject Experts, Members of the Academic Core Unit and teachers of the Directorate of Education.

The subject wise Support Material is developed for the betterment and enhancement of the academic performance of the students. It will give them an insight into the subject leading to complete understanding. It is hoped that the teachers and students will make optimum use of this material. This will help us achieve academic excellence.

I commend the efforts of the team who have worked with complete dedication to develop this matter well within time. This is another endeavor of the Directorate to give complete support to the learners all over Delhi.
DIRECTOR’S MESSAGE

Dear Students,

Through this Support Material, I am getting an opportunity to communicate directly with you and I want to take full advantage of this opportunity.

In Delhi, there are approximately 1020 other government schools like yours, which are run by Directorate of Education. The Head Quarters of Directorate of Education is situated at Old Secretariat, Delhi-54.

All the teachers in your school and officers in the Directorate work day and night so that the standard of our govt. schools may be uplifted and the teachers may adopt new methods and techniques to teach in order to ensure a bright future for the students.

Dear students, the book in your hand is also one such initiative of your Directorate. This material has been prepared specially for you by the subject experts. A huge amount of money and time has been spent to prepare this material. Moreover, every year, this material is reviewed and updated as per the CBSE syllabus so that the students can be updated for the annual examination.

Last, but not the least, this is the perfect time for you to build the foundation of your future. I have full faith in you and the capabilities of your teachers. Please make the fullest and best use of this Support Material.

[Signature]

DIRECTOR (EDUCATION)
It gives me immense pleasure and a sense of satisfaction to forward the support material for classes IX to XII in all subjects. The support material is continuously revised, redesigned and updated by a team of subject experts, members of Core Academic Unit and teachers from various schools of DOE.

Consistent use of support material by the students and teachers will make the year long journey seamless and enjoyable. The purpose of providing support material has always been to make available ready-to-use material which is matchless and most appropriate.

My commendation for all the team members for their valuable contribution.

Dr. Saroj Bala Sain
Addl.DE (School)
DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL
(2018-2019)

CHEMISTRY

Class : XII

NOT FOR SALE

PUBLISHED BY : DELHI BUREAU OF TEXTBOOKS
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Roop Narain Chauhan</td>
<td>Vice Principal</td>
</tr>
<tr>
<td></td>
<td>Group Leader (9868373636)</td>
<td>R. P. V. V., Sector-19 Dwarka, New Delhi</td>
</tr>
<tr>
<td>2.</td>
<td>Mukesh Kumar Kaushik</td>
<td>Lecturer</td>
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<td></td>
<td>(Member)</td>
<td>R. P. V. V., Narela, Delhi-40</td>
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<td>3.</td>
<td>Praveen Kumar Jain</td>
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<td>Ganesha Pal Rawat</td>
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<td>(Member)</td>
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</table>
## Chemistry (Code No. 043) Question Paper Design

**Class XII (2018-19)**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Typology of Questions</th>
<th>Very Short Answer (VSA)</th>
<th>Short Answer I (SA-I) 2 Marks</th>
<th>Short Answer II (SA-II) 3 Marks</th>
<th>Long Answer (LA) 5 marks</th>
<th>Total Marks</th>
<th>% Weighage</th>
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<tbody>
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<td>1.</td>
<td><strong>Remembering</strong> (Knowledge based Simple recall questions, to know specific facts, terms, concepts, principles, or theories, identify, define, or recite information).</td>
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<td>2</td>
<td>1</td>
<td>-</td>
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<td>2.</td>
<td><strong>Understanding</strong> (Comprehension-to be familiar with meaning and to understand conceptually, interpret, compare, contrast, explain, paraphrase, or interpret information)</td>
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<td>3.</td>
<td><strong>Application</strong> (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)</td>
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<td>4</td>
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<td>4.</td>
<td><strong>High order Thinking Skills</strong> (Analysis &amp; Synthesis Classify, compare, contrast or differentiate between different pieces of information, Organise and / or integrate unique places of information from a variety of sources)</td>
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<td>-</td>
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<td>1</td>
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<td>5.</td>
<td>Inferential and Evaluation and Multi-Disciplinary (Appraise, judge, and /or justify the value or worth of a decision or outcome, or to predict outcomes based on values)</td>
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<td>2</td>
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<td>-</td>
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<td>2. Solutions</td>
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<td>3. Electrochemistry</td>
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# CLASS XII (2018-19) (THEORY)

**Time : 3 Hours**  
Total Periods (Theory 160 + Practical 60)  
70 Marks

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<th>Title</th>
<th>No. of Periods</th>
<th>Marks</th>
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<td>Unit II</td>
<td>Solutions</td>
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<td><strong>70</strong></td>
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### QUESTION-WISE BREAK UP

<table>
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<tr>
<th>Type of Question</th>
<th>Mark per Question</th>
<th>Total No. of Question</th>
<th>Total Marks</th>
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<td>VSA</td>
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<td>5</td>
<td>05</td>
</tr>
<tr>
<td>SA-I</td>
<td>2</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>SA-II</td>
<td>3</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>LA</td>
<td>5</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>27</strong></td>
<td><strong>70</strong></td>
</tr>
</tbody>
</table>

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 = $2 \times N$ (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$_3$O$_4$, MgFe$_2$O$_4$ 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$_2$O, NaCl, C$_6$H$_6$ because they have all the electrons paired.

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

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

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,** $PE = \frac{Z \times \frac{4}{3} \pi r^3}{a^3} \times 100$

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

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

<table>
<thead>
<tr>
<th>Type of unit cell</th>
<th>Packing efficiency</th>
<th>Rank of unit cell (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>52.4%</td>
<td>1</td>
</tr>
<tr>
<td>BCC</td>
<td>68%</td>
<td>2</td>
</tr>
<tr>
<td>FCC</td>
<td>74%</td>
<td>4</td>
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</table>
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. CdCl₂

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 photovoltaic cell.

Q. 6. Analysis shows that a metal oxide has the empirical formula \( \text{M}_{0.98}\text{O}_{1.00} \). Calculate the percentage of \( \text{M}^{2+} \) and \( \text{M}^{3+} \) ions in the crystal.
Ans. Let the \( \text{M}^{2+} \) ion in the crystal be \( x \) and \( \text{M}^{3+} = 0.98 - x \)
Since, total charge on the compound must be zero,
So, \( 2x + 3(0.98 - x) - z = 0 \)
Or \( x = 0.94 \)
\( \% \) of \( \text{M}^{2+} = \frac{0.94}{0.98} \times 100 = 97.9\% \)
\( \% \) of \( \text{M}^{3+} = 100 - 97.9 = 2.1\% \)

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 SiO₂.
Q.11. Which point defect lowers the density of a crystal?
Aqs. Schottky defect/Vacancy defect.

Q.12. Why glass is called super cooled liquids?
Aqs. Hint: Its molecules move under gravity.

Q.13. Some of the very old glass objects appear slightly milky instead of being transparent. Why?
Aqs. Realignment of molecules takes place due to movement because of constant heating and cooling.

Q.14. What is anisotropy?
Aqs. 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?
Aqs. (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?
Aqs. (a) 14 (b) 9 (c) 8

Q.17. What are the co-ordination numbers of octahedral voids and tetrahedral voids?
Aqs. 6 and 4 respectively.

Q.18. Why common salt is sometimes yellow instead of being pure white?
Aqs. 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?
Aqs. No. of Y (ccp) = 4
No. of X (octahedral void) = 4

\[ \frac{X}{Y} = 4 : 4 \]

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 $\times \frac{1}{8}$ 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. $r = 0.144$ nm

$a = 2\sqrt{2}r$
$= 2 \times 1.414 \times 0.144$ nm
$= 0.407$ 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. CdCl₂ will introduce impurity defect if added to AgCl crystal. Explain.

**Ans.** Two Ag⁺ ions will be replaced by one Cd²⁺ ion to maintain electrical neutrality. Thus, a hole is created at the lattice site for every Cd²⁺ 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

No. of B = octahedral voids + \( \frac{\text{Tetrahedral}}{2} \)
\[ = 4 + \frac{8}{2} = 8 \]

\[ \text{A:B therefore, formula of the compound is } AB_2 \]

\[ 4:8 \]

\[ 1:2 \]

\[ AB_2 \]

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 = \(2 \times 4 = 8\)

No. of tetrahedral voids occupied by X = \(2/3 \times 8 = 16/3\)

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 \(N_A = 6.022 \times 10^{23} \text{ atoms mol}^{-1}\)).

Ans. \[ d = \frac{ZM}{a^3 \times N_A} \]
Here, \( Z = ?, a = 289 \text{ pm} = 289 \times 10^{-10} \text{ cm}, M = 52 \text{ g mol}^{-1}, d = 7.2 \text{ g cm}^{-3} \)

So,

\[
Z = \frac{d \times a^3 \times N_A}{M}
\]

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

Hence type of unit cell in BCC.

Q.41. An element crystallizes in FCC structure; 200 g of this element has \(4.12 \times 10^{24}\) 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 \(8.55 \text{ cm}^3\), calculate its atomic radius. (Atomic mass of Niobium = 92.9 \(u\), \(N_A = 6.022 \times 10^{23} \text{ atoms mol}^{-1}\))

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. (\(N_A = 6.022 \times 10^{23} \text{ atoms mol}^{-1}\))

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\(^{-1}\), \(N_A = 6.022 \times 10^{23} \text{ atoms mol}^{-1}\))

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 \(\text{Ni}_{0.96}\text{O}_{1.00}\). 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 1.00 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 \times 10^{-8} \text{ 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?

\[
\text{Hint: } \quad d = \frac{Z M}{a^3 \times N_A}
\]

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

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

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

Q.57. If NaCl is doped with 10^{-3} mol\% SrCl\(_2\). What is the concentration of cation valencies?

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

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. (\(N_A = 6.022 \times 10^{23} \text{ mol}^{-1}\), Atomic mass of K = 39 g mol\(^{-1}\), Br = 80 g mol\(^{-1}\))

\[
\text{Hint: } \quad \text{Calculate the value of } z = 4 \text{ so it has fcc lattice.}
\]

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

**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 \(5.46 \times 10^{-8}\) 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. \(6.03 \times 10^{23}\) mol\(^{-1}\)

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

Ans. \(1.6 \times 10^{-8}\) cm
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
   
   \[
   X_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad X_B = \frac{n_B}{n_A + n_B}
   \]

   \[X_A + X_B = 1\]

2. **Molarity (M)**
   
   \[\text{Moles of solute} \quad \text{mol L}^{-1} \quad \text{Volume of solution in litres}\]

3. **Molality (m)**
   
   \[\text{Moles of solute} \quad \text{mol kg}^{-1} \quad \text{Mass of solvent in kilograms}\]

4. **Parts per million (ppm)**
   
   \[\text{Number of parts of the compound} \quad \times 10^6 \quad \text{Total number of parts of all components of the solution}\]

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:**

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

   Where \( X_B \) is mole fraction of solute, \( i \) is van’t Hoff factor and \( \frac{p_A^0 - p_A}{p_A^0} \) is relative lowering of vapour pressure.

7. **Elevation in boiling point (\( \Delta T_b \))**

   \[
   \Delta T_b = iK_b m
   \]

   Where \( \Delta T_b = T_b - T_b^0 \)

   \( K_b \) = molal boiling point elevation constant
\[ m = \text{molality of solution} \]
\[ T_b = \text{Boiling point of solution} \]
\[ T_b^0 = \text{Boiling point of solvent} \]

8. **Depression in freezing point** \((\Delta T_f)\):

\[ \Delta T_f = i \cdot K_f \cdot m \]

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** \((\pi)\) of a solution:

\[ \pi V = i \cdot nRT \quad \text{or} \quad \pi = i \cdot CRT \]

where

- \(\pi\) = 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** \((i)\)

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

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

\[
i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}
\]

- \(i > 1\) 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 $i$.

$$ i = \frac{\text{normal molecular mass}}{\text{observed molecular mass}} = \frac{\text{no. of particles after association or dissociation}}{\text{no. of particles before dissociation or association}} $$

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. $N = M \times \text{Basicity or acidity}$

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 H₂SO₄ by weight \((d = 1.8 \text{ gm/ml})\) required to prepare 1 L of 0.2 M solution.

\[ M_1 \times V_1 = \frac{\text{Mass } \times d \times 10}{98} = M_2 \times V_2 \]

\[ = 14.5 \text{ ml} \]

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 PO₄³⁻ present in 4L of 10⁻⁵ M Ca₃(PO₄)₂.

Ans. \(8 \times 10⁻⁵\)

Q.17. Why anhydrous salts like NaCl or CaCl₂ are used to clear snow from roads on hills?

\[ \text{Hint: They depress freezing point of water.} \]

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

\[ \text{Hint: Boiling point increases and freezing point decreases.} \]

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

\[ \text{Hint: m, it is independent of temperature change.} \]

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

\[ \text{Hint: It depends upon number of moles of solute present in solution.} \]

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

\[ \text{Hint: – ve deviations} \]

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

\[ \text{Hint: Carboxylic acids or other example} \]
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 urca  (b) 0.1M BaCl₂  (c) 0.1M Na₂SO₄

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 – 8.0°C? (\( K_f = 1.86 \text{ K kg/mol} \))

**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 \((d = 1 \text{ g mL}^{-1})\).

Ans. Density of water = 1 g mL⁻¹

Mass of 1000 ml of water = \(V \times d\)

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

\[ = 1000 \text{ g} \]

Moles of water = \(\frac{1000}{18} = 55.55 \text{ mol}\)

Now, mole of \(\text{H}_2\text{O}\) 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 NH₄Cl 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 145°C and 190°C respectively. Which of them has higher vapour pressure at 80°C?

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

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. How is molar mass of solute is determined from the 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.

\[
\pi \propto C \\
\pi \propto T \\
\pi \propto CT \\
\pi = CRT \\
\pi = \frac{n_bRT}{V} \\
= \frac{n_b}{M_bV}RT \\
M_b = \frac{n_bRT}{\pi V}
\]
SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Determine the amount of CaCl\textsubscript{2} dissolved in 2.5L at 27\degree C such that its osmotic pressure is 0.75 atm at 27\degree C. (i for CaCl\textsubscript{2} = 2.47)

**Ans.** For CaCl\textsubscript{2},

\[
i = i = 2.47
\]

\[
\pi = iCRT
\]

\[
= i \frac{n_B}{V} \times RT
\]

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

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

\[
n_B = 0.0308 \text{ mol}
\]

Amount = 0.0308 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\textsubscript{2}SO\textsubscript{4} in 2 litre of water at 25\degree C assuming that it is completely dissociated.

**Ans.** If K\textsubscript{2}SO\textsubscript{4} is completely dissociated,

\[
\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}
\]

\[
i = 3
\]

Mol mass of K\textsubscript{2}SO\textsubscript{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 $6 \times 10^{-16}$, 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 → Cu$^{2+}$ + S$^{2-}$

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

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

= S \times S = S^2$

Solubility $S = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-16}}$

= $2.45 \times 10^{-8}$ 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 = $\frac{1}{1 + \frac{1000}{18}} = 0.0177$

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

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

$P_A = 12.08$ 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

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

\[
6.90 = \frac{30 \times 1000}{56 \times V}
\]

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

\[
D = \frac{M}{V}
\]

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

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,

\[
\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{422.6}{1.072} = 394.22 \text{ ml}
\]

\[
M = \frac{n_B}{V}
\]

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

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 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant \(K_b\) for chloroform is 3.63°C/m.

Ans. Elevation in boiling point \(\Delta T_b\) = 68.04 – 61.7 = 6.31°C

Mass of substance \(W_B\) = 6.21 g

Mass of CHCl\(_3\) \(W_A\) = 24.0 g

\(K_B\) = 3.63 °C/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\textsubscript{3}H\textsubscript{8}O\textsubscript{3}) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution? (K\textsubscript{b} = 0.512 K kg mol\textsuperscript{-1})

Ans. 37.73 g

Q.10. 18 g of glucose (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}) (molar mass = 180 g mol\textsuperscript{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil? (K\text{b for water} = 0.52 K kg mol\textsuperscript{-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\textsubscript{b} = 2.53 K kg mol\textsuperscript{-1}). What is molecular formula of sulphur? (Atomic mass s = 32 g mol\textsuperscript{-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\textsubscript{x}

Atomic mass of sulphur = 32

Molecular mass = 32 × x

32x = 253

x = \frac{253}{32} = 7.91 \approx 8

Molecular formula of sulphur = S\textsubscript{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 25°C. 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 × 10⁻³ g
Volume of water = 35.0 ml = 35 × 10⁻³ L
\[ \pi = 0.335 \text{ ton} = 0.335/760 \text{ atm} \]
Temp = 25 + 273 = 298 K
\[ \pi = \frac{W_A RT}{M_A \times V} \]
\[
\frac{0.335}{760} = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298}{M_A \times 35 \times 10^{-3}}
\]
Mₐ = 141933 g mol⁻³

Q. 3. (a) Define van’t Hoff factor.
(b) Calculate the freezing point depression expected for 0.0711M aqueous solution of Na₂SO₄. If this solution actually freezes at −0.320°C, what would be the value of van’t Hoff factor? (Kf = 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
\[ i = \frac{\text{Observed freezing point}}{\text{Calculate freezing point}} \]
\[ i = \frac{0.320}{0.132} = 2.42 \]

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 MgBr₂ in 200 g of water. (Molar mass of MgBr₂ = 184, Kf = 1.86 K kg mol⁻¹)
Ans. (a) \( i < 1 \) when solute is associated and \( i > 1 \) when solute is dissociated.
(b) \[ m = \frac{n_g \times 1000}{W_A \text{ (g)}} \]
\[ \frac{W_B \times 1000}{M_B \times W_A} = \frac{10.50 \times 1000}{184 \times 200} = 0.2853 \text{M} \]

MgBr\(_2\) ionizes as \(\text{MgBr}_2 \rightarrow \text{Mg}^{2+} + 2\text{Br}^-\)

\[ \begin{align*}
   i &= 3 \\
   \Delta T_f &= i \times K_f \times M \\
   &= 3 \times 1.86 \times 0.2855 \\
   &= 1.59
\end{align*} \]

Freezing point \(= 0 - 1.59^\circ C = -1.59^\circ C\)

Q. 5. (a) What is the value of \(i\) for \(\text{Al}_2(\text{SO}_4)_3\) 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. \((K_b = 0.512 \text{ K kg mol}^{-1} \text{ and molar mass of NaCl } = 58.44 \text{ g mol}^{-1})\)

Ans. (a) \(\text{Al}_2(\text{SO}_4)_3 \rightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-}\)

\[ \begin{align*}
   i &= 5 \\
   \Delta T_b &= \frac{iK_b \times 1000 \times W_B}{W_A \times M_B}
\end{align*} \]

(b)

\(\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-\)

\[ \begin{align*}
   i &= 2 \\
   \Delta T_b &= \frac{2 \times 0.512 \times 1000 \times 15}{250 \times 58.44} \\
   &= 1.05
\end{align*} \]

Boiling point of solution = 100 + 1.05

= 101.05^\circ C
**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):**

   \[ k = \frac{1}{\rho} = \frac{1}{R \times \Lambda} \]

   where R is Resistance, \( \frac{l}{A} \) = cell constant (G*) and \( \rho \) is resistivity.

2. **Relation between k and \( \Lambda_m \)**

   \[ \Lambda_m = \frac{1000 \times k}{C} \]

   where \( \Lambda_m \) is molar conductivity, \( k \) is conductivity and \( C \) is molar concentration.

**Kohlrausch’s law:**

(a) In general, if an electrolyte on dissociation gives \( \gamma_+ \) cations and \( \gamma_- \) anions, then its limiting molar conductivity (\( \Lambda_{m}^\circ \)) is given by

   \[ \Lambda_{m}^\circ = \gamma_+ \lambda_+^\circ + \gamma_- \lambda_-^\circ \]

Here, \( \lambda_+^\circ \) and \( \lambda_-^\circ \) are the limiting molar conductivities of cation and anion respectively and \( \gamma_+ \) and \( \gamma_- \) are the number of cations and anions furnished by one formula unit of the electrolyte.
(b) Degree of dissociation ($\alpha$) is given by :

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m}$$

Here, $\Lambda^c_m$ = is molar conductivity at the concentration $C$ and $\Lambda^o_m$ is limiting molar conductivity of the electrolyte.

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

$$K = \frac{C \alpha^2}{1 - \alpha} = \frac{C \left( \frac{\Lambda^c_m}{\Lambda^o_m} \right)^2}{1 - \frac{\Lambda^c_m}{\Lambda^o_m}}$$

**Dry cell :**

At anode (Oxidation)

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

At cathode (Reduction)

$$2\text{NH}_4^+ + 2\text{MnO}_2 + 2e^- \rightarrow 2\text{MnO (OH)} + 2\text{NH}_3$$

Overall

$$\text{Zn} \ (s) + 2\text{NH}_4^+ + 2\text{MnO}_2 \rightarrow \text{Zn}^{2+} + 2\text{MnO (OH)} + 2\text{NH}_3$$

**Mercury cell :**

At anode (Oxidation)

$$\text{Zn} \ (\text{Hg}) + 2\text{OH}^- \rightarrow \text{ZnO} \ (s) + \text{H}_2\text{O} + 2e^-$$

At cathode (Reduction)

$$\text{HgO} \ (s) + \text{H}_2\text{O} + 2e^- \rightarrow \text{Hg} \ (l) + 2\text{OH}^-$$

Overall

$$\text{Zn} \ (\text{Hg}) + \text{HgO} \ (s) \rightarrow \text{ZnO} \ (s) + \text{Hg} \ (l)$$

**Lead storage cell**

At anode (Oxidation)

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

$$\text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4$$

At cathode (Reduction)

$$\text{PbO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$$

$$\text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \ (s)$$
Overall

\[ \text{Pb(s) + PbO}_2\text{ (s) + 2H}_2\text{SO}_4\text{ (aq) } \xrightarrow{\text{Discharging}} \text{2PbSO}_4\text{ (s) + 2H}_2\text{O(l)}} \]

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

\[ E = E^0 - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} = E^0 - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \]

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

\[ E_{\text{cell}} = E^0_{\text{cell}} - \frac{2.303RT}{nF} \log [Q_c] = E^0 - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

**4. Relation between \( E^0_{\text{cell}} \) and equilibrium constant (\( K_c \)):**

\[ E^0_{\text{cell}} = \frac{2.303RT}{nF} \log K_c = \frac{0.059}{n} \log K_c \]

**5. \( \Delta G^0 = -nF E^0_{\text{cell}} \)**

where \( \Delta G^0 \) = standard Gibbs energy change and \( nF \) is the number of Faradays of charge passed. \( E^0_{\text{cell}} \) is standard cell potential.

\[ \Delta G^0 = -2.303RT \log K_c \]

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):

\[ 2\text{Fe (s) } \rightarrow 2\text{Fe}^{2+} + 4e^- \]

At cathode (Reduction):

\[ \text{O}_2\text{ (g) + 4H}^+\text{ (aq) + 4e}^- \rightarrow 2\text{H}_2\text{O} \]

Atmospheric oxidation:

\[ 2\text{Fe}^{2+}\text{ (aq) + 2H}_2\text{O (l) + }\frac{1}{2}\text{O}_2\text{ (g) } \rightarrow \text{Fe}_2\text{O}_3\text{ (s) + 4H}^+\text{ (aq)} \]

**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: \( \text{Cd} (s) + 2\text{OH}^- \xrightarrow{\text{Discharging}} \text{CdO} (s) + 2e^- \)

At cathode: \( \text{NiO}_2 + 2\text{H}_2\text{O} + 2e^- \xrightarrow{\text{Discharging}} 2\text{Ni(OH)}_2 + 2\text{OH}^- \)

Overall: \( \text{Cd} (s) + \text{NiO}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{Discharging}} \text{CdO} (s) + 2\text{Ni(OH)}_2 \)

Fuel cell:

At anode: \( 2\text{H}_2(g) + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 2e^- \)

At cathode: \( \text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \)

Overall: \( 2\text{H}_2(g) + \text{O}_2 \rightarrow 2\text{H}_2\text{O} (l) \)

\( E^o_{\text{cell}} = 0.9\text{V} \)

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. \( \Lambda^c_m = \frac{k}{C} \)

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

Ans. \( \Lambda^c_m = \Lambda_m^o - \Lambda \sqrt{C} \)

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. NH₄Cl is acidic in nature. It corrodes zinc container.

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

Ans. 2Fe + O₂ + 4H⁺ → 2Fe²⁺ + 2H₂O

Q.11. Write the reaction taking place in the cell : Al/Al³⁺ || Cu²⁺/Cu

Ans. 2Al + 3Cu²⁺ → 2Al³⁺ + 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 H₂ 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 Λₘ° for CH₃COOH 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 concentration in it.

Q.17. What is the role of ZnCl₂ in a dry cell?

Ans. ZnCl₂ combines with the NH₃ produced to form a complex salt [Zn(NH₃)₂]Cl₂.

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. $Fe_2O_3\cdot xH_2O$.

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:

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

Ans. Nernst equation is:

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

$E_{M^{n+}/M}^\circ$ 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:

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

[Given: $E_{cell}^\circ = 3.17$ V]
Ans. \( n = 2 \)

The Nernst equation for the cell is:

\[
E = E^0 - 0.059 \frac{0.059}{2} \log \left( \frac{\text{Mg}^{2+}}{\text{Ag}^+} \right)^2
\]

\[
= 3.17 - \frac{0.059}{2} \log \left( \frac{0.130}{0.0001} \right)^2
\]

\[
= 3.17 - 0.21 = 2.96 \text{V}
\]

Q. 3. Suggest a way to determine the \( \Lambda_m^o \) value of water.

Ans. \( \Lambda_m^o (\text{H}_2\text{O}) = \Lambda_m^o (\text{H}^+) + \Lambda_m^o (\text{OH}^-) \)

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

\[
\Lambda_m^o (\text{H}_2\text{O}) = \Lambda_m^o (\text{HCl}) + \Lambda_m^o (\text{NaOH}) - \Lambda_m^o (\text{NaCl})
\]

Q. 4. How much electricity in term of Faraday is required to produce 40 gram of Al from \( \text{Al}_2\text{O}_3 \)? (Atomic mass of Al = 27 g/mol)

Ans.

\[
\text{Al}^{3+} + 3e^- \rightarrow \text{Al}
\]

27 gram of Al require electricity = 3F

\[
\frac{3F}{27} \times 40 = 4.44 \text{ F}
\]

Q. 5. Predict the product of electrolysis of an aqueous solution of \( \text{CuCl}_2 \) with an inert electrode.

Ans. \( \text{CuCl}_2 (s) + \text{Aq} \rightarrow \text{Cu}^{2+} + 2\text{Cl}^- \)

\( \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \)

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

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

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

\( \text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + 1e^- \)

Thus, Cu will be deposited at cathode and \( \text{Cl}_2 \) will be liberated at anode.

Q. 6. Calculate \( \Lambda_m^o \) for \( \text{CaCl}_2 \) and \( \text{MgSO}_4 \) from the following data:

\( \Lambda_m^o (\text{Ca}^{2+}) = 119.0 \), \( \text{Mg}^{2+} = 106.0 \), \( \text{Cl}^- = 76.3 \) and \( \text{SO}_4^{2-} = 160.05 \text{ cm}^2 \text{ mol}^{-1} \)
Ans. $$\Lambda_m^{\circ}(\text{CaCl}_2) = \Lambda_m^{\circ}(\text{Ca}^{2+}) + 2\Lambda_m^{\circ}(\text{Cl}^-)$$
$$= 119 + (2 \times 76.3) = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\Lambda_m^{\circ}(\text{MgSO}_4) = \Lambda_m^{\circ}(\text{Mg}^{2+}) + 2\Lambda_m^{\circ}(\text{SO}_4^{2-})$$
$$= 106 + 160 = 266 \text{ S cm}^2 \text{ mol}^{-1}$$

Q. 7. If $$\Lambda_m^{\circ}$$ for AgNO$_3$, KCl and KNO$_3$ are 133.4, 149.9 and 144.9 S cm$^2$ mol$^{-1}$, calculate $$\Lambda_m^{\circ}$$ 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. $$\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$$
$$n = 1$$
$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[\text{H}^+]}$$
$$E = 0 - \frac{0.0591}{1} \times \text{pH}$$
$$E = -0.0591 \times 10$$
$$E = -0.591 \text{ V}$$

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. $$q = i \times t = 0.5 \times 2 \times 60 \times 60 = 3600 \text{ C}$$
96500 Coulombs are equal to 6.022 $\times$ 10$^{23}$e$^-$
So, 3600 Coulombs = $$\frac{6.022 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22} \text{ electrons}$$

Q.10. How much electricity is required in Coulomb for the oxidation of 1 mole of FeO to Fe$_2$O$_3$?
Ans. Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ + e$^-$
So, 1F = 1 $\times$ 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. Molar conductivity = $$\frac{k \times 1000}{M} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}}$$
$$= 124.0 \text{ S cm}^2 \text{ mol}^{-1}$$
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 \(0.146 \times 10^{-3}\) S cm\(^{-1}\).

Ans. \[\text{Cell constant} = \text{Conductivity} \times \text{Resistance}\]
\[= \frac{0.146 \times 10^{-3}}{1500} \text{S cm}^{-1} = 2.19 \text{ cm}^{-1}\]

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: \[2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)\]

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.
\[\Lambda_m^{\text{(Na}_2\text{SO}_4)} = 2\Lambda_m^{\text{(Na}^+)} + \Lambda_m^{\text{(SO}_4^{2-})}\]

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

Ans. At anode: \[\text{Zn (amalgam)} + 2OH^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^-\]

At cathode: \[\text{HgO (s)} + \text{H}_2\text{O (l)} + 2e^- \rightarrow \text{Hg (l)} + 2\text{OH}^- (aq)\]

The overall reaction is: \[\text{Zn (amalgam)} + \text{HgO (s)} \rightarrow \text{ZnO (s)} + \text{Hg (l)}\]

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

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

At cathode: \[2\text{H}^+ + 2e^- \rightarrow \text{H}_2 (g)\]

\[\text{Zn (s)} + 2\text{H}^+ (al) \rightarrow \text{Zn}^{2+} (aq) + \text{H}_2 (g)\]

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
\[\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad n = 2\]
\[ E_{\text{Cu}^{2+}/\text{Cu}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}]} = 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1} = 0.3104 \text{ V} \]

Q.19. Two metals A and B have reduction potential values – 0.76 V and + 0.34 V respectively. Which of these will liberate \( \text{H}_2 \) from dil. \( \text{H}_2\text{SO}_4 \)?

**Ans.** Metal having higher oxidation potential will liberate \( \text{H}_2 \) from \( \text{H}_2\text{SO}_4 \). Thus, A will liberate \( \text{H}_2 \) from \( \text{H}_2\text{SO}_4 \).

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: \( \text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2e^- \)

Cathode reaction: \( \text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \)

\[
\text{Pb (s)} + \text{PbO}_2 (s) + 2\text{H}_2\text{SO}_4 \xrightarrow{\text{Discharging}} \xrightarrow{\text{Recharging}} 2\text{PbSO}_4(_{\text{s}}) + 2\text{H}_2\text{O (l)}
\]

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

**Ans.** Because no ionic concentration in net cell reaction.

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:

\[ \text{Cu}|\text{Cu}^{2+} || \text{Cl}^{-}|\text{Cl}_2 (\text{Pt}) \]

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

**Ans.** Anode: \( \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \)

Cathode: \( \text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^{-} \)

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

**Ans.** Methane and methanol.

Q.26. \( E^0 \) values of \( \text{MnO}_4^- \), \( \text{Ce}^{4+} \) and \( \text{Cl}_2 \) are 1.507, 1.61 and 1.358 V respectively.

Arrange these in order of increasing strength as oxidizing agent.

**Ans.** \( \text{Cl}_2 < \text{MnO}_4^- < \text{Ce}^{4+} \)
Q.27. Draw a graph between $\Lambda_m^o$ and $\sqrt{C}$ for strong and weak electrolyte.

Ans.

Q.28. The conductivity of 0.02M solution of NaCl is $2.6 \times 10^2$ 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: \( \text{Ag (s)} \rightarrow \text{Ag}^+ + e^- \)

At cathode: \( \text{Ag}^+ + e^- \rightarrow \text{Ag (s)} \)

**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. 

\[ I = 1.5 \text{ Ampere} \]

\[ \text{Time} = 10 \times 60 \text{s} = 600 \text{s} \]

\[ Q = I \times t \]

\[ = 1.5 \times 600 = 900 \text{ C} \]

\( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu (s)} \)
2F amount of electricity deposit copper = \( \frac{63.5 \times 900}{2 \times 96500} \) = 0.296 g

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

\[ \text{Zn (s)} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag (s)} \]

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. \( \text{Zn (s)}||\text{Zn}^{2+} \text{(aq)} || \text{Ag}^-(\text{aq})|\text{Ag (s)} \)

(a) Zn electrode (anode)
(b) Ions are carriers of the current in the cell.
(c) At anode:
\[ \text{Zn (s)} \rightarrow \text{Zn}^{2+} + 2e^- \]
At cathode:
\[ \text{Ag}^+ + e^- \rightarrow \text{Ag (s)} \]

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

Ans. 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)
\[ 4\text{OH}^- - 4e^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]
At cathode (Reduction)
\[ \text{Ag}^+ + e^- \rightarrow \text{Ag (s)} \]
(b) At anode (Oxidation)
\[ \text{Cl}^- - e^- \rightarrow \text{Cl (g)} \]
Cl + Cl → Cl₂

At cathode (Reduction)

Cu²⁺ + 2e⁻ → Cu (s)

Q. 5. The standard reduction potential for Cu²⁺/Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. \( K_{sp} \) of Cu(OH)₂ is \( 1 \times 10^{-19} \).

Ans.

\[
\text{pH} = 14
\]

\[
[\text{H}^+] = 10^{-14}
\]

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

\[
K_w = [\text{H}^+][\text{OH}^-]
\]

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

Cu(OH)₂ → Cu²⁺ + 2 OH⁻

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

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

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

For the cell reaction,

Cu²⁺ + 2e⁻ → Cu (s)

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

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

\[
= 0.34 - \frac{0.059}{2} \times 19 = -0.22 \text{ V}
\]

Q. 6. Determine the values of equilibrium constant \( K_e \) and \( \Delta G^0 \) for the following reaction:

Ni (s) + 2Ag⁺ (aq) → Ni²⁺ (aq) + 2Ag (s) \hspace{1cm} E^0 = 1.05 \text{ V}

Ans.

\[
\Delta G^0 = -nFE^0_{cell}
\]

\[
n = 2, \ E^0_{cell} = 1.05 \text{ V}
\]

\[
F = 96500 \text{ C mol}^{-1}
\]

\[
\Delta G^0 = -2 \times 1.05 \times 96500
\]

\[
= -202.650 \text{ kJ}
\]

\[
\Delta G^0 = -RT \ln K_e
\]
\[
\ln K_c = \frac{\Delta G^\circ}{RT} = \frac{-202.650 \times 10^3}{8.314 \times 298}
\]

\[K_c = 3.32 \times 10^{35}\]

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

Ans.
\[
\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-
\]
\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-]
\]
\[
[\text{Cl}^-] = 1.0 \text{ M}
\]
\[
[\text{Ag}^+] = \frac{k_{sp}}{[\text{Cl}^-]} = \frac{1 \times 10^{-10}}{1} = 1 \times 10^{-10} \text{ M}
\]

Now,
\[
\text{Ag}^+ + e^- \rightarrow \text{Ag (s)}
\]
\[
E = E^\circ - \frac{0.059}{1} \log \frac{1}{[\text{Ag}^+]} = 0.80 - \frac{0.059}{1} \log \frac{1}{10^{-10}}
\]
\[
= 0.80 - 0.059 \times 10 = 0.21 \text{ V}
\]

Q. 8. Estimate the minimum potential difference needed to reduce \( \text{Al}_2\text{O}_3 \) at 500°C. The free energy change for the decomposition reaction:

\[
\frac{2}{3} \text{Al}_2\text{O}_3 \rightarrow \frac{4}{3} \text{Al} + \text{O}_2 \text{ is } \Delta G = +960 \text{ kJ, } F = 96500 \text{ C mol}^{-1}.
\]

Ans.
\[
\frac{2}{3} \text{Al}_2\text{O}_3 \rightarrow \frac{4}{3} \text{Al} + \text{O}_2
\]
\[
n = \frac{6 \times 2}{3} = 4e^-
\]
\[
\Delta G = -nFE
\]
\[
\Delta G = 960 \times 10^3 \text{ J, } n = 4, F = 96500 \text{ C mol}^{-1}
\]
\[
960 \times 10^3 = -4 \times 96500 \times E
\]
\[
E = -2.487 \text{ V}
\]

Minimum potential difference needed to reduce \( \text{Al}_2\text{O}_3 = -2.487 \text{ V.} \)
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. 
\[ w = z \times i \times t \]
\[ t = \frac{w}{z \times i} \]
\[ t = \frac{1.078 \times 1 \times 96500}{107.8 \times 2.5} = 386 \text{ seconds} \]
\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]
\[ w = \frac{63.5}{2 \times 96500} \times 2.5 \times 386 = 0.3175 \text{ gram} \]

Q.10. A solution of Ni(NO\textsubscript{3})\textsubscript{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:
\[ 2\text{Fe}^{3+} (aq) + 2\text{I}^- (aq) \rightarrow 2\text{Fe}^{2+} (aq) + \text{I}_2 (s) \] has \( E^\circ_{\text{cell}} = 0.236 \text{ V} \).

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

Ans. 
\[ n = 2 \]
\[ \Delta G^\circ = - nFE^\circ_{\text{cell}} = - 2 \times 96500 \times 0.236 \text{ J} = - 45.55 \text{ kJ/mol} \]
\[ \Delta G^\circ = - 2.303 \text{ RT log } K_c \]
\[ \log K_c = \frac{\Delta G^\circ}{-2.303 \text{ RT }} = \frac{45.55 \times 10^3}{2.303 \times 8.314 \times 298} = 7.983 \]
\[ K_c = \text{antilog}(7.983) = 9.616 \times 10^7 \]

Q.12. The molar conductivity of 0.025 mol L\textsuperscript{-1} methanoic acid is 46.1 S cm\textsuperscript{2} mol\textsuperscript{-1}. Calculate its degree of dissociation and dissociation constant. Given \( \Lambda^\circ (\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^1, \Lambda^\circ (\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^1. \)
Ans. \[ \Lambda_m^o (\text{HCOOH}) = \Lambda_m^o (\text{H}^+) + \Lambda_m^o (\text{HCOO}^-) \]
\[ = 349.6 + 54.6 \text{ S cm}^2 \text{ mol}^{-1} = 404.2 \text{ S cm}^2 \text{ mol}^{-1} \]
\[ \Lambda_m^o = 46.1 \text{ S cm}^2 \text{ mol}^{-1} \]
\[ \text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+ \]
\[ \alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{46.1}{404.2} = 0.114 \]

Initial conc. \[ C \text{ mol L}^{-1} \]
0 0

At equil. \[ C(1 - \alpha) \]
\[ C\alpha \]

\[ K_c = \frac{C\alpha^2}{1 - \alpha} = \frac{0.025 \times (0.114)^2}{1 - 0.114} \]
\[ = 3.67 \times 10^{-4} \]

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

\[ 2\text{Cr (s)} + 3\text{Cd}^{2+} (\text{aq}) \rightarrow 2\text{Cr}^{3+} (\text{aq}) + 3\text{Cd (s)} \]

Also calculate \( \Delta G^o \) and equilibrium constant of the reaction.

Ans. \[ E_{\text{cell}}^o = E_{\text{cathode}}^o - E_{\text{anode}}^o \]
\[ = -0.40 - (-0.74) = 0.34 \text{ V} \]
\[ \Delta G^o = -nFE_{\text{cell}}^o = -6 \times 96500 \times 0.34 = -196860 \]
\[ = -196860 \text{ J mol}^{-1} = -196.86 \text{ kJ/mol} \]
\[ = \Delta G^o = 2.303 \text{ RT log } K_c \]
\[ 196860 = 2.303 \times 8.314 \times 298 \log K_c \]
\[ \log K_c = 34.5014 \]
\[ K_c = \text{antilog } 34.5014 = 3.192 \times 10^{34} \]

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

Given : \[ E_{\text{Sn}^{4+/\text{Sn}^{2+}}}^o = 0.13 \text{V}, E_{\text{Zn}^{2+/\text{Zn}}}^o = -0.76 \text{V} \]

Will the cell potential \( \uparrow \) or \( \downarrow \) if the concentration of \( \text{Sn}^{4+} \) is increased?

Ans. \[ E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.0591}{n} \log \frac{\text{Sn}^{2+}}{\text{Sn}^{4+}} \times \frac{\text{Zn}^{2+}}{2} \]
\[ = 0.89 - \frac{0.0591}{2} \log \frac{0.5 \times 2}{1.5 \times 1} \]
\[ E = 0.89 - \frac{0.0591}{2} \log \frac{1}{1.5} \]
\[ = 0.895 \text{ V} \]

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

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

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

\[ \text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag} \]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}][\text{Ag}^+]^2}{[\text{Cu}][\text{Ag}^+]^2}
\]

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

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

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

\( \text{Cd}/\text{Cd}^{2+} \) \( (0.1M) || \text{H}^+ \) \( (0.2M)/\text{Pt}, \text{H}_2 \) \( (0.5 \text{ atm}) \)

Given \( E^\circ \) for \( \text{Cd}^{2+}/\text{Cd} = -0.403 \text{ V} \), \( R = 8.314 \text{ J} \text{mol}^{-1} \text{K}^{-1} \), \( F = 96500 \text{ C mol}^{-1} \).

**Ans.** The cell reaction is \( \text{Cd} + 2\text{H}^+ \) \( (0.2M) \rightarrow \text{Cd}^{2+} \) \( (0.1M) + \text{H}_2 \) \( (0.5 \text{ atm}) \)

\[
E^\circ_{\text{cell}} = 0 - (-0.403) = +0.403 \text{ V}
\]

\[
E_{\text{cell}} = 0.403 - \frac{2.303RT}{nF} \log \frac{[\text{Cd}^{2+}] \times P_{\text{H}_2}}{[\text{Cd}][\text{H}^+]^2}
\]

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

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

**Q.17.** The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is \( 5.55 \times 10^3 \text{ ohm} \). Calculate its resistivity, conductivity and molar conductivity.

**Ans.** Diameter = 1 cm, radius = 0.5 cm

\[
\text{Area} = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \text{ cm}^2
\]
\[ \rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \times 0.785}{50} = 87.135 \text{ ohm cm} \]

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

= 0.01148 ohm cm

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

Q.18. Conductivity of saturated solution of BaSO$_4$ at 315 K is $3.648 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ and that of water is $1.25 \times 10^{-6}$ 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. \[ \Lambda_m^o (\text{BaSO}_4) = \Lambda_m^o \text{ Ba}^{2+} + \Lambda_m^o \text{ SO}_4^{2-} = 110 + 136.6 = 246.6 \text{ ohm}^{-1} \text{ cm}^{-1} \]

\[ K_{\text{BaSO}_4} = K_{\text{BaSO}_4 \text{ (solution)}} - K_{\text{water}} = 3.648 \times 10^{-6} - 1.25 \times 10^{-6} \]

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

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

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

**LONG ANSWER TYPE QUESTIONS (5 Marks)**

Q. 1. Conductivity of 0.00241M acetic acid is $7.896 \times 10^{-5}$ S cm$^{-1}$. Calculate its molar conductivity and if \( \Lambda_m^o \) for acetic acid is 390.5 S cm$^2$ mol$^{-1}$, what is its dissociation constant?

Ans. \[ \Lambda_m^o = \frac{k \times 1000}{M} \]

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

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

\[ \alpha = \frac{\Lambda_m}{\Lambda_m^o} = \frac{32.76}{390.5} = 8.39 \times 10^{-2} \]
$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.39 \times 10^{-2})^3}{1 - 8.39 \times 10^{-2}} = 1.86 \times 10^{-5}$$

Q. 2. Three electrolytic cells A, B, C containing solution of ZnSO₄, AgNO₃ and CuSO₄ 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.  \[ \text{Ag}^+ + e^- \rightarrow \text{Ag (s)} \]

108 g of silver is deposited by 96500 C.

1.45 g silver is deposited by \[ \frac{96500 \times 1.45}{108} = 1295.6 \text{ C} \]

\[ Q = 1 \times t \]

\[ 1295.6 = 1.5 \times t \]

\[ t = \frac{12956}{1.5} = 863 \text{ s} \]

In cell A, the electrode reaction is \[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \]

2F of electricity deposit Zn = 65.3 g

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

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu (s)} \]

2F of electricity deposit Cu = 63.5 g

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 \( \Lambda_m^o \) for CH₃COOH.
(c) The $\Lambda_m^o$ for sodium acetate, HCl, NaCl are 91.0, 425.9 and 126.4 S cm$^{-2}$ mol$^{-1}$ respectively at 298 K. Calculate $\Lambda_m^o$ for CH$_3$COOH.

**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$_3$COOH = ?

$$\Lambda^o \text{CH}_3\text{COO}^- + \Lambda^o \text{H}^+ = \Lambda^o \text{CH}_3\text{COO}^- + \Lambda^o \text{Na}^+ + \Lambda^o \text{H}^+$$

$$+ \Lambda^o \text{Cl}^- - \Lambda^o \text{Na}^+ - \Lambda^o \text{Cl}^- \quad \ldots(i)$$

$$\Lambda_m^o \text{CH}_3\text{COOH} = \Lambda^o \text{CH}_3\text{COONa} + \Lambda^o \text{HCl} - \Lambda^o \text{NaCl}$$

(c) $\Lambda_m^o$ CH$_3$COOH = $\Lambda^o$ CH$_3$COONa + $\Lambda^o$ HCl − $\Lambda^o$ NaCl

$$= 91.0 + 425.9 - 126.4$$

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

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

(b) The $E^0$ 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 $\Delta G^o$ for the cell reaction.

**Ans.** (a) **Weak electrolyte**: The substance which partially ionized in solution is known as weak electrolyte. Example: NH$_4$OH.

**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

$E^o_{cell} = 0.52 - 0.16 = 0.36 \text{ V}$

$\Delta G^o = - nFE^o_{cell}$

$$= - 1 \times 96500 \times 0.36$$

$$= - 34740 \text{ J mol}^{-1}$$
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:

\[ \text{Zn/Zn}^{2+} (0.0004M) \ || \ \text{Cd}^{2+} (0.2M)/\text{Cd (s)} \]

Given: \( E^\circ_{\text{cell}} = 0.36 \) V

Ans. (a) At anode: \( \text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + 2\epsilon^- + \text{H}_2\text{O} \)

At cathode: \( \text{HgO (s)} + \text{H}_2\text{O} + 2\epsilon^- \rightarrow \text{Hg (l)} + 2\text{OH}^- \)

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

\( n = 2 \)

According to Nernst equation:

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \left( \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} \right) \]
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.

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

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

\[(\text{Rate})_t = (\text{Instantaneous rate}) \quad \frac{dx}{dt} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt}\]

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 molar 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 the equal to no of moles actually participating in the reaction.

For a reaction, \(aA + bB \rightarrow cC + dD\)
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.

\[ \text{Activation energy} = \text{Threshold energy} - \text{Kinetic energy} \]

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

Temperature coefficient = Rate constant at $T + 10°C$/Rate constant at $T°C$

**Arrhenius Equation**: \[ K = Ae^{-\frac{E_a}{RT}} \]

where, \( K = \text{Rate constant} \)

\( A = \text{Arrhenius energy (Frequency factor or pre-exponential factor)} \)

\( E_a = \text{Activation energy} \)

\( R = \text{Rate constant} \)

\( T = \text{Temperature} \)

\[ \frac{E_a}{RT} = \text{Fraction of molecules having energy equal to or more than activation energy} \]

\[ \log K = \log A - \frac{E_a}{2.303RT} \]

\[ \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \]
\[
\log \frac{K_2}{K_1} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{T_2 - T_1}{T_2 - T_1} \right]
\]

Where \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \)

\[
\log \frac{K_2}{K_1} = \frac{E_a}{19.147} \left[ \frac{T_2 - T_1}{T_2 - T_1} \right] = 0.0522E_a \left[ \frac{T_2 - T_1}{T_2 - T_1} \right]
\]

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) \( t_{1/2} = \frac{[R]_0}{2k} \), \( t_{1/2} \) 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:

\[
t_{1/2} = \frac{0.693}{k}
\]

*Pseudo chemical reaction*: The chemical reaction which looks like higher order reaction but in reality it follows lower order reaction.

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}
\]

Rate = \( k[\text{CH}_3\text{COOC}_2\text{H}_5]^1 \)

**Very Short Answer Type Questions (1 Mark)**

Q. 1. The gas phase decomposition of acetaldehyde

\[
\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}
\]

follows the rate law, \( \text{Rate} = k(P_{\text{CH}_3\text{CHO}})^{3/2} \), unit of \( P \) is atm and time is second.

What are the units of its rate constant?

**Ans.** \( \text{Atm}^{3/2} \text{ sec}^{-1} \)

Q. 2. State the order with respect to each reactant and overall reaction.

\[
\text{H}_2\text{O} + 3\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_3^-
\]

Rate = \( k[H_2O]^1[I]^- \)

**Ans.** Order of reaction = \( 1 + 1 = 2 \)
Q. 3. Give one example of pseudo first order reaction.

**Ans.** Hydrolysis of an ester:

\[ \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \]

Q. 4. The rate law for a reaction is

\[ \text{Rate} = K [A] [B]^{32} \]

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 \(3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3\), how are the rate of reaction expressions \(-\frac{d}{dt}[\text{H}_2]\) and \(\frac{d}{dt}[\text{NH}_3]\) inter-related?

**Ans.** \(\frac{1}{3} \frac{d}{dt}[\text{H}_2] = \frac{1}{2} \frac{d}{dt}[\text{NH}_3]\)

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 \(\Delta G\).

Q. 10. What value of \(k\) is predicted for the rate constant by Arrhenius equation is \(T \rightarrow \infty\)? Is this value physically reasonable?

**Ans.** From the equation \(k = Ae^{\frac{-E_a}{RT}}\) if \(T \rightarrow \infty \rightarrow k \rightarrow A\) so that \(E_a = 0\). This is not feasible.

Q. 11. Determine the order of reaction:

**Step 1.** \(2\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2\) Slow

**Step 2.** \(\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}\) Fast
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 10°.

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. \( \text{H}_2 + \text{Cl}_2 \xrightarrow{hv} 2\text{HCl} \) or any other example

Q.18. The rate constant of a reaction is \( 3 \times 10^2 \text{ min}^{-1} \). 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: \( \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \).

Q.21. Give one example of a reaction where order and molecularity are equal?

Ans. \( 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \) (Order = Molecularity = 2)
Q.22. For a reaction \( R \rightarrow P \), 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 \( 2A \rightarrow \text{Products} \), 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).

\[ \text{CH}_3\text{CHO} \xrightarrow{723 \text{K}} \text{CH}_4 + \text{CO} \]

Q.27. Decomposition reaction of ammonia on Pt surface has rate constant \( = 2.5 \times 10^3 \) 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 \( A + B \rightarrow \text{Product} \), the rate law is given by \( r = k[A]^{1/2} [B]^2 \). What is the order of the reaction?

Ans. Order of reaction = \( 1/2 + 2 = 2.5 \)

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. \( \frac{K_2}{K_1} = 4 \)

\( T_1 = 293 \text{ K}, T_2 = 313 \text{ K} \)

\( \log \frac{K_2}{K_1} = -\frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \)
Thus, on calculating and substituting values, we get:

\[ E_a = 52.86 \text{ KJ mol}^{-1} \]

**Q. 2. If the decomposition of nitrogen oxide as**

\[ 2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2 \]

**follows a first order kinetics.**

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

\[ \text{Rate} = K[\text{N}_2\text{O}_5] \]

\[ K = \frac{\text{Rate}}{[\text{N}_2\text{O}_5]} \]

\[ = \frac{1.5 \times 10^{-6}}{0.05} \]

\[ K = 3.0 \times 10^{-5} \]

(b) What concentration of \(\text{N}_2\text{O}_5\) would give a rate of \(2.45 \times 10^{-5}\) mol L\(^{-1}\) s\(^{-1}\)?

\[ \text{Rate} = 2.45 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \]

\[ [\text{N}_2\text{O}_5] = \frac{\text{Rate}}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}} \]

\[ = 0.82 \text{ M} \]

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

<table>
<thead>
<tr>
<th>Order</th>
<th>Molecularity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. It is the sum of the powers of concentration terms in the rate law expression.</td>
<td>It is the number of reacting species undergoing simultaneously collision in a reaction.</td>
</tr>
<tr>
<td>2. It is determined experimentally.</td>
<td>2. It is a theoretical concept.</td>
</tr>
<tr>
<td>3. Order of reaction need not to be a whole number.</td>
<td>3. It is whole number only.</td>
</tr>
<tr>
<td>4. Order of reaction can be zero.</td>
<td>4. It can’t be zero or fractional.</td>
</tr>
</tbody>
</table>
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,

\[ K = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1} \]

\[ [A]_0 = 0.10 \text{ M} \quad [A] = 0.075 \text{ M} \]

\[ t = \frac{[A]_0 - [A]}{K} = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s} \]

Q. 5. For the reaction:

\[ C_{12}H_{22}O_{11} + H_{2}O \xrightarrow{\text{H}^+} C_{6}H_{12}O_{6} + C_{6}H_{12}O_{6} \]

(a) Rate of reaction expression.

(b) Molecularity

**Ans.** (a) Rate = \( \frac{d}{dt} \left[ C_{12}H_{22}O_{11} \right] = -\frac{d}{dt} \left[ H_{2}O \right] \)

\[ = \frac{d}{dt} \left[ C_{6}H_{12}O_{6} \right] = \frac{d}{dt} \left[ C_{6}H_{12}O_{6} \right] \]

(b) Molecularity = 2

Q. 6. Consider the decomposition reaction:

\[ 2H_{2}O_{2} \xrightarrow{\text{OH}^{-}/\text{I}^{-}} 2H_{2}O + O_{2} \]

This reaction takes place in two steps as given below:

Step 1. \( H_{2}O_{2} + I^- \rightarrow H_{2}O + IO^- \) (slow)

Step 2. \( H_{2}O_{2} + IO^- \rightarrow H_{2}O + I^- + O_2 \) (fast)

(a) Determine rate law expression.

(b) Determine the order of reaction.

**Ans.** (a) Rate = \( K [H_{2}O_{2}] [I^-] \) because second step is rate determining step.

(b) Order = 1 + 1 = 2

Q. 7. The decomposition of hydrocarbon follows the equation \( K = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000/kT} \). Calculate \( E_a \).

**Ans.** \( K = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000/kT} \)

Comparing the equation with Arrhenius equation,
\[ K = A e^{-E_a/RT} \]

\[ \frac{-E_a}{R} = -28000 \text{ K} \]

\[ E_a = 28000 \times 8.314 = 232192 \text{ J mol}^{-1} \]

**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.**

Rate = \( k[A]^2 \)

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 \( \frac{3}{4} \) of the reaction to complete is \( t_2 \). How are \( t_1 \) and \( t_2 \) related?

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

**Q. 10.**

![Graph showing the concentration of A over time](image)

(a) What is the order of the reaction?

(b) What is the slope of the curve?

**Ans.** (a) Zero order reaction.

(b) \( [R] = [R_0] - kt \)

\[ \therefore \text{Slope} = -k \]

**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 \([R] = 0\)

\[
\therefore \quad k t = [R]_0
\]

Or

\[
t = \frac{[R]_0}{k}
\]

Q.12. For the reaction \(N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g)\)

How is the rate of formation of ammonia related to the rate of disappearance of \(H_2\)?

Ans. Rate of reaction \(= \frac{1}{3} \frac{\Delta [H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [NH_3]}{\Delta t}\)

Or \(\frac{\Delta [NH_3]}{\Delta t} = \frac{2}{3} \frac{\Delta [H_2]}{\Delta t}\)

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 \(A (g) \rightarrow \text{Products}\)

\[\text{Rate} = k[A]^n\]  

...(i)

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

\[\frac{\text{Rate}}{2} = k \left( \frac{A}{2} \right)^n\]  

...(ii)

Dividing equation (i) by equation (ii),

\[(2)^1 = (2)^n\]

Or

\[n = 1\]

Q.14. A reaction which is first order with respect to \(A\) has rate constant 6 min\(^{-1}\). If we start with \([A] = 0.5 \text{ mol L}^{-1}\), when would \([A]\) reach the value of 0.05 \text{ M L}^{-1}\?  

Ans.

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

\[k = 6 \text{ min}^{-1}, [A]_0 = 0.5, [A] = 0.05, t = ?\]
\[ t = \frac{2.303}{6} \log \frac{0.5}{0.05} = \frac{2.303}{6} \log 10 = 0.3838 \text{ min} \]

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 \(1.15 \times 10^{-3} \text{ s}^{-1}\). How long will 5 gram of this reactant take to reduce to 3 grams?

Ans. \(t = 444 \text{ seconds}\)

Q.17. \(4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}\). If rate of formation of NO is \(6 \times 10^{-4} \text{ atm min}^{-1}\), calculate the rate of formation of \(\text{H}_2\text{O}\).

Ans. \(9.0 \times 10^{-4} \text{ atm min}^{-1}\)

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 \(K = (4.5 \times 10^{11} \text{ sec}^{-1}) \ e^{-28000K/T}\). Calculate the value of \(E_a\).

Ans. 232.79 kJ/mol

Q.20. Consider a certain reaction \(A \rightarrow \text{Product}\) with \(K = 2.0 \times 10^2 \text{ s}^{-1}\). Calculate the concentration of A remaining after 100 s, if the initial concentration of A is \(1.0 \text{ mol L}^{-1}\).

Ans. \([A] = 0.135 \text{ M}\)

Q.21. Explain with an example, what is a pseudo first order reaction? The graphs (A and B) given below are plots of rate of reaction Vs concentration of the reactant. Predict the order from the graphs.

[Diagram showing two rate concentration 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 \( \text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO} \), the experimentally determined rate expression below 400 K is \( \text{rate} = k[\text{NO}_2]^2 \). 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.

\[
t = \frac{2.303}{K} \log \left( \frac{R_0}{R} \right)
\]

\[
t = \frac{2.303}{10} \log \left( \frac{R_0}{R} \right)
\]

\[
t = \frac{2.303}{60} \log 10
\]

\[
t = \frac{2.303}{60}
\]

\[= 3.38 \times 10^2 \text{ s}^{-1}
\]

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.**

\[ K = \frac{0.693}{t_{1/2}} \]

\[ = \frac{0.693}{69.3} \text{ min} \]

\[ = 10^2 \text{ min}^{-1} \]

\[ T = \frac{2.303}{K} \log \left[ \frac{R_0}{[R]} \right] \]

\[ = \frac{2.303}{10^{-2}} \log 5 \]

\[ = 160.9 \text{ min} \]

**Q. 4.** The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is \(1.8 \times 10^3\) sec\(^{-1}\). Calculate the frequency factor \(A\).

**Ans.** Given, \(E_a = 94.14 \times 10^3 \text{ J mol}^{-1}\), \(T = 40 + 273 = 313 \text{ K}\), \(K = 1.8 \times 10^3 \text{ sec}^{-1}\)

By using, \(K = Ae^{-E_a/RT}\) \(\Rightarrow \ln K = \ln A - \frac{E_a}{RT}\)

Or \(\log K = \log A - \frac{E_a}{2.303RT}\)

Or \(\log \left(1.8 \times 10^{-3}\right) + \frac{94.19 \times 10^3}{2.303 \times 8.314 \times 313} = \log A\)

Or \(A = \text{antilog (10.9635)} = 9.194 \times 10^{10} \text{ sec}^{-1}\)

**Q. 5.** 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. 6.** 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. \(2.824 \times 10^{10}\)

Q. 7. The initial concentration of \(\text{N}_2\text{O}_5\) in the first order reaction \(\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2\) was \(1.24 \times 10^{-2}\) mol L\(^{-1}\) at 318 K. The concentration of \(\text{N}_2\text{O}_5\) after 60 minutes was \(0.20 \times 10^{-2}\) mol L\(^{-1}\). Calculate the rate constant of the reaction at 318 K.

Ans. 

\[
K = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = \frac{2.303}{60} \log \frac{1.24 \times 10^{-2}}{0.2 \times 10^{-2}} \\
= \frac{2.303}{60} \log 6.2 = \frac{2.303}{60} \times 0.7924 \text{ min}^{-1} \\
= 0.0304 \text{ min}^{-1}
\]

Q. 8. The following data were obtained during the first order thermal decomposition of \(\text{N}_2\text{O}_5\) at constant volume:

\[
2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2
\]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Time per second</th>
<th>Total pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.512</td>
</tr>
</tbody>
</table>

Calculate rate constant.

Ans. \(4.98 \times 10^{-4}\) s\(^{-1}\)

Q. 9. 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. 10. For a first order reaction, calculate the ratio between the time taken to complete \(\frac{3}{4}\) of the reaction and the time taken to complete half of the reaction.

Ans. Two

Q. 11. The following results have been obtained during the kinetics studies of the reaction:

\[
2\text{A} + \text{B} \rightarrow \text{C} + \text{D}
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A] mol L(^{-1})</th>
<th>[B] mol L(^{-1})</th>
<th>Initial rate of formation of D mol L(^{-1}) min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.1</td>
<td>0.1</td>
<td>(6.0 \times 10^{-3})</td>
</tr>
<tr>
<td>II</td>
<td>0.3</td>
<td>0.2</td>
<td>(7.2 \times 10^{-2})</td>
</tr>
<tr>
<td>III</td>
<td>0.3</td>
<td>0.4</td>
<td>(2.88 \times 10^{-1})</td>
</tr>
<tr>
<td>IV</td>
<td>0.4</td>
<td>0.1</td>
<td>(2.40 \times 10^{-1})</td>
</tr>
</tbody>
</table>

Determine the rate law and the rate constant for the reaction.
Ans. Rate = $K[A][B]^2$

Q. 12. 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. 13. The decomposition of A into product has value of $K$ as $4.5 \times 10^3$ sec$^{-1}$ at 10° C and energy of activation 60 kJ/mol. At what temperature would $K$ be $1.5 \times 10^4$ sec$^{-1}$.

Ans. 24° C

Q. 14. (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. 15. For a chemical reaction $R \rightarrow P$, 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. 17. 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. 18. In a pseudo first order reaction of hydrolysis of an ester in H$_2$O, the following results were obtained:

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester (M/L)</td>
<td>0.55</td>
<td>0.31</td>
<td>0.17</td>
<td>0.085</td>
</tr>
</tbody>
</table>
(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.

\[
\text{Ans. (a)} \quad \text{Average rate during 30-60 sec.} = \frac{0.17 - 0.31}{60 - 30} = 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}
\]

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

\[
K_{60} = \frac{2.303}{60} \log \frac{0.55}{0.17}
\]

\[
K_{90} = \frac{2.303}{90} \log \frac{0.55}{0.085}
\]

Average \(K = 1.98 \times 10^2 \text{ sec}^{-1}\)

Q. 19. Following reaction takes place in one step:

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2
\]

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?

\[
\text{Ans.} \quad 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2
\]

\[
dx/dt = K*\text{[NO]}^2\text{[O}_2]^1
\]

[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. 20. The decomposition of NH\(_3\) on platinum surface is a zero order reaction. What are the rate of production of N\(_2\) and H\(_2\)? \([K = 2.5 \times 10^{-4}]\)

\[
\text{Ans.} \quad 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2
\]

\[
- \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{NH}_2]}{dt} + \frac{1}{3} \frac{d[\text{H}_2]}{dt}
\]

\[
\frac{d[\text{NH}_3]}{dt} = \text{rate} = k \times [\text{NH}_3]^0
\]

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

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

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

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

**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? \(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\).

**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, \(T_1 = 298 \text{ K}, T_2 = 308 \text{ K}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\)

\[
\frac{K_2}{K_1} = 2
\]

\[
\log 2 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{298} - \frac{1}{308} \right]
\]

\[
0.3010 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right]
\]

\[
E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}
\]
= 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,

\[ \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{H^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \]

excess
Rate = \( K[\text{CH}_3\text{COOC}_2\text{H}_5] \)
Order = 1

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

So, \( E_a = -2.303 \times R \times \text{Slope} \)
\[ = -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 4250 \]
\[ = 81375.3 \text{ J mol}^{-1} \]
\[ = 81.375 \text{ KJ mol}^{-1} \]

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) \( K = (\text{mol})^{1-n} L^{n-1} \text{ S}^{-1} \)

For zero order, \( n = 0 \)

So, \( K = (\text{mol})^{1-0} L^{0-1} \text{ S}^{-1} = \text{ S}^{-1} \text{ mol} L^{-1} \)

For first order, \( n = 1 \)

\( K = (\text{mol})^{1-1} L^{1-1} \text{ S}^{-1} \)

So, \( K = (\text{mol})^{1-1} L^{1-1} \text{ S}^{-1} \)
\[ = \text{ S}^{-1} \]
(b) For a first order reaction,

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

\[ [A]_0 = a, \quad [A] = a - \frac{a \times 99}{100} = 0.01a \]

\[ t(99\%) = \frac{2.303}{K} \log \frac{a}{0.01a} \]

\[ = \frac{2.303}{K} \log 100 \]

\[ = \frac{2.303}{K} \times 2 \]

...(i)

For 90% completion of reaction,

\[ [A] = a - \frac{a \times 99}{100} = 0.1a \]

\[ t(90\%) = \frac{2.303}{K} \log \frac{a}{0.1a} \]

\[ = \frac{2.303}{K} \times 1 \]

...(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. = \( a \)

Conc. after 40 mins. = \( a - \frac{a \times 30}{100} \)

\[ = 0.70a \]

\[ K = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \]
\[ \frac{2.303}{40} \log \frac{a}{0.70a} = \frac{2.303}{40} \log \frac{1}{0.70} = \frac{2.303}{40} \times 0.1549 = 8.92 \times 10^{-3} \text{ min}^{-1} \\
\frac{t_{1/2}}{K} = 0.693 \Rightarrow \frac{0.693}{8.92 \times 10^{-3}} = 77.7 \text{ min} \]

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 \( \text{SO}_2\text{Cl}_2 \) at a constant volume:

\( \text{SO}_2\text{Cl}_2 (g) \rightarrow \text{SO}_2 (g) + \text{Cl}_2 (g) \)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Time/s</th>
<th>Total p/atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Calculate the rate of the reaction when total pressure is 0.65 atm.

Ans. (a) First order reaction

\[ K = \text{mol}^{1-n} \text{L}^{n} \text{S}^{-1} \]

\[ n = 1 \]

\[ K = (\text{mol})^{1-1} \text{L}^{1} \text{S}^{-1} = \text{S}^{-1} \]

\[ k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_i} \]
\[
\frac{2.303}{100} \log \frac{0.5}{(2 \times 0.5 - 0.6)} = \frac{2.303}{100} \log \frac{0.5}{0.4} = \frac{2.303}{100} \times 0.969 = 2.23 \times 10^{-3} \text{ s}^{-1}
\]

Now, \( \text{Rate} = P_{\text{SO}_2\text{Cl}_2} \)

Pressure of \( \text{SO}_2\text{Cl}_2 \) when total pressure = 0.65 atm

\[
P_{\text{SO}_2\text{Cl}_2} = 2P_i - P_t
= 2 \times 0.5 - 0.65
= 0.35 \text{ atm}
\]

Rate \( = 2.23 \times 10^{-3} \times 0.35 \)
\( = 7.8 \times 10^{-4} \text{ atm s}^{-1} \)

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 20° C ?

(b) \( \text{A + 2B} \rightarrow 3\text{C} + 2\text{D} \)

The rate of disappearance of B is \( 1 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1} \). What will be (i) rate of reaction (ii) rate of change in the concentration of A and C ?

Ans. (a) \( 2.35 \times 10^{13} \) times

\[
[\text{Hint : } \log \frac{K_2}{K_1} = \frac{E_a - E_p}{2.303RT} \Rightarrow \log \frac{K_2}{K_1} = \frac{75 \times 10^3}{2.303 \times 8.314 \times 293}]
\]

(b) \( (5 \times 10^{-3}, 5 \times 10^{-3}, 15 \times 10^{-3}) \text{ M L}^{-1} \text{ sec}^{-1} \)

Q. 7. (a) For the reaction \( 2\text{A} + \text{B} \rightarrow \text{A}_2\text{B} \)

the rate = \( k[A][B]^2 \) with \( k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ sec}^{-1} \). Calculate the initial rate of reaction when \( [A] = 0.1 \text{ mol L}^{-1} \), \( [B] = 0.2 \text{ mol L}^{-1} \). Calculate the rate of reaction after \( [A] \) is reduced to 0.06 mol L\(^{-1}\).

(b) (i) The activation energy for the reaction \( 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \) 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.**  (b)(ii) \( K = Ae^{-E_a/RT} \) 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:

<table>
<thead>
<tr>
<th>[R] molar</th>
<th>1.0</th>
<th>0.75</th>
<th>0.40</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t ) (in min)</td>
<td>0.0</td>
<td>0.05</td>
<td>0.12</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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. ]
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 forces.

4. Water vapours are adsorbed in silica gel but absorbed in CaCl₂.

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

\[
\frac{x}{m} = kP^{1/n} \quad (n > 1)
\]

\[\text{i.e.,} \quad \log \left( \frac{x}{m} \right) = \log k + \frac{1}{n} \log P\]

\[
\text{log } \frac{x}{m} \quad \text{slope} = \frac{1}{n}
\]

\[
\text{log } k \quad \text{log } P
\]

The plot of \( \log \frac{x}{m} \) vs \( \log P \) gives a straight line with slope = \( \frac{1}{n} \) 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 **gold 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 NH₃ 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.
   
   \[ \frac{x}{m} = kp^{1/n} \quad (n > 1), \quad \log \frac{x}{m} = \log k + \frac{1}{n} \log P \]

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.
   
   \[ \text{Hint: } \text{SO}_2 + 2\text{H}_2\text{S} \xrightarrow{\text{oxidation}} 3\text{S}_{(\text{sol})} + 2\text{H}_2\text{O} \]

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: \( \text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O} \) 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) \( K_3[\text{Fe(CN)}_6] \)?

[Hint: \( K_3[\text{Fe(CN)}_6] \)]

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 ppt’s 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?

![Diagram](image_url)

Give reasons for the origin of charge.

Ans.  (i) $I^-$ ions are adsorbed on AgI, forming negatively charged colloid.
(ii) $Ag^+$ ions are adsorbed on AgI, forming positively charged colloid.

Reason for origin of charge is the preferential adsorption of common ions of the electrolyte present in excess.

Q. 4. 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.
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 \( \text{CaCl}_2 \): Absorption, as it forms \( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \)

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) + \( \text{H}_2 \) (g) \( \xrightarrow{\text{Ni} (s)} \) Vegetable ghee (s)
(b) \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \) (aq) + \( \text{H}_2\text{O} \) (l) \( \xrightarrow{\text{H}_2\text{SO}_4 \text{(aq)}} \) \( \text{C}_6\text{H}_{12}\text{O}_6 \) (aq) + \( \text{C}_6\text{H}_{12}\text{O}_6 \) (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 45° 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.

$$\frac{1}{n} = \tan 45° = 1, \log k = 0.3010, k = 2, p = 0.5 \text{ atm}$$

$$\frac{x}{m} = kp^{1/n} = 2 \times (0.5)^{1} = 1.0$$

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) $2\text{AuCl}_3 + 3\text{SnCl}_2 \xrightarrow{\text{Reduction}} 2\text{Au (sol)} + 3\text{SnCl}_4$

(b) $\text{FeCl}_3 + 3\text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{Fe(OH)}_3 \text{ (sol)} \text{ (Or Fe}_2\text{O}_3x\text{H}_2\text{O) + 3HCl}$]
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 tannin 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 stabilises 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. Enzymes 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) $C_2H_6$ 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 ethene 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) \[
\begin{align*}
\text{CH} & \equiv \text{CH} + \text{H}_2 & \xrightarrow{\text{Pd}} & \text{CH}_2 \equiv \text{CH}_2 \\
& \xrightarrow{\text{BaSO}_4, \text{quinoline}} & \xrightarrow{\text{Pd}} & \text{CH}_3 \equiv \text{CH}_3 \\
\text{CH} & \equiv \text{CH} + \text{H}_2 & \xrightarrow{\text{Pd}} & \text{CH}_2 \equiv \text{CH}_2
\end{align*}
\]
(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.

\[
\begin{align*}
\text{Alcohols} & \xrightarrow{\text{ZSM-5, Dehydration}} \text{Hydrocarbons}
\end{align*}
\]

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., \( \text{Na}^+ < \text{Ca}^{++} < \text{Al}^{3+} \)  
  For negatively charged sol
- \( \text{Cl}^- < \text{CO}_3^{2-} < \text{PO}_4^{3-} < [\text{Fe(CN)}_6]^{4-} \)  
  For positive sol
Flow-sheet diagram of metallurgical process is given below:

**Step 1. Crushing**
and grinding

**Step 2. Concentration**
of the ore

**Step 3. Working of**
the concentrated ore
(oxidation and
reduction process)

**Step 4. Purification**
and refining

1. Ore
   - Powdered Ore
     - Gravity separation
     - Magnetic separation
     - Froth flotation process
     - Leaching
     - Concentrated Ore
       - Roasting
       - Calcination
       - Conversion into metal oxide (Oxidation)
       - Smelting
       - Hydrometallurgy
       - Auto-reduction
       - Electrolytic reduction
       - Crude Metal
         - Liqation
         - Distillation
         - Poling
         - Electrolytic refining
         - Zone refining
         - Vapour phase refining
         - Chromatographic methods
         - Pure Metal
## General Types of Ores of Metals

<table>
<thead>
<tr>
<th>Type of Ore</th>
<th>Metal</th>
<th>Name of ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Oxides</td>
<td>Iron</td>
<td>Haematite, Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>Aluminium</td>
<td>Bauxite, Al$_2$O$_3$.2H$_2$O</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>Cuprite, Cu$_2$O</td>
</tr>
<tr>
<td></td>
<td>Zinc</td>
<td>Zincite, ZnO</td>
</tr>
<tr>
<td></td>
<td>Manganese</td>
<td>Pyrolusite, MnO$_2$</td>
</tr>
<tr>
<td>2. Sulphides</td>
<td>Copper</td>
<td>Copper pyrites, CuFeS$_2$</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>Galena, PbS</td>
</tr>
<tr>
<td></td>
<td>Zinc</td>
<td>Zinc blende, ZnS</td>
</tr>
<tr>
<td></td>
<td>Mercury</td>
<td>Cinnabar, HgS</td>
</tr>
<tr>
<td>3. Carbonates</td>
<td>Iron</td>
<td>Siderite, FeCO$_3$</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>Malachite, CuCO$_3$.Cu(OH)$_2$</td>
</tr>
<tr>
<td></td>
<td>Calcium</td>
<td>Limestone, CaCO$_3$</td>
</tr>
<tr>
<td></td>
<td>Magnesium</td>
<td>Dolomite, MgCO$_3$.CaCO$_3$</td>
</tr>
<tr>
<td>4. Chloride</td>
<td>Sodium</td>
<td>Rock salt, NaCl</td>
</tr>
<tr>
<td></td>
<td>Magnesium</td>
<td>Carnallite, KCl, MgCl$_2$.6H$_2$O</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>Horn silver, AgCl</td>
</tr>
<tr>
<td>5. Sulphates</td>
<td>Calcium</td>
<td>Gypsum, CaSO$_4$.2H$_2$O</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>Anglesite, PbSO$_4$</td>
</tr>
<tr>
<td>6. Silicates</td>
<td>Magnesium</td>
<td>Calcium magnesium silicate, CaSiO$_2$.3MgSiO$_2$ (Asbestos)</td>
</tr>
</tbody>
</table>
### Various Types of Steel

<table>
<thead>
<tr>
<th>Type of Steel</th>
<th>Carbon content</th>
<th>Properties</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild Steel</td>
<td>0.2-0.5%</td>
<td>(i) It can be hardened by heat treatment.</td>
<td>(i) Lightly stressed machine fittings, turbine, motors, steel, railway axels, crank shafts, fish plates, cross heads, etc.</td>
</tr>
<tr>
<td>(Medium carbon)</td>
<td></td>
<td>(ii) It has a good machining property.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii) It is very good for welding.</td>
<td></td>
</tr>
<tr>
<td>Hard Steel</td>
<td>0.5-0.7%</td>
<td>(i) It can be imparted desired hardness by heat treatment.</td>
<td>Wheels for railways service, cushion springs, clutch springs, dies, set screws, etc.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) It can be welded with a great care.</td>
<td></td>
</tr>
<tr>
<td>Chrome Steel</td>
<td>1.5-2% Cr</td>
<td>Extremely hard</td>
<td>For making armour – piercing projectiles, crushing machinery and cutlery.</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>11.5% Cr</td>
<td>Resists corrosion</td>
<td>For making cutlery, utensils, surgical instruments, automobile parts and cycle parts.</td>
</tr>
<tr>
<td></td>
<td>2% Ni</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**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. \( \Delta G \) should be –ve or \( \log K = + \text{ve} \).

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. \( \text{SiO}_2, \text{Fe}_2\text{O}_3, \) and \( \text{TiO}_2 \).

Q. 9. What is the composition of copper matte?

[ Hint: \( \text{Cu}_2\text{S and FeS} \) ]

Q. 10. Which form of copper is called blister copper?

[ Hint: The solidified copper obtained has blistered appearance due to the evolution of \( \text{SO}_2 \), so it is called blistered copper. ]


[ 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. \( \text{NaCN} \)

Q. 13. What are the constituents of German silver?
Ans. \( \text{Cu} = 25-30\%, \text{Zn} = 25-30\%, \text{Ni} = 40-50\% \)

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,
\( \text{Cu}^{2+} (aq) + \text{H}_2 (g) \rightarrow \text{Cu} (s) + 2\text{H}^+ (g) \)

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 \( \text{Al}_2\text{O}_3 \), ]
Q. 17. Which method of purification is represented by the following reaction:

\[ \text{Ti}_2(\text{s}) + 2\text{I}_2(\text{g}) \xrightarrow{\text{impure}} \text{TiI}_4(\text{g}) \xrightarrow{\Delta} \text{Ti}_2(\text{s}) + 2\text{I}_2(\text{g}) \text{ pure} \]

[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 molten 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. 

\[ 2\text{CuS} (s) + \text{C} (s) \rightarrow \text{CS}_2 (l) + 2\text{Cu} (s) \]

\[ \text{CuO} (s) + \text{C} (s) \rightarrow \text{CO} (g) + \text{Cu} (s) \]

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) \( \text{Fe}_2\text{O}_3 \)
(b) \( \text{Fe}_3\text{O}_4 \)
(c) \( \text{Fe}_2\text{O}_3\cdot2\text{H}_2\text{O} \)
(d) \( \text{FeCO}_3 \)

Q. 8. Give equations for the industrial extraction of zinc from calamine.

Ans. 

\[ \text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2 \] (Calcination)

\[ \text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO} \] (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.

\[ \text{Hint:} \quad (i) \quad \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \]

(ii) \( 3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \)

(iii) \( \text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2 \)

(iv) \( \text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \)

(v) \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)

(vi) \( \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \)

Q. 11. How are impurities separated from bauxite ore to get pure alumina?

\[ \text{Hint:} \quad \text{By leaching.} \]

(i) \( \text{Al}_2\text{O}_3 (s) + 2\text{NaOH} (aq) + 3\text{H}_2\text{O} (l) \rightarrow 2\text{Na}[\text{Al(OH)}_4] (aq) \)

(ii) \( 2\text{Na}[\text{Al(OH)}_4] (aq) + \text{CO}_2 (g) \rightarrow \text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O} (s) + 2\text{NaHCO}_3 (aq) \)

(iii) \( \text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 (s) + x\text{H}_2\text{O} (g) \) (alumina)
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.

\[ \text{ZnO + C} \xrightarrow{975 \text{ K}} \text{Zn + CO} \]

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: $E^\circ_{Fe^{2+}/2e} = − ve, E^\circ_{Cu^{2+}/Cu} = + ve$]

Q. 16. Gibbs energy of formation $G_f$ of MgO (s) and CO (g) at 1273 K and 2273 K are given below:

- $G_f [\text{MgO (s)}] = − 941 \text{ kJ mol}^{-1} \text{ at 1273 K}$
- $G_f [\text{CO (g)}] = − 439 \text{ kJ mol}^{-1} \text{ at 1273 K}$
- $G_f [\text{MgO (s)}] = − 314 \text{ kJ mol}^{-1} \text{ at 2273 K}$
- $G_f [\text{CO (g)}] = − 628 \text{ kJ mol}^{-1} \text{ at 2273 K}$

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, MgO (s) + C (s) $\rightarrow$ Mg (s) + CO (g)

At 1273 K, $G_r = G_f [\text{CO (g)}] - G_f [\text{MgO (s)}] = − 439 - (− 941) \text{ kJ mol}^{-1} = 502 \text{ kJ mol}^{-1}$

At 2273 K, $G_r = - 628 - (− 314) \text{ kJ mol}^{-1} = - 314 \text{ kJ mol}^{-1}$

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) \(2\text{CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{O}_2\)
(ii) \(\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2\)
(iii) \(\text{Cu}_2\text{O} + \text{C} \rightarrow 2\text{Cu} + \text{CO}\)
(iv) \(2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + 2\text{SO}_2\)]

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:

\[
\text{Ag} + \text{NaCN} + [A] + \text{H}_2\text{O} [B] + \text{OH}^- + \text{Na}^+ [C] + [B][D] + \text{Ag}
\]

Ans. 
[A] = O_2
[B] = Na[Ag(CN)_2]
[C] = Zn
[D] = Na_2[Zn(CN)_4]

Q. 5. In the cyanamide extraction process of silver ore argentite from, name the oxidizing and reducing agents. Write the chemical equations of the reactions involved.

[Hint : \(4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Na}[\text{Ag(CN)}_2] + 4\text{NaOH}\)
\(2[\text{Ag(CN)}_2]^- (\text{aq}) + \text{Zn} (\text{s}) \rightarrow [\text{Zn(CN)}_4]^{2-} (\text{aq}) + 2\text{Ag} (\text{s})\)
(i) Oxidising agent = O_2 (ii) Reducing agent = Zn]
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 PCl₅, PF₅ and PF₅⁻. Why?
   
   (ii) Sulphur (S) forms SF₆ but oxygen does not form OF₆. 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 π-π bond(s) with itself, (*e.g.*, C=≡C, C≡N, 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 π d-d bonds with oxygen.

Nitrogen rarely forms π-d bonds with heavier elements as in case of trisilylamine (SiH₃)₃N.
Now, the following questions can be explained using the above mentioned reasoning:

(i) Nitrogen forms N₂ but phosphorus forms P₄ at room temperature. Why?
(ii) Oxygen exists as O₂ but sulphur as S₈. Why?
(iii) Explain why (CH₃)₃P=O is known but (CH₃)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, ICl₄⁻/XeF₄, BrO₃⁻/XeO₃, BH₄⁻/NH₄⁺ 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 ns² electrons of heavier elements strongly and the tendency of ns² 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) NaBiO₃ 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) $AsCl_4$ 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 atom, 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 NH₃ molecule than PH₃ molecule. Because of more Ip-bp repulsion, the N– H bonds are pushed closer to a lesser extent than in PH₃. 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 PH₄⁺ ion is higher than in PH₃. Why?

(ii) H– O– H bond in H₂O is greater than H– S– H angle in H₂S. 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:

- PH₃ < AsH₃ < SbH₃ < NH₃  
  Melting point  
- PH₃ < AsH₃ < NH₃ < SbH₃  
  Boiling point  
- H₂S < H₂Se < H₂Te < H₂O  
  Melting point and boiling point  
- HCl < HBr < HI < HF  
  Boiling point  
- HCl < HBr < HF < HI  
  Melting point

(i) NH₃ has higher boiling point than PH₃.

(ii) H₂O is liquid and H₂S is gas or H₂S is more volatile than H₂O.

**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, while thermal stability decreases down the group, reducing power and acid strength of hydrides increases down the group.
The following questions can be explained using the above concepts.

**Explain why :**

(i) HF is weaker acid than HCl.
(ii) Among hydrogen halides, HI is the strongest reducing agent.
(iii) \( \text{H}_2\text{Te} \) is more acidic than \( \text{H}_2\text{S} \).
(iv) \( \text{NH}_3 \) is mild reducing agent while \( \text{BiH}_3 \) is the strongest reducing agent among the group-15 hydrides.
(v) \( \text{H}_2\text{S} \) is weaker reducing agent than \( \text{H}_2\text{Te} \).

**Basic nature of hydrides \( \text{EH}_3 \) of group 15 elements**

All the hydrides \( \text{EH}_3 \) 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 \( \text{PH}_3 \), the lone pair of electrons is present in large and more diffuse 3s orbital which is non-directional. As a result, \( \text{PH}_3 \) is less basic than \( \text{NH}_3 \) and basic character decreases down the group. \( \text{NH}_3 \) donates electron pair more readily than \( \text{PH}_3 \). \( \text{(SiH}_3\text{)}_3\text{N} \) has less Lewis basic nature than that of \( \text{(CH}_3\text{)}_3\text{N} \) because lone pair of electrons in p-orbital of N atom in \( \text{(SiH}_3\text{)}_3\text{N} \) is transferred to the vacant d-orbital of Si atom forming dπ-pπ bond.

**Covalent/Ionic Character of Halides**

Pentahalides are more covalent than trihalides since the element (E) in higher oxidation state (+ 5) in pentahalides has more polarizing power than element (E) in lower oxidation state (+ 3) in trihalides, similarly, \( \text{SnCl}_4 \), \( \text{PbCl}_2 \), \( \text{SbCl}_3 \) and \( \text{UF}_4 \) 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) \( \text{SnCl}_2 \) has more b.p. than \( \text{SnCl}_4 \).
(ii) \( \text{SbCl}_5 \) is more covalent than \( \text{SbCl}_3 \).
(iii) \( \text{PCl}_5 \) has lower boiling point than that of \( \text{PCl}_3 \).

**Oxoacids of N, P and halogens :**

\[
\begin{align*}
\text{HNO}_3 & \\
\text{H}_2\text{SO}_3 & \\
\text{H}_2\text{SO}_4 & 
\end{align*}
\]
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**

\[ \text{X(g)} \xrightarrow{-\Delta_{\text{el}} H} \text{X(g)} \]

\[ + \frac{1}{2} \Delta_{\text{diss}} H^0 \]

\[ \text{aq} \xrightarrow{-\Delta_{\text{hyd}} H^0} \]

\[ \frac{1}{2} \text{X}_2(\text{g}) \xrightarrow{\Delta_{\text{el}} H^0} \text{X(aq)} \]

The more negative the value of \( \Delta_{\text{H}} H^0 = \frac{1}{2} \Delta_{\text{diss}} H^0 - \Delta_{\text{el}} H^0 - \Delta_{\text{hyd}} H^0 \) the higher will be oxidizing property of the halogen and more positive will be standard reduction potential \( E_{\text{red}}^0 \) of the halogen.

Following questions can be explained on the basis of parameters, like \( \Delta_{\text{diss}} H^0, \Delta_{\text{el}} H^0 \) and \( \Delta_{\text{hyd}} H^0 \).
(i) Why does F\textsubscript{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\textsubscript{2}) is a stronger oxidizing agent than Cl\textsubscript{2} gas. Why?

**Some Important Reactions**

1. \((\text{NH}_4\textsubscript{2} \text{Cr}_2\text{O}_7) \xrightarrow{\text{Heat}} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3\)

2. \(\text{FeCl}_3\text{ (aq)} + \text{NH}_4\text{OH} \text{ (aq)} \rightarrow \text{Fe}_2\text{O}_3\cdot x\text{H}_2\text{O} \text{ (s)} + \text{NH}_4\text{Cl} \text{ (aq)}\)

3. \(\text{Cu}^{2+} \text{ (aq)} + 4\text{NH}_3 \text{ (aq)} \rightarrow \left[\text{Cu}\left(\text{NH}_3\right)_4\right]^{2+} \text{ (aq)}\)

4. \(\text{AgCl} \text{ (s)} + 2\text{NH}_3 \text{ (aq)} \rightarrow [\text{Ag}\left(\text{NH}_3\right)_2]\text{Cl}\)

5. \(2\text{Pb}\left(\text{NO}_3\right)\text{ (s)} \xrightarrow{673 K} 4\text{NO}_2 + 4\text{PbO} + \text{O}_2\)

6. \(4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5\)

7. \(3\text{Cu} + 8\text{HNO}_3\text{ (dil.)} \rightarrow 3\text{Cu(NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}\)

8. \(\text{Cu} + 4\text{HNO}_3\text{ (conc.)} \rightarrow \text{Cu(NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}\)

9. \(4\text{Zn} + 10\text{HNO}_3\text{ (dil.)} \rightarrow 4\text{Zn(NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}\)

10. \(\text{Zn} + 4\text{HNO}_3\text{ (conc.)} \rightarrow \text{Zn(NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}\)

11. \(\text{I}_2 + 10\text{HNO}_3\text{ (conc.)} \rightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}\)

12. \(\text{S}_8 + 48\text{HNO}_3\text{ (conc.)} \rightarrow 8\text{H}_2\text{SO}_4 + 48\text{NO}_2 + 16\text{H}_2\text{O}\)

13. \(\text{P}_4 + 20\text{HNO}_3\text{ (conc.)} \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}\)

14. Chemistry of ring test:
\[\text{NO}_3^- + 3\text{Fe}^{3+} + 4\text{H}^+ \rightarrow \text{NO} + 3\text{Fe}^{3+} + 2\text{H}_2\text{O}\]
\[\left[\text{Fe}(\text{H}_2\text{O})_6\right]^{2+} + \text{NO} \rightarrow \left[\text{Fe}(\text{H}_2\text{O})_5\text{NO}\right]^{2+} + \text{H}_2\text{O}\]

15. \(\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2\)

16. \(\text{P}_4 + 8\text{SOCl}_2 \rightarrow 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2\)

17. \(\text{P}_4 + 10\text{SO}_2\text{Cl}_2 \rightarrow 4\text{PCl}_5 + 10\text{SO}_2\)

18. \(\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 3\text{HCl}\)

19. \(\text{PCl}_5 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 3\text{HCl}\)

20. \(4\text{H}_3\text{PO}_4 \xrightarrow{\text{Heat}} 3\text{H}_2\text{PO}_4 + \text{PH}_3\)

21. \(4\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2} 2\text{Cl}_2 + 2\text{H}_2\text{O}\)

22. \(2\text{Fe}^{3+} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + \text{SO}_4^{2-} + 4\text{H}^+\)

23. \(5\text{SO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{Mn}^{2+}\)

24. \(2\text{F}_2\text{ (g)} + 2\text{H}_2\text{O} \text{ (l)} \rightarrow 4\text{H}^+ \text{ (aq)} + 4\text{F}^- \text{ (aq)} + \text{O}_2 \text{ (g)}\)

25. \(\text{X}_2\text{ (g)} + \text{H}_2\text{O} \text{ (l)} \rightarrow \text{HX} \text{ (aq)} + \text{HXO} \text{ (aq)} \text{ (X = Cl, Br)}\)

26. \(4\text{I}^- \text{ (aq)} + 4\text{H}^+ \text{ (aq)} + \text{O}_2 \rightarrow 2\text{I}_2 \text{ (s)} + 2\text{H}_2\text{O} \text{ (l)}\)
27. \( \text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} \)

28. \( 2\text{NaOH (dil)} + \text{X}_2 \xrightarrow{\text{Cold}} \text{NaX} + \text{NaOX} + \text{H}_2\text{O} \)  

29. \( 6\text{NaOH (conc)} + 3\text{X}_2 \xrightarrow{\text{heat}} 5\text{NaX} + \text{NaXO}_3 + 3\text{H}_2\text{O} \)  
\( (\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2) \)

30. \( 2\text{Ca(OH)}_2 + 2\text{Cl}_2 \rightarrow \text{Ca(OCl)}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O} \)

31. \( \text{NaCl} + \text{H}_2\text{SO}_4 \xrightarrow{\text{heat}} \text{NaHSO}_4 + \text{HCl} \)

32. \( \text{XeF}_2 + \text{PF}_5 \rightarrow \text{[XeF]}^4\text{[PF}_6]^{	ext{-}} \)

33. \( \text{XeF}_6 + \text{MF} \rightarrow \text{M}^+\text{[XeF}_7]^{	ext{-}} \) \( (\text{M} = \text{Na}, \text{K}, \text{Rb or Cs}) \)

34. \( 6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 2\text{O}_2 \)

35. \( \text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF} \)

36. \( \text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF} \)

37. \( \text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF} \)

\[ \text{NH}_3 \quad \text{P}\text{H}_3 \quad \text{Sp}^3 \text{(Pyramidal)} \]
\[ \text{PCl}_3 \quad \text{Sp}^3 \text{(Pyramidal)} \]

\[ \text{SF}_6 \quad \text{Sp}^3\text{d}^2 \text{(Octahedral)} \]

Oxides of Nitrogen
\( :\text{N} = 0 \)
Nitric oxide (colourless) 
paramagnetic

\[ \text{NO} \]
\( \text{Sp}^2 \text{(NO})_2 \) Bentmolecule 
(brown) Paramagnetic

\[ \text{N} \equiv \text{N} \rightarrow \text{O} \]
\( (\text{N}_2\text{O}) \) Colourless 
Linear

\[ \text{N}_2\text{O}_4 \] (Colourless) 
(diamagnetic)

\[ \text{N}_2\text{O}_5 \] (Colourless) 
(diamagnetic)

\[ (\text{N}_2\text{O}_3) \] Pale blue solid
Oxy-acids of Nitrogen

\[
\begin{align*}
\text{(HNO}_3) & \quad \text{Colourless} \\
\text{(HNO}_2) & \quad \text{Pale blue} \\
\text{Hyponitrous acid} & \\
\text{Resonating structure of NO}_3^- &
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \quad \text{(Phosphoric acid) tribasic} \\
\text{H}_3\text{PO}_3 & \quad \text{Phosphoric acid (Dibasic)} \\
\text{H}_4\text{P}_3\text{O}_7 & \quad \text{Pyrophosphoric acid (tetrabasic)} \\
\text{H}_4\text{P}_2\text{O}_6 & \quad \text{Hypophosphoric acid (tetrabasic)} \\
\text{H}_3\text{PO}_2 & \quad \text{(Hypophosphoric acid) (Monobasic)} \\
\text{Cyclic meta phosphoric acid (HPO}_3\text{)}_n &
\end{align*}
\]

\[
\begin{align*}
\text{sp}^3 & \quad \text{Bent molecules} \\
\text{H}_2\text{S (sp}^3\text{)} & \quad \text{V-shape} \\
\text{H}_2\text{O (sp}^3\text{)} & \quad \text{V-shape} \\
\text{Planer Sp}^3 &
\end{align*}
\]
**General principles and processes of Block Elements**

- **SF₄**
  - Trigonal pyramidal sp³d

- **ClO₂**
  - $\sigma - \sigma^*$

- **ClₙOₙ**
  - $\sigma - \sigma^*$

- **H₂SO₄**
  - Sulphuric acid

- **H₂S₂O₃**
  - Thiosulphuric acid

- **H₂SO₃**
  - Sulphurous acid

- **H₂SO₃ (Caro's acid)**
  - Peroxomonosulphuric acid

- **H₂S₂O₈ (Marshall's acid)**
  - Peroxodisulphuric acid

- **(H₂S₂O₈) Cl₂O**

- **Dithionic acid (H₂S₂O₈)**
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?
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 \( \text{E}_2 \) at room temperature. Assign a reason.

[Hint: p-p multiple bonds are formed by N due to its small size.]

Q. 5. The ionization enthalpies of group 15 elements are higher than those of corresponding members of group 14 and 16 elements. Assign the reason.

[Hint: Due to their stable electronic configuration (ns\(^2\)np\(^3\)].

Q. 6. The boiling point of PH\(_3\) is lesser than NH\(_3\). Why?

[Hint: NH\(_3\) molecules are stabilized by intermolecular H-bonding, while PH\(_3\) by weak van der Waals’s forces.]

Q. 7. NO\(_2\) dimerises to form N\(_2\)O\(_4\). Why?

[Hint: Due to presence of odd electron on N.]

Q. 8. Draw the structure of N\(_2\)O\(_5\) molecule.

Ans.

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{N} & \rightarrow & \text{N} & \rightarrow & \text{O} \\
\end{array}
\]

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\(_3\)PO\(_3\)?

[Hint: 4H\(_3\)PO\(_3\) \rightarrow 3H\(_3\)PO\(_4\) + PH\(_3\)]

Q. 12. How does NH\(_3\) acts as a complexing agent?

[Hint: Metal hydroxides are dissolved in excess of NH\(_4\)OH. 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\(_2\)O \rightarrow POCl\(_3\) + 2DCI]

Q. 14. What is laughing gas? How is it prepared?

[Hint: N\(_2\)O, NH\(_4\)NO\(_3\) \rightarrow N\(_2\)O + 2H\(_2\)O]
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: $4\text{AgNO}_3 + \text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ag} + 4\text{HNO}_3 + \text{H}_3\text{PO}_4$]

Q. 17. Draw the structure of $\text{H}_4\text{P}_2\text{O}_7$ and find out its basicity.

[Hint: HO – P – O – 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, $\text{PCl}_5$ behaves as an ionic species.

[Hint: It exists as an ionic solid [PCl$_4^-$][PCl$_6^{3-}$]]

Q. 21. Give reason: $\text{BiCl}_3$ is less covalent than $\text{PCl}_3$.

[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 $\text{N}_2\text{O}$.

(ii) Nitrogen monoxide/Nitrogen (II) oxide/Nitric oxide NO.]
SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Complete the following reactions:

1. (i) \((\text{NH}_4)_2 \text{Cr}_2\text{O}_7 \xrightarrow{\text{heat}}\)
   (ii) \(\text{NH}_4\text{Cl (aq)} + \text{NaNO}_2 (aq) \rightarrow\)

2. (i) \(\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow\)
   (ii) \(\text{FeCl}_3 (aq) + \text{NH}_4\text{OH (aq)} \rightarrow\)

3. (i) \(\text{Ca}_3\text{P}_2 + \text{H}_2\text{O (l)} \rightarrow\)
   (ii) \(\text{I}_2 + \text{HNO}_3 (\text{conc.}) \rightarrow\)

4. (i) \(\text{Ba(N}_3\text{)}_2 \xrightarrow{\text{heat}}\)
   (ii) \(4\text{H}_3\text{PO}_3 \xrightarrow{\text{heat}}\)

5. (i) \(\text{PH}_4\text{I} + \text{KOH} \rightarrow\)
   (ii) \(\text{HgCl}_2 + \text{PH}_3 \rightarrow\)

6. (i) \(\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow\)
   (ii) \(\text{PCl}_5 + \text{H}_2\text{O} \rightarrow\)

7. (i) \(\text{NO}_3^- + \text{Fe}^{2+} + \text{H}^+ \rightarrow\)
   (ii) \(\text{Zn} + \text{HNO}_3 (\text{dil.}) \rightarrow\)

8. (i) \(\text{Zn} + \text{HNO}_3 (\text{conc.}) \rightarrow\)
   (ii) \(\text{P}_4 + \text{HNO}_3 (\text{conc.}) \rightarrow\)

9. (i) \(\text{NH}_3 + \text{O}_2 \xrightarrow{\text{pt/Rh}}\)
   (ii) \(\text{P}_4 + \text{NaOH} + \text{H}_2\text{O} \rightarrow\)

10. (i) \(\text{NH}_3 \text{ (excess)} + \text{Cl}_2 \rightarrow\)
    (ii) \(\text{NH}_3 + \text{Cl}_2 \text{ (excess)} \rightarrow\)

11. (i) \(\text{P}_4 + \text{HNO}_3 (\text{conc.}) \rightarrow\)
    (ii) \(\text{Cu} + \text{HNO}_3 (\text{conc.}) \rightarrow\)

Q. 12. Why is red phosphorus denser and less chemically reactive than white phosphorus?

[Hint: Because it have polymeric structure consisting chains of \(\text{P}_4\) 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 \(\text{NH}_3\) to \(\text{BiH}_3\). Why?

(ii) Phosphorus show marked tendency for catenation. Why?
[Hint: (i) Because from NH₃ to BiH₃ thermal stability decreases hence acidic character increases from NH₃ to BiH₃,
(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:
NCl₃, PCl₃, AsCl₃, SbCl₃

[Hint: NCl₃ < PCl₃ < AsCl₃ < SbCl₃]

Q. 15. How many P – O – P bonds are there in (i) H₄P₂O₇ (ii) P₄O₁₀?

[Hint: (i) H₄P₂O₇ = 01 (ii) P₄O₁₀ = 05]

Q. 16. At low temperature, NO₂ becomes colourless. Why?

[Hint: NO₂ gets condensed to N₂O₄]

Q. 17. Give chemical reaction in support of the statement that all the bonds in PCl₅ molecule are not equivalent.

[Hint: PCl₅ dissociates into PCl₃ and Cl₂ on heating.]

\[ \text{PCl}_5 \xrightarrow{\Delta} \text{PCl}_3 + \text{Cl}_2 \]

Q. 18. (i) What is the covalency of N in N₂O₅?

(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 PCl₅, while N cannot expand its octet.]

Q. 19. Arrange the following in the decreasing order of their basicity. Assign the reason:
PH₃, NH₃, SbH₃, AsH₃, BiH₃

[Hint: NH₃ > PH₃ > AsH₃ > SbH₃ > BiH₃, small size, more charge density]

Q. 20. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber’s process.

[Hint: N₂(g) + 3H₂(g) \xrightarrow{\text{Fe}} \xrightarrow{\text{Mo}} 2\text{NH}_3(g)
(i) High pressure (200 atm).
(ii) Moderate temperature (700 K).
(iii) Presence of catalyst Fe, with small amount of K₂O and Al₂O₃ to increase the rate of attainment of equilibrium.]
Q. 21. Explain the Ostwald’s process to manufacture nitric acid. Give any two uses of HNO₃.

\[ \text{Hint} : \ 4\text{NH}_3 \ (g) + 5\text{O}_2 \ (g) \xrightarrow{\text{Pt.} 500\text{K} \ 9 \text{bar}} 4\text{NO} \ (g) + 6\text{H}_2\text{O} \ (l) \]

\[ 2\text{NO} \ (g) + \text{O}_2 \ (g) \rightarrow 2\text{NO}_2 \ (g) \]

\[ 3\text{NO}_2 \ (g) + \text{H}_2\text{O} \ (l) \rightarrow 2\text{HNO}_3 \ (aq) + \text{NO} \ (g) \]

(68% by mass)

Uses : (i) Used in the manufacture of fertilizers, explosives.
(ii) Used as lab reagent.

Q. 22. Why does PCl₃ fumes in moisture? Give reaction also.

\[ \text{Hint} : \ \text{PCl}_3 \ \text{hydrolyses in the presence of moisture giving fumes of HCl.} \]

\[ \text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl} \uparrow \]

Q. 23. Draw the structure of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why?

\[ \text{Hint} : \ \text{White phosphorus exists as discrete P}_4 \ \text{tetrahedral molecule, while red phosphorus is polymeric consisting of chains of P}_4 \ \text{tetrahedra linked together.} \]

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 HNO₃ prepared commercially?
(ii) Write chemical equations of the reactions involved.
(iii) What concentration by mass of HNO₃ can be obtained?
[Hint: Refer to Q. 21 SA-I type]

Q. 2. An unknown salt X reacts with hot conc. H₂SO₄ 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. H₂SO₄ along the sides of the test tube, a brown complex Y is formed at the interface between the solution and H₂SO₄. Identify X and Y and write the chemical equation involved in the reaction.

\[ \text{Hint:} \ X = \text{NO}_3^- \text{salt,} \quad [Y = \text{[Fe(H}_2\text{O)}_6\text{(NO)}]^{2+}] \]

\[ \text{NO}_3^- + 3\text{Fe}^{2+} + 4\text{H}^+ \rightarrow \text{NO} + 3\text{Fe}^{3+} + 2\text{H}_2\text{O} \]

\[ \text{[Fe(H}_2\text{O)}_6\text{(NO)}]^{2+} + \text{NO} \rightarrow \text{[Fe(H}_2\text{O)}_5\text{(NO)}]^{2+} + \text{H}_2\text{O} \]

(Brown complex)
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) $4\text{Zn} + 10\text{HNO}_3 $ (dil.) $\rightarrow 4\text{Zn(NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}$
(ii) $3\text{Cu} + 8\text{HNO}_3 $ (dil.) $\rightarrow 3\text{Cu(NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
(iii) $\text{I}_2 + 10\text{HNO}_3 $ (conc.) $\rightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$

Q. 5. A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous 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).


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$_3$P = O exist but R$_3$N = O does not? (R = an alkyl group).
(iii) Why is N$_2$P unreactive at room temperature?

*Hint*: (i) Due to its small size and high electronegativity, N forms $p\pi - p\pi$ multiple bond (N ≡ N) whereas P does not form $p\pi - p\pi$ bonds but forms P–P single bond.
(ii) In R$_3$N = O, N should have a covalence of 5 so the compound R$_3$N = O does not exist since maximum covalence shown by N cannot exceed 4.
(iii) Due to N – N triple bond
GROUP 16 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why SF₄ is easily hydrolysed, whereas SF₆ is resistant to hydrolysis?

[Hint : Water molecule cannot attack ‘S’ atom due to steric hinderance and ‘S’ atom is also coordinately saturated in SF₆ 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 H₂S₂O₄ and find the number of S – S bond, if any.

[Hint :]

\[
\begin{array}{c}
\text{O} \\
\text{HO} \quad - \quad \text{S} \quad - \quad \text{O} \quad - \quad \text{O} \quad - \quad \text{S} \quad - \quad \text{OH} \\
\text{O} \\
\end{array}
\]

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 Fe³⁺ ions to Fe²⁺ ions.

\[2\text{Fe}^{3+} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + \text{SO}_4^{2-} + 4\text{H}^+\]}

Q. 5. All the bonds in SF₄ are not equivalent. Why?

[Hint : It is having see-saw shape. (4BP + 1LP)]

Q. 6. O₃ acts as a powerful oxidizing agent. Why?

[Hint : Due to the ease with which it liberates atoms of nascent oxygen.]

\[\text{O}_3 \rightarrow \text{O}_2 + [\text{O}]\]

Q. 7. Which one of the following is not oxidized by O₃? State the reason:

KI, FeSO₄, K₂MnO₄, KMnO₄

[Hint : KMnO₄, 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 SO₂ molecule have equal strength?

[Hint: Due to resonance, two S – O bonds have partial double bond character, hence have equal strength.]

Q. 12. \( K_a_2 \ll K_a_1 \) for \( H_2SO_4 \) in water, why?

[Hint: \( H_2SO_4 \) (aq) + \( H_2O \) (l) \( \rightarrow \) \( H_3O^+ \) (aq) + \( HSO_4^- \) (aq); \( K_a_1 > 10 \)

\( HSO_4^- \) (aq) + \( H_2O \) (l) \( \rightarrow \) \( H_3O^+ \) (aq) + \( SO_4^{2-} \) (aq); \( K_a_2 = 10^{-2} \)

\( K_a_2 \) is less than \( K_a_1 \) 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 \( p\pi-p\pi \) 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 ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Write the chemical equations of the following reactions:
   (a) Sucrose is heated with conc. \( H_2SO_4 \).
   (b) Sodium nitrate is heated with conc. \( H_2SO_4 \).

[Hint: (a) \( C_{12}H_{22}O_{11}(\text{conc.} \ H_2SO_4) \rightarrow 12C + 11H_2O \)
(b) \( NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \).]
Q. 2. 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 (V₂O₅).

\[2\text{SO}_2 (g) + \text{O}_2 (g) \rightarrow 2\text{SO}_3 (g) \Delta H^\circ = -196.6 \text{ KJ mol}^{-1}\]

Q. 3. Complete the following reactions :

(a) PbS + O₃ →
(b) KI + H₂O + O₃ →
(c) MnO₄⁻ + SO₂ + H₂O →
(d) S₈ + H₂SO₄ (conc.) →

Q. 4. Explain why :

(a) H₂S is more acidic than H₂O.
(b) Two S – O bonds in SO₂ are identical.
(c) SF₆ is inert and stable but SF₄ 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 SF₄ cannot offer much steric hindrance, hence reactive.]

Q. 5. How is O₃ estimated quantitatively ?

[Hint : O₃ reacts with an excess of KI solution buffered with a borate buffer, I₂ is liberated which is titrated against standard solution of sodium thiosulphate.]

\[2\text{I}^- (aq) + \text{H}_2\text{O} (l) + \text{O}_2 (g) \rightarrow \text{I}_2 (s) + \text{O}_3 (g) + 2\text{OH}^- (aq)\]

Q. 6. Explain why O₃ is thermodynamically less stable than O₂ ?

[Hint : Because O₃ is endothermic compound/decomposition of O₃ is exothermic and \(\Delta G\) is negative/decomposition of O₃ is spontaneous.]

Q. 7. Draw the structure of :

(i) H₂SO₅
(ii) SO₃²⁻

[Hint : (i) HO – S – O – O – H (ii)]
SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (i) How does O₃ react with lead sulphide? Write chemical equation.
(ii) What happens when SO₂ is passed in acidified KMnO₄ solution?
(iii) SO₂ behaves with lime water similar to CO₂. Explain why?

[Hint: (i) PbS (s) + 4O₃ (g) → PbSO₄ (s) + 4O₂ (g)
(ii) It decolourises acidified KMnO₄ solution.
SO₂ + 2MnO₄⁻ + 2H₂O → 5SO₄²⁻ + 4H⁺ + 2Mn²⁺
(iii) It turns lime water milky due to the formation of insoluble CaSO₃.
Ca(OH)₂ + SO₂ → CaSO₃ + H₂O
(milkiness)

Q. 2. Complete the reactions:
(i) CaF₂ + H₂SO₄ (conc.) →
(ii) C₁₂H₂₂O₁₁ + H₂SO₄ (conc.) →
(iii) SO₂ + MnO₄⁻ + H₂O →

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. KMnO₄ solution. Identify the solid ‘A’ and the gas ‘B’ and write the reaction involved.

[Hint: A = S₈; B = SO₂ (g)]
(i) How is SO₂ prepared in laboratory?
(ii) What happens when SO₂ is passed through water and reacts with NaOH? Write balanced equation.
(iii) Write its any two uses.

[Hint: (i) Na₂SO₃ (s) + H₂SO₄ (aq) → SO₂ (g) + Na₂SO₄ (aq) + H₂O (l)
(ii) 2NaOH + SO₂ (g) → Na₂SO₃ (aq) + H₂O
Na₂SO₃ (aq) + SO₂ + H₂O → 2NaHSO₃ (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) H₂O is less acidic than H₂Te.
(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) \(4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2\)

(ii) \(2\text{SO}_2 (g) + \text{O}_2 (g) \rightarrow 2\text{SO}_3 (g)\)

(iii) \(\text{SO}_3 + \text{H}_2\text{SO}_4 (98\%) \rightarrow \text{H}_2\text{S}_2\text{O}_7 (\text{oleum})\)

(iv) \(\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4\)]

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: \(K_a (\text{HF}) = 7 \times 10^{-4}\) \(K_a (\text{HI}) = 7 \times 10^{11}\)

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: \(\text{KI} + \text{I}_2 \rightarrow \text{KI}_3\)]

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 \(\text{H}_2\text{SO}_4\) forming \(\text{Br}_2\).]

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: \(\text{I}_2\text{O}_5\).]
Q. 10. Arrange the following oxoacids of chlorine in increasing order of acid strength:

\[ \text{HOCl, HOClO, HOClO}_2, \text{HOClO}_3 \]

[Hint: HOCl < HOClO < HOClO\(_2\) < HOClO\(_3\)]

Q. 11. Why does fluorine not play the role of a central atom in interhalogen compounds?

[Hint: Due to smallest size of F. and high electronegativity]

Q. 12. Fluorine exhibit only – 1 oxidation state whereas other halogens exhibit +ve oxidation states also. Explain why?

[Hint: Due to absence of vacant d-orbitals in the octet of F.]

Q. 13. \(\text{ClF}_3\) exists but \(\text{FCl}_3\) 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. \(\text{ClF}_3\) 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 \(\text{NaCl}\) is heated with \(\text{H}_2\text{SO}_4\) in the presence of \(\text{MnO}_2\)?

[Hint: \(4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{MnCl}_2 + 4\text{NaHSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2\)]

Q. 17. With what neutral molecule \(\text{ClO}^-\) is isoelectronic?

[Hint: \(\text{ClF}\) or \(\text{OF}_2\).]

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 \(\text{F}_2\) is less than that of \(\text{Cl}_2\). Explain why?

[Hint: \(\text{F}_2\) is having higher electron-electron repulsion due to its smaller size, as compared to \(\text{Cl}_2\).]

**SHORT ANSWER-I TYPE QUESTIONS (2 Marks)**

Q. 1. (i) Interhalogen compounds are more reactive than halogens except \(\text{F}_2\). Why?

(ii) Give one important use of \(\text{ClF}_3\).
[Hint: (i) Because X – X bond in interhalogens is weaker than X – X bond in halogens except F – F bond.

(ii) ClF₃ is used for the production of UF₆.]

Q. 2. (i) Write the composition of bleaching powder.

(ii) What happens when NaCl is heated with conc. H₂SO₄ in the presence of MnO₂. Write the chemical equation.

[Hint: (i) Ca(OCl)₂ CaCl₂ Ca(OH)₂ 2H₂O]

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 + H₂SO₄ (conc.) → NaHSO₄ + HCl]

Q. 4. NO₂ readily disminide, whereas ClO₂ does not. Why?

[Hint: Due to bigger size of Cl than N.]

Q. 5. Compare the oxidizing powers of F₂ and Cl₂ 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 often used instead of F₂? Write chemical equation showing their use as fluorinating agents.

[Hint: U(s) + 3ClF₃(l) → UF₆(g) + 3ClF(g)]

Q. 7. Draw the structure of BrF₃.

```
F
```

F → Br→ Bent T - shaped

Complete the following reactions:

8. (i) Al₂O₃ (s) + NaOH (aq) + H₂O (l) →

(ii) HCl + O₂ →

9. (i) Ca(OH)₂ + Cl₂ →

(ii) N₂ (excess) + Cl₂ →

10. (i) Na₂SO₃ + Cl₂ + H₂O →

(ii) N₂ + Cl₂ (excess) →
11. (i) \( \text{Cl}_2 + \text{NaOH (cold & dil.)} \rightarrow \)
   (ii) \( \text{Cl}_2 + \text{NaOH (hot & conc.)} \rightarrow \)

12. (i) \( \text{Fe} + \text{HCl} \rightarrow \)
   (ii) \( \text{Cl}_2 + \text{F}_2 \text{ (excess)} \rightarrow \)

13. (i) \( \text{U} + \text{ClF}_3 \rightarrow \)
   (ii) \( \text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2 \rightarrow \)

Q. 14. Draw the structure of : (a) \( \text{I}_3^- \) (b) \( \text{ICl}_2^- \).

   \( \text{Hint :} \)

   \[
   \begin{array}{c}
   \text{Linear} \\
   \text{[I – I} \leftarrow \text{I}^-]
   \end{array}
   \quad \begin{array}{c}
   \text{Linear} \\
   \text{[Cl – I} \leftarrow \text{Cl}^-]
   \end{array}
   \]

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 \( \text{Cl}_2 \) makes it colourless.

   \( \text{[Hint : (i) According to Fajan’s Rule, bigger ions are more polarized than the smaller ions by a particular cation.} \)

   (ii) \( \text{ClO}_4^- \) is more resonance stabilized than \( \text{SO}_4^{2-} \) since dispersal of negative charge is more effective in \( \text{ClO}_4^- \) as compared with \( \text{SO}_4^{2-} \).

   (iii) \( 2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2 \)

   \( 5\text{Cl}_2 \text{ (excess)} + \text{I}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{HIO}_3 + 10\text{HCl} \)

   (colourless)

Q. 2. \( \text{X}_2 \) is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in \( \text{H}_2\text{O} \) to give a solution which turns blue litmus red. When \( \text{X}_2 \) is passed through \( \text{NaBr} \) solution, \( \text{Br}_2 \) is obtained.

   (i) Identify \( \text{X}_2 \), name the group to which it belongs.

   (ii) What are the products obtained when \( \text{X}_2 \) reacts with \( \text{H}_2\text{O} \) ? Write chemical equation.
(iii) What happens when \( X_2 \) reacts with hot and conc. NaOH? Give equation.

[Hint: (i) \( \text{Cl}_2 \), 17 group.
(ii) \( \text{Cl}_2 (g) + 2\text{H}_2\text{O} (l) \rightarrow \text{HCl} (aq) + \text{HOCl} (aq) \)
(iii) \( 3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O} \]

Q. 3. Arrange the following in the order of the property indicated for each set:

(i) \( \text{F}_2, \text{Cl}_2, \text{Br}_2, \text{I}_2 \) (Increasing bond dissociation energy)
(ii) \( \text{HF}, \text{HCl}, \text{HBr}, \text{HI} \) (decreasing acid strength)
(iii) \( \text{NH}_3, \text{PH}_3, \text{AsH}_3, \text{SbH}_3, \text{BiH}_3 \) (Decreasing base strength)

[Hint: (i) \( \text{F}_2 \) has exceptionally low bond dissociation enthalpy. Lone pairs in \( \text{F}_2 \) molecule are much closer to each other than in \( \text{Cl}_2 \) molecule. Stronger electron-electron repulsions among the lone pairs in \( \text{F}_2 \) molecule make its bond dissociation enthalpy exceptionally low, \( \text{I}_2 < \text{F}_2 < \text{Br}_2 < \text{Cl}_2 \)

(ii) Acid strength depends upon \( \text{H} - \text{X} \) bond dissociation enthalpy. As the size of ‘\( X \)’ atom increases, bond dissociation enthalpy of \( \text{H} - \text{X} \) decreases. \( \text{HI} > \text{HBr} > \text{HCl} > \text{HF} \)

(iii) Electron availability on the central atom ‘\( E \)’ in \( \text{EH}_3 \) decreases down the group.] \( \text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3 \)

Q. 4. Draw the structure of:

(i) Hypochlorous acid
(ii) Chlorous acid
(iii) Perchloric acid

\[ \text{Hint}: \]

\[ \text{(a) } \begin{array}{c} \text{H} \\ \text{O} \text{Cl} \end{array} \quad \text{(b) } \begin{array}{c} \text{H} \\ \text{O} \text{Cl} \text{O} \end{array} \quad \text{(c) } \begin{array}{c} \text{O} \\ \text{H} \end{array} \]

Q. 5. Which is more acidic among \( \text{HClO}_4 \) and \( \text{HIO}_4 \)? Why?

[Hint: \( \text{HClO}_4 \) is more acidic than \( \text{HIO}_4 \). Because Cl is more electronegative than Br, due to which \( \text{ClO}_4 \) group have more tendency to withdraw electrons of O–H bond towards itself as compared to \( \text{BrO}_3 \) group.]

GROUP 18 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What inspired N. Barlett for carrying out reaction between Xe and PtF\(_6\)?

[Hint: Almost same ionization enthalpy of oxygen and Xe.]
Q. 2. Predict the shape and the bond angle (90° or more or less) in the following case:

\[ \text{XeF}_2 \text{ and the angle } \text{F} - \text{Xe} - \text{F} \]

[Hint : Linear, 180°]

Q. 3. Structure of Xenon fluoride cannot be explained by valence bond approach. Why?

[Hint : Due to fully filled octet of Xe.]

Q. 4. Why do some noble gases form compounds with fluorine and oxygen only?

[Hint : Due to high electronegativity of F and oxygen.]

Q. 5. XeF\(_2\) has a straight linear structure and not a bent angular structure. Why?

[Hint : In XeF\(_2\), 2 bond pairs and 3 lone pairs are present hence linear structure.]

Q. 6. Why do noble gases have very low boiling point?

[Hint : Because noble gases are stabilized by weak van der Waal’s forces.]

Q. 7. Write the chemical equation involved in the preparation of XeF\(_4\).

[Hint : Xe (g) + 2F\(_2\) (g) \rightarrow XeF\(_4\) (s)]

Ratio 1 : 5

SHORT ANSWER-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\(_2\)O (l) \rightarrow 2Xe (g) + 4HF (aq) + O\(_2\) (g)

(ii) Xe + PtF\(_6\) \rightarrow Xe\(^+\)[PtF\(_6\)]\(^-\)]
Q. 4. Complete the reactions:
   (i) \( \text{XeF}_6 + \text{H}_2\text{O} \rightarrow \)
   (ii) \( \text{XeF}_6 + \text{H}_2\text{O} \rightarrow \)

Q. 5. Draw the structure of \( \text{BrF}_3, \text{XeOF}_4, \text{XeO}_3 \) using VSEPR theory.

   \[ \text{Hint} : \]
   \[
   \begin{align*}
   & \text{Br} \quad \text{F} \quad \text{F} \\
   & \text{F} \\
   & \text{F} \\
   & \text{F} \\
   \end{align*}
   \]

Q. 6. Account for the following:
   (i) \( \text{XeF}_2 \) has linear structure and not a bent structure.
   (ii) The majority of known noble gas compounds are those of Xenon. Why?

   \[ \text{Hint} : \text{(ii) Xe has low ionization enthalpy as compared to other noble gases.} \]

Q. 7. Write the chemical reactions:
   (i) \( \text{XeF}_2 (s) + \text{H}_2\text{O} (l) \rightarrow \)
   (ii) \( \text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \)

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.

   \[ \text{Hint} : \text{(i) Due to their electron configuration.} \]
   (ii) Due to its less solubility in blood.
   (iii) Due to its high ionization enthalpy.\]

Q. 2. Draw the structure of:
   (i) \( \text{XeOF}_4 \)  (ii) \( \text{XeF}_6 \)  (iii) \( \text{XeO}_3 \)

   \[ \text{Hint} : \]
   \[
   \begin{align*}
   & \text{F} \quad \text{Xe} \quad \text{F} \\
   & \text{F} \quad \text{F} \\
   & \text{O} \\
   & \text{F} \\
   \end{align*}
   \]

   \[
   \begin{align*}
   & \text{F} \quad \text{Xe} \quad \text{F} \\
   & \text{F} \quad \text{F} \\
   & \text{F} \\
   & \text{O} \\
   & \text{O} \\
   \end{align*}
   \]

   \[
   \begin{align*}
   & \text{F} \quad \text{Xe} \quad \text{F} \\
   & \text{F} \quad \text{F} \\
   & \text{O} \\
   \end{align*}
   \]
Q. 3. Complete the reactions:
   (i) \( \text{XeF}_2 + \text{NaF} \rightarrow \)
   (ii) \( \text{XeF}_4 + \text{SbF}_5 \rightarrow \)
   (iii) \( \text{XeF}_4 + \text{H}_2\text{O} \rightarrow \)

Q. 4. (i) How is \( \text{XeO}_3 \) prepared from \( \text{XeF}_6 \)? Write the chemical equation for the reaction.

(ii) Draw the structure of \( \text{XeF}_4 \).

[Hint: (i) \( \text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF} \)
Or
\( 6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2 \)]

(ii) \[
\begin{array}{c}
\text{F} \\
\text{Xe} \\
\text{F} \\
\end{array}
\]

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How is \( \text{PH}_3 \) prepared in the laboratory? How is it purified? How does the solution of \( \text{PH}_3 \) in water react on irradiation with light and on adsorption in \( \text{CuSO}_4 \)? How can you prove that \( \text{PH}_3 \) is basic in nature?

Write chemical equations for all the reactions involved.

[Hint: \( \text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2 \)
It is purified by absorbing it in HI to form \( \text{PH}_4\text{I} \) which on treating with KOH gives off phosphine.

\( \text{PH}_4\text{I} + \text{KOH} \rightarrow \text{KI} + \text{H}_2\text{O} + \text{PH}_3 \)
\( \text{PH}_3 \) in water decomposes into red phosphorus and hydrogen in presence of light.

\( 4\text{PH}_3 \rightarrow \text{P}_4 + 6\text{H}_2 \)
Reaction with \( \text{CuSO}_4 \):

\( 3\text{CuSO}_4 + 3\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4 \)]

Q. 2. Identify A, B, C, D and E in the following sequence of reactions:

A \( \xrightarrow{\text{Cl}_2} \) B \( \xrightarrow{\text{H}_2\text{O}} \) C (Acid)

\( \text{Excess of Cl}_2 \)

B \( \xrightarrow{\text{CH}_3\text{COOH}} \) C

\( \text{E (Acid)} \)

D \( \xrightarrow{\text{CH}_3\text{COOH}} \) \( \text{CH}_3\text{COCl} \)

(White solid)

(Excess of Cl)

(Yellowish)

(Colourless Oily liquid)
Complete the reactions of the above mentioned sequence.

*Hint*: A is P₄, B is PCl₃.

\[
P Cl₃ + 3H₂O \rightarrow H₃PO₃ + 3HCl
\]

(C)

\[
3CH₃COOH + PCl₃ \rightarrow 3CH₃COCl + H₃PO₃
\]

(D)

\[
P₄ + 10Cl₂ \rightarrow 4PCl₅, \quad PCl₅ + 4H₂O \rightarrow H₃PO₄ + 3HCl
\]

(E)

Q. 3. Write the structure of A, B, C, D and E in the following sequence of reactions:

\[
NH₃ + O₂ \rightarrow A + H₂O
\]

(A)

\[
A + O₂ \rightarrow B \text{ (Brown fumes)}
\]

(B)

\[
B + H₂O \rightarrow C + A \text{ (C is an oxoacid)}
\]

(C)

\[
C + I⁻ \rightarrow D \text{ (Violet vapours)}
\]

(Q. 3. 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 HNO₃.

\[
2NO + O₂ \rightarrow 2NO₂
\]

(A)

\[
3NO₂ + H₂O \rightarrow 2HNO₃ + NO
\]

(B)

\[
6I⁻ + 2NO₃⁻ + 8H⁺ \rightarrow 3I₂ + 2NO + 4H₂O
\]

(Q. 4. A waxy translucent solid, M, insoluble in water but soluble in CS₂, 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 CS₂ and does not glow in dark. Identify R and draw its structure.

*Hint*: (a) M is white phosphorus.

\[
P₄ + 3NaOH + 3H₂O \rightarrow PH₃ + 3NaH₂PO₂
\]

(N)
\[ P_4 + 5O_2 \rightarrow P_4O_{10} \]

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 \( XeF_2 \) react 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) \( \text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+[\text{PF}_6]^- \)

(d) He is used in filling balloons/used by scuba divers.

    Ne is used in discharge tubes, advertisement display purposes.

(e) \( 6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2 \)
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 $(n-1)d^{1−10}ns^{n−2}$ 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

<table>
<thead>
<tr>
<th>3rd group $n^2$</th>
<th>4th group $n^2d^1$</th>
<th>5th group $n^2d^2$</th>
<th>6th group $n^2d^3$</th>
<th>7th group $n^2d^4$</th>
<th>8th group $n^2d^5$</th>
<th>9th group $n^2d^6$</th>
<th>10th group $n^2d^7$</th>
<th>11th group $n^2d^8^0$</th>
<th>12th group $n^2d^9^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(n−1)$</td>
<td>$(n−1)$</td>
<td>$(n−1)$</td>
<td>$(n−1)$</td>
<td>$(n−1)$</td>
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</tr>
<tr>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
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<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
</tbody>
</table>

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 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

**(iv) Oxidation States**

- Transition metals show 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 M²⁺ ions in solution and their standard electrode potentials.

  - If sum of the first and second ionization enthalpies is greater than hydration enthalpy standard potential \((E^0_{M^{2+}/M})\) 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 TiX₄, VF₅ and CrF₆. The + 7 state for Mn is not represented in simple halides but MnO₄⁻ is known and beyond Mn no metal has a trihalide except FeX₃ and CoF₃ and increasing order of oxidizing power in the series VO₂⁺ ≪ Cr₂O₇²⁻ ≪ MnO₄⁻.

**(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 $\text{V}_2\text{O}_5$, 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 ($\text{K}_2\text{Cr}_2\text{O}_7$)**

(i) **Ore**

Ferrochrome or chromate ($\text{FeO}_\text{Cr}_2\text{O}_5$) or ($\text{FeCr}_2\text{O}_4$)
(ii) Preparation

\[ 4\text{FeO} + 8\text{Na}_2\text{Cr}_2\text{O}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2 \]  
(yellow)

\[ 2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O} \]  
(orange)

\[ \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl} \]

Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

\[
\begin{array}{c}
\text{O} \\
\text{Cr} \\
\text{O}
\end{array}
\]  
\[ \text{chromate ion sp}^3 \]

\[
\begin{array}{c}
\text{O} \\
\text{Cr} \\
\text{O} \\
\text{O}
\end{array}
\]  
\[ \text{dichromate ion sp}^3 \]

(iii) Properties

Sodium and potassium dichromates are strong oxidizing agents, thus, acidified \( \text{K}_2\text{Cr}_2\text{O}_7 \) will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2 \]

\[ \text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{S} + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O} \]

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{Sn}^{2+} \rightarrow 3\text{Sn}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

(iv) Uses

(a) \( \text{K}_2\text{Cr}_2\text{O}_7 \) 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 (\( \text{KMnO}_4 \))

(i) Ore

Pyrolusite (\( \text{MnO}_2 \))

(ii) Preparation

\[ 2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} \]  
(green)

\[ 3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^{-} + \text{MnO}_2 + 2\text{H}_2\text{O} \]
(iii) Commercial preparation

\[ \text{MnO}_2 \xrightarrow{\text{Fused with KOH oxidised with air or KNO}_3} \text{MnO}_4^{2-} \]
\[ \text{MnO}_4^{-} \xrightarrow{\text{Electrolytic oxidation (alkaline medium)}} \text{MnO}_4^{-} \text{Permanganate ion (purple)} \]

(iv) Properties

KMnO\(_4\) acts as a strong oxidizing agent.

(a) In presence of dilute H\(_2\)SO\(_4\), KMnO\(_4\) is reduced to manganous salt.

\[ \text{MnO}_4^{-} + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

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

\[ \text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2 + 2\text{e}^- \]
\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \]
\[ \text{NO}_2^{-} \rightarrow \text{NO}_3^{-} + 2\text{e}^- \]
\[ 2\text{I}^{-} \rightarrow \text{I}_2 + 2\text{e}^- \]

To acidify KMnO\(_4\), only H\(_2\)SO\(_4\) 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\(_2\).

\[ \text{MnO}_4^{-} + 3\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{OH}^- \]

Alkaline or neutral KMnO\(_4\) solution oxidizes I\(^-\) to IO\(_3\)\(^-\), S\(_2\)O\(_3\)\(^{2-}\) 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\(^{14}\), 5d\(^{0}\), 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 $f^4$ type (Yb$^{3+}$ and Lu$^{3+}$) are all paramagnetic. The paramagnetism arises to maximum in neodymium.
• Oxidation states $\rightarrow$ Ce$^{4+}$; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^\circ_{value}$ 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, Eu$^2+$ is a strong reducing agent changing to the common +3 state. Similarly, Yb$^{3+}$ which has $f^4$ configuration is a reductant, Tb$^{5+}$ has half-filled $f$-orbitals and is an oxidant.

• Lanthanoid are very reactive metals like alkaline earth metals.

\[
\begin{align*}
\text{M} & \overset{+\text{O}_2}{\rightarrow} \text{M}_2\text{O}_3 \\
\text{M} & \overset{+\text{N}_2}{\rightarrow} \text{MN} \\
\text{M} & \overset{+\text{S}}{\rightarrow} \text{M}_2\text{S}_3 \\
\text{M} & \overset{+\text{C}}{\rightarrow} \text{MC}_2 \\
\text{M} & \overset{+\text{X}}{\rightarrow} \text{MX}_3 \\
\text{M} & \overset{+\text{H}_2\text{O}}{\rightarrow} \text{M(OH)}_3+\text{H}_2
\end{align*}
\]

• Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigarette and gas lighters, toys, tank and tracer bullets.

**Actinoids**

• General configuration [Rn] 5f$^{1-14}$, 6d$^{0-2}$, 7s$^2$.
• Actinoids exhibit a range of oxidation states due to comparable energies of 5f, 6d and 7s orbitals. The general 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$_2$O is blue while CuSO$_4$ is colourless?

Ans. Because water molecules act as ligands and results in crystal field splitting of $d$-orbitals of Cu$^{2+}$ ion.
Q. 2. Which element among 3d series exhibit highest oxidation state?

Ans. Mn

Q. 3. In 3d series (Sc to Zn), the enthalpy of atomization of Zn is low. Why?

Ans. Due to absence of unpaired electrons.

Q. 4. Which element among 3d series exhibit only one oxidation state?

Ans. Sc

Q. 5. Why is the 3rd ionization energy of Mn (Z = 25) is unexpectedly high?

Ans. Due to half-filled electronic configuration.


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 synergetic bonding with metal ion.

Q. 8. Why can’t HCl acid be used to acidify KMnO₄ solution?

Ans. Because KMnO₄ oxidize HCl into Cl₂.

Q. 9. Name one ore of Mn and Cr.

Ans. Mn : MnO₂
Cr : FeCr₂O₄

Q. 10. Why Mn²⁺ compounds are more stable than Fe²⁺ compounds towards oxidation to their +3 state?

Ans. Mn¹² 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 lighter 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 Cr₂O₇²⁻ ion.

Ans. 1

Q. 15. What is effect of increasing pH on K₂Cr₂O₇ solution?

Ans. It changes into K₂CrO₄ solution/orange colour change into yellow colour.
Q. 16. Why is Ce⁴⁺ in aqueous solution a good oxidizing agent?
Ans. Because Ce⁴⁺ is most stable in Ce³⁺ 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 Cu²⁺ state.

Q. 20. Arrange the given in increasing order of acidic character:
CrO₃, CrO₂, Cr₂O₃.
Ans. CrO < Cr₂O₃ < CrO₃

Q. 21. Why KMnO₄ or MnO₄⁻ 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 KMnO₄ is used in cleaning surgical instruments in hospitals?
Ans. This is because KMnO₄ 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 Δₜₚₜₐₜₜ 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.

Ans. Cu²⁺ = [Ar] 3d⁸4s⁰
Co³⁺ = [Ar] 3d⁷
Q. 7. Balance the following equations:
   (a) $\text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+ \rightarrow$
   (b) $\text{Cr}_2\text{O}_7^{2-} + \text{Sn}^{2+} + \text{H}^+ \rightarrow$

   Ans. (a) $\text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+}$
   (b) $\text{Cr}_2\text{O}_7^{2-} + \text{Sn}^{2+} + \text{H}^+ \rightarrow \text{Cr}^{3+} + \text{Sn}^{4+}$

Q. 8. Briefly explain why electronic configuration of lanthanoids are not known with certainty?

   Ans. $4f/5d$ subshells are very close in energy. +ve electrons can jump from $4f$ to $5d$ or vice-versa.

Q. 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 $\text{K}_2\text{Cr}_2\text{O}_4$ solution?

   Ans. $\text{K}_2\text{Cr}_2\text{O}_4$ solution changes into $\text{K}_2\text{Cr}_2\text{O}_7$/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$_3$H,


   Ans. Due to weak interatomic attraction/low boiling point.

Q. 14. Why is first ionization energy of $5d$ elements higher than those of $3d$ and $4d$ 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 $\text{HNO}_3$ with Zn are given:
   (a) $\text{Zn} + \text{conc. HNO}_3 \rightarrow \text{Zn(NO}_3)_2 + X + \text{H}_2\text{O}$
   (b) $\text{Zn} + \text{dil. HNO}_3 \rightarrow \text{Zn(NO}_3)_2 + Y + \text{H}_2\text{O}$

   Identify X and Y.

   Ans. $X = \text{NO}_2$
   $Y = \text{N}_2\text{O}$
Q. 17. Complete the equations:

(a) \[ \text{KMnO}_4 \xrightarrow{\text{\Delta}} \]

(b) \[ 3\text{K}_2\text{MnO}_4 \xrightarrow{\text{on standing for long time in acidic medium}} \]

Ans. (a) \[ 2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2 \]

(b) \[ 3\text{K}_2\text{MnO}_4 \rightarrow \text{MnO}_4^{-} + \text{MnO}_2 + 2\text{H}_2\text{O} \]

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 3d electrons in the following ions:

\[ \text{Cu}^{2+}, \text{Sc}^{3+} \]

(b) Why do transition metals form alloy?

(c) Why Zn^{2+} salts are white?

Ans. (a) Cu^{2+} : 9 electrons

Sc^{3+} : 0 electron

(b) Transition metals have similar atomic radii.

(c) Absence of unpaired electron.

Q. 2. Complete and balance the following equations:

(a) \[ \text{MnO}_4^{2-} + \text{H}^+ \rightarrow \]

(b) \[ \text{KMnO}_4 \xrightarrow{\text{heat}} \]

(c) \[ \text{MnO}_4^{-} + \text{FeC}_2\text{O}_4 \xrightarrow{\text{H}^+} \]

Ans. (a) \[ 3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^{-} + \text{MnO}_2 + 2\text{H}_2\text{O} \]

(b) \[ 2\text{KMnO}_4 \xrightarrow{\text{heat}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2 \]

(c) \[ \text{MnO}_4^{-} + \text{FeC}_2\text{O}_4 + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+} + \text{CO}_2 \]

Q. 3. Describe the oxidizing action of K_2 Cr_2 O_7 with the following. Write ionic equations for its reaction (acidic medium) with:

(a) \text{I}^{-}  \hspace{1cm} (b) \text{Iron(II)} \hspace{1cm} (c) \text{H}_2\text{S}


Ans. (a) It liberates I\(_2\) form I\(^-\).
\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2
\]
(b) It oxidizes Fe\(^{2+}\) to Fe\(^{3+}\).
\[
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+}
\]
(b) It oxidizes H\(_2\)S to sulphur.
\[
\text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{S} + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{S}
\]

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) \(s^{8}\)Ce = [Xe] 4f\(^5\) 5d\(^1\) 6s\(^2\)
Ce\(^{3+}\) = 4f\(^1\) one unpaired electron
\[
\mu = \sqrt{n(n+2)} = 1.73 \text{ BM}
\]
(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 NH₃.
   \[
   \text{AgCl} + 2\text{NH}_3 \rightarrow [\text{Ag(NH}_3)_2]\text{Cl}
   \]
   (b) \( \text{Cu}^+ : 3d^9 4s^0 \) – All electrons are paired.
   \( \text{Cu}^{+2} : 3d^9 \) – Here, one unpaired electron is present.
   (c) Due to resonance.

Q. 8. The \( E^0 \) values in respect of electrodes of Cr, Mn and iron are:
   \[
   \begin{align*}
   \text{Cr}^{+3}/\text{Cr}^{+2} &= -0.4 \text{ V} \\
   \text{Mn}^{+3}/\text{Mn}^{+2} &= +1.5 \text{ V} \\
   \text{Fe}^{+3}/\text{Fe}^{+2} &= +0.8 \text{ V}
   \end{align*}
   \]
   Compare the feasibilities of further oxidation of these ions.

Ans. \( \text{Cr}^{+3} \) is more stable than \( \text{Cr}^{+2} \).
(\( \text{Mn}^{+3} \) is more stable than \( \text{Mn}^{+2} \).
(\( \text{Fe}^{+3} \) is more stable than \( \text{Fe}^{+2} \).
Order of feasibility of +2 oxidation state is:
(\( \text{Mn}^{+2} > \text{Fe}^{+2} > \text{Cr}^{+2} \)

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 1st ionization energy of the 5d series are higher than 3d and 4d transition elements in respective groups.
   (c) \( \text{Ce}^{+3} \) can be easily oxidized to \( \text{Ce}^{+4} \).

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 : \text{FeCr}_2\text{O}_4 \quad B : \text{Na}_2\text{CrO}_4 \quad C : \text{Na}_2\text{Cr}_2\text{O}_7
4FeCr₂O₄ + 8Na₂CO₃ + 7O₂ → 8Na₂CrO₄ + 2Fe₂O₃ + 8CO₂

(A) \hspace{1cm} (B)
Na₂CrO₄ + H₂SO₄ → Na₂Cr₂O₇ + Na₂SO₄ + H₂O

(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 : MnO₂ \hspace{1cm} B : K₂MnO₄ \hspace{1cm} C : KMnO₄

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. A violet compound of manganess (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 KNO₃ to give compound (B). On heating compound (C) with conc. H₂SO₄ and NaCl, Cl₂ gas is liberated and compound (D) of manganese is formed. Identify A, B, C, D along with reactions involved.

Ans. A : KMnO₄ \hspace{1cm} B : K₂MnO₄ \hspace{1cm} C : MnO₂ \hspace{1cm} D : MnCl₂

KMnO₄ \xrightarrow{Δ} K₂MnO₄ + MnO₂ + O₂

(A) \hspace{1cm} (B)
MnO₂ + KOH + KNO₃ → K₂MnO₄

(C) \hspace{1cm} (B)
MnO₂ + NaCl + conc. H₂SO₄ → MnCl₂

(C) \hspace{1cm} (D)

Q. 2. (a) What is meant by disproportionation of an oxidation state? Give one example.

(b) Draw the structures of Cr₂O₇²⁻, CrO₄²⁻, MnO₄⁻.

(c) What is the effect of lanthanoids contraction beyond lanthanoid?

Ans. (a) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.

2Cu⁺ → Cu⁺² + Cu

(b) ![Cr₂O₇²⁻](image) ![CrO₄²⁻](image) ![MnO₄⁻](image)

(c) Size of respective 4d and 5d series elements becomes comparable from fourth group onwards (e.g., Zr and Hf).
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,

\[ K_4[\text{Fe(CN)}_6] + H_2O \rightarrow 4K^+ + [\text{Fe(CN)}_6]^{4-} \]

2. Types of Complex

(i) Anionic complex

\[ K_3[\text{Fe(C}_2\text{O}_4)_3] \rightarrow 3K^+ + [\text{Fe(C}_2\text{O}_4)_3]^{3-} \]

anionic complex

(ii) Cationic complex

\[ [\text{CoCl}_2(\text{en})_2]\text{Cl} \rightarrow [\text{CoCl}_2(\text{en})_2]^+ + \text{Cl}^- \]

cationic complex

(iii) Neutral complex

\[ [\text{Ni(CO)}_4] \]

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., oxalate ion

\[ \begin{array}{c}
\text{COO}^- \\
\text{COO}^- \\
\text{Oxalate ion}
\end{array} \]

<table>
<thead>
<tr>
<th>CH₂ – NH₂</th>
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<tr>
<td>CH₂ – NH₂</td>
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ethylene diamine
(iii) Polydentate, a ligand which is bound to a metal ion through a several donor atoms.

* e.g., ethylene diamine tetraacetate ion \([\text{EDTA}]^{4-}\).

(iv) Ambidentate ligands, which can ligate through two different atoms.

* e.g., \(\text{NO}_2^-, \text{ONO}, \text{SCN}^-, \text{NCS}\) 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.,* \(\text{Co(NH}_3)_6^{3+}\) are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups *e.g.,* \([\text{Co(NH}_3)_4\text{Cl}_2]^+\), are known as heteroleptic.

5. Nomenclature of Coordination Compounds

**Cationic Complex**

\([\text{Cr(NH}_3)_3(\text{H}_2\text{O})_2]\text{Cl}_2\)

triamminetriaqua chromium (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**

\(\text{K}_3[\text{Fe(CN)}_6]\)

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**

\([\text{Pt(NH}_3)_2\text{Cl(NO}_2\text{)}]\)

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.*, \([\text{Pt(NH}_3)_2\text{Cl}_2]\)

(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.*, \([\text{Pt(NH}_3)(\text{Br})(\text{Cl})(\text{Py})]\)

(iii) **Octahedral complexes of formula** \([MX_2L_4]\), in which the two ligands X may be oriented *cis* or *trans* to each other.

   *e.g.*, \([\text{Co(NH}_3)_4\text{Cl}_2]^-\)

(iv) **Octahedral complexes of formula** \([MX_2A_4]\) where X are unidentates and A are didentate and form *cis* and *trans* isomers.

   *e.g.*, \([\text{CoCl}_2(\text{en})_2]\)

(v) **Octahedral coordination entities of the type** \([Ma,b]\) like \([\text{Co(NH}_3)_3(\text{NO}_2)_3]\).

   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 meridional (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.*, \([\text{Co(en)}_3]^{3+}\), \([\text{PtCl}_2(\text{en})_2]^{2+}\) 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.

\[ \text{e.g., } [\text{Co(NH}_3\text{)}_5(\text{NO}_2\text{})]\text{Cl}_2 \]
\[ [\text{Co(NH}_3\text{)}_5(\text{ONO})]\text{Cl}_2 \]

(ii) **Coordination isomerism**, arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

\[ \text{e.g., } [\text{Co(NH}_3\text{)}_6][\text{Cr(CN)}_6] \]
\[ [\text{Cr(NH}_3\text{)}_6][\text{Co(CN)}_6] \]

(iii) **Ionisation isomerism**, when the ionisable anion exchange with anion ligand.

\[ \text{e.g., } [\text{CO(NH}_3\text{)}_5\text{SO}_4]\text{Br} \text{ and } [\text{Co(NH}_3\text{)}_5\text{Br}]\text{SO}_4 \]

(iv) **Solvent isomerism**, is also known as ‘hydrate isomerism’. In this case water is involved as a solvent.

\[ \text{e.g., } [\text{Cr(H}_2\text{O)}_6]\text{Cl}_3, [\text{Cr(H}_2\text{O)}_5\text{Cl}]\text{.H}_2\text{O}, [\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\text{Cl.2H}_2\text{O} \]

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 3d series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

(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 \((sp^d d^2)\). Generally halides \((F^-, Cl^-, Br^-, I^-)\), \(SCN^-\), \(S^{2-}\) form outer orbital complexes and other ligands form inner orbital complexes.

\[ \text{e.g., Inner orbital complex, } [\text{Co(NH}_3\text{)}_6]^{3+} \]
Orbitals of Co$^3+$ ion

$3d$ $4s$ $4p$

$d^2sp^3$ hybridizes orbitals of Co$^{3+}$

$[\text{Co(NH}_3\text{)}_6]^{3-}$

six pairs of electrons from six NH$_3$ molecules

All electrons are paired therefore, complex will be diamagnetic in nature.

*e.g.* **Outer orbital complex**, $[\text{CoF}_6]^{3-}$

Orbitals of Co$^{3-}$ ion

$3d$

$4s$ $4p$ $4d$

$sp^3d^2$ hybridizes orbitals of Co$^{3-}$

$[\text{CoF}_6]^{3-}$

Six pairs of electrons from six F$^-$ ions

Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.
Complexes with coordination number : 4

1. \([\text{Ni(CN)}_4]^{2-}\)

Orbitals of Ni\(^{2+}\) ion

- \(3d\)
- \(4s\)
- \(4p\)

\(d^3p^3\) hybridizes orbitals of Ni\(^{2+}\)

\([\text{Ni(CN)}_4]^{2-}\)

- \(3d\)
- \(4p\)

Four pairs of electrons from 4 CN\(^{-}\) group

All electrons are paired. Complex will be diamagnetic in nature.

2. \([\text{CoCl}_4]^{-}\)

Orbitals of Co\(^{3+}\) ion

- \(3d\)
- \(4s\)
- \(4p\)

\(sp^3\) hybridizes orbitals of Co\(^{3+}\)

\([\text{CoCl}_4]^{-}\)

- \(3d\)
- \(4s\)
- \(4p\)

Four pairs of electrons from 4 Cl\(^{-}\)

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 $\Delta_o$ (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 \( d^0 \) ions, so the ions having \( d^1 \) to \( d^0 \) configuration are coloured. On the other hand, the ions \( d^0 \) and \( d^{10} \) configuration do not show \( d-d \) transition.

9. Importance and Applications of Coordination Compounds

- Hardness of water is estimated by simple titration with Na\(_2\)EDTA. The Ca\(^{2+}\) and Mg\(^{2+}\) ions form stable complexes with EDTA.

- Some important extraction processes of metals, like those of silver and gold make use of complex formation.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to \([\text{Ni(CO)}_4]\), which is decomposed to yield pure nickel.

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, \([(\text{Ph}_3\text{P})_2\text{RhCl}]\), a Wilkinson catalyst, is used for the hydrogenation of alkenes.

**Supplementary List of Ligands**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>F(^-)</th>
<th>Cl(^-)</th>
<th>Br(^-)</th>
<th>I(^-)</th>
<th>OH(^-)</th>
<th>CN(^-)</th>
<th>O(^2-)</th>
<th>O(^2-)</th>
<th>CO(^2-)</th>
<th>PH(^3-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>fluoro</td>
<td>chloro</td>
<td>bromo</td>
<td>iodo</td>
<td>hydroxy</td>
<td>cyano</td>
<td>oxo</td>
<td>super-oxo</td>
<td>carboxyl</td>
<td>phosphine</td>
</tr>
<tr>
<td>Ligand</td>
<td>SO(_4^{2-})</td>
<td>NO(_3^-)</td>
<td>ONO(^-)</td>
<td>SCN(^-)</td>
<td>NCS</td>
<td>CH(_3)COO(^-)</td>
<td>C(_3)H(_4)N</td>
<td>S(^2-)</td>
<td>SO(_4^{2-})</td>
<td>NO(_3^-)</td>
</tr>
<tr>
<td>Name</td>
<td>sulfoxide</td>
<td>nitrito</td>
<td>thiocyanato</td>
<td>iso-thiocyanato</td>
<td>acetate</td>
<td>pyridine (Py)</td>
<td>sulfoxide</td>
<td>thiosulphato</td>
<td>nitrato</td>
<td>sulphite</td>
</tr>
<tr>
<td>Ligand</td>
<td>NC=</td>
<td>(C(_3)H(_2))(_2)P</td>
<td>CS</td>
<td>NH(^3-)</td>
<td>NH(^3-)</td>
<td>H(_2)NCSNH(_2)</td>
<td>C(_6)O(_4)^{2-})</td>
<td>H(_2)O</td>
<td>NH(_3)</td>
<td>CO</td>
</tr>
<tr>
<td>Name</td>
<td>iso-cyano</td>
<td>triphenylphosphine</td>
<td>thiocarboxyl</td>
<td>amido</td>
<td>imido</td>
<td>thiourea (tu)</td>
<td>oxalate (ox)</td>
<td>aqua</td>
<td>ammine</td>
<td>carboxyl</td>
</tr>
</tbody>
</table>

H\(_2\)N–CH\(_2\)–CH\(_2\)–NH\(_2\)
Ethylene diamine (en)

CH\(_2\)–N\(\sim\)
CH\(_3\)COO\(^-\)
CH\(_2\)–N\(\sim\)
CH\(_3\)COO\(^-\)

Ethylene diamine triacetate ion EDTA\(^{2-}\)

H\(_2\)NCH\(_2\)CH\(_2\)NHCH\(_2\)CH\(_2\)NH\(_2\)
Diethylenetriamine (dieno)

CH\(_2\)–N\(\sim\)
CH\(_2\)COO\(^-\)
CH\(_2\)–N\(\sim\)
CH\(_2\)COO\(^-\)

Ethylene diamine triacetate ion EDTA\(^{2-}\)
H₂N – CH₂ – COO⁻  
Glycinato (gly)  

CH₂NHCH₂CH₂NH₂  

\[ \text{CH₃ – C – CH = C – CH₃} \]  

| O | O⁶ |  

\[ \text{CH₃ – C = N – O} \]  

2,2’ Bipyridyl  

\[ \text{N} \]  

\[ \text{N} \]

**VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)**

Q. 1. Write the oxidation state of Nickel in \([\text{Ni(CO)}₄]^-\).  
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 \([\text{PtCl₂(en)}₂(\text{NO₃})₂]^-\).  
Ans. Dichlorodibis(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 simultaneusly 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 \([\text{Ni(NH₃)}₄]^{2+}\)?  
Ans. Not possible because all 4 ligands are same.

Q. 8. Write IUPAC name of \([\text{Co(C₂O₄)}₃]^{3-}\).  
Ans. Trioxalatocobalate(III) ion.

Q. 9. Give an example of coordination isomerism.  
Ans. \([\text{Co(NH₃)}₆][\text{Cr(CN)}₆]\)

Q. 10. Name an ionization isomer of \([\text{Cr(H₂O)}₅\text{Br}]\text{SO₄}^-\).  
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. K₄[Fe(CN)₆]

Q. 13. Which of these cannot act as a ligand?  
\(\text{NH}_₂\), H₂O, CO, \(\text{NH}_₄^+\)  
Ans. \(\text{NH}_₄^+\) 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. [(Ph₃P)₃RhCl]

Q. 17. Which of the two is more stable – K₄[Fe(CN)₆] Or K₄[Fe(CN)₆] ?
Ans. K₄[Fe(CN)₆] because Fe has d⁸ configuration in this case.

Q. 18. How many moles of AgCl will be precipitated when an excess of AgNO₃ is added to a molar solution of [CrCl(H₂O)₅]Cl₂ ?
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(NH₃)₅Cl]⁺, [Co(NH₃)₆]Cl₂, [Co(NH₃)₄]Cl₃
Ans. [Co(NH₃)₅Cl]⁺ < [Co(NH₃)₆]Cl₂ < [Co(NH₃)₄]Cl₃

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) [FeF₆]⁻³
Ans. (i) Fe²⁺ → 3d⁶. CN⁻ is a strong ligand so e⁻ pair 4p, no unpaired e⁻ then magnetic moment is zero

(ii) \[ \mu_{BH} = \sqrt{n(n+1)} = 0 \]
    \[ n = 5, \text{So} \quad \mu = \sqrt{n(n+2)} \]
    \[ \mu = \sqrt{5(5+2)} \]
    \[ \mu = \sqrt{35} \approx 5.96 \text{ BM} \]

Q. 2. Explain the following:
   (i) NH₃ act as a ligand but NH₄⁺ does not.
   (ii) CN⁻ is a ambidentate ligand.
Ans. (i) NH₃ has one lone pair while NH₄⁺ 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) \([\text{Ni(CO)}_4]\)  
(ii) \([\text{Fe(H}_2\text{O)}_6]^{3+}\)

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 complexed lead-EDTA is eliminated in urine.


Ans. Homolectic: When metal atom/ion is linked with one type of ligands. Example, [Ni(CO)]

Heterolectic: With the more than one kind of ligands. Example, [Co(NH)_4Cl]^{+}.

Q. 7. \([\text{NiCl)}_2\] is paramagnetic while \([\text{Ni(CO)}_4]\) is diamagnetic though both are tetrahedral. Why?

Ans. In \([\text{NiCl)}_2\]^-2, Ni has 3d^84s^0 configuration, Cl^- can’t pair up while in \([\text{Ni(CO)}_4]\), Ni has 3d^84s^2 configuration, CO pair up electrons.

Q. 8. The oxidation number of cobalt in the complex:

(i) K[Co(CO)]
(ii) [Co(C_2O_4)]^{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.

\[
\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Ag(S}_2\text{O}_3)_2] + \text{NaBr}
\]

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. CuSO₄ is colourless while CuSO₄·5H₂O is coloured. Why?

Ans. CuSO₄ does not has any ligand, so splitting of d-orbital take place while
CuSO₄·5H₂O 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(NH₃)₅NO₂]Cl₂,
   (i) Identify the ligand.
   (ii) Oxidation number of metal ion.

Ans. (i) NH₃, NO₂⁻
(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) C₂O₄⁻²  (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 CoCl₃·4NH₃. It does not liberate
NH₃ but forms a precipitate with AgNO₃. Write the structure and IUPAC
name of the complex compound. Does it show geometrical isomerism?

Ans. Formula: [Co(NH₃)₄Cl₂]Cl
Name: Tetraaminedichlorocobalt(III) chloride
Yes, it show geometrical isomerism.

Q. 2. Why does a tetrahedral complex of the type [MA₂B₂] not show geometrical
isomerism?

Ans. Because all position of tetrahedral is same in orientation.
Q. 3. The molar conductivity of the complex CoCl₃·4NH₃·2H₂O 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 A₅B or AB₃ type, formula is [Co(NH₃)₆(H₂O)₂]Cl₃.
Name: Tetraaminediaqua cobalt (III) chloride
Geometrical isomer: 2 (cis and trans)

Q. 4. [Ti(H₂O)₆]³⁺ is coloured while [Sc(H₂O)₆]³⁺ is colourless. Why?

Ans. [Ti(H₂O)₆]³⁺: In this core Ti³⁺ has one unpaired e⁻ while Sc³⁺ 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(NH₃)₅Cl]SO₄
   (ii) [Co(en)₃]⁺³
   (iii) [Co(NH₃)₆][Cr(CN)₆]

Ans. (i) Ionization
   (ii) Optical
   (iii) Coordination isomerism

Q. 7. Explain the following:
   (i) CO is stronger ligand than NH₃.
   (ii) Low spin octahedral complexes of nickel are not known.
   (iii) Aqueous solution of [Ti(H₂O)₆]³⁺ is coloured.

Ans. (i) CO has high value of crystal field splitting energy than Cl.
   (ii) Ni has d⁶ configuration which does not affect by field strength of ligand.
   (iii) In this case, Ti³⁺ has t₂g⁷ e_g⁰ configuration. It can perform d-d transition.

Q. 8. Write all the geometrical isomers of [Pt(NH₃)₅(Br)(Cl)(Py)] and how many of these will exhibit optical isomerism? Here, Py = Pyridine.
Ans. 3 isomers are possible.

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 \( \Delta_a > p \):

(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 \( \Delta_a > p \) then

\[
\begin{array}{c}
\text{eg} \\
\text{t}_{2g}
\end{array}
\]

(ii) \( d^4sp^3 \)

(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 \( M^{2+} \) ion when:

(a) \( p > \Delta_a \)

(b) \( \Delta_a > p \)

Ans. (i) The metal carbon bond in metal carbonyls possess both \( \sigma \) and \( \pi \) character. The \( M - C \) \( \sigma \) bond if formed by the \( M \leftarrow C \equiv O \) while \( M - C \) \( \pi \) bond if formed by the donation of a pair of electron from filled \( d \)-orbital of metal to antibonding \( \pi^* \) orbital of CO.

\[
\begin{array}{c}
\text{eg} \\
\text{t}_{2g}
\end{array}
\]

(a) \( t_{2g}^3 e_g^2 \)  

(b) \( t_{2g}^5 e_g^0 \)
Q. 3.  (i) [Fe(CN)₆]⁴⁻ and [Fe(H₂O)₆]³⁺ are of different colours in dilute solution. Why?

(ii) A complex is prepared by mixing CoCl₃ and NH₃ in the molar ratio of 1 : 4. 0.1M solution of this complex was found to be freeze at – 0.372° C. What is the formula of the complex? Kᵣ = 1.86°C/M

Ans.  (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN⁻ and H₂O has different crystal field splitting energy.

(ii) ΔTᵣ = i.Kᵣ.m

i = 2 means complex dissociate into two ions.

Hence the formula is [Co(NH₃)₄Cl₂]Cl
UNIT 10
HALOALKANES AND HALOARENES

Points to Remember

1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[\text{C}_n\text{H}_{2n+1}\text{X}]$. ($\text{X} = \text{F, Cl, Br or I}$)
2. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula $\text{Ar} - \text{X}$.
3. Since halogen is more electronegative than C, hence C – X bond is polar.

4. Named Reactions:
   (a) Sandmeyer Reaction:
   $\text{NH}_2\text{H}_2\text{NNO}_2\text{HX}_{273-278\text{K}} \xrightarrow{\text{N}_2\text{I}^+\text{X}^-} \xrightarrow{\text{Cu}_2\text{X}_2} \text{R} + \text{N}_2$ (X = Cl, Br)

   (b) Finkelstein Reaction:
   $\text{R} - \text{X} + \text{NaI} \xrightarrow{\text{dry acetone}} \text{R} - \text{I} + \text{NaX}$ (X = Cl, Br)

   (c) Swartz Reaction:
   $\text{CH}_3 - \text{Br} + \text{AgF} \rightarrow \text{CH}_3 - \text{F} + \text{AgBr}$
   Instead of Ag – F, other metallic fluoride like Hg$_2$F$_2$, CoF$_2$ or SbF$_3$ can also be used.

   (d) Wurtz Reaction:
   $2\text{R} - \text{X} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{R} - \text{R} + 2\text{NaX}$

   (e) Wurtz-Fittig Reaction:
   $\xrightarrow{\text{dry ether}} \text{R} + 2\text{NaX}$

   (f) Fittig Reaction:
   $\xrightarrow{\text{dry ether}} \text{biphenyl or diphenyl}$
5. **Nucleophilic Substitution Reactions**:

\[
\text{Nu}^\ominus + \text{C} - X \xrightarrow{\text{S}^2_\text{N}_2} \text{C} - \text{Nu} + X^\ominus
\]

**haloalkane**

(a) **Substitution nucleophilic bimolecular** \((S^2_N)\):

1. **1° haloalkane**
2. Bimolecular, 2nd order
3. One step

**Order of reactivity**: 1° > 2° > 3°

**Deciding factor**: Steric hindrance

(a) **Substitution nucleophilic unimolecular** \((S^1_N)\):

1. **3° haloalkane**
2. Unimolecular, 1st order
3. Two steps

**Order of reactivity**: 3° > 2° > 1°

**Deciding factor**: Stability of carbo cation

* Allylic \(\text{CH}_2 = \text{CH} - \text{CH}_2\) and benzylic \(\text{C}_6\text{H}_5\text{CH}_2\) halides undergo reaction via \(S^1_N\) 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. \(\text{CHCl}_3\) is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

\[
2\text{CHCl}_3 + \text{O}_2 \xrightarrow{\text{light}} 2\text{COCl}_2 + 2\text{HCl}
\]

Chloroform \hspace{1cm} Carbonyl chloride (phosgene)
9. Reaction of Haloalkanes:

$$\text{R-X} \rightarrow \begin{cases} 
\text{NaOH or KOH} & \text{R-OH} \\
\text{NaI} & \text{R-I} \\
\text{KCN} & \text{RCN} \\
\text{AgCN} & \text{RNC} \\
\text{KNO}_2 & \text{R-O-N = O} \\
\text{AgNO}_2 & \text{R-NO}_2 \\
\text{LAH} & \text{RH} \\
\text{NH}_3 & \text{R-NH}_2 \\
\text{Mg} & \text{R-MgX} \\
\text{Na, D.E.} & \text{R-R} \\
\text{NaOR} & \text{R-O-R'} \\
\text{R'COOAg} & \text{R'COOR}
\end{cases}$$

10. Electrophilic Substitution Reaction of Haloarenes:

$$\text{Cl}_2 \text{ (anhyd AlCl}_3) \rightarrow \begin{cases} 
\text{Cl} & \text{Cl} \rightarrow \text{Cl} & \text{Cl} \\
\text{concHNO}_3 \text{ or concH}_2\text{SO}_4 & \text{Cl} & \text{Cl} \rightarrow \text{NO}_2 & \text{Cl} & \text{NO}_2 \\
\text{concH}_2\text{SO}_4 & \text{Cl} & \text{SO}_3\text{H} \rightarrow \text{Cl} & \text{SO}_3\text{H} \\
\text{CH}_3\text{Cl} \text{ (anhyd AlCl}_3) & \text{Cl} & \text{CH}_3 \rightarrow \text{Cl} & \text{CH}_3 \\
\text{CH}_3\text{COCl} \text{ (anhyd AlCl}_3) & \text{Cl} & \text{COCH}_3 \rightarrow \text{Cl} & \text{COCH}_3 \\
\text{chlorination} & \text{Nitration} & \text{Sulphonation} & \text{Friedel craft Alkylation} & \text{Friedel craft acylation}
\end{cases}$$
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**  
(ii) **α-elimination**

**Saytzaiff’s Rule**

\[
\text{OH} + \text{H} \xrightarrow{\text{H}} \xrightarrow{\Delta} \text{CH}_2 = \text{CH}_2 + \text{KBr} + \text{H}_2
\]

\[
\text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 \xrightarrow{\text{Aloc,KOH}} \text{CH}_2 = \text{CH}_2 + \text{KBr} + \text{H}_2
\]

81% More highly substituted Alkenes, More stable

12. **Distinguishing test for alkyl chlorides, bromides and iodide**: Alkyl chlorides react with AgNO₃ to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with AgNO₃ to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with AgNO₃ to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.

E.g., \[\text{CH}_3 - \text{Cl} \xrightarrow{\text{HNO}_3, \text{AgNO}_3} \text{AgCl} \downarrow\]

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:

![Chemical structure](image)

*[Hint: 1-chloro-2, 3-dibromo-2-methyl pentane]*

Q. 2. Identify A and B in each of the following processes:

\[\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{NaCN}} A \xrightarrow{\text{Reduction Na/H}_2} B\]

*[Hint: A : CH₃ - CH₂ - CN; B : CH₃CH₂CH₂NH₂]*
Q. 3. Draw the structure of 4-bromo-3-methylpent-2-ene.

\[ \text{Hint : } \text{CH}_3 - \text{CH} = \text{C} - \text{CH} - \text{CH}_3 \]

\[ \text{CH}_3 \text{Br} \]

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 C₄H₂Cl is optically active. What is its structure?

\[ \text{Hint : } \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \]

\[ \text{Cl} \]

Q. 7. An organic compound ‘A’ on treatment with KCN gave B which on hydrolysis with dil. HCl gave acetic acid. Identify A.

\[ \text{Hint : A : CH}_3\text{Cl} \]

Q. 8. Write IUPAC name of iodoform.

\[ \text{Hint : Triiodomethane} \]

Q. 9. Which one of the following two substances undergo SN¹ reaction faster and why?

\[ \begin{align*}
\text{Cl} & \quad \text{Or} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad (2°)
\end{align*} \]

\[ \text{Hint : } \]

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:

\[ \text{Hint : 3-bromo-2-methylprop-1-ene} \]

Q. 12. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions:

\[ \text{CH}_3\text{F, CH}_3\text{I, CH}_3\text{Br, CH}_3\text{Cl} \]

\[ \text{Hint : CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I} \]

Q. 13. Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why?

Q. 14. Complete the reaction:

\[ \begin{align*}
\text{Br} & \quad \text{heat or} \\
\text{Br}_2 & \quad \text{Uv light} \\
\text{Br} & \quad \text{Br}
\end{align*} \]

\[ \text{Hint : } \]

\[ \begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*} \]
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: AgNO₃ test]

Q. 17. Why iodoform show antiseptic properties?

[Hint: Due to free liberated iodine.]

Q. 18. The presence of nitro group (−NO₂) 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 (SOCl₂) is preferred. Give reason.

**SHORT ANSWER-I TYPE QUESTIONS (2 Marks)**

Q. 1. Complete the following reactions:

(i) C₆H₅N₂Cl + KI →
(ii) \( \text{H}_2\text{C}=\text{C}=\text{H} + \text{Br}_2 \rightarrow \text{CCl}_4 \)

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 haloarenes.]

Q. 4. Which of the following compounds would undergo \( S_N^1 \) reaction faster and why?

\[ \text{CH₂Cl} \quad \text{CH₂Cl} \]

(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 AlCl₃.

Q. 8. (i) An alkyl halide having molecular formula C₄H₉Cl is optically active. What is its structure?
(ii) Alkyl iodides develop colouration on long standing particularly in light. Explain.
   [Hint: (i) CH₃ – CH(Cl) – CH₂ – CH₃
   (ii) Due to decomposition by light and produce I₂.]

Q. 9. Tert-butyl bromide reacts with aq. NaOH by S_N¹ mechanism while n-butylbromide reacts with S_N² 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) \[
\begin{align*}
\text{Br} & \quad \text{NO}_2 \\
& \quad + \text{Mg} \quad \text{dry} \\
& \quad \text{ether} \\
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH}_3 \\
\text{Br} & \quad \text{alc. KOH} \\
& \quad \text{HBr} \\
& \quad \text{H}_2\text{O}_2 \\
& \quad \text{B} \\
\end{align*}
\]

Q. 12. (i) Arrange the following halides in order of increasing S_N¹ reactivity:
CH₃Cl, CH₃Br, CH₃CH₂Cl, (CH₃)₂CHCl
(ii) Which out of 1-bromobutane & 2-bromobutane would react faster by S_N² pathway and why?

Q. 13. Identify the products:
\[
\begin{align*}
\text{CH}_2\text{Cl} & \quad \text{anhy. AlCl}_3 \quad \text{A} \quad \text{Cl}_2 (1 \text{ mole}) \quad \text{B} \\
& \quad \text{hv} \quad \text{aq. KOH} \quad \text{C} \quad \text{HBr} \quad \text{D} \\
\end{align*}
\]

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 PCl₅ to give compound B. Compound B reacts with Na/ether to give n-butane. What are compounds A and B?

[Hint : A = C₂H₅OH, B = C₂H₅Cl]

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) AgNO₂
(ii) Na/dry ether]

Q. 18. Draw structure of monohalo product in each of the following:

(i) \[
\begin{array}{c}
\text{OH} \quad \text{SOCl₂} \quad \text{CH₂CH = CH₂ + HBr} \\
\text{Cl}
\end{array}
\]
(i) \[
\begin{array}{c}
\text{Cl} \\
\text{CH₃CH₂CH₂HBr}
\end{array}
\]

Ans. (i) \[
\begin{array}{c}
\text{Cl}
\end{array}
\]
(ii) \[
\begin{array}{c}
\text{CH₃CH₂CH₂HBr}
\end{array}
\]

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, C₆H₅CH(CH₃)Br and C₆H₅CH(C₆H₅)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?

\[ \text{CH}_3\text{CHClCH}_3\text{CH}_3 \text{ or CH}_3\text{CH}_2\text{CH}_2\text{Cl} \]

(iii) Which one undergo \( S_N^2 \) substitution reaction faster and why?

\[ \text{I} \quad \text{or} \quad \text{Cl} \]

Q. 4. Complete the following reactions:

(i) \[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{SOCl}_2} \text{A} \xrightarrow{\text{KCN}} \text{B} \]

(ii) \[ (\text{CH}_3)_2\text{CHBr} + \text{Na} \rightarrow \]

(iii) \[ \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{AgNO}_3} \]

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 \( \text{C}_2\text{H}_8 \) on treatment with dil. \( \text{H}_2\text{SO}_4 \) give another compound ‘B’. B on treatment with conc. \( \text{HCl} \) and anhy. \( \text{ZnCl}_2 \) 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:

\[ \text{2-propanol} \xrightarrow{\text{SOCl}_2} \text{A} \xrightarrow{\text{Mg}} \text{B} \xrightarrow{\text{H}_2\text{O}} \text{C} \]

Q. 10. Account for the following:

(i) A small amount of ethyl alcohol is added to \( \text{CHCl}_3 \) stored for use as an anaesthetic.

(ii) After using \( \text{CCl}_4 \) 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 COCl₂ to ethyl carbonate.

(ii) To sweep out COCl₂ formed by CCl₄ vapour and H₂O 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 haloalkanes are polar in character but 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’ (C₄H₈) is added with HBr in accordance with Markonikov’s rule to give compound ‘B’ which on hydrolysis with aqueous alkali forms tertiary alcohol ‘C’ (C₄H₁₀O). Identify A, B and C.

**Q. 16.** (i) Which isomer of C₄H₃Cl 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) ![CH(CH₃)₂ + Br₂ → Δ](image)

(ii) ![CH₂CH₂OH + HBr](image)
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) \[ C_6H_6 + Cl_2/Fe \rightarrow X \rightarrow CuCN_{Pyridine} \rightarrow Y \rightarrow H^+, H_2O \]
(ii) \[ C_2H_4 + HBr \rightarrow X \rightarrow \text{aq. KOH} \rightarrow Y \rightarrow I_2, NaOH \rightarrow Z \]
(iii) \[ CH_3CH_2Br + AgCN \rightarrow A \]
(iv) \[ 3\text{-ethylpent-2-ene} + Br_2/H_2O \rightarrow B \]

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 CHCl₃ as anaesthetic is not preferred.

Q. 5.  (i) A primary alkyl halide (A), C₄H₉Br 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), C₈H₁₈ 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 AgNO₃ on heating while CHCl₃ does not. Why?

[Hint : A : \( \text{CH}_3 \quad \text{CH} \quad \text{CH} \quad \text{CH}_2 \text{Br} \)]

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 sp² hybridised which is smaller in size than sp³ present in haloalkanes. So C–Cl bond in aryl halides is shorter and stronger.

Q. 2. Why do haloarenes under go nucleophillic substitution whereas haloarenes under go electrophillic 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.

\[ \text{R-X + KOH} \rightarrow \text{R-OH + KX} \]
Where as in alcoholic KOH, C₂H₅O⁻ ion is produced which is a strong base hence β-elimination took place to form alkane

\[
\text{C}_2\text{H}_5\text{OH} + \text{KOH} \rightarrow \text{C}_2\text{H}_5\text{O}^- + \text{K}^+
\]

\[
\text{CH}_3\text{CH}_2\text{Cl} + \text{alcoholic KOH} \rightarrow \text{CH}_2 = \text{CH}_2 + \text{C}_2\text{H}_5\text{OH}
\]

**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.

\[
\text{H}_2\text{C} = \text{C} \quad \text{H}_2\text{C} = \text{CH} = \text{Cl}
\]

**Q. 6**  Arrange the following compounds according to reactivity towards nucleophile substitution reaction with reagents mentioned :-

(i)  4-nitrochlorobenzene > 2,4 dinitrochlorobenzene > 2,4,6, trinitrochlorobenzene with CH₃ONa

**Ans.**  2,4,6, trinitrochlorobenzene > 2,4 dinitrochlorobenzene > 4- nitrochlorobenzene

**Q. 7**  Why Grignard reagent should be prepared under an hydrous conditions?

**Ans.**  Grignard reagent react with H₂O 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 I₂ 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 CH₃Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_n,1 reactions are accompanied by racemization in optically active alkyl halides.

**Ans.**

(i)  In chlorobenzene, each carbon atom is sp² hybridised/ resonating structures / partial donable bond character.

(ii) Due to + R effect in chlorobenzene / difference in hybridization i.e., sp² and sp³ respectively.

(iii) Due to formation of planer carbocation.
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](image1)
   ![Catechol](image2)
   ![Pyrogallol](image3)

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°.

![Structure](image4)

6. **Isomerism**:
   (i) Functional isomerism
   (ii) Chain isomerism
   (iii) Positional isomerism

7. **General Methods of Preparation**:
   (i) **Acid catalysed hydration of alkenes**:

   $$\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{dil.} \text{H}_2\text{SO}_4} \text{CH}_3 - \text{CH} - \text{CH}_3$$

   (ii) **Hydroboration oxidation**:

   $$3\text{CH}_3 - \text{CH} = \text{CH}_2 + \frac{3}{2}\text{B}_2\text{H}_6 \xrightarrow{\text{DE}} (\text{CH}_3 - \text{CH}_2 - \text{CH}_2)\text{B} \xrightarrow{\text{OH}^-} \text{H}_2\text{O}_2$$

   $$\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH} + \text{H}_3\text{BO}_3$$
(iii) From carbonyl compounds with Grignard’s reagent:

\[
\begin{align*}
R - C = O + R\text{MgBr} & \xrightarrow{\text{Dry ether}} [\text{OMgBr}]^+ \\
& \xrightarrow{H_2O^+} \text{RCH}_2\text{OH} \\
R - C - \text{OH} + \text{MgBr} & \xrightarrow{\text{OH}} \text{RCH}_2\text{OH}
\end{align*}
\]

Formaldehyde gives \(1^\circ\) alcohol and ketones gives tertiary alcohol.

(iv) By reduction of carbonyl compounds:

\[
\begin{align*}
\text{RCHO} + 2[H] & \xrightarrow{\text{Pd}} \text{RCH}_2\text{OH} \\
\text{R - C = O + 2[H]} & \xrightarrow{\text{NaBH}_4} \text{RCH}_2\text{OH} \\
\text{R - C = O + 2[H]} & \xrightarrow{\text{NaBH}_4} \text{RCHOH}
\end{align*}
\]

(v) By reduction of esters with LiAlH\(_4\) or Na/C\(_2\)H\(_5\)OH:

\[
\begin{align*}
\text{R - C - OR' + 4[H]} & \xrightarrow{\text{LiAlH}_4} \text{RCH}_2\text{OH} + \text{R' - OH}
\end{align*}
\]

(vi) By hydrolysis of esters:

\[
\begin{align*}
\text{R - C - O - R' + H}_2\text{O} & \xrightarrow{\text{conc H}_2\text{SO}_4} \text{R - C - OH} + \text{R' - OH}
\end{align*}
\]

(vii) From alkyl halides:

\[
\text{R - X + KOH (aq)} \rightarrow \text{R - OH} + \text{KX}
\]

(viii) By reduction of acids and their derivatives:

\[
\begin{align*}
\text{R - COOH} & \xrightarrow{\text{LiAlH}_4} \text{RCH}_2\text{OH} \\
\text{R - COCl} + 2\text{H}_2 & \xrightarrow{\text{Ni}} \text{RCH}_2\text{OH} + \text{HCl}
\end{align*}
\]

(ix) From \(1^\circ\) amines:

\[
\begin{align*}
\text{R - NH}_2 & \xrightarrow{\text{NaNO}_2 + \text{HCl}} \text{ROH} + \text{H}_2\text{O} + \text{N}_2
\end{align*}
\]
1. **Reimer Tiemann Reaction**

   ![Chemical Reaction Diagram]

   - **OH**
   - **CHCl₃ + aq NaOH**
   - **Intermediate**
   - **NaOH**
   - **H⁺**
   - **Salicyaldehyde**

2. **Kolbe reaction**

   ![Chemical Reaction Diagram]

   - **OH**
   - **NaOH**
   - **ONA**
   - **(i) CO₂**
   - **(ii) H⁺**
   - **2-Hydroxybenzolic acid**
   - **(Salicylic acid)**

3. **Friedel craft reaction**

   ![Chemical Reaction Diagram]

   - **OCH₃**
   - **+ CH₃Cl**
   - **Anhyd. AlCl₃, CS₂**
   - **2-Methoxytoluen**
   - **(Minor)**
   - **4-Methoxytoluen**
   - **(Major)**

   ![Chemical Reaction Diagram]

   - **OCH₃**
   - **+ CH₃COCl**
   - **Anhyd. AlCl₃**
   - **Ethanoyl chloride**
   - **2-Methoxyacetophenone**
   - **(Minor)**
   - **4-Methoxyacetophenone**
   - **(Major)**
4. Williamson synthesis: Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide is called Williamson synthesis.

\[
\begin{align*}
R - X + R' - O - Na & \rightarrow R - O - R' + NaX \\
CH_3I + CH_3CH_2ONa & \rightarrow CH_3OCH_2 - CH_3 + NaI \\
CH_3CH_2 - I + & \rightarrow + NaI
\end{align*}
\]

Both simple and mixed ether can be produced.

Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN² or SN¹ mechanism.

**MECHANISMS**

1. **Hydration of Alkene**:

\[
\begin{align*}
\text{C} = \text{C} & \quad + \quad \text{H}_2\text{O} \quad \xleftarrow{\text{H}^+} \quad \text{C} - \text{C} \\
\quad \text{H} & \quad \text{OH} \\
\quad \text{CH}_3\text{CH} = \text{CH} + \text{H}_2\text{O} & \quad \xleftarrow{\text{H}^+} \quad \text{CH}_3 - \text{CH} - \text{CH}_3 \\
\quad \text{OH}
\end{align*}
\]

**Mechanism**

The mechanism of the reaction involves the following three steps:

**Step 1:** Protonation of alkene to form carbocation by electrophilic attack of H₃O⁺.

\[
\begin{align*}
\text{H}_2\text{O} + \text{H}^+ & \rightarrow \text{H}_3\text{O}^+ \\
\text{C} = \text{C} & \quad + \quad \text{H} - \xrightarrow{\text{H}^+} \quad \text{C} - \text{C} + \quad \text{H}_2\text{O}^+
\end{align*}
\]

**Step 2:** Nucleophilic attack of water on carbocation.

\[
\begin{align*}
\quad \text{H} & \quad \xleftarrow{\text{H}^+} \quad \text{C} - \text{C} \quad + \quad \text{H}_2\text{O}^+ \\
\quad \text{C} - \text{C} & \quad + \quad \text{H}_2\text{O}^+
\end{align*}
\]

**Step 3:** Deprotonation to form an alcohol.

\[
\begin{align*}
\quad \text{H} & \quad \xleftarrow{\text{H}^+} \quad \text{C} - \text{O}^-' - \text{H} \quad + \quad \text{H}_2\text{O}^- \\
\quad \text{C} & \quad + \quad \text{H}_2\text{O}^- \\
\quad \text{C} - \text{C} & \quad \xrightarrow{\text{H}^+} \quad \text{C} - \text{C} + \quad \text{H}_3\text{O}^+
\end{align*}
\]
2. **Dehydration Reaction**

\[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4, 413 \text{ k}} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \]

**Mechanism:**

**Step 1:** \( \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{O} - \text{H} \)

**Step 2:** \( \text{CH}_3\text{CH}_2\text{O} - \text{H} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{O} - \text{H} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \)

**Step 3:** \( \text{CH}_3\text{CH}_2\text{O} - \text{H} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}^+ \)

(2) \( \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4, 443 \text{ K}} \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O} \)

**Step 1:** \( \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+ \xrightarrow{\text{Fast}} \text{CH}_3\text{CH}_2\text{O} - \text{H} \)

**Step 2:** \( \text{CH}_3\text{CH}_2\text{O} - \text{H} \xrightarrow{\text{Slow}} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \)

**Step 3:** \( \text{H} \rightarrow \text{CH}_2 = \text{CH} + \text{H}^+ \)
IMPORTANT PREPARATIONS

(1) **Preparation of Phenol from Cumene**

\[
\text{Cumene} + \text{O}_3 \xrightarrow{} \text{Cumene Hydroperoxide} \xrightarrow{\text{H}^+} \text{Phenol} + \text{CH}_3\text{COCH}_3
\]

(2) **Preparation of Aspirin**

\[
\text{Salicylic acid} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{H}^+} \text{Acetylsalicylic acid (Aspirin)} + \text{CH}_3\text{COOH}
\]

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 \((\text{ZnCl}_2 + \text{HCl})\).
   (3rd turbidity – instant, 2nd - 5 minutes, 1st - 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

\[
\begin{align*}
\text{O} & \\
\text{CH}_3-C & \quad \text{or} \quad \text{CH}_3-\text{CH}-
\end{align*}
\]

15. Presence of EWGs increase the acid strength of phenols while EDGs decrease the acid strength.

   \[
   \begin{align*}
   \text{EWG} : & \quad -\text{NO}_2, -\text{X}, -\text{CN}, -\text{COOH} \text{ etc.} \\
   \text{EDG} : & \quad -\text{R}, -\text{OR}, -\text{OH}, -\text{NH}_2 \text{ etc.}
   \end{align*}
\]
16. 3rd alcohols are resistant to oxidation due to lack of \(\alpha\)-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:

$$\text{HC - CH - CH}_2 - \text{CH - CH - CH}_2\text{OH} \quad \text{CH}_3 \quad \text{OH} \quad \text{CH}_3$$

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 phenoxy ion by resonance.

Q. 4. Arrange the following in decreasing order of their acidic character:

(i) $\text{CH}_3\text{O-} - \text{OH}$  
(ii) $\text{C}_6\text{H}_5\text{OH}$  
(iii) $\text{O}_2\text{N-} - \text{OH}$

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$_2$SO$_4$ + 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 $\text{CH}_3\text{CH}_2\text{OH}$ heated with red P and HI?

Ans. $\text{C}_2\text{H}_5\text{OH} + 2\text{HI} \xrightarrow{\text{Red P}} \text{C}_2\text{H}_6 + \text{I}_2 + \text{H}_2\text{O}$

Q. 10. Complete the following reaction:

$$\text{OH} \quad + \text{HNO}_3 \xrightarrow{\text{conc. H}_2\text{SO}_4} \quad \text{?} + \text{H}_2\text{O}$$
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. \[ \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Conc. } \text{H}_2\text{SO}_4, 443 \text{ K}} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \]

Q. 13. Explain Kolbe’s reaction with example.

Ans. \[ \text{C}_6\text{H}_5\text{Na} + \text{CO}_2 \xrightarrow{400 \text{ K}, 4-7 \text{ atm}} \text{C}_6\text{H}_5\text{ONa} \xrightarrow{\text{dilHCl}} \text{C}_6\text{H}_5\text{COOH} \]

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-Tiemann reaction

(ii) Williamson’s synthesis

Ans. (i) \[ \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{CHCl}_3 + \text{NaOH(aq)}} \text{C}_6\text{H}_5\text{O}^+\text{CHCl}_2 \]

(ii) \[ \text{C}_6\text{H}_5\text{ONa} + \text{CH}_3\text{Br} \rightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{NaBr} \]

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)  \( \text{Phenol} + \text{FeCl}_3 \rightarrow \)

(ii)  \( \text{C}_6\text{H}_5\text{OH} + \text{CHCl}_3 + \text{NaOH} \xrightarrow{340\, \text{K}} \)

(iii)  \( \text{C}_6\text{H}_5\text{OH} + \text{Br}_2 \, (\text{aq}) \rightarrow \)

(iv)  \( \text{O} + \text{CO}_2 \xrightarrow{400\, \text{K}, 4-7\, \text{atm}} \)

Ans.

(i)  \( [(\text{C}_6\text{H}_5\text{O})_3\text{Fe}] + 3\text{HCl} \)

(ii)  \( \text{CHO} + \text{NaCl} + \text{H}_2\text{O} \)

(iii)  \( \text{Br} + \text{HBr} \)

(iv)  \( \text{COONa} \)

Q. 4. Write:

(i)  Friedel-Crafts reaction

(ii)  Coupling reaction

Ans.

(i)  \( \text{Anhyd. AlCl}_3 \xrightarrow{\text{CH}_3\text{Cl}} \text{CH}_3 \)

(ii)  \( \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{pH}=9-10} \text{OH} + \text{HCl} \)

Q. 5. Give one reaction of alcohol involving cleavage of:

(i)  \( \text{C} - \text{O} \) bond

(ii)  \( \text{O} - \text{H} \) bond

Ans.

(i)  \( \text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_3 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{POCl}_3 + \text{HCl} \)

(ii)  \( \text{CH}_3\text{CH}_2\text{OH} + \text{Na} \rightarrow \text{CH}_3\text{CH}_2\text{ONa} + \text{H}_2 \)

Q. 6. Etherial solution of an organic compound ‘X’ when heated with Mg gave ‘Y’. ‘Y’ on treatment with \( \text{CH}_3\text{CHO} \) followed by acid hydrolysis gave 2-propanol. Identify the compound ‘X’. What is ‘Y’ known as?
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 CH₃OH.
(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) CH₃CH = CH₂ + H₂O $\xrightarrow{H_{2}SO_{4}(dil.)}$ CH₃CH – CH₃

(ii) CO₂ + C₆H₅OH $\xrightarrow{NaOH, \Delta}$ C₆H₅COOH

Q. 10. Write mechanism of reaction of HI with methoxymethane.

Ans. CH₃ – O – CH₃ + H – I $\xrightarrow{\text{H}}$ CH₃ – O – CH₃ + H – I

I + CH₃ – O – CH₃ $\xrightarrow{\text{I}}$ CH₃I + CH₃OH
Q. 11. Arrange in order of boiling points:
   (i) \( \text{C}_2\text{H}_4\text{O} - \text{O} - \text{C}_2\text{H}_4, \text{C}_4\text{H}_8\text{COOH}, \text{C}_4\text{H}_8\text{OH} \)
   (ii) \( \text{C}_3\text{H}_7\text{CHO}, \text{CH}_3\text{COC}_2\text{H}_5, \text{C}_2\text{H}_5\text{COOCH}_3, (\text{CH}_3\text{CO})_2\text{O} \)
   
   Ans. (i) \( \text{C}_4\text{H}_8\text{COOH} > \text{C}_4\text{H}_8\text{OH} > \text{C}_2\text{H}_4 - \text{O} - \text{C}_2\text{H}_4 \)
   (ii) \( (\text{CH}_3\text{CO})_2\text{O} > \text{C}_2\text{H}_5\text{COOCH}_3 > \text{CH}_3\text{COC}_2\text{H}_5 > \text{C}_3\text{H}_7\text{CHO} \)

Q. 12. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

   (i) \( \text{Br} + \text{CH}_3\text{ONa} \)
   (ii) \( \text{ONO}_2 \) + \( \text{CH}_3\text{Br} \)

   Ans. (ii) \( \text{ONO}_2 \) + \( \text{CH}_3\text{Br} \rightarrow \text{OCH}_3 \)

   It is because of double bond character, (C – Br) bond in \( \text{Br} \) due to resonance it is less reactive towards SN, RXN.


   Ans. Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides \( \left( \text{C} - \text{O} - \text{C} \right) \).

Q. 14. How will you distinguish between \( \text{CH}_3\text{OH} \) and \( \text{C}_2\text{H}_5\text{OH} \)?

   Ans. \( \text{C}_2\text{H}_5\text{OH} + 4\text{I}_2 + 3\text{Na}_2\text{CO}_3 \xrightarrow{\text{warm}} \text{CHI}_3 + \text{HCOONa} + 5\text{NaI} + 2\text{H}_2\text{O} + 3\text{CO}_2 \)

   CH\(_3\)OH 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) NaBH₄, sodium borohydride.
(iii) Br₂ (water)

Q. 2. Write structures of the major products of the following:
(i) Mononitrilation of 3-methylphenol
(ii) Dinitration of 3-methylphenol
(iii) Mononitrilation of phenyl ethanoate

Ans. – OH and – CH₃ are o- and p-directing groups. The products are:

(i)

(ii)

(iii)

Q. 3. Complete the following reactions:
(i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \xrightarrow{\text{Pd/H}_2/\text{Ni}} \)
(ii) \( \text{CH}_3\text{CH} = \text{CHCH}_2\text{OH} \xrightarrow{\text{PCC}} \)
(iii) \( \text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{(1) \text{B}_2\text{H}_6} \xrightarrow{(2) 3\text{H}_2\text{O}_2/\text{OH}^-} \)
(iv) \( \text{C}_6\text{H}_5\text{OH} \xrightarrow{(1) \text{aq.NaOH}} \xrightarrow{(2) \text{CO}_2/\text{H}^+} \)
(v) \( \text{CH}_2\text{Br} - \text{CH}_2\text{Br} \xrightarrow{\text{KOH}} \)
(vi) \( \text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{HNO}_2} \)

Ans. (i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)
(ii) \( \text{CH}_3\text{CH} = \text{CHCH}_2^- \text{OH} \)
(iii) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)
Q. 4. Give equations of the following reactions:

(i) Oxidation of propan-1-ol with alkaline KMnO₄ solution.
(ii) Bromine in CS₂ with phenol.
(iii) Treating phenol with chloroform in presence of aqueous NaOH.

Ans.

(i) \[
\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH} + 2[\text{O}] \xrightarrow{\text{alkaline KMnO}_4} \text{CH}_3\text{CH}_2\text{COO}^-\text{K}^+
\]

(ii) \[
\text{ phenol } + \text{Br}_2 \xrightarrow{\text{CS}_2} \text{ phenol} + \text{Br}
\]

(iii) \[
\text{ phenol } + \text{CHCl}_3, \text{NaOH, 343K} \xrightarrow{\text{Reimer-Tiemann reaction}} \text{ phenol} + \text{CHO}
\]

Q. 5. Describe the following reactions with examples:

(i) Reimer-Tiemann reaction
(ii) Kolbe’s reaction
(iii) Friedel Crafts acylation of anisole

Ans.

(i) \[
\text{ phenol } + \text{CHCl}_3, \text{NaOH} \xrightarrow{} \text{ phenol} + \text{CHO}
\]

(ii) \[
\text{ phenol } + \text{CO}_2 \xrightarrow{400 \text{K, 4-7 atm}} \text{ phenol} + \text{H}_2\text{O}
\]

(iii) \[
\text{ phenol } + \text{Br}_2 \xrightarrow{\text{CH}_3\text{COOH}} \text{ phenol} + \text{Br}
\]

[10%] [90%]

Salicylic acid
Q. 6. Dehydration of alcohols to form an alkene is always carried out with conc. \( \text{H}_2\text{SO}_4 \) and not with conc. \( \text{HCl} \) or \( \text{HNO}_3 \). Explain.

Ans. In acidic medium alcohols protonated then loses \( \text{H}_2\text{O} \) to form a carbo cation. If \( \text{HCl} \) \( \text{Cl}^- \) strong nucleophile cause nucleophilic substitution, \( \text{HNO}_3 \) causes oxidation.

Q. 7. How will you convert:

(i) Phenol to cyclohexanol
(ii) Benzyl chloride to benzyl alcohol
(iii) Anisole to phenol

Ans. (i) \[ \text{Ph} + \text{H}_2 \xrightarrow{\text{Ni}} \text{CyH}_6 \]

(ii) \[ \text{Ph-CH}_2\text{Cl} + \text{KOH (aq)} \rightarrow \text{Ph-CH}_2\text{OH} + \text{KCl} \]

(iii) \[ \text{Ph} + \text{HI} \rightarrow \text{C} + \text{CH}_3\text{I} \]

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. An alcohol \( \text{A} (\text{C}_4\text{H}_{10}\text{O}) \) on oxidation with acidified \( \text{K}_2\text{Cr}_2\text{O}_7 \) gives carboxylic acid ‘B’ \( (\text{C}_4\text{H}_6\text{O}_2) \). Compound ‘A’ when dehydrated with conc. \( \text{H}_2\text{SO}_4 \) at 443 K gives compound ‘C’ with aqueous \( \text{H}_2\text{SO}_4 \). ‘C’ gives compound ‘D’ \( (\text{C}_4\text{H}_{10}\text{O}) \) 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 : \((\text{CH}_3)_2\text{CHCH}_2\text{OH}\)  
B : \(\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}\)  
C : \((\text{CH}_3)_2\text{C} = \text{CH}_2\)  
D : \((\text{CH}_3)_3 - \text{C} - \text{OH}\)

Q. 2. An ether ‘A’ \( (\text{C}_4\text{H}_{12}\text{O}) \) 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 : \(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3\)  
B : \(\text{CH}_3\text{CH}_2\text{OH}\)  
C : \(\text{CH}_3\text{CHOHCH}_3\)  
D : \(\text{CH}_3\text{COOH}\)  
E : \(\text{CH}_3\text{COCH}_3\)
Q. 3. Which of the following compounds gives fastest reaction with HBr and why?

(i) (CH$_3$)$_3$COH
(ii) CH$_3$CH$_2$CH$_2$OH
(iii) CH$_3$CHCH$_3$
(iv) CH$_3$CHCH$_2$OH

Ans. (i) (CH$_3$)$_3$C – OH
Due to formation of EDG and formation of cation.

Q. 4. Phenol, C$_6$H$_5$OH 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) [Phenolic SO$_3$H]
(Z) (Picric acid) [Phenolic NO$_2$]

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 $\xrightarrow{Zymase}$

(ii) [Ring] + Br$_2$ $\xrightarrow{H_2O}$ ?

(iii) [Ring] + COOH $\xrightarrow{(CH_3CO)_2O, H^+}$ ?

(iv) CH$_3$CHOCH$_2$CH$_3$ $\xrightarrow{HI}$ ?

(v) Phenol + Zn (dust) $\rightarrow$

(vi) Phenol + Na $\rightarrow$

(vii) R$_2$CHOH + HCl + ZnCl$_2$ $\rightarrow$ R$_2$CHCl + .......... (anhydrous)

(viii) R – CHOH – R $\xrightarrow{[O]}$
(ix) $\text{CH}_3 - \text{CH} - \text{CH}_3 \xrightarrow{\text{SOCl}_2} \text{CH}_3 - \text{CH} - \text{CH}_3^+ + $ \\
(x) $\text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow{\text{Bleaching powder}}$ \\

**Ans.** 
(i) $\text{C}_2\text{H}_5\text{OH}$  
(ii) 

(iii) 

(iv) $(\text{CH}_3)_2\text{CHOH}$ and $\text{CH}_3\text{CH}_2\text{I}$  
(v) $\text{C}_6\text{H}_6$  
(vi) $\text{C}_6\text{H}_5\text{ONa}$  
(vii) $\text{H}_2\text{O}$  
(viii) $\text{R} - \text{C} - \text{R}$  
(ix) $\text{SO}_2$  
(x) $\text{CHCl}_3$
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 BaSO₄ prevent reduction of R–CHO to R–CH₂OH.
3. In the reaction of toluene with CrO₃, acetic anhydride is used to protect benzaldehyde by forming benzylidenecacetate to avoid its oxidation to benzoic acid.
4. Order of reactivity of aldehydes and ketones towards nucleophilic addition is:
   (i) HCHO > CH₃CHO > CH₃CH₂CHO.
   (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 at least one α–H atom get condensed in presence of a base. This is known as Aldol condensation.
7. Aldol condensation involves carbanion as an 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 (C₁₂–C₁₈) 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.

\[ \begin{array}{c}
C \quad \sigma \\
\pi \\
O 
\end{array} \]

17. General Methods of Preparation:

(i) Controlled oxidation of $1^o$ alcohols:

\[ \text{RCH}_2\text{OH} \xrightarrow{\text{PCC/CrO}_3} \text{RCHO} \]  
(Collin’s reagent)

(ii) Dehydrogenation of $1^o$ alcohols:

\[ \text{RCH}_2\text{OH} \xrightarrow{\text{Cu573 K}} \text{RCHO} + \text{H}_2 \]

(iii) From Rosenmund reaction/reduction:

\[ \text{RCOCl} + \text{H}_2 \xrightarrow{\text{Pd/BaSO}_4} \text{RCHO} + \text{HCl} \]

(iv) Hydration of alkynes:

\[ \text{CH} \equiv \text{CH} \xrightarrow{1\% \ HgSO}_4\text{[CH}_2 = \text{CHOH]} \xrightarrow{\text{Tautomerism}} \text{CH}_3\text{CHO} \]

(v) Reductive ozonolysis of alkenes:

\[ \text{R} = \text{CH} = \text{CH} = \text{R} \xrightarrow{\text{(i) }} \text{O}_2 \xrightarrow{\text{Zn/H}_2\text{O}} 2\text{RCHO} + \text{H}_2\text{O}_2 \]

(vi) From salts of fatty acids:

\[ (\text{RCOO})_2\text{Ca} + (\text{HCOO})_2\text{Ca} \xrightarrow{\text{D Dist.}} 2\text{RCHO} + 2\text{CaCO}_3 \]

(vii) Stephen’s reduction of nitrile compounds:

\[ \text{R} = \text{C} \equiv \text{N} \xrightarrow{\text{SnCl}_4/HCl}} \text{[R} = \text{CH} = \text{NH}_2\text{HCl]} \xrightarrow{\text{H}_3\text{O}^+} \text{RCHO} + \text{NH}_4\text{Cl} \]

(viii) Hydrolysis of germinal halides:

\[ \text{R} \equiv \text{CHCl} \xrightarrow{\text{aq KOH}} \text{RCHO} + \text{H}_2\text{O} \]

(ix) From Grignard’s reagent:

\[ \text{H} \equiv \text{C} \equiv \text{N} + \text{R} \equiv \text{MgX} \xrightarrow{\text{Dryether}} \text{H} \equiv \text{C} = \text{N} \equiv \text{R} \xrightarrow{\text{H}_2\text{O}^+} \text{RCHO} + \text{NH}_3 + \text{Mg(OH)X} \]
General Methods of Preparation of Ketones only

(i) Dehydrogenation of 2° alcohols:

\[
R - \text{CHOL} - R \xrightarrow{\text{Cu}_{\text{573K}}} R - \overset{\text{O}}{\text{C}} - R + H_2
\]

(ii) Hydration of alkynes:

\[
R - C \equiv CH \xrightarrow{\text{H}_2\text{O} / \text{Zn}} \left\{ \begin{array}{c}
\text{OH} \\
\text{R} \overset{\text{O}}{\equiv} \overset{\text{CH}_2}{\text{C}} \end{array} \right\} \xrightarrow{\text{Tautomerism}} R - C - \text{CH}_3
\]

Ozonolysis of Alkene

(iii) \( R \xrightarrow{\text{O}_3} \overset{\text{O}}{\text{C}} = \overset{\text{R}'}{\text{C}} \xrightarrow{\text{H}_2\text{O}/\text{Zn}} 2R - C - R + H_2\text{O}_2 \)

(iv) From Grignard's reagents:

\[
\text{R'MgX} + R - C \equiv N \rightarrow \left\{ \begin{array}{c}
\text{R'} \\
\text{R} - C = N - \text{MgX} \end{array} \right\} \xrightarrow{\text{H}_2\text{O}} R - C = O + \text{NH}_3 + \text{Mg(OH)X}
\]

(iv) From acid chlorides:

\[
\text{RCOCl} + R_2\text{Cd} \rightarrow 2R - C - R' + \text{CdCl}_2
\]

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. **ROSMUND REDUCTION:**

Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes

\[
\text{O} \quad \text{C} - \text{Cl} + 2\text{[H]} \xrightarrow{\text{Pd-BaSO}_4} \text{CHO}
\]

Benzoyl chloride \[\rightarrow\] 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.

\[
\text{RCN} + \text{SnCl}_2 + \text{HCl} \xrightarrow{\text{RCH} = \text{NH}} \text{H}_2\text{O}^+ \xrightarrow{\text{RCHO}}
\]

3. **ETARD REACTION**

On treating toluene with chromyl chloride \(\text{CrO}_2\text{Cl}_2\), the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

\[
\text{O} \quad \text{C} - \text{Cl} + 2\text{[H]} \xrightarrow{\text{Pd-BaSO}_4} \text{CHO}
\]

Benzoyl chloride \[\rightarrow\] Benzaldehyde

OR

\[
\text{CH}_3 \quad + \text{CrO}_2\text{Cl}_2 \xrightarrow{\text{CS}_2} \text{CH(O\text{CrOHCl}_2)} \xrightarrow{\text{H}_2\text{O}^+} \text{CHO}
\]

Toluene \[\rightarrow\] Chromium complex \[\rightarrow\] 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.
5. **WOLFF-KISHNER REDUCTION**

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol.

\[ \text{> C}=\text{O} \xrightarrow{\text{Zn} - \text{Hg, HCl}} \text{CH}_3 + \text{H}_2\text{O} \quad \text{Alkanes} \]

\[ \text{> C}=\text{O} \xrightarrow{\text{NH}_2 - \text{NH}_2, \text{KOH/Ethylene glycol, heat}} \text{CH}_3 + \text{H}_2\text{O} \quad \text{Alkanes} \]

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 ethydes (aldol) or β-hydroxy ketones (ketol).

\[
2\text{CH}_3 - \text{CHO} \xrightarrow{\text{NaOH, dil}} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 - \text{CHO} \xrightarrow{\text{Heat, -H}_2\text{O}} \text{CH}_3 - \text{CH} = \text{CH} - \text{CHO} \\
\text{(Aldol)} \quad \text{But} - 2 - \text{enal}
\]

\[
2\text{CH}_3 - \text{CO} - \text{CH}_3 \xrightarrow{\text{Ba(OH)}_2} \text{CH}_3 - \text{C} - \text{CH}_3 - \text{CO} - \text{CH}_3 \xrightarrow{\text{Heat, -H}_2\text{O}} \text{CH}_3 - \text{C} = \text{CH} - \text{CO} - \text{CH}_3 \\
\text{(Ketal)} \quad \text{4-Methyl pent-3-en-2-one}
\]

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.

\[
\text{CH}_3\text{CHO} + \text{CH}_3 - \text{CH}_2 - \text{CHO} \xrightarrow{1 \text{NaOH, 2 } \Delta} \text{CH}_3\text{CH} = \text{CH} - \text{CHO} + \text{CH}_3\text{CH}_2\text{CH} = \text{C} - \text{CHO} \\
\text{But-2-enal} \quad \text{2-Methylpent-2-enal}
\]

\[
\text{CH}_3 - \text{CH} = \text{C} - \text{CHO} + \text{CH}_3\text{CH}_2\text{CH} = \text{CHCHO} \\
\text{Pent-2-enal} \quad \text{2-Methylbut-2-enal}
\]

8. **CANNIZZARO REACTION**

Aldehydes which do not have an a-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali, to yield carboxylic acid salt and an alcohol respectively.
H-CHO + H-CHO + Conc.KOH $\rightarrow$ CH$_3$OH + HCOOK

\[ \text{CHO + NaOH (con.)} \xrightarrow{\text{Methanol}} \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COONa}^- \]
Benzaldehyde

\[ \text{Benzyl alcohol Sodium benzoate} \]

**CARBOXYLIC ACID**

1. **HELL-VOLHARD-ZELINSKY REACTION (HVZ)**

   Carboxylic acids having an - hydrogen are halogenated at the - position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give a -halocarboxylic acids.

   \[ \text{RCH}_2 - \text{COOH} \xrightarrow{\text{i) X}_2/ \text{Red phosphorus}} \text{R - CH - COOH} \xrightarrow{\text{ii) H}_2\text{O}} X \]
   \[ X = \text{Cl, Br} \]
   \[ \alpha - \text{halocarboxylic acids} \]

2. **ESTERIFICATION**

   Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc.$\text{H}_2\text{SO}_4$ as catalyst to form esters.

   \[ \text{RCOOH + R'O} \xrightarrow{\text{H}^+} \text{RCOOR'} + \text{H}_2\text{O} \]

18. Vinegar is 8 to 10% solution of CH$_3$COOH.

19. $\alpha$-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 \hspace{1cm} Oxalic acid 1, 2 ethanedioic acid
   HOOC – CH$_2$ – COOH \hspace{1cm} Malonic acid 1, 3 propanedioic acid
   HOOC – (CH$_2$)$_2$ – COOH \hspace{1cm} Succinic acid 1, 4 butanedioic acid
   HOOC – (CH$_2$)$_3$ – COOH \hspace{1cm} Glutonic acid 1, 5 pentamideoic acid
   HOOC – (CH$_2$)$_4$ – COOH \hspace{1cm} 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:
   \[(\text{CH}_3)_2\text{CHCOOH}, \text{CH}_3\text{CH}_2\text{CH(Br)COOH}, \text{CH}_3\text{CH(Br)CH}_2\text{COOH}\]
   
   Ans. \((\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH(Br)CH}_2\text{COOH} < \text{CH}_3\text{CH(Br)COOH}\)

Q. 2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.
   
   Ans. \(\begin{array}{c}
   \text{Cl} \\
   \text{O} \\
   \text{CH}_3 \quad \text{C} \quad \text{CH}_3
   \end{array}\)

Q. 3. Which type of aldehyde can go Cannizzaro reaction?
   
   Ans. Aromatic and aliphatic aldehydes which do not contain \(\alpha\)-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:
   \[\text{CH}_3\text{CHO}, \text{CH}_3\text{COCH}_3, \text{HCHO}, \text{C}_2\text{H}_5\text{COCH}_3\]
   
   Ans. \(\text{C}_2\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}\)

Q. 6. Mention industrial product obtained from HCHO.
   
   Ans. Bakelite

Q. 7. Arrange the following compounds in increasing order of their boiling point:
   \[\text{CH}_3\text{CHO, CH}_3\text{CH}_2\text{OH, CH}_3 – \text{O} – \text{CH}_3, \text{CH}_3 – \text{CH}_2 – \text{CH}_3\]
   
   Ans. \(\text{CH}_3 – \text{CH}_2 – \text{CH}_3 < \text{CH}_3 – \text{O} – \text{CH}_3 < \text{CH}_3\text{CHO} < \text{CH}_3\text{CH}_2\text{OH}\)

Q. 8. How is acetone obtained from ethanol?
   
   Ans. \(\text{CH}_3 – \text{CH}_2 – \text{OH} \xrightarrow{\text{Cu, 573K}} \text{CH}_3 – \text{C} – \text{H} \xrightarrow{(\text{i})\text{CH}_3\text{MgBr}} \xrightarrow{(\text{ii})\text{H}_2\text{O/H}^+} \text{CH}_3 – \text{CH} – \text{CH}_3 \xrightarrow{\text{Cu, 573K}} \text{CH}_3 \text{C} = \text{O}\)
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. \[ 2\text{CH}_3\text{COCl} + \text{Cd}[\text{CH}_3]_2 \xrightarrow{\text{dry \ ether}} 2\text{CH}_3 - \text{C} - \text{CH}_3 + \text{CdCl}_2 \]

Q. 11. What happens when \( \text{CH}_3\text{CHO} \) is treated with \( \text{K}_2\text{Cr}_2\text{O}_7 \) in presence of \( \text{H}_2\text{SO}_4 \)?
Ans. \( \text{CH}_3\text{CHO} + [\text{O}] \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4} \text{CH}_3\text{COOH} \)

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 \( \text{CH}_3\text{COOH} \) is treated with \( \text{PCl}_5 \)?
Ans. \( \text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl} \)

Q. 14. What product is obtained when ethyl benzene is oxidized with alkaline \( \text{KMnO}_4 \)?
Ans. Benzoic acid (\( \text{C}_6\text{H}_5\text{COOH} \)) is obtained.

Q. 15. \( \text{CH}_3\text{CHO} \) is more reactive than \( \text{CH}_3\text{COCH}_3 \) towards reaction with HCN. Give reason.
Ans. Because the positive charge on carbonyl carbon of \( \text{CH}_3\text{CHO} \) decreases to lesser extent due to one ERG (–\( \text{CH}_3 \)) and hence 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:
\[ \text{HOOC – CH = CH - COOH} \]
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 C₆H₅COOH 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) C₂H₂ → CH₃COOH

(ii) C₆H₅CONH₂ → C₆H₅COOH

Ans. (i) CH₂CH₂SO₄\text{HgSO₄} CH₃CHO \xrightarrow{\text{dil H₂SO₄}} CH₃COOH

(ii) C₆H₅CONH₂ + HNO₂ → C₆H₅COOH + N₂ + H₂O

Q. 2. Complete the following:

(i) COOH

\xrightarrow{\text{SO₃/H₂SO₄}}

(ii) COOH

\xrightarrow{\text{conc. HNO₃ (conc. H₂SO₄)}}

Ans. (i) COOH

\xrightarrow{\text{SO₃H}}

(ii) COOH

\xrightarrow{\text{NO₂}}

Q. 3. An organic compound X has molecular formula C₅H₁₀O. 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.
An. Ketone give +ve test with Iodoform. It is methyl-ketone.

\[ \text{CH}_3 - \overset{\text{O}}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \text{ and } \text{CH}_3 - \overset{\text{O}}{\text{C}} - \text{CH} - \text{CH}_3 \] are possible structures of the compound.

Q. 4. Give the chemical test to distinguish between:

(i) \( \text{CH}_3\text{CHO and CH}_3 - \overset{\text{C}}{\text{C}} - \text{CH}_3 \)
(ii) \( \text{CH}_3\text{CHO and C}_6\text{H}_5\text{CHO} \)

An. (i) \( \text{CH}_3\text{CHO} \) gives Tollen’s reagent test.

\[ \text{CH}_3\text{CHO} + 2\text{AgNO}_3 + 2\text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COOH} + 2\text{Ag} + 2\text{NH}_4\text{NO}_3 + 2\text{H}_2\text{O} \]

Silver mirror

(ii) \( \text{CH}_3\text{CHO} \) gives brick red ppt.

\[ \text{CH}_3\text{CHO} + 2\text{CuSO}_4 + 4\text{NaOH} \rightarrow \text{CH}_3\text{COOH} + \text{Cu}_2\text{O} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

Brick red ppt.

Q. 5. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

An. Carbon atom of carbonyl is \( \text{C}_6\text{H}_5\text{CHO} \) is less reactive than that of propanal. \( \text{C}_6\text{H}_5\text{CHO} \) less polar due to resonance.

Q. 6. Which acid of each pair shown here would you expect to be stronger?

(i) \( \text{CH}_3\text{CO}_2\text{H or CH}_2\text{FCO}_2\text{H} \)

(ii) \( \text{CH}_2\text{FCO}_2\text{H or CH}_2\text{ClCO}_2\text{H} \)

(iii) \( \text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H or CH}_3\text{CHFCH}_2\text{CO}_2\text{H} \)

(iv) \( \text{F}_3\text{C-COOH or H}_5\text{C-COOH} \)

An. (i) \( \text{FCH}_2\text{COOH} \) (ii) \( \text{CH}_2\text{FCOOH} \)

(iii) \( \text{CH}_3 - \overset{\text{F}}{\text{CH}} - \text{CH}_2\text{COOH} \)
Q. 7. Carboxylic acids do not give reactions of aldehydes and ketones why?

Ans. It is due to resonance R – C \equiv O \rightleftharpoons R – C = O \rightleftharpoons R – C = O^+ \overset{\text{Position of } > \text{ C = O group}}{\text{keep changing.}}

Q. 8. Write IUPAC name of the following:

(i) \begin{align*}
\text{OCOCH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{align*}

(ii) \begin{align*}
\text{COOH} \\
\text{I} \\
\text{Br} \\
\text{Cl}
\end{align*}

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\textsubscript{6}H\textsubscript{5}CHO with CrO\textsubscript{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\textsubscript{2}H\textsubscript{5}OH and CH\textsubscript{3}CHO

(ii) C\textsubscript{6}H\textsubscript{5}COCH\textsubscript{3} and C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CHO

Ans. (i) C\textsubscript{2}H\textsubscript{5}OH evolves H\textsubscript{2} gas with Na, CH\textsubscript{3}CHO not.
(ii) Acetophenone will give yellow ppt. of iodoform while C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CHO will not.

Q. 11. Complete the following reactions by identifying A, B and C:

(i) A + Hydrogen (g) $\xrightarrow{\text{Pd/BaSO}_4}$ (CH\textsubscript{3})\textsubscript{2}CH – CHO

(ii) \begin{align*}
\text{CH}_3 \quad | \\
\text{CH}_3 \quad | \\
\text{CH}_3 \quad | \\
\text{CH}_3 \quad \text{O}
\end{align*} + NaO\textsubscript{I} $\rightarrow$ B + C

Ans. (i) ‘A’ is \begin{align*}
\text{CH}_3 \quad | \\
\text{CH} \quad | \\
\text{C} \quad | \\
\text{Cl}
\end{align*}
(ii) ‘B’ is CH₃ and ‘C’ is CH₃ – C – C – ONa
    \[\text{O} \quad \text{CH₃}\]

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.


Ans. In case of aldehyde reaction is reversible.

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{O} & \quad \text{H}_2\text{O} & \quad \rightleftharpoons & \quad \text{R} & \quad \text{C} & \quad \text{OH} & \quad \text{OH} \\
\text{H} & \quad & & & & & & \end{align*}
\]

In case of CCl₃CHO, Cl atoms increases +ve charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.

\[
\text{Cl} \quad \overset{\delta^+}{\text{O}} \quad \overset{\delta^-}{\text{Cl}} \quad \text{Cl} \quad \text{C} \quad \text{H} \quad \text{Cl} \quad \text{H}_2\text{O} \quad \text{CCl₃-CHO} \cdot \text{H}_2\text{O} \quad \text{Chloral hydrate}
\]

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 – NH₂ groups in semicarbazide. However, only one is involved in formation of semi carbazole.

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 – NH₂ group attached to C = O is involved in resonance. As result electron density on these NH₂ group decreases and hence does not act as nucleophile.

\[
\text{H}_2\text{N} \quad \overset{\delta^-}{\text{C}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}} \quad \overset{\delta^-}{\text{NH}}
\]

Q. 15. Aldehydes are easily oxidisable yet propanal can conveniently be prepared by the oxidation of propanol by acidic K$_2$Cr$_2$O$_7$.

**Ans.** Aldehydes having boiling points less than 373 K can be removed by distillation therefore propanal can easily be prepared from propanol by distillation from the alcohol dichromate solution.

Q. 16. Do the following conversions in not more than two steps
   (i) Benzoic acid to Benzaldehyde (ii) Propanone to propene

**Ans.**
   (i) C$_6$H$_5$COOH $\xrightarrow{\text{SOCl}_2}$ C$_6$H$_5$COCl $\xrightarrow{\text{Pol}–\text{BaSO}_4\text{H}_2}$ C$_6$H$_5$CHO
   (ii) CH$_3$COCH$_3$ $\xrightarrow{\text{NaBH}_4}$ CH$_3$CHCH$_3$ $\xrightarrow{\text{C}_{\text{onc.}}\text{H}_2\text{SO}_4}$ CH$_3$CH = CH$_2$

Q. 17. Write the reactions involved in the following reactions:
   (i) Clemmensen reduction (ii) Cannizzoro reaction

**Ans.**
   (i) $\overrightarrow{\text{C} = \text{O}}$ $\xrightarrow{\text{Zn} – \text{Hg} \text{HCl}}$ $\overrightarrow{\text{CH}_2 \ + \ \text{H}_2\text{O}}$
   (ii) $\overrightarrow{\text{H}}$ $\overrightarrow{\text{H}}$ $\overrightarrow{\text{C} = \text{O}}$ $\ + $ $\overrightarrow{\text{H}}$ $\ + $ $\overrightarrow{\text{C} = \text{O}}$ $\xrightarrow{\text{Conc.} \ \text{KOH}}$ CH$_3$OH + HCOO$^-\text{K}^+$

Q. 18. Convert the following (i) Ethyl benzene to benzoic acid (ii) Ethanal to but-2-enal

**Ans.**
   (i) C$_6$H$_5$C$_2$H$_5$ $\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+}$ C$_6$H$_5$COOH
   (ii) $2\text{CH}_3\text{CHO}$ $\xrightarrow{\text{NaOH}}$ $\text{dil.}$ $\text{CH}_3\text{CHCH}_2\text{CHO}$ $\xrightarrow{\text{H}_2\text{O}^+ / \Delta}$ CH$_2$CH = 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$_2$COOH $\xrightarrow{\text{(i) } \text{X}_2/\text{RedP}}$ RCHCOOH $\xrightarrow{\text{(ii) } \text{H}_2\text{O}}$ X = Cl, Br
   (ii) $\overrightarrow{\text{C} = \text{O}}$ $\xrightarrow{\text{(i) } \text{NH}_2\text{NH}_2}$ $\overrightarrow{\text{CH}_2 \ + \ \text{N}_2}$
   (ii) $\xrightarrow{\text{(ii) } \text{KOH/Ethylene glycol, heat}}$
Q. 2. Predict the organic products of the following reactions:

(i) \[ \text{CH}_2\text{CH}_3 \xrightarrow{\text{KMnO}_4, \text{KOH, } \Delta} \]

(ii) \[ \text{COOH} \xrightarrow{\text{SOCl}_2, \Delta} \]

(iii) \[ \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{H}_2\text{NCONHNH}_2} \]

(iv) \[ \xrightarrow{\text{+}} \]

(v) \[ \xrightarrow{(\text{Ag(NH}_3)_2)^+} \]

(vi) \[ \xrightarrow{\text{NaCN/HCl}} \]

Ans. (i) \[ \text{C}_6\text{H}_5 - \text{COOK} \]

(ii) \[ \text{COCl} \]

(iii) \[ \text{C}_6\text{H}_5\text{CH} = \text{N} - \text{NHCONH}_2 \]

(iv) \[ \text{C}_6\text{H}_5\text{COCl/AlCl}_3 \]

(v) \[ \text{COO}^- \]
Q. 3. Write chemical reaction to affect the following transformations:

(i) Butan-1-ol → Butanoic acid

(ii) Benzyl alcohol to pheynylethanoic acid

(iii) 3-Nitrobenzobenzene to 3-nitrobenzoic acid

(iv) 4-methylacetophenone to Terephthalic acid

(v) Cyclohexene → Hexane-1, 6 dioic acid

(vi) Butanal → Butanoic acid

Ans. (i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CrO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \)

(ii) \( \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CN} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH} \)

(iii) \( \text{Br} \text{ ether} \rightarrow \text{MgBr} \text{ (dry.ice)} \rightarrow \text{CO}_2 \rightarrow \text{H}_3\text{O}^+ \)

(iv) \( \text{CH}_3 \rightarrow \text{KMnO}_4/\text{KOH} \rightarrow \text{COOK} \rightarrow \text{dilH}_2\text{SO}_4 \rightarrow \text{COOH} \)

Dipotassium benzene 1, 4 dicarboxylate

Terephthalic acid

(v) \( \text{Cyclohexene} + \text{KMnO}_4, \text{dilH}_2\text{SO}_4 \rightarrow \text{COOH} \rightarrow \text{Hexane-1, 6 dioic acid} \) (adipic acid)

(vi) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{Amm, AgNO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \)
Q. 4. Draw the structure of the following derivatives:
   (i) 2, 4-dinitrophenylhydrazone of C₆H₅CHO
   (ii) Cyclopropanone oxime
   (iii) Acetaldehyedimethylacetal
   (iv) Semicarbazone to cyclobutanone
   (v) Ethylene ketal of hexan-3-one
   (vi) Methylhemiacetal of formaldehyde

   Ans. (i) \( \text{C}_6\text{H}_5 - \text{CH} = \text{N} - \text{NH} \begin{array}{c} \text{NO}_2 \\ \text{NOH} \end{array} \)

   (ii)

   (iii) \( \text{CH}_3 - \text{CH} - \text{OCH}_3 \)

   (iv)

   (v) \( \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \)

   (vi) \( \text{H} - \text{C} - \text{OCH}_3 \)

Q. 5. Draw the structure of a carbonyl group and indicate:
   (i) hybridized state of carbon
   (ii) the \( \sigma \) and \( \pi \) bonds
   (iii) the electrophilic and nucleophilic centres

   Ans. (i) \( \overset{3\delta}{\text{C}} \overset{\pi}{\text{O}} \) - hybridized state of ‘C’ is sp²
Q. 6. Complete the following as missing starting material, reagent or products:

(i) \[
\text{\underbrace{\text{O}_3}}_{\text{O}} \xrightarrow{\text{Zn – H}_2\text{O}} \text{2} \text{O} = \text{O}
\]

(ii) \[
\text{C} = \text{CH}_2 \xrightarrow{\text{KMnO}_4, \text{KOH} \Delta} \text{CHO}
\]

(iii) \[
\text{CH}_2\text{OH} \xrightarrow{\text{COOK}} \text{C}_\text{O}
\]

Ans. (i) 1, 2 Dicyclohexylethene (Ozonolysis)

(ii) B\textsubscript{2}H\textsubscript{6}/THF, H\textsubscript{2}O\textsubscript{2}/OH\textsubscript{-}, PCC (Hydroboration)

(iii) Potassium benzoate (Oxidation)

Q. 7. How can the following be converted:

(i) Ethanol $\rightarrow$ Acetone
(ii) Benzene $\rightarrow$ Acetophenone
(iii) Benzoic acid $\rightarrow$ Benzaldehyde

Ans. (i) \[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{CrO}_3\text{ or Pcc}} \text{CH}_3\text{CHO} \xrightarrow{\text{CH}_3\text{MgBr, Dry ether}} \text{CH}_3 - \text{CH} - \text{OMgBr} \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3
\]

(ii) \[
\text{CH}_3 - \text{CO} - \text{CH}_3 \xrightarrow{\text{CrO}_2} \text{CH}_3 - \text{CH} - \text{OH}
\]

(iii) \[
\text{CH}_3 - \text{CO} - \text{CH}_3 \xrightarrow{\text{Cl}_2, \text{Cu}} \text{CH}_3 - \text{CO} - \text{CH}_3
\]
Q. 8. Give reasons for the following:

(i) Carboxylic acids do not give characteristic reactions of carbonyl group.

(ii) Treatment of C₆H₅CHO 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 - C = O\(\overset{\text{O}}{\text{OH}}\) \(\overset{\text{O}^-}{\text{OH}}\) 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 NaHCO₃ whereas impurities do not.

Q. 9. Write tests to distinguish between:

(i) CH₃CHO and C₆H₅CHO

(ii) C₆H₅-OH and CH₃COOH

(iii) Pentanal and Pentan-2-one

Ans. (i) CH₃CHO gives brick red ppt. with Fehling, C₆H₅CHO not.

(ii) Phenol does not give brisk effervescence but CH₃COOH gives this test with NaHCO₃.

(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

\[
\text{CHO} \xrightarrow{(O)} \text{COOH} + \text{NaOH} \xrightarrow{\Delta} \text{COONa} + \text{NaOH}/\text{CaO} \xrightarrow{\Delta} \\
\text{HCl} + \text{CH}_2=\text{CH}-\text{CH}_2\xrightarrow{\Delta} \text{CH}_3\text{COOH} + \text{CO}_2
\]

Malonic acid

\[
\xrightarrow{\text{OH}^-} \xrightarrow{\text{D}} \xrightarrow{\text{H}^+} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

2-Butanol

Q. 11. Write the structures of organic compound A to F in the following sequence of reactions:

\[
\text{OH} \xrightarrow{\text{Zn}} \xrightarrow{\Delta} \xrightarrow{\text{concHNO}_3/\text{H}_2\text{SO}_4} \xrightarrow{\text{Br}_2} \xrightarrow{\text{H}_2/\text{pt-v}} \xrightarrow{\text{HNO}_2/\text{HCl}} \xrightarrow{\text{H}_2\text{O}^+} 
\]

\[
\text{C} \xrightarrow{\text{D}} \xrightarrow{\text{E}} \xrightarrow{\text{F}} 
\]

Ans. A = C\text{}_6\text{H}_6 \quad B = C\text{}_6\text{H}_5\text{NO}_2 \quad C = \begin{array}{c} \text{NO}_2 \\ \text{Br} \end{array} \\
\begin{array}{c} \text{D} = \begin{array}{c} \text{NH}_2 \\ \text{Br} \end{array} \\ \text{E} = \begin{array}{c} \text{N}^+\text{Cl}^- \\ \text{Br} \end{array} \\ \text{F} = \begin{array}{c} \text{OH} \\ \text{Br} \end{array} \end{array}

Q. 12. Complete the following:

(i) CH\text{}_3\text{CONH}_2 + \text{HNO}_2 →
(ii) \( \text{CH}_3\text{CONH}_2 + \text{NaOH} + \text{Br}_2 \rightarrow \)

\[
\begin{array}{c}
\text{COOH} \\
| \\
\text{HNO}_3/\text{H}_2\text{SO}_4 \\
\end{array}
\]

(iii) \( \text{COOH} \rightarrow \text{NO}_2 \) + \( \text{H}_2\text{O} \)

Ans. (i) \( \text{CH}_3\text{COOH} + \text{N}_2 + \text{H}_2\text{O} \)

(ii) \( \text{CH}_3\text{NH}_2 + \text{Na}_2\text{CO}_3 + \text{NaBr} + \text{H}_2\text{O} \)

Q. 13. Write the structures of A, B, C, D and E in the following reactions:

\[
\begin{align*}
\text{C}_6\text{H}_6 & \xrightarrow{\text{CH}_3\text{COCl}} \text{anhyd.} \xrightarrow{\text{AlCl}_3} \xrightarrow{\text{NaOI}} \text{A} \\
\text{Zn–Hg} & \xrightarrow{\text{HCl}} \xrightarrow{(1) \text{KMnO}_4 – \text{KOH}} \xrightarrow{(2) \text{H}_3\text{O}} \text{B} \\
\text{D} & \xrightarrow{\text{E}} \\
\text{NaOI} & \xrightarrow{\text{D} + \text{E}} \\
\end{align*}
\]

Ans. A = \( \text{CH}_3\text{COCH}_3 \)

B = \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \)

C = \( \text{C}_6\text{H}_5\text{COOH} \)

D = \( \text{C}_6\text{H}_5\text{COONa} \)

E = \( \text{CHI}_3 \)

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 \( \alpha \)-hydrogen.
Q. 2. An organic compound ‘A’ (C₃H₆O) is resistant to oxidation but forms compound ‘B’ (C₃H₈O) 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.

Q. 3. (a) Write the products of the following reactions:

(i) \[ \ce{O + H_2N-OH \rightarrow H^+} \]

(ii) \[ \ce{2C_6H_5CHO + NaOH \rightarrow Conc.} \]

(iii) \[ \ce{CH_3COOH \rightarrow Cl_2/P} \]

(b) Give simple tests to distinguish between the following pairs of compounds.

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and propanone

Ans. (a) (i) \[ \ce{O \rightarrow NOH} \] (ii) \[ \ce{CH_2OH \rightarrow COO^-Na^+} \]

(ii) Cl-CH₂COOH
(b) (i) Add NaHCO₃, benzoic acid will give brisk effervescence 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 CH₃COOH? 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) CH₃ - C - OH → CH₃ - C - O - O - CH₃

(b) CH₃ - C - OH + PCl₅ → CH₃COCl + POCl₃ + 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) CH₃CONH₂ + HNO₂ → (ii) CH₃COCl + H₂O (steam) →

(iii) CH₃MgBr \( \xrightarrow{(i) \text{CO}_2/\text{H}^+} \) (ii) H₂O/\text{H}^+ → (iv) CH₃COOH + NH₃ \( \xrightarrow{\Delta} \)

(v) CH₃COOH + C₂H₅OH \( \xrightarrow{\text{conc. H}_2\text{SO}_4} \) (vi) HCHO + NH₃ →

(vii) CH₃CHO \( \xrightarrow{\text{LiAlH}_4} \) (viii) CH₃CHO \( \xrightarrow{\text{CH}_2\text{OH}} \) \( \xrightarrow{\text{CH}_2\text{OH}} \)

(ix) CH₃COR + NaOI → (x) C₆H₅CHO + NH₂ - NH₂ →

Ans. (i) CH₃COOH

(ii) CH₃COOH

(iii) CH₃COOH

(iv) CH₃CONH₂

(v) CH₃COOC₂H₅

(vi) (CH₂)₆N₄ (Urotropine)

(vii) CH₃CH₂OH

(viii) CH₂-O

(ix) CH₂-O

(x) CH-CH₃
(ix) CH$_3$

(x) $\text{C}_6\text{H}_5\text{CH}$

```
\|N
\|N\text{H}_2
```

Q. 6. Give reasons for the following:

(i) $\text{C}_6\text{H}_5\text{COOH}$ is weaker than formic acid.
(ii) HCOOH and CH$_3$COOH differentiated by Tollen’s reagent.
(iii) R – COOH do not give characteristic reaction with $> \text{C} = \text{O}$.
(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$_3$COOH.
(iii) $> \text{C} = \text{O}$ 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$_2$COOH
(d) Write the product in the following reaction

$$\text{CH}_3\text{CH} = \text{CHCH}_2\text{CN} \overset{(1) \text{DIBAL - H}}{\rightarrow} \text{(2) H}_2\text{O}$$

(e) How can you distinguish between propanal and propanone?

**Ans.**

(a) HCHO + HCHO $\overset{\text{Conc. NaOH}}{\rightarrow}$ HCOONa + CH$_3$OH
(b) CH$_3$CH = N–NHCONH$_2$
(c) Stronger –I effect of fluorine makes F-CH$_2$COOH to be stronger acid than Cl–CH$_2$COOH and less pka
(d) CH$_3$CH = CHCH$_2$CHO
(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 $\tilde{\text{N}}\text{H}_3$.

2. Functional groups of $1^\text{o}$, $2^\text{o}$ and $3^\text{o}$ amines are respectively as given below:

   $\tilde{\text{N}}\text{H}_2$, $\tilde{\text{N}}\text{H}$ and $\tilde{\text{N}}$.

3. Gabriel phthalimide synthesis can’t be used for the preparation of $2^\text{o}$ and $3^\text{o}$ amines. It gives aliphatic primary amine only.

4. Hoffmann’s bromamide reaction gives $1^\text{o}$ 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 $\tilde{\text{N}}\text{H}_3$.

   (ii) In aqueous solution medium, the order is $2^\text{o} > 1^\text{o} > 3^\text{o}$ (for $\text{CH}_3$ group) and $2^\text{o} > 3^\text{o} > 1^\text{o}$ for $\text{C}_2\text{H}_5$ group.

   (iii) In non-aqueous medium or gaseous phase, the order is $3^\text{o} > 2^\text{o} > 1^\text{o}$.

6. Basic strength of aromatic amines:

   (i) Aromatic amines are weaker bases than $\tilde{\text{N}}\text{H}_3$.

   (ii) ERGs like $\text{CH}_3$, $\text{OR}$, $\text{NH}_3$ etc. increase basic strength while EWGs like $\text{NO}_2$, $\text{CN}$ 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. $1^\text{o}$, $2^\text{o}$ and $3^\text{o}$ amines can be distinguished by Hinsberg’s test.

9. Hinsberg’s reagent is benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$).

10. $3^\text{o}$ amines like trimethylamine are used as insect attractants.

11. Diazonium salts are represented by the general formula $[\text{Ar N} \equiv \text{N}]^+ \text{X}^-$. 
12. **Structure of amines**: Pyramidal for trimethyl amine \((\text{CH}_3)_3 \text{N}\). They are Lewis bases.

![Diagram of trimethyl amine](image)

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 with 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.

\[
\begin{align*}
\text{Phthalimide} & \quad \xrightarrow{\text{KOH}} \quad \text{N-K}^- \\
\text{N-Alkylphthalimide} & \quad \xrightarrow{R-X} \quad \text{N-R}
\end{align*}
\]

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 that present in the amide.

\[
R - C - NH_2 + Br_2 + 4NaOH \rightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O
\]

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 (C₆H₅SO₂Cl), 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.

\[
\begin{align*}
\text{Sulphonyl chloride} & \quad + \quad \text{Primary amine} \\
\text{Sulphonamide} & \quad + \quad \text{HCl}
\end{align*}
\]

*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-diethylbenzenesulphonamide is formed.

\[
\begin{align*}
\text{O} & \quad \text{S} & \quad \text{H} & \quad \text{N} & \quad \text{C}_2\text{H}_5 \\
\text{O} & \quad \text{Cl} & \quad \text{C}_2\text{H}_5 & \quad \text{H}_2\text{C} & \quad \text{O} & \quad \text{S} & \quad \text{N} & \quad \text{C}_2\text{H}_5 & \quad \text{HCl} \\
\end{align*}
\]

\[\text{N, N-Diethylbenzenesulphonamide}\]

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.

\[
\begin{align*}
\text{Ar}^+ & \quad \text{N}_2 & \quad \text{ArCl} & \quad \text{+} & \quad \text{N}_2 & \quad \text{CuCl/HCl} \\
\text{Ar}^+ & \quad \text{N}_2 & \quad \text{ArBr} & \quad \text{+} & \quad \text{N}_2 & \quad \text{CuBr/HBr} \\
\text{Ar}^+ & \quad \text{N}_2 & \quad \text{ArCN} & \quad \text{+} & \quad \text{N}_2 & \quad \text{CuCN/KCN} \\
\end{align*}
\]

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.

\[
\begin{align*}
\text{Cu/HCl} & \quad \text{ArCl} & \quad \text{+} & \quad \text{N}_2 & \quad \text{+} & \quad \text{CuX} \\
\text{Cu/HBr} & \quad \text{ArBr} & \quad \text{+} & \quad \text{N}_2 & \quad \text{+} & \quad \text{CuX} \\
\end{align*}
\]

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.

\[
\begin{align*}
\text{N} &= \text{N} \\
\text{N} &= \text{N}
\end{align*}
\]

\( P \)-Hydroxyazobenzene (orange dye)

\[
\begin{align*}
\text{N} &= \text{N} \\
\text{N} &= \text{N}
\end{align*}
\]

\( p \)-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 \( \text{CH}_3\text{NC} \).

Ans. Methane carbamylamine.

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 \( \text{CH}_3 - \text{N} - \text{C} - \text{CH}_2 - \text{CH}_3 \).

\( \text{CH}_3\text{C}_2\text{H}_5 \)

Ans. 3-Methyl-N,N-dimethyl pentanamine

Q. 5. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., \( [\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_2]^+\text{Cl}^- \).
Q. 6. What is Hinsberg’s reagent?
Ans. Benzene sulphonyl chloride, \( \text{SO}_2\text{Cl} \)

Q. 7. Why aniline dissolves in HCl?
Ans. \( \text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} \rightarrow [\text{C}_6\text{H}_5\text{NH}_3]^+\text{Cl}^- \).
It dissolves due to its basic nature.

Q. 8. How will you test the presence of primary amine?
Ans. By carbyl amine test.

\[
\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{RN} = \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}
\]

Q. 9. What is vapour phase nitration?
Ans. \( \text{CH}_4 + \text{HNO}_3 \xrightarrow{623 \text{K}} \text{CH}_3\text{NO}_2 \)
(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. \( \text{H}_2\text{SO}_4 + \text{HNO}_3 \) 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 \( \text{CH}_3 - \text{C} - \text{CH}_3 \) to give product containing \( > \text{C} = \text{N} - \)?
(i) \( \text{C}_6\text{H}_5\text{NH}_2 \)       (ii) \( (\text{CH}_3)_3\text{N} \)
(iii) \( \text{C}_6\text{H}_5\text{NHC}_6\text{H}_5 \)       (iv) \( \text{C}_6\text{H}_5\text{NHNH}_2 \)
Ans. \( \text{C}_6\text{H}_5\text{NH}_2 \) and \( \text{C}_6\text{H}_5\text{NHNH}_2 \).

Q. 13. How will you give expression for \( K_b \) to indicate its basic strength?
Ans. \[
K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{R} - \text{NH}_2]}
\]

Q. 14. What happens when aniline is treated with bromine?
Q. 15. Write a chemical equation to illustrate the ammonolysis.

**Ans.** For alcohols:

\[
\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{NH}_3, \text{AlCl}_3, 620\text{K}} \text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{H}_2\text{O}} (\text{C}_2\text{H}_5)_2\text{NH} \xrightarrow{\text{H}_2\text{O}} (\text{C}_2\text{H}_5)_3\text{N}
\]

For alkyl halides:

\[
\text{C}_2\text{H}_5\text{I} \xrightarrow{\text{NH}_3, 373\text{K}} \text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{C}_2\text{H}_5\text{I}} (\text{C}_2\text{H}_5)_2\text{NH} \xrightarrow{\text{C}_2\text{H}_5\text{I}} (\text{C}_2\text{H}_5)_3\text{N} \xrightarrow{\text{C}_2\text{H}_5\text{I}} [(\text{C}_2\text{H}_5)_3\text{N}]^+ \text{I}^-
\]

Q. 16. Write the structure of p-toluidine.

**Ans.**

\[
\text{CH}_3 \quad \text{NH}_2
\]

Q. 17. Prepare/convert nitrobenzene into aniline.

**Ans.**

\[
\text{NO}_2 \xrightarrow{\text{H}_2, \text{Ni}} \text{NH}_2
\]

Q. 18. Convert \(\text{C}_6\text{H}_5\text{COOH}\) to \(\text{C}_6\text{H}_5\text{NH}_2\).

**Ans.**

\[
\text{COOH} \xrightarrow{\Delta, \text{NH}_3\text{(aq)}} \text{CONH}_2 \xrightarrow{\Delta, \text{Br}_2, \text{KOH}} \text{NH}_2
\]

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:

\(\text{C}_6\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}, \text{C}_2\text{H}_5\text{NH}_2\)

**Ans.** \(\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2\)
SHORT ANSWER TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following acid-base reactions and name the products:

(i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow \)

(ii) \((\text{CH}_3\text{CH}_2)_3\text{N} + \text{HCl} \rightarrow \)

Ans. (i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3\text{Cl}^- \) (n-propyl ammonium chloride)

(ii) \((\text{CH}_3\text{CH}_2)_3\text{N}^+\text{HCl}^- \) (Triethyl ammonium chloride)

Q. 2. Write chemical reaction of \( \text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl} \) and name product obtained.

Ans. \( \text{C}_6\text{H}_5\text{NH}^- + \text{H}_2\text{N}^- \rightarrow \text{C}_6\text{H}_5\text{CONH}^- + \text{HCl} \)

N-phenyl benzoamide

Q. 3. How will you convert:

(i) 3-methylaniline \( \rightarrow \) 3-nitrotoluene

(ii) Aniline \( \rightarrow \) 1, 3, 5-tribromobenzene

Ans. (i) \[
\begin{align*}
\text{NH}_2 \\
\text{CH}_3 \\
\end{align*}
\]
Diazoo
\[
\begin{align*}
\text{N}_2\text{BF}_4^- \\
\text{CH}_3 \\
\end{align*}
\]
\[
\begin{align*}
\text{NO}_2 \\
\text{CH}_3 \\
\end{align*}
\]
NaNO\textsubscript{2}/Cu
\[
\begin{align*}
\text{N}_2 \\
\text{NaBF}_4 \\
\end{align*}
\]

(ii) \[
\begin{align*}
\text{NH}_2 \\
\text{Br}_2/\text{H}_2\text{O} \\
\text{Br} \\
\text{Br} \\
\end{align*}
\]
Diazoo
\[
\begin{align*}
\text{N}_2\text{Cl}^- \\
\text{Br} \\
\text{Br} \\
\text{Br} \\
\end{align*}
\]
NaNO\textsubscript{2}/HCl
\[
\begin{align*}
\text{Br} \\
\text{H}_3\text{PO}_2 + \text{H}_2\text{O} \\
\text{Cu}^{+} \\
\text{Br} \\
\text{Br} \\
\end{align*}
\]

Q. 4. How will you convert:

(i) Propanoic acid \( \rightarrow \) Ethanoic acid

(ii) Nitromethane \( \rightarrow \) Dimethylamine

Ans. (i) \[
\begin{align*}
\text{C}_3\text{H}_7\text{COOH} \xrightarrow{\text{NH}_2/\text{H}_2}\text{O} \xrightarrow{\text{H}_2/\text{Ni}} \text{C}_3\text{H}_7\text{CONH}_2 \\
\text{Br} \xrightarrow{\text{H}_2\text{O}/\text{KOH}} \text{C}_3\text{H}_7\text{NH}_3 \\
\text{H}_2\text{O}/\text{KOH} \xrightarrow{\text{H}_2\text{O}/\text{Cu}_2} \text{CH}_3\text{CHO} \\
\text{CH}_3\text{CHO} \xrightarrow{\text{H}_2/\text{Ni}} \text{CH}_3\text{COOH} \\
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_3\text{NO}_2 \xrightarrow{\text{H}_2/\text{Ni}} \text{CH}_3\text{NH}_2 \\
\text{CH}_3\text{OH} \xrightarrow{\text{CH}_3\text{OH} \xrightarrow{\text{H}_2\text{O}/\text{Cu}_2} \text{CH}_3\text{CHO} \xrightarrow{\text{H}_2/\text{Ni}} \text{CH}_3\text{COOH} \\
\end{align*}
\]

Q. 5. Draw the structures of the following compounds:

(i) N-isopropylaniline

(ii) t-butylamine
Q. 6. Why $\text{C}_6\text{H}_5\text{N}^+(\text{CH}_3)_3\text{OH}^-$ a stronger base than $\text{NH}_4\text{OH}$ ?

**Ans.** Due to – I effect of phenyl group, it decreases $\varepsilon^-$ density on nitrogen atom but no such group in $\text{NH}_4\text{OH}$.

Q. 7. Explain Kb order : $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$ 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 $\text{H}_2\text{O}$.

(iii) Steric effects of alkyl groups.

Q. 8. Distinguish between $1^\circ$, $2^\circ$ and $3^\circ$ amines by HNO$_2$ acid test.

**Ans.** $1^\circ$ gives $\text{N}_2$ gas. $2^\circ$ gives yellow oily compound. $3^\circ$ form water soluble salts.

$\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HNO}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{N}_2 + \text{H}_2\text{O}$

$\text{R}_2\text{NH} + \text{HNO}_2 \rightarrow \text{R}_2\text{N} - \text{N} = \text{O} + \text{H}_2\text{O}$

$(\text{CH}_3\text{CH}_2)_3\text{N} + \text{HNO}_2 \rightarrow [(\text{CH}_3\text{CH}_2)_3\text{NH}] \text{NO}_2^-$

Soluble in water

Q. 9. A compound ‘A’ having molecular formula $\text{C}_3\text{H}_7\text{ON}$ reacts with $\text{Br}_2$ in presence of NaOH to give compound ‘B’. This compound ‘B’ reacts with HNO$_2$ to form alcohol and $\text{N}_2$ gas. Identify compound ‘A’ and ‘B’ and write the reaction involved.

**Ans.** ‘A’ is $\text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow{\text{Br}_2, \text{NaOH}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{C}_2\text{H}_5\text{OH} + \text{N}_2 + \text{H}_2$ (B)

Q. 10. Write chemical equation for the following conversions :

(i) \[ \text{CH}_3 - \text{CH}_2 - \text{Cl} \rightarrow \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \]

(ii) \[ \text{C}_6\text{H}_5 - \text{CH}_2 - \text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 - \text{NH}_2 \]

**Ans.** (i) With NaCN and reduction.

\[ \text{i.e.,} \quad \text{C}_2\text{H}_5\text{Cl} \xrightarrow{\text{Ethanol, NaCN}} \text{C}_2\text{H}_5 - \text{C} \equiv \text{N} \xrightarrow{\text{red}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \]
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 $^\oplus$ NH$_3$ 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) $-\text{NH}_2$ 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) $\text{C}_6\text{H}_5\text{N}^{\ominus}\text{Cl} + \text{H}_{\text{NH}_2} \xrightarrow{\text{alkaline} (\text{pH 4-5})} \text{C}_6\text{H}_5\text{N} = \text{N} \text{NH}_2 + \text{HCl}$

(ii) Ammonolysis: $R - X + \text{NH}_3 \rightarrow R - \text{NH}_2 + HX$

$\text{RNH}_2 + R - X \rightarrow (\text{R}_2\text{N}) + \text{HX}$

$(\text{R}_2\text{NH} + R - X \rightarrow (\text{R})_3\text{N} + \text{HX}$

$(\text{R})_3\text{N} + R - X \rightarrow [\text{R}_2\text{N}]^\ominus\text{X}^-$
Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.

Ans. By Gabriel Phthalimide Reaction

\[
\begin{align*}
\text{C}_2\text{H}_5\text{NH}_2 + \text{PhCOOH} & \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{PhCONH}_2 \xrightarrow{\text{N}^+\text{C}_2\text{H}_5} \\
\text{C}_2\text{H}_5\text{NH}_2 + \text{PhCOOH} & \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{PhCONH}_2 \xrightarrow{\text{N}^+\text{C}_2\text{H}_5}
\end{align*}
\]

**ANSWER-II TYPE QUESTIONS (3 Marks)**

Q. 1. What happens when:

(i) An alkyl halide reacts with AgNO\textsubscript{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) \[ R - X + \text{AgNO}_2 \xrightarrow{-\text{AgX}} R - \text{NO}_2 \xrightarrow{\text{Sn/HCl}/[\text{HI}]} R - \text{NH}_2 \]

(ii) \[ R - X + \text{AgCN} \xrightarrow{-\text{AgX}} \text{RNC} \xrightarrow{\text{H}_2\text{O}/\text{H}^+} \text{RNH}_2 + \text{HCOOH} \]

(iii) \[ \text{CH}_3\text{MgBr} + \text{CN} - \text{Cl} \rightarrow \text{CH}_3\text{CN} + \text{Mg}\text{<Cl} <\text{Br} \]

Q. 2. How would you prepare:

(i) \( \text{C}_6\text{H}_5\text{NH}_2 \) from \( \text{C}_6\text{H}_5\text{NO}_2 \)

(ii) \( \text{CH}_3\text{NH}_2 \) from \( \text{C}_2\text{H}_5\text{NH}_2 \)

(iii) \( \text{C}_2\text{H}_5\text{NH}_2 \) from \( \text{CH}_3\text{NH}_2 \)

Ans. (i) \[ \text{NO}_2 \xrightarrow{\text{Sn/HCl}/6[\text{HI}]} \text{NH}_2 + 2\text{H}_2\text{O} \]

(ii) \[ \text{C}_2\text{H}_5\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{(O)}/\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3} \text{CH}_3\text{COONH}_4 \xrightarrow{\Delta/\text{H}_2\text{O}} \text{CH}_3\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{CH}_3\text{NH}_2 \]

(iii) \[ \text{CH}_3\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{CH}_3\text{OH} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3\text{CN} \xrightarrow{[\text{H}]} \text{CH}_3\text{CH}_2\text{NH}_2 \]
Q. 3. Write the structure of the products in each case:

(i) \( \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} \text{A} \)

(ii) \( \text{CH}_3\text{CONHC}_6\text{H}_5 \xrightarrow{\text{Br}_2/\text{Fe}} \)

(iii) \( \text{CH}_3\text{CH}_2\text{CN} \xrightarrow{\text{H}_2\text{O/H}^+} \)

Ans. (i) \( \text{CH}_3\text{CH}_2\text{NHCOCCH}_3, \text{CH}_3\text{COOH} \)

(ii) \( \text{Br}, \quad \text{Br} \)

(iii) \( \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+ \)

Q. 4. Write the structures of A, B and C in following

(i) \( \text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{NaOH}} \text{A} \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{B} \xrightarrow{\text{KI}} \text{C} \)

(ii) \( \text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \text{A} \xrightarrow{\text{LiAIH}_4} \text{B} \xrightarrow{\text{CHCl}_3/\text{AlCl}_3/\text{H}_2\text{O}} \text{C} \)

Ans. (i) \( \text{C}_6\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-, \text{C}_6\text{H}_5\text{I} \)

(ii) \( \text{CH}_3\text{CN}, \text{CH}_3\text{CH}_2\text{NH}_2, \text{CH}_3\text{CH}_2\text{NC} \)

Q. 5. Write the structure of reagents/organic compounds ‘A’ to ‘F’:

Ans. \( \text{A} \xrightarrow{\text{NaOH/Br}_2/\text{H}_2\text{O}} \text{B} \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{C} \xrightarrow{\text{Cl}_2/\text{Fe}} \text{E} \xrightarrow{\text{H}_2/\text{pt}} \text{F} \)

A: \( \text{CONH}_2, \text{NH}_2, \text{N}_2\text{Cl}, \text{KCN}, \text{Cu}, \) (A)

B: \( \text{NH}_2, \) (B)

C: \( \text{N}_2\text{Cl} \) (C)

D: \( \text{KCN}, \text{Cu} \) (D)

E: \( \text{CN} \) (E)

F: \( \text{CN} \) (F)

m-chlorobenzonitrosole (F)
LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Arrange the following:

(i) In decreasing order of pKb values:

\[ \text{C}_2\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{NHCH}_3, (\text{C}_2\text{H}_5)_2\text{NH} \text{ and C}_6\text{H}_5\text{NH}_2 \]

(ii) In increasing order of basic strength:

(a) Aniline, p-nitroaniline and p-toluidine

(b) \[ \text{C}_6\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{NHCH}_3, \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \]

(iii) In decreasing order of basic strength:

\[ \text{C}_6\text{H}_5\text{NH}_2, \text{C}_6\text{H}_5\text{N(CH}_3)_2, (\text{C}_2\text{H}_5)_2\text{NH}, \text{CH}_3\text{NH}_2 \]

(iv) Decreasing order of basic strength in gas phase:

\[ \text{C}_2\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}, (\text{C}_2\text{H}_5)_3\text{N} \text{ and NH}_3 \]

(v) Increasing order of boiling point:

\[ \text{C}_2\text{H}_5\text{OH}, (\text{CH}_3)_2\text{NH}, \text{C}_2\text{H}_5\text{NH}_2 \]

Ans. (i) \[ \text{C}_6\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} \]

(ii) (a) p-nitroaniline < aniline < p-toluidine

(b) \[ \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \]

(iii) (\text{C}_2\text{H}_5)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{C}_6\text{H}_5\text{N(CH}_3)_2 > \text{C}_6\text{H}_5\text{NH}_2 \]

(iv) (\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 \]

(v) \[ (\text{CH}_3)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH} \]

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) \[ \text{CH}_3\text{COOH} + \text{HN}_3 \xrightarrow{\text{Conc. H}_2\text{SO}_4, \text{heat}} \text{CH}_3\text{NH}_2 + \text{N}_2 + \text{CO}_2 \]

Ethanoic acid Hydrazoic acid Methylamine
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.

\[ RCH_2NH_2 + CHCl_3 + 3KOH \text{ (alc.)} \xrightarrow{\Delta} RCH_2NC + 3KCl + 3H_2O \]

\( \text{Aniline} + CHCl_3 + 3KOH \text{ (alc)} \xrightarrow{\Delta} \text{Phenyl isocyanate} \)

(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.

\[ \text{Aniline} + \text{NaNO}_2 + \text{HCl} \xrightarrow{273 - 278 K} \text{Benzenediazonium chloride} \]

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.

\[
\text{O} \\
\text{R} - \text{C} - \text{NH}_2 + \text{Br}_2 + 4\text{KOH} \rightarrow \text{RNH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}
\]

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.

\[
\text{N}^+ = \text{NCl}^- + \text{PhOH} \xrightarrow{\text{NaOH}} \text{Ph} = \text{N} \text{N}^- \text{PhOH} \text{(Azo dye)}
\]

(e) **Ammonolysis**: Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.

\[
\text{RCH}_2\text{Cl} + \text{NH}_3 \xrightarrow{-\text{HCl}} \text{RCH}_2\text{NH}_2 \xrightarrow{-\text{HCl}} (\text{RCH}_2\text{})\text{Cl} \xrightarrow{-\text{HCl}} (\text{RCH}_2\text{})\text{H} \xrightarrow{-\text{HCl}} (\text{RCH}_2\text{})_3\text{N}
\]

Q. 4. Complete the following reactions:

(i) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4 \text{ (conc.)} \rightarrow \)

(ii) \( \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \)

(iii) \( \text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \)

(iv) \( \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow \)

(v) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH (alc.)} \rightarrow \)

**Ans.**

(i) \[
\left[ \begin{array}{c}
\text{O} \\
\text{R} - \text{C} - \text{NH}_2 \\
\end{array} \right] \xrightarrow{\Delta} \left[ \begin{array}{c}
\text{O} \\
\text{R} - \text{C} - \text{NH}_2 \\
\end{array} \right] \\
\]

(ii) \( \text{C}_6\text{H}_6 + \text{N}_2 + \text{HCl} + \text{CH}_3\text{CHO} \)
(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) \( CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_3, 0^\circ C} C \)

(iii) \( C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_3, 273 K} B \xrightarrow{H_2O/H^+} C \)

(iv) \( CH_3COOH \xrightarrow{NH_3, \Delta} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_3/HCl} C \)

(v) \( CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH^-} B \xrightarrow{NaOH/Br_2} C \)

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 \( \rightarrow m \)-bromophenol

(iii) \( C_6H_5COOH \rightarrow C_6H_5NH_2 \)

(iv) Aniline \( \rightarrow 2, 4, 6 \) tribromoaniline

(v) Benzylchloride \( \rightarrow 2 \)-phenyl ethanamine

Ans. (i) \[ \text{Nitrobenzene} \xrightarrow{\text{Sn/HCl, 6[H]}} \text{NH}_2 \xrightarrow{\text{NaNO}_2/\text{HCl, 273 K}} \text{N}_2\text{Cl} \xrightarrow{\text{KCN}} \text{CN} \xrightarrow{\text{H}_2\text{O}} \text{COOH} \]
Q. 7. Given reasons : (i) Acetylation of aniline reduces its activating effect.

(ii) \( \text{CH}_3\text{NH}_2 \) is more basic than \( \text{C}_6\text{H}_5\text{NH}_2 \)

(iii) Although \(-\text{NH}_2 \) group is o/p directing, yet aniline on nitration gives a significant amount of \( m \)-nitroaniline

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
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 Tollens’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 Tollens’s reagent. They do not have free aldehydic group. *E.g.*, sucrose.

4. **Glucose**: It is a monosaccharide with molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$.

5. **Preparation**:
   
   (i) From sucrose:
   
   $$\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$$

   (only from sucrose)

   glucose Fructose

   (ii) From starch:
   
   $$\left(\text{C}_6\text{H}_{10}\text{O}_5\right)_n + n\text{H}_2\text{O} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow 2\text{C}_6\text{H}_{12}\text{O}_6$$

   glucose

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 :

\[
\text{CHO} \\
\text{H-\text{C-OH}} \\
\text{HO-\text{C-H}} \\
\text{H-\text{C-OH}} \\
\text{H-\text{C-OH}} \\
\text{\text{CH}_2\text{OH}}
\]

\[
\text{D-(+)-glucose}
\]

\[
\text{HI} \rightarrow \text{CH}_3-(\text{CH}_2)_2\text{CH}_3 \text{  \(n\)-hexane}
\]

\[
\text{NH}_2\text{OH} \rightarrow \text{CH = NOH} \\
\text{(CHOH)}_4 \\
\text{CH}_2\text{OH} \text{  glucose oxime}
\]

\[
\text{Br}_2 - \text{H}_2\text{O} \rightarrow \text{COOH} \\
\text{(CHOH)}_4 \\
\text{CH}_2\text{OH} \text{  gluconic acid}
\]

\[
\text{HNO}_3 \rightarrow \text{COOH} \\
\text{(CHOH)}_4 \\
\text{COOH} \text{  saccharic acid}
\]

\[
\text{(CH}_3\text{CO})_2\text{O} \rightarrow \text{CHO} \\
\text{(CHOCOCH}_3)_4 \\
\text{CH}_2\text{OCOCH}_3 \text{  glucose pentaacetate}
\]

\[
\text{HCN} \rightarrow \text{CH}_3\text{OH} \\
\text{CH}_3\text{CN} \\
\text{(CHOH)}_4 \\
\text{CH}_2\text{OH} \text{  glucose cyanohydrin}
\]
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 NaHSO₃.

(b) The pentacetate of glucose does not react with NH₂OH, 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 (-NH₂) 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

<table>
<thead>
<tr>
<th>Fibrous Protein</th>
<th>Glubular Protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Polypeptide chains run par’allel or anti-parallel and held together by hydrogen and disulphide bonds.</td>
<td>(i) Chains of polypeptide coil around to give a spherical shape.</td>
</tr>
<tr>
<td>(ii) Generally insoluble in water e.g., keratin, collagen, myosin, fibroin.</td>
<td>(ii) Usually soluble in water, e.g., insulin, thyroglobin, albumin, haemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.</td>
</tr>
</tbody>
</table>
11. **Structure and shape of protein** (Ref. page no. 416 NCERT Book)

<table>
<thead>
<tr>
<th>Primary structure</th>
<th>Secondary structure</th>
<th>Tertiary structure</th>
<th>Quaternary structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>The specific sequence of amino acids in the poly-peptide chain. Change in amino acids sequence changes the protein completely. They have covalent bonds.</td>
<td>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.</td>
<td>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.</td>
<td>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.</td>
</tr>
</tbody>
</table>

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 be supplied regularly in diet as they are excreted in urine and cannot be stored (except vitamin B₁₂) 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
B₁ | Beri-beri
B₂ | Ariboflavinosis, cheilosis, burning sensation of skin
B₁₂ | 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 + Phosphoric acid

19. | **DNA** | **RNA**
---|---
(i) | Double helical. | (i) | Single stranded.
(ii) | Sugar is 2-deoxyribose. | (ii) | Sugar is ribose.
(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.

Ans.

\[ \text{\(\alpha\)-D(+) Glucopyranose} \]

\[ \text{\(\beta\)-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 denatured 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 B₁₂.

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:

\[
\text{NH}_2\text{CH}-\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2\text{CH}\{-\text{OH}\} + \text{H}_3\text{O}^+
\]

\[
\text{NH}_2\text{CH}-\text{COOH} \rightleftharpoons \text{NH}_3\text{CH}-\text{COOH} + \text{H}^+
\]
SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Define the following terms in relation to proteins :

(i) Peptide linkage  (ii) Denaturation


(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 NaHSO₃.

(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.


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 C₁ 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 avitaminosis.

Q. 11. What are anomers? Give the structures of two anomers of glucose.

Ans. Monosaccharides which differs in configuration at functional gp-c-atom (C₁ and C₂), e.g., α-glucose and β-glucose.
Q. 12. Write the hydrolysed product of:

(i) Maltose

(ii) Cellulose

Ans. (i) $\alpha$-D-glucose

(ii) $\beta$-D-glucose


(ii) Explain why glucose penta acetate does not react with hydroxylamine?

Ans. (i) $\left(\begin{array}{c}
\text{CHO} \\
\text{H} \quad \text{C} \quad \text{O} \\
\text{O} \\
\text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{CH}_3
\end{array}\right)$

(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
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.  Amylose: 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\text{a} values.

\textbf{Ans.} (i) \[ \text{NH}_2 - \text{CH} - \text{COO}^- \xrightarrow{\text{R}} \text{NH}_3 - \text{CH} - \text{COO}^- \xrightarrow{\text{OH}} \text{R} \text{ migrate towards anode} \]

\[ + \text{H}_2\text{O} \]

\[ \text{migrate (neutral)} \]

\[ \xrightarrow{\text{H}^+} \text{R} \text{ migrate towards cathode} \]

(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\text{o} & 3\text{o} structures are destroyed and 1\text{o} 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\text{o} 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-galactose.

(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<sub>1</sub> & B<sub>2</sub> = Nitrogenous bone

(Adenine, guanine, Cytosine 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 isolectric 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 B₁

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 $\text{Br}_2$, 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, Albumin

(ii) $C₆H₁₂O₆ + \text{Br}_2$, water $\rightarrow$ 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,
\( \alpha \)-D glucose ⇔ Equilibrium mixture ⇔ \( \beta (D) \) glucose

\([\alpha]_D = +111^\circ \quad [\alpha]_D = +52.5^\circ \quad [\alpha]_D = +19.2^\circ \)

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.
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, polyester, 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) **Branches**: This contain linear chains having some branches, e.g., amyllopectin, 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 tensile 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

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of Polymer</th>
<th>Structure</th>
<th>Monomer</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polythene</td>
<td>((-\text{CH}_2-\text{CH}_2-)_n)</td>
<td>CH(_2)=CH(_2)</td>
<td>As insulator, ant corrosive, packing material, household and laboratory wares.</td>
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<tr>
<td>2.</td>
<td>Polystyrene</td>
<td>({\text{CH} - \text{CH}_2}_n)</td>
<td>CH = CH(_2) (\bigg</td>
<td>\bigg</td>
</tr>
<tr>
<td>3.</td>
<td>Polyvinyl chloride</td>
<td>((- \text{CH}_2-\text{CH}_2-)_n)</td>
<td>CH(_2)=CHCl</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>4.</td>
<td>Polytetrafluoroethylene (PTFE) or Teflon</td>
<td>((- \text{CF}_2-\text{CF}_2-)_n)</td>
<td>CF(_2) = CF(_2)</td>
<td>TFE</td>
</tr>
<tr>
<td>5.</td>
<td>NOVOLAC</td>
<td>(\bigg(\text{OH} \bigg</td>
<td>\bigg</td>
<td>\text{CH}_2 \bigg</td>
</tr>
<tr>
<td>6.</td>
<td>Polycryliclonitrile (Orion) (Acrilian)</td>
<td>((- \text{CH}_2-\text{CH}_2-)_n)</td>
<td>CH(_2)=CHCN</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>7.</td>
<td>Styrene butadiene rubber (SBR or Buna-S)</td>
<td>((-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-)) (\bigg</td>
<td>\bigg</td>
<td>) (\text{C}_6\text{H}_5)</td>
</tr>
<tr>
<td>8.</td>
<td>Nitrile rubber (Buna-N)</td>
<td>(-CH₂-CH-C=C-CH₂)ₙ</td>
<td>(a) CH₂ = CH – CH = CH₂</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>CN</td>
<td>(b) CH = CH₂</td>
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<td>In making oil seals, manufacture of hoses and tank linings.</td>
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<td>9.</td>
<td>Neoprene</td>
<td>(- CH₂ = C = CH – CH₂)ₙ</td>
<td>CH₂ = C – CH = CH₂</td>
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<td></td>
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<td>Cl</td>
<td>Cl</td>
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<td></td>
<td></td>
<td></td>
<td>Chloroprene</td>
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<td>As insulator, making conveyor belts and printing rollers.</td>
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<td>10.</td>
<td>Natural rubber (NR)</td>
<td>(CH₃)₂C=CH₂</td>
<td>CH₃</td>
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<td></td>
<td></td>
<td></td>
<td>CH₃</td>
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<td></td>
<td></td>
<td>Isoprene</td>
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<td>In making erasers, tyres, tubes, vulcanised rubber etc.</td>
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<td>11.</td>
<td>Terylene (Dacron)</td>
<td>O</td>
<td>O</td>
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<td></td>
<td></td>
<td>OCH₂-CH₂-O-C₆H₄-C₆H₄-CH₂</td>
<td>(a) HOOC-CH₂-CH₂-COOH</td>
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<td>(b) HO – CH₃ – CH₂ – OH</td>
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<td>For making fibres, safety belts, tyre cords, tents etc.</td>
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<td>12.</td>
<td>Polypropene = P Propene</td>
<td>CH₃</td>
<td>Propen</td>
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<td></td>
<td></td>
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<td>CH₃ – CH = CH₂</td>
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<td></td>
<td>Ropes, toys, pipes, fibre etc. strings.</td>
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<td>13.</td>
<td>Glyptal</td>
<td>O</td>
<td>O</td>
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<td></td>
<td>OCH₂-CH₂-OOC-CH₂-C₆H₄-CH₂</td>
<td>(a) HOOC-CH₂-CH₂-COOH</td>
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<td>(b) HO – CH₂ – CH₂ – OH</td>
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<td>As binding material in preparation of mixed plastics and plants.</td>
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<td>14.</td>
<td>Nylon 6</td>
<td>(NH – [CH₂]₅ – C –)ₙ</td>
<td>Capralactum</td>
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<td>15.</td>
<td>Nylon 66</td>
<td>(NH –[CH₃]₅-NH–[CH₂]₅-NH₃)ₙ</td>
<td>(a) HOOC – (CH₂)ₙ – COOH</td>
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<td></td>
<td></td>
<td></td>
<td>(b) H₂N – (CH₂)ₙ – NH₂</td>
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<td>In making brushes, synthetic fibres, parachutes, ropes and carpets.</td>
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<td>16.</td>
<td>Bakellite</td>
<td>OH</td>
<td>OH</td>
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<td></td>
<td></td>
<td>CH₂-CH₂-OH</td>
<td>a) HCHO</td>
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<td>CH₂-CH₂-CH₂</td>
<td>b) C₆H₄OH</td>
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<td>For making gears, protective coating and electrical fittings.</td>
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<td>17.</td>
<td>Urea formaldehyde resin</td>
<td>(– NH – CO – NH – CH₂ –)ₙ</td>
<td>(a) HCHO</td>
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<td>(b) NH₂CONH₂</td>
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<td>For making unbreakable cups and laminated sheets.</td>
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<td>18.</td>
<td>Melamine formaldehyde resin</td>
<td>(NH₂-N=NH)ₙ</td>
<td>(a) H₂N-N=NH₂</td>
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<td></td>
<td></td>
<td>(b) HCHO</td>
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<td></td>
<td>In making plastic crockery, unbreakable cups and plates.</td>
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<td></td>
<td></td>
<td>R</td>
<td>OH</td>
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<td></td>
<td></td>
<td>CH₃-CH₂-CO₂H</td>
<td>a) R = CH₃C₂H₅</td>
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<td></td>
<td>(b) HCHO</td>
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<td></td>
<td></td>
<td>As packaging, orthopaedic devices and in controlled drug release.</td>
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</tbody>
</table>
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. \( \text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2 + \text{H}_2\text{C} = \text{CH} \) \\
1,3 Butadiene \\
Acrylonitrile

Q. 5. Is \( \text{H}_2\text{CCH(C}_6\text{H}_5)_n \) 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. \( \text{HNCONHCH}_2 \) \\
It is used in unbreakable crockery.

Q. 7. Is \( \text{H}_2\text{C-CHCl}_n \) 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
Q. 11. Name a natural elastomer.

Ans. Natural rubber.

Q. 12. Write name of a synthetic polymer which is an ester.

Ans. Terylene.


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 (10³-10⁷ 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., "CH₂-C₁₂H₂₅".

Q. 22. Give chemical name of teflon.

Ans. Polytetrafluoroethylene.
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) H₂C = CH  
       Cl

Vinyl chloride  Caprolactum

Q. 2. What is the repeating unit in the condensation polymer obtained by combining HOOCC₂H₂COOH (succinic acid) and H₂NCH₂CH₂NH₂ (ethylene diamine)?

Ans. nHOOCC₂H₂COOH+nH₂NCH₂CH₂NH₂ → (C = CH₂ₐₙ-NH₂)ₙ

Q. 3. Draw the structure of monomers of the following polymers:

(i) Teflon         (ii) Polythene

Ans. (i) F₂C = CF₂ Tetrafluoroethene

(ii) H₂C = CH₂ 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.,

\[
\text{nHOOC}-(\text{CH}_2)_4\text{COOH} + \text{nH}_2\text{N}-(\text{CH}_2)_6\text{NH}_2
\]

\[
\xrightarrow{\text{O O H H}} \text{+ C -(CH}_2)_4\text{C - N -(CH}_2)_6\text{N}_n -(2n-1)\text{H}_2\text{O}
\]

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:

H₂C = CH – CH – CH₂ and

1, 3-Butadiene

and

Styrene
(ii) Neoprene:

\[
\begin{align*}
\text{Cl} \\
\text{H}_2\text{C} = \text{C} - \text{CH} = \text{CH}_2 \\
\text{Chloroprene}
\end{align*}
\]

(iii) Nylon-6:

\[
\begin{align*}
\text{H} \\
\text{N} \quad \text{O} \\
\text{Caprolactum}
\end{align*}
\]

Q. 2. Write names and structure of monomers of following polymers:

(i) Bakelite
(ii) Nylon-6
(iii) Polythene

Ans. (i) Phenol and formaldehyde

\[
\text{C}_6\text{H}_5\text{OH} + \text{HCHO}
\]

(ii) Caprolactum

(iii) Ethene

\[
\text{H}_2\text{C} = \text{CH}_2
\]

Q. 3. Write names and structure of monomers of following polymers:

(i) Polystyrene
(ii) Dacron
(iii) Teflon

Ans. (i) Styrene

\[
\begin{align*}
\text{HC} = \text{CH}_2 \\
\text{Styrene}
\end{align*}
\]

(ii) Ethylene glycol + Terephthalic acid

\[
\text{HOH}_2\text{C} \cdot \text{CH}_2\text{OH} + \text{HOOC}-\text{COOCOH}
\]
(iii) Tetrafluoroethene

\[ \text{F}_2\text{C} = \text{CF}_2 \]

Q. 4. (i) What is the role of t-butyl peroxide in the polymerisation of ethane?

(ii) Identify the monomers in the following polymer:

\[ \text{HN(CH}_2\text{)}_6\text{NHCO(CH}_2\text{)}_4\text{CO} \]

(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

\[ \text{C}_6\text{H}_5\text{C} - \text{O} - \text{O} - \text{C} - \text{C}_6\text{H}_5 \rightarrow 2\text{C}_6\text{H}_5 = \text{C} - \text{O} \rightarrow 2\text{C}_6\text{H}_5 \times \text{Phenylradical} \]

\[ \text{C}_6\text{H}_5 + \text{H}_2\text{C} = \text{C}_2 \rightarrow \text{C}_6\text{H}_3\text{CH}_2\text{CH}_2 \]

(ii) Chain propagating step

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2 + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_2 \]

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \]

(iii) Chain terminating step

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 + \text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \]

Q. 6. Write chemical equation for the synthesis of:

(i) Nylon-6, 6

(ii) Neoprene

(iii) Terylene
Ans. (i)  Nylon-6, 6 :

\[
n\text{HOOC–(CH}_2\text{)}_4\text{COOH} + n\text{H}_2\text{N(CH}_2\text{)}_6\text{NH}_2 \rightarrow \text{C–}-(\text{CH}_2\text{)}_4\text{C–N–(CH}_2\text{)}_6\text{N}_n \quad \text{Nylon 6, 6}
\]

Adipic acid  Hexamethylene diamine

(ii)  Neoprene :

\[
\text{Cl}
\]

\[
\text{H}_2\text{C} = \text{C} - \text{CH} = \text{CH}_2 \quad \text{Chloroprene}
\]

\[
\text{Cl}
\]

\[
\text{H}_2\text{C} = \text{C} = \text{CHCH}_2\gamma_n \quad \text{Neoprene}
\]

(iii)  Terylene :

\[
n\text{H}_2\text{O} - \text{CH}_2\text{CH}_2\text{OH} + \text{Ethylene glycol}
\]

\[
n[\text{HO–C–C–OH}] \quad \text{Terephthalic acid}
\]

\[
\rightarrow \quad \text{O–CH}_2\text{CH}_2\text{O–C–C}_n
\]

\[
\text{Tereylene}
\]

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.

\[
n\text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{H}_2\text{C} = \text{CH}_2 \gamma_n
\]

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.
Q. 9. A monomer of a polymer on ozonolysis gives two moles of \( \text{CH}_2\text{O} \) and one mol of \( \text{CH}_3\text{C}\text{CHO} \). Write the structure of monomer and polymer and each step of reaction.

**Ans.** Structure of monomer:

\[
\text{CH}_3
\]

\[
\text{CH}_2\text{O} + \text{O} = \text{C} - \text{CH}_3 + \text{OCH}_2
\]

Structure of polymer:

\[
\mathrm{CH}_2 = \mathrm{C} - \mathrm{CH} = \mathrm{CH}_2
\]

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.

\[
n\text{HOH}_2\text{C} - \text{CH}_2\text{OH} + n\text{HO} - \text{C} - \text{OH} \rightarrow \left[ \begin{array}{c}
\text{O} - \text{CH}_2\text{CH}_2 - \text{O} - \text{C} - \text{C} - \text{O} \\
\text{Dacron}
\end{array} \right]
\]

(ii) **Nylon-6** : By condensation polymerisation.

\[
\text{H}_2\text{O} \xrightarrow{533-543K} [\text{H}_3\text{N}^+(\text{CH}_2)_5\text{COO}^-] \rightarrow \mathrm{N} - (\text{CH}_2)_5 \mathrm{C} \uparrow
\]

Nylon-6
(iii) Buna-N: By addition polymerisation.

\[
nH_2C = CHCH = CH_2 + nH_2C = CHCN \\ 1, 3 - Butadiene \\ Acrylonitrile \\ \rightarrow \left\{ HC - CH = CH - CH_2CH_2CH_2CHCN \right\}^n \\
\text{Buna - N}
\]

(iv) Glyptal: By condensation polymerisation.

\[
nH_2OHCCHOH_2 + n \quad \text{HOOC } \quad \text{COOH} \\ \text{Ethylene glycol} \quad \text{Phthalic acid} \\ \rightarrow \quad O\text{-CH}_2\text{CH}_2\text{O} - \text{C} \quad \text{O} \quad \text{O} \\
\text{Glyptal}
\]

(v) PHBV: By condensation polymerisation.

\[
n\text{HO} - \text{CHCH}_2\text{COOH} + n\text{HO} - \text{CHCH}_2\text{COOH} \\ \text{3-hydroxybutanoic acid} \quad \text{3-hydroxyvaleric acid} \\ \rightarrow \quad \text{OCHCH}_2\text{C} - \text{O} - \text{CHCH}_2\text{C} \\
\text{PHBV}
\]
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 interfere 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, ipronizid, 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, Ofloxaclin.

        **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, tetracycline.

    (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** : Those are prepared by using a 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.

\[
\text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}_2\text{OSO}_3\text{H} \rightarrow \text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}_2\text{OSO}_3\text{Na}^+
\]

(lauryl alcohol) (sodium lauryl sulphonate)

(ii) **Cationic detergents** : They are quaternary 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 tetramethyloctyl-benzene sulphonate. It creates water pollution.

**VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)**

Q. 1. Write the formula and IUPAC name of aspirin.

\[
\text{O} \quad \text{O} \quad \text{C--CH}_3
\]

[Hint : \( \text{IUPAC name : 2-Acetooxybenzoic acid} \)]
Q. 2. Name the type of drugs having following structural formula:

\[
\text{SO}_2\text{NHR} \\
\text{NH}_2
\]

[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.]


[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.]


[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. 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.18. 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.19. What type of drug is chloramphenicol?

[Hint: Bacteriostatic broad spectrum antibiotic.]

Q.20. Name a chemical used as an antiseptic as well as disinfectant.

[Hint: Phenol. (0.2% solution antiseptic and 1% solution disinfectant)]

Q.21. Give two examples of antidepressants.

[Hint: Iproniazid, Phenelzine.]

Q.22. Name the antioxidants commonly used to increase the storage of butter.

[Hint: BHA (Butylated Hydroxy anisole).]

Q.23. Give the name of medicine having – As = As – linkage.

[Hint: Arsphenamine.]
Q.24. Which antibiotic is supposed to be toxic towards certain strains of cancer cells?

[Hint: Dysidazirine.]

Q.25. Name one antioxidant used in wine, butter and beers.

[Hint: BHA, BHT.]

Q.26. Hair shampoos belong to which class of synthetic detergent?

[Hint: They belong to cationic detergents. E.g., Cetyltrimethyl-ammonium bromide.]

Q.27. Dishwashing soaps are synthetic detergents. What is their chemical nature?

[Hint: They are non-ionic detergents. E.g., Polyethylene glycol-stearate.]

Q.28. 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.29. 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.]

**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., Brompheniramine, 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 minimising the branching of the hydrocarbon chain, as unbranched chains can be biodegraded.]

Q.12. If water contains dissolved calcium hydrogen carbonate, 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. 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. 18. 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. 19. 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, chloramphenicol, 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 sweeteners.]

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) Pheneizine (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) Joint 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 differ 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) \( \text{CH}_3 (\text{CH}_2)_10 \text{CH}_2 \text{OSO}_3^-\text{Na}^+ \)
(ii) \( [\text{CH}_3 - (\text{CH}_2)_{18}\text{N(CH}_3)_2]^-\text{Br}^- \)
(iii) \( \text{C}_9\text{H}_{10} \begin{array}{c}
\text{O(CH}_2\text{CH}_2\text{O)}_n\text{CH}_2\text{CH}_2\text{OH}
\end{array} \)

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.
SOLVED SAMPLE PAPER
Chemistry-XII (Theory)
CBSE : 2014 (DELHI)

Time allowed

Max. Marks = 70

General Instructions :

(i) All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Give one example each of ‘oil in water’ and ‘water in oil’ emulsion. 1
2. Which reducing agent is employed to get copper from the leached low grade copper ore? 1
3. Which of the following is more stable complex and why? 1
   \[ [\text{Co(NH}_3\text{)}_6]^3+ \text{ and } [\text{Co(en})_3]^3+ \]
4. Write the IUPAC name of the compound. 1
   \[ \text{CH}_3 \text{– CH – CH}_2 \text{ – COOH} \]
5. Which of the following isomers is more volatile: 1
   o-nitrophenol or p-nitrophenol?
6. What are isotonic solutions? 1
7. Arrange the following compounds in increasing order of solubility in water: 1
   \[ \text{C}_6\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}, \text{C}_2\text{H}_5\text{NH}_2 \]
8. Which of the two components of starch is water soluble? 1
9. An element with density 11.2 g cm\(^{-3}\) forms a f.c.c. lattice with edge length of 4 10-8 cm. Calculate the atomic mass of the element.

\[ \text{(Given : } \text{NA} = 6.022 \times 10^{23} \text{ mol}^{-1} \text{)} \]

10. Examine the given defective crystal

\[
\begin{array}{cccc}
\text{A}^+ & \text{B}^- & \text{A}^+ & \text{B}^-\\
\text{B}^- & 0 & \text{B}^- & \text{A}^+ & \text{B}^- \\
\text{A}^+ & \text{B}^- & \text{A}^+ & 0 & \text{A}^+ \\
\text{B}^- & \text{A}^+ & \text{B}^- & \text{A}^+ & \text{B}^- \\
\end{array}
\]

Answer the following questions:

(i) What type of stoichiometric defect is shown by the crystal?
(ii) How is the density of the crystal affected by this defect?
(iii) What type of ionic substances show such defect?

11. Calculate the mass of compound (molar mass = 256 g mol\(^{-1}\)) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K (\(K_f = 5.12 \text{ K kg mol}^{-1}\)).

12. Define an ideal solution and write one of its characteristics.

13. Write two differences between ‘order of reaction’ and ‘molecularity of reaction’.

14. Outline the principles behind the refining of metals by the following methods:

(i) Zone refining method
(ii) Chromatographic method

15. Complete the following chemical equations:

(i) \( \text{Ca}_3\text{P}_2 + \text{H}_2\text{O} \rightarrow \)

(ii) \( \text{Cu} + \text{H}_2\text{SO}_4 (\text{conc.}) \rightarrow \)

OR

Arrange the following in the order of property indicated against each set:

(i) \( \text{HF, HCl, HBr, HI} \) – increasing bond dissociation enthalpy.

(ii) \( \text{H}_2\text{O, H}_2\text{S, H}_2\text{Se, H}_2\text{Te} \) – increasing acidic character.

16. Write the IUPAC name of the complex \([\text{Cr(NH}_3)_4\text{Cl}_2]^+\). What type of isomerism does it exhibit?
17. (i) Which alkyl halide from the following pairs is chiral and undergoes faster $S_N^2$ reaction?

\[ \begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*} \]

(ii) Out of SN$^1$ and SN$^2$, which reaction occurs with
(a) Inversion of configuration
(b) Racemisation

18. Draw the structure of major monohalo product in each of the following reactions:
(i) \[ \text{Cyclic structure} \quad \text{SOCl}_2 \]
(ii) \[ \text{Cyclic structure} \quad \text{H}_2\text{O}_2 \quad \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{H}_2\text{Br} \quad \text{Peroxide} \]

19. (a) In reference to Freundlich adsorption isotherm with the expression for adsorption of gases on solids in the form of an equation.
(b) Write an important characteristic of lyophilic sols.
(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid.

20. (a) Draw the structures of the following molecules:
(i) XeOF$_4$  (ii) H$_2$SO$_4$
(b) Write the structural difference between white phosphorus and red phosphorus.

21. Account for the following:
(i) PCl$_5$ is more covalent than PCl$_3$.
(ii) Iron on reaction with HCl forms FeCl$_2$ and not FeCl$_3$.
(iii) The two O-O bond lengths in the ozone molecule are equal.

22. The following data were obtained during the first order thermal decomposition of SO$_2$Cl$_2$ at a constant volume:
\[ \text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g) \]
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time/s – 1</th>
<th>Total pressure/atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Calculate the rate constant.

(Given: \( \log 4 = 0.6021, \log 2 = 0.3010 \))

23. (i) Give two examples of macromolecules that are chosen as drug targets.

(ii) What are antiseptics? Given an example.

(iii) Why is use of aspartame limited to cold foods and soft drinks?

24. (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 the structure of glucose?

25. After the ban on plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on the environment and Yamuna River. To make the awareness more impactful, they organized a rally by joining hands with other schools and distributed paper bags to street vendors, shopkeepers, and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River.

After reading the above passage, answer the following questions:

(i) What values are shown by the students?

(ii) What are biodegradable polymers? Give one example.

(iii) Is polythene a condensation or an addition polymer?

26. (a) Write the mechanism of the following reaction:

\[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{HBr}} \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} \]

(b) Write the equation involved in Reimer-Tiemann reaction.

27. Give the structures of A, B and C in the following reactions:

(i) \( \text{CH}_3\text{Br} \xrightarrow{\text{KCN}} A \xrightarrow{\text{LiAlH}_4} B \xrightarrow{\text{HNO}_3, 273K} C \)

(ii) \( \text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3, \Delta} A \xrightarrow{\text{Br}_2 + \text{KOH}} B \xrightarrow{\text{CHCl}_3 + \text{NaOH}} C \)
OR

How will you convert the following:

(i) Nitrobenzene into aniline
(ii) Ethanoic acid into methanamine
(iii) Aniline into N-phenylethanamide

(Write the chemical equations involved.)

28. (a) Define the following terms:

(i) Limiting molar conductivity
(ii) Fuel cell

(b) Resistance of a conductivity cell filled with 0.1 mol L⁻¹ KCl solution is 10 Ω. If the resistance of the same cell when filled with 0.02 mol L⁻¹ KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L⁻¹ KCl solution. The conductivity of 0.1 mol L⁻¹ KCl solution is 1.29 \( \times 10^{-2} \) Ω⁻¹ cm⁻¹.

OR

(a) Stanle Faraday’s first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mlo of \( \text{Cu}^{2+} \) to \( \text{Cu} \).

(b) Caluclate emf of the following cell at 298 K:

\[ \text{Mg} (s) \ | \text{Mg}^{2+} (0.1 \text{ M}) \ || \text{Cu}^{2+} (0.01) \ | \text{Cu}(s) \]

[Given \( E_{\text{cell}} = +2.71 \text{ V} \), \( 1 \text{ F} = 96500 \text{ C mol}^{-1} \)]

29. (a) How do you prepare:

(i) \( \text{K}_2\text{MnO}_4 \) from \( \text{MnO}_2 \)?
(ii) \( \text{Na}_2\text{Cr}_2\text{O}_7 \) from \( \text{Na}_2\text{CrO}_4 \)?

(b) Account for the following:

(i) \( \text{Mn}^{2+} \) is more stable than \( \text{Fe}^{2+} \) towards oxidation to +3 state.
(ii) The enthalpy of atomization is lowest for \( \text{Zn} \) is 3d series of the transition elements.
(iii) Actinoid elements show wide range of oxidation states.

OR

(i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?
(ii) Which transition metal of 3d series has positive E \( (M^{2+}/M) \) value and why?

(iii) Out of Cr\(^{3+}\) and Mn\(^{3+}\), which is a stronger oxidizing agent and why?

(iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

\[ \text{MnO}_4^- + 8 \text{H}^+ + 5e^- \rightarrow \]

30. (a) Write the products of the following reactions:

(i) \[ \text{O} + \text{H}_2\text{N} \rightarrow \text{OH} \rightarrow \text{H}^+ \]

(ii) \[ 2\text{C}_6\text{H}_5\text{CHO} + \text{conc. NaOH} \rightarrow \]

(iii) \[ \text{CH}_3\text{COOH} \xrightleftharpoons[\text{Cl}_2/\text{P}]{\text{Cl}_2/\text{P}} \]

(b) Given simple chemical tests to distinguish between the following pairs of compounds:

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and Propanone

OR

(a) Account for the following:

(i) \( \text{CH}_2\text{CHO} \) is more reactive than \( \text{CH}_3\text{COCH}_3 \) towards reaction with HCN.

(ii) Carboxylic acid is a stronger acid than phenol.

(b) Write the chemical equation to illustrate the following name reactions:

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction
<table>
<thead>
<tr>
<th>Qn</th>
<th>Answers</th>
<th>Marks</th>
</tr>
</thead>
</table>
| 1  | Oil in water: milk / vanishing cream (any one)  
    Water in oil: butter / cold cream (any one) | ½       |
| 2  | Hydrogen / Iron                                                        | 1       |
| 3  | [Co(en)₃]³⁺: because (en) is a chelating ligand / bidentate ligand     | ½, ½    |
| 4  | 3-hydroxybutanoic acid / 3-hydroxybutan-1-oic acid                    | 1       |
| 5  | o - nitrophenol                                                        | 1       |
| 6  | Solutions with sameosmotic pressure                                   | 1       |
| 7  | C₆H₆NH₂<(C₂H₅)₂NH< C₂H₅NH₂                                            | 1       |
| 8  | Amylose                                                                | 1       |
| 9  | d = 1 1.2 g/cm³  
    z = 4  
    a = 4 \( \times 10^{-8} \) cm  
    \[ d = \frac{z \times M}{N_a \times a^3} \] | ½       |

\[
11.2 = \frac{4 \times M}{6.022 \times 10^{23}} \times (4 \times 10^{-8})^3
\]

\[
M = \frac{11.2 \times 6.022 \times 10^{23}}{4} \times 4 \times 10^{-8} \times 4 \times 10^{-8} \times 4 \times 10^{-8}
\]

\[
M = 107. \text{ gmol}^{-1} \text{ or } 107.9 \text{ U}
\]

| 10 | (i) Schottky defect  
    (ii) Decreases  
    (iii) Alkali metal halides/ Ionic substances having almost similar size of cations and anions (NaCl/KCl) | 1, ½, ½ |
11. \[ \Delta T_f = \frac{K_f \times W_2 \times 1000}{w_1 \times M_2} \]

\[ 0.48K = 5.12K \text{ kgmol}^{-1} \quad \frac{W_2}{75 \times 256} \times 1000 \]

\[ W_2 = \frac{0.48 \times 75 \times 256}{5.12 \times 1000} \]

\[ W_2 = 1.8g \]

12. Solutions which obey Raoult’s law over the entire range of concentration
   A-A or B-B ~A-B interactions
   \[ \Delta H_{\text{mix}} = 0 \]
   \[ \Delta V_{\text{mix}} = 0 \]
   (any one)

13. (i) Order of reaction is meant for elementary as well as for complex reactions but molecular for elementary reactions.
   (ii) Order can be zero or fraction but molecularity cannot be zero or fraction. (or any other difference)

14. (i) Impurities are more soluble in melt than in solid state of the metal.
   (ii) Different components of a mixture are differently adsorbed on an adsorbent

15. (i) \[ \text{Ca}_4 \text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca(OH)}_2 + 2\text{PH}_3 \]
   (ii) \[ \text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2 \]
   (give full credit even if correct products are mentioned)

OR

(i) \[ \text{HI} < \text{HBr} < \text{HCl} < \text{HF} \]
   (ii) \[ \text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} \]
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>16.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>Tetraamminedichloridochromium (III) ion</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>Geometrical isomerism / cis - trans</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>(b) is chiral OR</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(a) undergoes faster $S_n^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>(a) $S_n^2$</td>
<td>$\frac{1}{2}, \frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) $S_n^1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>Cl</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>$\text{CH}_2-\text{CH}_2-\text{CH}_2$ Br</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>$x = Kp \frac{1}{n}$ or $\log (x/m) = \log K + \frac{1}{n} \log p$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>Reversible in nature/ stable sol/ solvent loving (or any other)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>Associated colloid - Soap/ micelles; Multimolecular colloid - $S_8$ / gold sol. (or any other)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (i)</td>
<td></td>
<td></td>
<td>1 + 1</td>
</tr>
<tr>
<td>(b) White phosphorus</td>
<td>Red phosphorus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>It exists as discrete tetrahedral $P_4$ unit</td>
<td>It exists in the form of polymeric chain.</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>OR correct structures.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>Because +5 oxidation state is more covalent than +3/ high charge to size ratio / high polarizing power</td>
<td>$\frac{1}{2}, \frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>Because $\text{HC}1$ is a mild oxidising agent/ formation of hydrogen gas prevents the formation of $\text{FeCl}_3$.</td>
<td>$\frac{1}{2}, \frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td>(iii)</td>
<td>Because of resonance in $\text{O}_3$ molecule.</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
### 22. \( \text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2 \)

<table>
<thead>
<tr>
<th>Time</th>
<th>Partial Pressure</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0s</td>
<td>0.4 atm</td>
<td>At t = 0s</td>
</tr>
<tr>
<td>100s</td>
<td>(0.4 - x) atm</td>
<td>At t = 100s</td>
</tr>
</tbody>
</table>

\[ Pt = 0.4 - x + x + x \]
\[ Pt = 0.4 + x \]

\[ 0.7 = 0.4 + x \]

\[ x = 0.3 \]

\[ k = \frac{2.303}{t} \log \left( \frac{pi}{2pi \cdot pt} \right) \]

\[ k = \frac{2.303}{t} \log \frac{0.4}{0.8 - 0.7} \]

\[ k = \frac{2.303}{100} \log \frac{0.4}{0.1} \]

\[ k = \frac{2.303}{100} \times 0.6021 = 1.39 \times 10^{-2} \text{ s}^{-1} \]

### 23. (a) carbohydrates, lipids, oprotens, enzymes, nucleic acids (any two)

(b) Antiseptics are the chemical substances which are used to kill or prevent the growth of microbes. Eg – Dettol / Iodoform / Boric acid/ phenol (or any other correct example)

(c) Becasue it is unstable at cooking temperature.

### 24. (a) Vitamin A

(b) Uracil

(c) It suggests that six carbon atoms are in straight chain 
\( / \text{CHO} - (\text{CHOH})_4 - \text{CH}_2\text{OH} / \)

### 25. (i) Concern towards environment / caring / socially aware / team work, (atleast two values)

(ii) Polymers which can be degraded by the action of microorganisms. Eg. PHBV, Nylon -2-nylon- 6/ any natural polymer

(iii) Addition polymer.
26. (a) \( \text{HBr} \rightarrow \text{H}^+ + \text{Br}^- \)

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{H}} + \text{H}^+ &\rightarrow \text{CH}_3 - \text{CH}_2 - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{H}} \\
\text{CH}_3 - \text{CH}_2 - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{H}} &\rightarrow \text{CH}_3 - \text{CH}_2 + \text{H}_2\text{O} \\
\text{CH}_3 - \text{CH}_2 &\rightarrow \text{CH}_3 - \text{CH}_2 - \text{Br} \\
\text{Br}^- + \overset{\cdot}{\text{CH}}_2 - \overset{\cdot}{\text{O}} - \overset{\cdot}{\text{H}} &\rightarrow \text{Br} - \text{CH}_2 + \text{H}_2\text{O}
\end{align*}
\]

(b) (where \( R = -\text{CH}_3 \))

\[
\begin{align*}
\text{OH} &\rightarrow \overset{\cdot}{\text{O}} \text{Na}^+ \\
\text{CHCl}_3 + \text{aq NaOH} &\rightarrow \overset{\cdot}{\text{O}} \text{Na}^+ \\
\overset{\cdot}{\text{O}} \text{Na}^+ &\rightarrow \overset{\cdot}{\text{O}} \text{CHO} \\
\text{CHO} &\rightarrow \text{Salicylaldehyde}
\end{align*}
\]

27. (a) \( \text{CH}_3 \text{Br} \xrightarrow{\text{KCN}} \text{CH}_3 \text{CN} \xrightarrow{\text{LiAlH}_4} \text{CH}_3 \text{CH}_2 \text{NH}_2 \xrightarrow{\text{HNO}_2} \text{CH}_3 \text{CH}_2 \text{OH} \xrightarrow{273K} \text{CH}_3 \text{CH}_2 \text{OH} \)

(b) \( \text{CH}_3 \text{COOH} \xrightarrow{\Delta} \text{CH}_3 \text{CONH}_2 \xrightarrow{\text{KOH}} \text{Br}_2 \xrightarrow{\text{NaOH}} \text{CH}_3 \text{NH}_2 \xrightarrow{\text{CHCl}_3} \text{CH}_3 \text{NC} \)

\[
\begin{align*}
\text{CH}_3 \text{Br} &\rightarrow \text{CH}_3 \text{CN} \\
\text{CH}_3 \text{CH}_2 \text{NH}_2 &\rightarrow \text{CH}_3 \text{CH}_2 \text{OH} \\
\text{HNO}_2 &\rightarrow \text{CH}_3 \text{CH}_2 \text{OH} \\
\text{CH}_3 \text{CONH}_2 &\rightarrow \text{Br}_2 \\
\text{Br}_2 &\rightarrow \text{CH}_3 \text{NH}_2 \\
\text{CHCl}_3 &\rightarrow \text{CH}_3 \text{NC}
\end{align*}
\]

27. (i) \( \text{NO}_2 \xrightarrow{\text{Sn/HCl}} \text{NH}_2 \)

(ii) \( \text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CONH}_2 \xrightarrow{\text{Br}_2} \text{CH}_3\text{NH}_2 \)

(iii) \( \text{NO}_2 \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} \text{NH} - \overset{\cdot}{\text{C}} - \overset{\cdot}{\text{CH}}_3 \)

\[
\begin{align*}
\text{OR} \\
\text{OR}
\end{align*}
\]

\[
\begin{align*}
\text{OR} \\
\text{OR} \\
\text{OR}
\end{align*}
\]
28. (a) (i) Limiting molar conductivity – when concentration approaches zero the conductivity is known as limiting molar conductivity.

(ii) Fuel cell – are the cells which convert the energy of combustion of fuels to electrical energy.

(b) Cell constant = \( G^\# = \text{conductivity} \div \text{resistance} \)
\[
= 1.26 \text{ S/m} \quad 100 \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}
\]
Conductivity of 0.02 mol L\(^{-1}\) KCl solution = cell constant / resistance
\[
K = \frac{G^\#}{R} = \frac{129 \text{ m}^{-1}}{520 \Omega} = 0.248 \text{ S m}^{-1} = 0.248 \times 10^{-2} \text{ S cm}^{-1}
\]
Concentration = 0.02 mol L\(^{-1}\)
\[
= 1000 \quad 0.02 \text{ mol m}^{-3}
\]
\[
= 20 \text{ mol m}^{-3}
\]
Molar conductivity = \( A_m = \frac{\Lambda^*}{C} \)
\[
= \frac{248 \times 10^{-2} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}}
\]
\[
= 124 \quad 10^{-4} \text{ S m}^{2} \text{ mol}^{-1} = 124 \text{ S cm}^{2} \text{ mol}^{-1} \text{d}
\]

OR

28. (a) The amount of substance deposited at any electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.
(aq. Solution or melt)
Charge = \( Q = 2F \)

(b) \( E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \)
\[
E_{cell} = 2.71 - \frac{0.059}{2} \log \frac{0.10}{0.01}
\]
\[
E_{cell} = 2.71 - \frac{0.059}{2} \log 10
\]
\[
= 2.71 - 0.0295 = 2.68 \text{ V}
\]
29. (a) (i) $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
   (ii) $2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$
(b) (i) Because of 3d5 (half filled) stable configuration of Mn$^{2+}$
   (ii) Because in zince there is no unpaired electron / there is no contribution form the inner d electrons.
   (iii) Because of comparable energies of 7s, 6d and 5f orbitals.

OR

29. (i) Mn, because of presence of 5 unpaired electrons in 3d subshell
   (ii) Cu, because enthalpy of atomization and ionisation enthalpy is not compensated by enthalpy of hydration.
   (iii) Mn$^{3+}$, because Mn$^{2+}$ is more stable due to its half filled (3d5) configuration
   (iv) Eu$^{2+}$ (Eu)
   (v) $\text{MnO}_4^{-} + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

30. (a) (i) ![Chemical Structure](image)
   (ii) ![Chemical Structure](image)
   (iii) $\text{Cl} - \text{CH}_2 - \text{COOH}$
(b) (i) Add NaHCO$_3$, benzoic acid will give brisk effervescence whereas benzaldehyde will not give this test. (or any other test)
   (ii) Add tollen's reagent, propanal will give silver mirror whereas propanone will not give this test. (or any other test)
30. (a) (i) Because the positive charge on carbonyl carbon of \( \text{CH}_3\text{CHO} \) decreases to a lesser extent due to one electron releasing (+I effect) \( \text{CH}_3 \) group as compared to \( \text{CH}_3\text{COCH}_3 \) (two electron releasing \( \text{CH}_3 \) group) and hence more reactive.

(ii) Because carboxylate ion (conjugate base) is more resonance stabilized than phenoide ion.

(b) (i) \[ \text{C} = \text{O} \xrightarrow{\text{NH}_2\text{NH}_2 - \text{H}_2\text{O}} \text{C} = \text{NNH}_2 \xrightarrow{\text{KOH/ethylene glycol, heat}} \text{CH}_2 + \text{N}_2 \]

(ii) \[ \text{CH}_3 - \text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CHO} \]

(or any other example) 1

(iii) \[ \text{H} \xrightarrow{\text{C} = \text{O} + \text{H}} \text{H} \xrightarrow{\text{C} = \text{O} + \text{Conc. KOH}} \text{H} - \text{C} - \text{OH} + \text{H} - \text{C} \]

(or any other example) 1
General Instructions:

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carry 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. What is the basicity of H₃PO₄?

2. Write the IUPAC name of the given compound:

   \[
   \begin{array}{c}
   \text{NO}_2 \\
   \text{OH} \\
   \text{NO}_2
   \end{array}
   \]

3. Which would undergo S₈2 reaction faster in the following pair and why?

   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{CH}_3 - \text{CH}_2 - \text{Br}
   \end{array}
   \quad \text{and} \quad \begin{array}{c}
   \text{CH}_3 - \text{C} - \text{CH}_3 \\
   \text{Br}
   \end{array}
   \]

4. Out of BaCl₂ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal Sol? Give reason.

5. What is the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy l/3rd of tetrahedral voids?

6. What are the transition elements? Write two characteristics of the transition elements.

   (i) Write down the IUPAC name of the following complex:

   \[\text{[Cr(NH₃)₂Cl₂(en)]Cl} \quad (\text{en} = \text{ethylenediamine})\]

   (ii) Write the formula for the following complex:

   Pentaamminenitrito-o-Cobalt (III).
8. Name the reagents used in the following reactions:
   (i) \( \text{CH}_3\text{COCH}_3 \xrightarrow{?} \text{CH}_3 - \text{CH} - \text{CH}_3 \) (ii) \( \text{CH}_3 - \text{CO} - \text{CH}_3 \xrightarrow{\text{OH}} \text{C}_6\text{H}_5 - \text{COO}^-\text{K}^+ \)

9. What is meant by positive deviations from Raoult’s law? Give an example. What is the sign of \( \Delta_{\text{mix}}\text{H} \) for positive deviation?

   OR

   Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult’s law? Give an example.

10. (a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

   \[
   \begin{align*}
   \text{Ag}^+(\text{aq}) + \text{e}^- & \rightarrow \text{Ag}(\text{s}) & \text{E} &= +0.80 \text{ V} \\
   \text{H}^+(\text{aq}) + \text{e}^- & \rightarrow \frac{1}{2}\text{H}_2(\text{g}) & \text{E} &= 0.00 \text{ V}
   \end{align*}
   \]

   On the basis of their standard reduction electrode potential (E) values, which reaction is feasible at the cathode and why?

   (b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration?

11. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van’t Hoff factor and predict the nature of solute (associated or dissociated).

   (Given) : Molar mass of benzoic acid = 122 g mol\(^{-1}\), \( K_f \) for benzene = 4.9 K kg mol\(^{-1}\))

12. (i) Indicate the principle behind the method used for the refining of zinc.

   (ii) What is the role of silica in the extraction of copper?

   (iii) Which form of the iron is the purest form of commercial iron?

13. An element with molar mass 27 g mol\(^{-1}\) forms a cubic unit cell with edge length 4.05 \(\times\) \(10^{-8}\) cm. If its density is 2.7 g cm\(^{-3}\), what is the nature of the cubic unit cell?

14. (a) How would you account for the following:

   (i) Actinoid contraction is greater than lanthanoid contraction.

   (ii) Transition metals form coloured compounds.

   (b) Complete the following equation:

   \[ 2\text{MnO}_4^- + 6\text{H}^+ + 5\text{NO}_2^- \rightarrow \]
15. (i) Draw the geometrical isomers of complex \([\text{Pt(NH}_3)_2\text{Cl}_2]\).

(ii) On the basis of crystal field theory, write the electronic configuration for \(d^4\) ion if \(\Delta_0 < P\).

(iii) Write the hybridization and magnetic behaviour of the complex \([\text{Ni(CO)}_4]\).
   (At.no. of Ni = 28)

16. Calculate emf of the following cell at 25°C:
   \[
   \text{Fe | Fe}^{2+} (0.001 \text{ M}) \parallel \text{H}^+ (0.01 \text{ M}) | \text{H}_2(g) \text{ (1 bar)} | \text{Pt(s)}
   \]
   \[
   E (\text{Fe}^{2+} | \text{Fe}) = -0.44 \text{ V} \quad E (\text{H}^+ | \text{H}_2) = 0.00 \text{ V}
   \]

17. Give reasons for the following observations:
(i) Leather gets hardened after tanning.
(ii) Lyophilic sol is more stable than lyophobic sol.
(iii) It is necessary to remove CO when ammonia is prepared by Haber’s process.

18. Write the names and structures of the monomers of the following polymers:
   (i) Nylon–6, 6
   (ii) PHBV
   (iii) Neoprene

19. Predict the products of the following reactions:
   \[
   \begin{align*}
   \text{CH}_3 - \text{C} &= \text{O} \quad \text{(i) } \text{H}_2\text{N} - \text{NH}_2 \\
   \text{CH}_3 &\quad \text{(ii) KOH/Glycol, } \Delta
   \end{align*}
   \]

20. How do you convert the following:
   (i) Phenol to anisole
   (ii) Propan-2-ol to 2-methylpropan-2-ol
   (iii) Aniline to phenol
      (a) Write the mechanism of the following reaction:
      (b) Write the equation involved in the acetylation of Salicylic acid.

21. (i) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?
(ii) What is the difference between fibrous protein and globular protein?
(iii) Write the name of vitamin whose deficiency causes bone deformities in children.
22. Give reasons:
   (a) n-Butyl bromide has higher boiling point than t-butyl bromide.
   (b) Racemic mixture is optically inactive.
   (c) The presence of nitro group (−NO₂) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

23. Mr. Roy, the principal of one reputed school organized a seminar in which he invited parents and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in schools and to introduce healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following:
   (i) What are the values (at least two) displayed by Mr. Roy?
   (ii) As a student, how can you spread awareness about this issue?
   (iii) What are tranquilizers? Give an example.
   (iv) Why is use of aspartame limited to cold foods and drinks?

24. (a) Account for the following:
   (i) Acidic character increases from HF to HI.
   (ii) There is large difference between the melting and boiling points of oxygen and sulphur.
   (iii) Nitrogen does not form pentahalide.

   (b) Draw the structures of the following:
   (i) ClF₃
   (ii) XeF₄

   OR

   (i) Which allotrope of phosphorus is more reactive and why?
   (ii) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers?
   (iii) F₂ has lower bond dissociation enthalpy than Cl₂. Why?
(iv) Which noble gas is used in filling balloons for meteorological observations?

(v) Complete the equation:
\[ \text{XeF}_2 + \text{PF}_3 \rightarrow \]

25. An aromatic compound ‘A’ of molecular formula C₇H₇ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:

\[
(C_7H_7ON) \xrightarrow{\text{Br}_2 + \text{KOH}} C_6H_5NH_2 \quad \xrightarrow{\text{NaNO}_2 + \text{HCl}} \quad B \quad \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} C
\]

\[
\text{CHCl}_3 + \text{NaOH} \quad \text{KI}
\]

D \quad E

OR

(a) Write the structures of main products when aniline reacts with the following reagents:

(i) \( \text{Br}_2 \) water

(ii) \( \text{HCl} \)

(iii) \( (\text{CH}_3\text{CO})_2\text{O} / \text{pyridine} \)

(b) Arrange the following in the increasing order of their boiling point:

\( C_2H_5NH_2, C_2H_5OH, (\text{CH}_3)_3\text{N} \)

(c) Give a simple chemical test to distinguish between the following pair of compounds:

\( (\text{CH}_3)_2\text{NH} \) and \( (\text{CH}_3)_3\text{N} \)

26. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>30</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CH}_3\text{COOCH}_3])/mol L(^{-1})</td>
<td>0.60</td>
<td>0.30</td>
<td>0.15</td>
</tr>
</tbody>
</table>

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(Given $\log 2 = 0.3010$, $\log 4 = 0.6021$)

26. (a) For a reaction $A + B \rightarrow P$, the rate is given by
\[
\text{Rate} = k[A][B]^2
\]
(i) How is the rate of reaction affected if the concentration of $B$ is doubled?
(ii) What is the overall order of reaction if $A$ is present in large excess?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction, ($\log 2 = 0.3010$)
## MARKING SCHEME

**CBSE DELHI-2015**

<table>
<thead>
<tr>
<th>Ques.</th>
<th>Value points</th>
<th>Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2, 5 – dinitrophenol</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>CH₃-CH₂-Br</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Because it is a primary halide / (1 ) halide</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>BaCl₂ because it has greater charge / +2 charge</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>X₂Y₃</td>
<td>1</td>
</tr>
</tbody>
</table>
| 6.    | Elements which have partially filled d-orbital in its ground states or any one of its oxidation states.  
       | (1) Variable oxidation states  
       | (2) Form coloured ion  
       | Or any other two correct characteristics |       |
| 7.    | (1) Diammine dichlorido ethylene diamine chromium (III) chloride  
       | (2) [Co(NH₃)₅(ONO)]²⁺ | 1+1   |
| 8.    | (i) LiAlH₄ / NaBH₄/H₂, Pt  
       | (ii) KMnO₄, KOH | 1     |
| 9     | When vapour pressure of solution is higher than that predicted by Raoult’s law / the intermolecular attractive forces between the solute-solvent/(A-B) molecules are weaker than those between the solute-solute and solvent-solvent molecules/A-A or B-B molecules. Eg. ethanol-acetone/ethanol-cyclohexane/CS₂-acetone or any other correct example Δₘᵢₓ H is positive | 1     |
|       |               | ½     |
|       |               | ½     |

**OR**

(a) Azeotropes are binary mixtures having the same composition in the liquid and vapour phase and boil at a constant temperature.  
(b) minimum boiling azeotrop  
   eg- ethanol + water or any other example | 1     |
<p>|                                           | ½     |
|                                           | ½     |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>(i) $\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)}$</td>
<td>$\frac{1}{2} = 4 = 2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reaction with higher E value / $\Delta G$ negative</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ii) Molar conductivity of a solution at infinite dilution or when concentration approaches zero</td>
<td>Number of ions per unit volume decreases</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$\Delta T_f = i K_f m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta T_f = i K_f \frac{W_b \times 1000}{M_b \times W_a}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.62 \text{K} = i \times 4.9 \text{K kg mol}^{-1}$</td>
<td>$\frac{3.9 \text{g}}{122 \text{gmol}^{-1}} \times 1000$</td>
<td>$\frac{49 \text{kg}}{1$</td>
</tr>
<tr>
<td></td>
<td>$1 = 0.506$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Or by any other correct method</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>As $i &lt; 1$, therefore solute gets associated.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>(i) Zinc being low boiling will distil first leaving behind impurities/ or on electrolysis the pure metal gets deposited on cathode from anode.</td>
<td>$\frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ii) Silica acts as flux to remove iron oxide which is an impurity as slag or $\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(iii) Wrought iron</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>$d = \frac{z \times M}{a^3 N_A}$</td>
<td>$\frac{1}{2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$z = \frac{d a^3 N_A}{M}$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$z = \frac{2.7 \text{g cm}^{-3} \times 6.022 \times 10^{23} \text{mol}^{-1} \times (4.05 \times 10^{-8} \text{cm})^3}{27 \text{g mol}^{-1}}$</td>
<td></td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$= 3.999 \sim 4$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Face centered cubic cell/ fee</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(i) 5f orbital electrons have poor shielding effect than 4f</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ii) due to d-d transition / or the energy of excitation of an electron from lower d orbital to higher d-orbital lies in the visible region /presence of unpaired electrons in the d-orbital.</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) $2 \text{MnO}_4^- + 6 \text{H}^+ + 5 \text{NO}_2 \rightarrow 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O} + 5 \text{NO}_3^-$</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
15. (i) \[ \text{cis-isomer} \quad \begin{array}{c} \text{Pt} \\ \text{Cl} \\ \text{Cl} \end{array} \quad \begin{array}{c} \text{H}_2\text{N} \\ \text{NH}_3 \end{array} \quad \begin{array}{c} \text{Cl} \\ \text{Pt} \\ \text{NH}_3 \end{array} \quad \text{trans-isomer} \]

(ii) \[ t_g^3 g_l^1 \]

(iii) \[ \text{sp}^3, \text{diamagnetic} \]

16. The cell reaction: \( \text{Fe}(s) + 2\text{H}^+ \text{(aq)} \xrightleftharpoons{\text{®}} \text{Fe}^{2+} \text{(aq)} + \text{H}_2 \text{(g)} \)

\[
E_{\text{cell}} = E^\circ_{c} - E^\circ_{a} \\
= [0 - (-0.44)] \text{V} = 0.44 \text{V}
\]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \left[ \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \right] \\
= 0.44 \text{V} - \frac{0.059}{2} \log (0.001) \\
= 0.44 \text{V} - \frac{0.059}{2} \log (10) \\
= 0.44 \text{V} - 0.0295 \text{V} \\
= \boxed{0.410 \text{V}}
\]

17. (i) mutual coagulation

(ii) strong interaction between dispersed phase and dispersion medium or solvated layer

(iii) CO acts as a poison for catalyst

18. (i) Hexamethylene diamine \( \text{NH}_2(\text{CH}_2)_6 \text{NH}_2 \) and adipic acid \( \text{HOOC} - (\text{CH}_2)_4 - \text{COOH} \)

(ii) 3 hydroxybutanoic acid \( \text{CH}_3\text{CH}((\text{OH})\text{CH}_2\text{COOH} \) and 3 hydroxypentanoic acid \( \text{CH}_3\text{CH}_2\text{CH}((\text{OH})\text{CH}_2\text{COOH} \)

(iii) Chloroprene \( \text{H}_2\text{C} = \text{C(Cl)} \text{ CH} = \text{CH}_2 \)

IUPAC names are accepted

\textbf{Note:} mark for name Is and mark for structure / s

\[ \frac{1}{2} \times 6 = 3 \]
### 19. 
(i) CH$_3$CH$_2$CH$_3$  
(ii) C$_6$H$_5$COONa + CH$_3$  
(iii) CH$_4$  

### 20. 
(i) $\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{ONa}$ \(\xrightarrow{\text{CH}_3\text{X}}\) $\text{C}_6\text{H}_5\text{OCH}_3$  
$\text{C}_6\text{H}_5\text{OH} + \text{Na} \rightarrow \text{C}_6\text{H}_5\text{ONa}$ \(\xrightarrow{\text{CH}_3\text{X}}\) $\text{C}_6\text{H}_5\text{OCH}_3$  
(ii) $\text{CH}_3\text{CH(ОН)CH}_3 \xrightarrow{\text{CrO}_3, \text{Cu}/573K} \text{CH}_3\text{COCH}_3$ \(\xrightarrow{(i) \text{CH}_3\text{MgX}, (ii) \text{H}_2\text{O}}\) (CH$_3$)$_2$C(ОН)CH$_3$  
(iii) $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{NaNO}_3, \text{HCl} 273K} \text{C}_6\text{H}_5\text{N}_2\text{Cl}$ \(\xrightarrow{\text{H}_2\text{O} \text{warm}}\) $\text{C}_6\text{H}_5\text{OH}$  

OR  
(a) $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{H} + \text{H}^+ \rightarrow \text{CH}_3 - \text{CH}_2 - \text{O} - \text{H}$  
(b) $\text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2\text{CH}_3 + \text{H}^+$  

(Acetyl chloride instead of acetic anhydride may be used)

### 21. 
(i) Maltose  
(ii) Fibrous proteins: parallel polypeptide chain, insoluble in water  
Globular proteins: spherical shape, soluble in water, (or any 1 suitable difference)  
(iii) Vitamin D

### 22. 
(i) Larger surface area, higher van der Waals’ forces, higher the boiling point  
(ii) Rotation due to one enantiomer is cancelled by another enantiomer  
(iii) $-\text{NO}_2$ acts as Electron withdrawing group or $-\text{I}$ effect
23.  
(i) Concern for students health, Application of knowledge of chemistry to daily life, empathy, caring or any other  
(ii) Through posters, nukkad natak in community, social media, play in assembly or any other  
(iii) Tranquilizers are drugs used for treatment of stress or mild and severe mental disorders. Eg: equanil (or any other suitable example)  
(iv) Aspartame is unstable at cooking temperature.  

24.  
(a) (i) Due to decrease in bond dissociation enthalpy from HF to HI, there is an increase in acidic character observed.  
(ii) Oxygen exists as diatomic O₂ molecule while sulphur as polyatomic S₈  
(iii) Due to non availability of d orbitals  

---

### OR

(i) White Phosphorus because it is less stable due to angular strain  
(ii) Nitrogen oxides emitted by supersonic jet planes are responsible for depletion of ozone layer.  
\[ \text{or } NO + O_3 \rightarrow NO_2 + O_2 \]  
(iii) due to small size of F, large inter electronic repulsion/electrom-electron repulsion among the lone pairs of fluorine  
(iv) Helium  
(v) \[ \text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+ [\text{PF}_6]^− \]
25. 

(a) (i) OR

(b) \((\text{CH}_3)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH}\)

(c) By Hinsberg test secondary amines \((\text{CH}_3)_2\text{NH}\) shows ppt formation which is insoluble ... tertiary amines \((\text{CH}_3)_3\text{N}\) do not react with benzene sulphonyl chloride

26. 

(a) \[
k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}
\]

\[
k = \frac{2.303}{30} \log \frac{0.60}{0.30}
\]

\[
k = \frac{2.303}{30} \times 0.301 = 0.023 \text{ s}^{-1}
\]

\[
k = \frac{2.303}{60} \log \frac{0.60}{0.15}
\]

\[
k = \frac{2.303}{60} \times 0.6021 = 0.023 \text{ s}^{-1}
\]

As \(k\) is constant in both the readings, hence it is a pseudofirst order reaction.

(ii) Rate = \(-\Delta[R]/\Delta t\)

\[
= -\frac{[0.15 - 0.30]}{60 - 30}
\]

\[
= 0.005 \text{ mol L}^{-1} \text{ s}^{-1}
\]
26. (a) (i) Rate will increase 4 times of the actual rate of reaction.
(ii) Second order reaction

(b) \( t_{1/2} = \frac{0.693}{k} \)

30 min = \( \frac{0.693}{k} \)  

\( k = 0.023 \text{ min}^{-1} \)

\[ k = \frac{2.303}{t} \log \left( \frac{[A_0]}{[A]} \right) \]

\[ t = \frac{2.303}{0.0231} \log \left( \frac{100}{10} \right) \]

\( t = 99.7 \text{ min} \)
SOLVED SAMPLE PAPER
CBSE DELHI-2016

General Instructions:
(i) All questions are compulsory.
(ii) Questions number 1 to 5 are very short-answer questions and carry 1 mark each.
(iii) Questions number 6 to 10 are short-answer questions and carry 2 marks each.
(iv) Questions number 11 to 22 are also short-answer questions and carry 3 marks each.
(v) Questions number 23 is a value based question and carry 4 marks.
(vi) Questions number 24 to 26 are long-answer questions and carry 5 marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Out of CH₃ – CH – CH₂ – Cl and CH₃ – CH₂ – CH – Cl, which is more reactive towards S_N_1 reaction and why?

2. On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved which forms a blue coloured complex with Cu²⁺ ion. Identify the gas.

3. What type of magnetism is shown by a substance if magnetic moments of domains are arranged in same direction?

4. Write the IUPAC name of the given compound:

```
  Br     
 /       
 /       
NH₂     
Br     
|       |
|       |
Br 
```

5. Write the main reason for the stability of colloidal sols.

6. From the given cells:
   Lead storage cell, Mercury cell, Fuel cell and Dry cell
   Answer the following:
   (i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo Space Programme?

(iii) Which cell is used in automobiles and inverters?

(iv) Which cell does not have long life?

7. When chromite ore FeCr$_2$O$_4$ is fused with NaOH in presence of air, a yellow coloured compound (A) is obtained which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms a orange coloured crystalline compound (C).

(i) Write the formulae of the compounds (A), (B) and (C).

(ii) Write one use of compound (C).

OR

Complete the following chemical equations:

(i) $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow$

(ii) $\text{Cr}_2\text{O}_7^{2-} + 3\text{Sn}^{2+} + 14\text{H}^+ \rightarrow$

8. When a co-ordination compound CrCl$_3$6H$_2$O is mixed with AgNO$_3$, 2 moles of AgCl are precipitated per mole of the compound. Write

(i) Structural formula of the complex.

(ii) IUPAC name of the complex.

9. For reaction: $2\text{NH}_3 (g) \xrightarrow{\text{Pt}} \xrightarrow{\text{Rate} = k} \text{N}_2 (g) + 3\text{H}_2 (g)$

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

10. Write the mechanism of the following reaction:

$2\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Conc.} \text{H}_2\text{SO}_4} \xrightarrow{41\text{K}} \text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$

11. Give reasons:

(i) C–Cl bond length in chlorobenzene is shorter than C–Cl bond length in CH$_3$–Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) $S_N1$ reactions are accompanied by racemization in optically active alkyl halides.

12. An element crystallizes in a f.c.c. lattice with cell edge of 250 pm. Calculate the density if 300 g of this element contain $2 \times 10^{24}$ atoms.
13. The rate constant for the first order decomposition of \( \text{H}_2\text{O}_2 \) is given by the following equation:

\[
\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{K}
\]

**OR**

Calculate \( E_a \) for this reaction and rate constant \( k \) if its half-life period be 200 minutes. (Given: \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \))

14. (i) Differentiate between adsorption and absorption.
(ii) Out of \( \text{MgCl}_2 \) and \( \text{AlCl}_3 \), which one is more effective in causing coagulation of negatively charged sol and why?
(iii) Out of sulphur sol and proteins, which one forms multimolecular colloids?

15. (i) Name the method of refining of metals such as Germanium.
(ii) In the extraction of Al, impure \( \text{Al}_2\text{O}_3 \) is dissolved in conc. \( \text{NaOH} \) to form sodium aluminate and leaving impurities behind. What is the name of this process?
(iii) What is the role of coke in the extraction of iron from its oxides?

16. Calculate e.m.f of the following cell at 298 K:

\[
2\text{Cr(s)} + 3\text{Fe}^{2+}(0.1\text{M}) \rightarrow 2\text{Cr}^{3+}(0.01\text{M}) + 3\text{Fe(s)}
\]

Given: \( E(\text{Cr}^{3+}/\text{Cr}) = -0.74 \text{ V} \quad E(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V} \)

17. Give reasons:
(i) \( \text{Mn} \) shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
(ii) Transition metals show variable oxidation states.
(iii) Actinoids show irregularities in their electronic configurations.

18. Write the main product(s) in each of the following reactions:

(i) \[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{O} \quad \text{CH}_3 + \text{H}\text{I} \\
\text{CH}_3
\end{align*}
\]

(ii) \[
\begin{align*}
\text{CH}_3 - \text{CH} = \text{CH}_2 & \quad \frac{(i) \text{B}_2\text{H}_6}{(ii) 3\text{H}_2\text{O}_2 / \text{OH}^-} \\
\end{align*}
\]
(iii) $C_6H_5 - OH \xrightarrow{(i) \text{aq. NaOH}} (ii) CO_2, H^+$

19. Write the structures of A, B and C in the following:

(i) $\text{C}_6\text{H}_5\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{ar.KoH}} A \xrightarrow{\text{NaNO}_2 + \text{HCl}} B \xrightarrow{0 - 5^\circ \text{C}} KI \xrightarrow{} C$

(ii) $\text{CH}_3 - \text{Cl} \xrightarrow{\text{KCN}} A \xrightarrow{\text{LiAlH}_4} B \xrightarrow{\text{CHCl}_3 + \text{alc.KoH}} C$

20. (i) What is the role of t-buty1 peroxide in the polymerization of ethene?
(ii) Identify the monomers in the following polymer:
$[-\text{NH} - \text{(CH}_3)_6 - \text{NH} - \text{CO} - \text{(CH}_2)_4 - \text{CO}]_n$
(iii) Arrange the following polymers in the increasing order of their intermolecular forces:

Polystyrene, Terylene, Buna-S

OR

Write the mechanism of free radical polymerization of ethene.

21. (i) Write the name of two monosaccharides obtained on hydrolysis of lactose sugar.
(ii) Why Vitamin C cannot be stored in our body?
(iii) What is the difference between a nucleoside and nucleotide?

22. (a) For the complex $[\text{Fe(CN)}_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex. (At. number : Fe = 26).
(b) Draw one of the geometrical isomers of the complex $[\text{Pt(en)}_2\text{Cl}_2]^{2+}$ which is optically active.

23. Due to hectic and busy schedule, Mr. Angad made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Deepak, a close friend of Mr. Angad, advised him to stop taking sleeping pills and suggested to change his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Angad followed his friend’s advice and after few days he started feeling better.

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr. Deepak?
(ii) Why is it not advisable to take sleeping pills without consulting doctor?
(iii) What are tranquilizers? Give two examples.

24. (a) Account for the following:
   (i) Ozone is thermodynamically unstable.
   (ii) Solid PCl₅ is ionic in nature.
   (iii) Fluorine forms only one oxoacid HOF.

(b) Draw the structure of
   (i) BrF₅
   (ii) XeF₄

OR

(i) Compare the oxidizing action of F₂ and Cl₂ by considering parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy.

(ii) Write the conditions to maximize the yield of H₂SO₄ by contact process.

(iii) Arrange the following in the increasing order of property mentioned:
   (a) H₃PO₃, H₃PO₄, H₃PO₅ (Reducing character)
   (b) NH₃, PH₃, AsH₃, SbH₃, BiH₃ (Base strength)

25. (a) Write the structures of A, B, C, D and E in the following reactions:

\[
\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} + \text{Anhyd. AlCl}_3 \rightarrow \text{A} \xrightarrow{\text{Zn–Hg/ conc. HCl}} \text{B} \xrightarrow{(i) \text{KMnO}_4 – KOH, } \text{C} \xrightarrow{(ii) \text{H}_3\text{O}^+} \text{D + E}
\]

OR

(a) Write the chemical equation for the reaction involved in Cannizzaro reaction.

(b) Draw the structure of the semicarbazone of ethanal.

(c) Why pKa of F-CH₂-COOH is lower than that of Cl – CH₂ – COOH?

(d) Write the product in the following reaction:

\[
\text{CH}_3 – \text{CH} = \text{CH} – \text{CH}_2\text{CN} \xrightarrow{(i) \text{DIBAL – H}} \xrightarrow{(ii) \text{H}_2\text{O}}
\]
26. (a) Calculate the freezing point of solution when 1.9 g of MgCl$_2$ (M=95 g mol$^{-1}$) was dissolved in 50 g of water, assuming MgCl$_2$ undergoes complete ionization.

(K$_f$ for water = 1.86 K kg mol$^{-1}$)

(b) (i) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?

(ii) What happens when the external pressure applied becomes more than the osmotic pressure of solution?

OR

(a) When 2.56 g of sulphur was dissolved in 100 g of CS$_2$, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S$_x$).

(K$_f$ for CS$_2$ = 3.83 K kg mol$^{-1}$, Atomic mass of Sulphur = 32 g mol$^{-1}$)

(b) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing

(i) 1.2% sodium chloride solution?

(ii) 0.4% sodium chloride solution?
<table>
<thead>
<tr>
<th>Q.No</th>
<th>VALUE POINTS</th>
<th>MARKS</th>
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<tbody>
<tr>
<td>1.</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH(Cl)CH&lt;sub&gt;3&lt;/sub&gt;; secondary halide/ 2&lt;sup&gt;o&lt;/sup&gt; carbocation is more stable</td>
<td>1</td>
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<tr>
<td>2.</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1</td>
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<tr>
<td>3.</td>
<td>Ferromagnetism</td>
<td>1</td>
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<td>4.</td>
<td>2, 4, 6-Tribromoaniline / 2, 4, 6-Tribromobenzenamine</td>
<td>1</td>
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<tr>
<td>5.</td>
<td>Like Charged particles cause repulsion/ Brownian motion/ solvation</td>
<td>1</td>
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<tr>
<td>6.</td>
<td>(i) Mercury cell</td>
<td>½</td>
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<td></td>
<td>(ii) Fuel cell</td>
<td>½</td>
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<td></td>
<td>(iii) Lead storage battery</td>
<td>½</td>
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<td></td>
<td>(iv) Dry cell</td>
<td>½</td>
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<tr>
<td>7.</td>
<td>A-Na&lt;sub&gt;2&lt;/sub&gt;CrO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>½</td>
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<td></td>
<td>B-Na&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>½</td>
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<tr>
<td></td>
<td>C-K&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>½</td>
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<tr>
<td></td>
<td>Use-strong oxidising agent / as a primary standard in volumetric analysis</td>
<td>½</td>
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<td></td>
<td>OR</td>
<td></td>
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<tr>
<td>8</td>
<td>8MnO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; + 3S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O  → 8MnO&lt;sub&gt;2&lt;/sub&gt; + 6SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; + 2OH&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1</td>
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<td></td>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; + 14 H&lt;sup&gt;+&lt;/sup&gt; + 3 Sn&lt;sup&gt;2+&lt;/sup&gt;  → 2Cr&lt;sup&gt;3+&lt;/sup&gt; + 3Sn&lt;sup&gt;4+&lt;/sup&gt; + 7H&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>8</td>
<td>(i) [Cr(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;5&lt;/sub&gt;Cl]&lt;Cl&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1</td>
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<td></td>
<td>(ii) pentaquacloridoChromium</td>
<td>1</td>
</tr>
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<td></td>
<td>(iii) chloride monohydrate (or chloride hydrate)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(no deduction for not writing hydrate)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(i) zero order, bimolecular/unimolecular</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(ii) mol L&lt;sup&gt;-1&lt;/sup&gt; S&lt;sup&gt;-1&lt;/sup&gt;</td>
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</table>
10. 

(i) \[ \text{CH}_3 - \text{CH}_2 - \overset{\cdot}{\text{O}} - \text{H} + \text{H}^+ \rightarrow \text{CH}_3 - \text{CH}_2 - \overset{\cdot}{\text{O}} - \text{H} \]

(ii) \[ \text{CH}_3\text{CH}_2 - \overset{\cdot}{\text{O}}^+ + \text{CH}_2 - \overset{\cdot}{\text{O}} - \text{H} \rightarrow \text{CH}_3\text{CH}_2 - \overset{\cdot}{\text{O}} - \text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \]

(iii) \[ \text{CH}_3\text{CH}_2 - \overset{\cdot}{\text{O}} - \text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2 - \overset{\cdot}{\text{O}} - \text{CH}_2\text{CH}_3 + \text{H}^+ \]

11. 

(i) In chlorobenzene, each carbon atom is sp hybridised /resonating structures /partial double bond character.

(ii) Due to +R effect in chlorobenzene/ difference in hybridization i.e. sp² and sp³ respectively/ -I and +R effect oppose each other while -I effect is the only contributing factor in cyclohexane.

(iii) Due to formation of planar carbocation/ Carbon in

12. 

2 \(10^{24}\) atoms weigh = 300g

6.022 \(10^{23}\) atoms weigh = \((300 \times 6.022 \times 10^{23})/2 \times 10^{24}\)

= 90.3g

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

= 4 \(90.3/(250 \times 10^{-10})^3\) \(N_0\)

= 38.4 g cm\(^{-3}\) (or any other correct method)

13. 

log \(k = \log A - E_a/2.303RT\)

\(E_a / 2.303RT = 1.0 \times 10^4 \text{ K/T}\)

\(E_a = 1.0 \times 10^4 \times 2.303 = 8.314\)

= 191471.4 J/mol

\(t_{1/2} = 0.693/k\)

\(k = 0.693/200 \text{ min}\)

= 0.0034 mn\(^{-1}\)
### 14.

<table>
<thead>
<tr>
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<th>Adsorption</th>
<th>Absorption</th>
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<tr>
<td><strong>Surface phenomena</strong></td>
<td>The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption.</td>
<td>The substance is uniformly distributed throughout the bulk of the solid essentially a bulk phenomenon. (any one difference)</td>
</tr>
</tbody>
</table>

(ii) AlCl₃, more positive charge/Hardy-Schulze rule  
(iii) Sulphur

\[ \frac{1}{2}+\frac{1}{2} \]

### 15.

(i) Zone-: refining  
(ii) Leaching/Bayer’s process  
(iii) Reducing agent / to form CO which acts as a reducing agent.

### 16.

(i) \[ E_{\text{cell}}^0 = E_{c}^0 - E_{a}^0 \]
= \((-0.44) - (-0.74)\) V
= 0.30V

\[ E_{\text{cell}} = E^0 - \frac{0.059}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]} \]
\[ E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{6} \log \left[ \frac{[0.01]^2}{[0.1]^3} \right] \]
= 0.30\((-0.059/6)\)
= 0.3098V

\[ \frac{1}{2} \]

### 17.

(i) Ability of oxygen to form multiple bond/ \( p\pi d\pi \) bond.

(ii) Partially filled d orbitals / due to comparable energies of ns and (n-1) d orbitals

(iii) Due to relative stabilities of the \( f^0, f^7 \) and \( f^{14} \) occupancies of the 5f orbitals/ Comparable energies of 7s, 6d, 5f orbitals.
### 18.
(i) \( \text{CH}_2\text{OH} , \text{(CH}_2\text{)}_3\text{C-I} \)
(ii) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)
(iii) \[
\begin{array}{c}
\text{OH} \\
\text{COOH}
\end{array}
\]

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### 19.
(i) \( \text{C}_9\text{H}_5\text{NH}_2, \text{C}_9\text{H}_5\text{N}_2^\text{+Cl}, \text{C}_9\text{H}_5\text{I} \)
(ii) \( \text{CH}_3\text{CN}, \text{CH}_3\text{CH}_2\text{NH}_2, \text{CH}_3\text{CH}_2\text{NC} \)

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### 20.
(a) Catalyst/initiator of free radical
(b) Hexamethylene diamine and adipic acid/structure/IUPAC name
(c) Buna-S<olystrene<Terylene

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**OR**

### 20

**Chain initiation steps**

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**Chain propagating step**

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**Chain terminating step**

For termination fo the long chain, these free radicals can combine in different ways to form polythene One mode of termination of chain is shown as under:

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### 21.
(i) \( \beta-D \) glucose and \( \beta-D \)-galactose / glucose and galactose
(ii) water soluble, excreted out of the body
(iii) In nucleotide, phosphoric acid/phosphate group attached to the nucleoside / structures of both nucleotide and nucleoside / nucleotide = base + sugar + phosphate group, nucleoside= base + sugar.

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</table>
22. **d^2sp^3**, Paramagnetic, low spin  

![Chemical Structure](image)

\[ 2^+ \]

- en
- Pt

1,\(1/2,1/2\)

1

23. (i) Aware, concerned or any other correct two values.  
(ii) Side effects, unknown health problems  
(iii) Neurologically active drugs/ stress relievers  
Example - Valium, equanil  
(or any other correct two example)  

1  
1  
1  
\(1/2+1/2\)

24. (a) i. Endothermic compound / decomposition of ozone is exothermic in nature and \(\Delta G\) is negative / decomposition of ozone is spontaneous.  
ii. Exists as \([\text{PCl}_4]^+ [\text{PCl}_6]^-%\)  
iii. Shows only -1 oxidation state / most electronegative element/ absence of d-orbitals  
(i)  

![Chemical Structure](image)

(ii)  

![Chemical Structure](image)

1  
1  
1

OR

24. (i) \(\text{F}_2\) is the stronger oxidising agent than chlorine  
(a) low enthalpy of dissociation of F-F bond  
(b) less negative electron gain enthalpy of F  
(c) high hydration enthalpy of F ion  
(ii) low temperature, high pressure and presence of catalyst iii)  
(iii) (a) \(\text{H}_3\text{PO}_4 < \text{H}_3\text{PO}_3 < \text{H}_3\text{PO}_2\)  
(b) \(\text{BiH}_3 < \text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3\)  

\(1/2 \times 4 = 2\)

1  
1
| 25. | A -C₆H₅COCH₃  | 1 |
|     | B-C₆H₅CH₂CH₃  | 1 |
|     | C-C₆H₅COOH     | 1 |
|     | D, E -C₆H₅COONa , CHI₃ | 1+1 |

|     | OR |
| 25. |     |
| (a) | HCHO +HCHO $\xrightarrow{\text{conc NaOH}}$ HCOONa + CH₃OH |
|     | (or any other example) | 1 |
| (b) | CH₃CH = N-NHCONH₂ | 1 |
| (c) | Stronger -I effect of fluorine ,stronger acid less $pK_a$ \text{ / strong electron withdrawing power of fluorine.} | 1 |
| (d) | CH₃CH=CHCH₂ CHO | 1 |
| (e) | Silver mirror formed on adding ammonical silver nitrate to propanal and not with propanone (or any other correct test) | 1 |

| 26. |     |
| (a) | $\Delta T_f = i \frac{K_f W_b \times 1000}{M_b \times W_a}$ |
|     | $\Delta T_f = 3\ (1.86\ 1.9/95\ 50)\ 1000$ |
|     | = 2.23K |
|     | $T_f - \Delta T_f = 273.15- 2.23 / 273- 2.23$ |
|     | $T_f = 270.92$ K or 270.77K |
| (b) | (i) 2M glucose; More Number of particles / less vapour pressure \text{ /} $\frac{1}{2}+\frac{1}{2}$ |
|     | (ii) Reverse Osmosis | 1 |
26. \[
\Delta T_f = i \frac{K_f W_b \times 1000}{M_b \times W_a}
\]

0.383 = (3.83 \times 2.56/M \times 100) \times 1000  

M = 256  
S \times = 256  
32 \times = 256  
x = 8  
(b) (i) Shrinks  
(ii) swells
General Instructions:
(i) All questions are compulsory.
(ii) Questions number 1 to 5 are very short-answer questions and carry 1 mark each.
(iii) Questions number 6 to 10 are short-answer questions and carry 2 marks each.
(iv) Questions number 11 to 22 are also short-answer questions and carry 3 marks each.
(v) Questions number 23 is a value based question and carry 4 marks.
(vi) Questions number 24 to 26 are long-answer questions and carry 5 marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Write the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number. 1

2. Write IUPAC name of the following compound: 
(CH₃CH₂)₂NCH₃
For a reaction R → P, half-life (t₁/₂) is observed to be independent of the initial concentration of reactants. What is the order of reaction? 1

3. Write the structure of 1-Bromo-4-chlorobut-2-ene. 1

4. Write one similarity between Physisorption and Chemisorption. 1

6. Complete the following reactions:
   (i) NH₃ + 3Cl₂(excess) →
   (ii) XeF₆ + 2H₂O →

OR

What happens when
(i) (NH₄)₂Cr₂O₇ is heated?
(ii) H₃PO₃ is heated?
Write the equations. 2

7. Define the following terms:
   (i) Colligative properties
   (ii) Molality (m)
8. Draw the structures of the following:
   (i)  $\text{H}_2\text{S}_2\text{O}_7$
   (ii) $\text{XeF}_6$

9. Calculate the degree of dissociation ($\alpha$) of acetic acid if its molar conductivity ($\lambda$) is $39.05 \text{ S cm}^2\text{mol}^{-1}$.
   Given $\lambda (\text{H}^+) = 349.6 \text{ S cm}^2\text{mol}^{-1}$ and $\lambda (\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2\text{mol}^{-1}$

10. Write the equations involved in the following reactions:
    (i) Wolff-Kishner reduction
    (ii) Etard reaction

11. 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.
    Given: (Molar mass of sucrose = 342 g mol$^{-1}$)
       (Molar mass of glucose = 180 g mol$^{-1}$)
    (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.
       (Given: Molar mass of Ag = 108 g mol$^{-1}$ IF = 96500 C mol$^{-1}$)
    (b) Define fuel cell.

13. (i) What type of isomerism is shown by the complex $[\text{Co(NH}_3)_6]\text{Cr(CN)}_6$?
    (ii) Why a solution of $[\text{Ni(H}_2\text{O})_6]^{2+}$ is green while a solution of $[\text{Ni(CN)}_4]^{2-}$ is colourless? (At. no. of Ni = 28)
    (iii) Write the IUPAC name of the following complex:
           $[\text{Co(NH}_3)_5(\text{CO}_3)]\text{Cl}$

14. Write one difference in each of the following:
    (i) Lyophobic sol and Lyophilic sol
    (ii) Solution and Colloid
    (iii) Homogeneous catalysis and Heterogeneous catalysis

15. Following data are obtained for the reaction:
    $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}_2$

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>300</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{N}_2\text{O}_5]/\text{mol L}^{-1}$</td>
<td>1.6 10$^{-2}$</td>
<td>0.8 10$^{-2}$</td>
<td>0.4 10$^{-2}$</td>
</tr>
</tbody>
</table>
(a) Show that it follows first order reaction.
(b) Calculate the half-life.
   (Given log 2 = 0.3010 log 4 = 0.6021)

16. Following compounds are given to you:
    2-Bromopentane, 2-Bromo-2 methylbutane, 1-Bromopentane
    (i) Write the compound which is most reactive towards $S_N^2$ reaction.
    (ii) Write the compound which is optically active.
    (iii) Write the compound which is most reactive towards $\beta$-elimination reaction.

17. (a) Write the principle of method used for the refining of germanium.
(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?

18. Write structures of compounds A, B and C in each of the following reactions:
    (i) $\text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{Mg/dry ether}} \text{A} \xrightarrow{(a) \text{CO}_2(g)} \xrightarrow{(b) \text{H}_2\text{O}^+} \text{B} \xrightarrow{\text{PCl}_3} \text{C}$
    (ii) $\text{CH}_3\text{CN} \xrightarrow{(a) \text{SNCl}_2/\text{HCl}} \xrightarrow{(b) \text{H}_2\text{O}^+} \text{A} \xrightarrow{\text{dil. NaOH}} \xrightarrow{\Delta} \text{B} \xrightarrow{\Delta} \text{C}$
    OR
Do the following conversions in not more than two steps:
(i) Benzoic acid to benzaldehyde
(ii) Ethyl benzene to Benzoic acid
(iii) Prapanone to Propene

19. Write the structures of the monomers used for getting the following polymers:
    (i) Dacron
    (ii) Melamine - formaldehyde polymer
    (iii) Buna-N
20. Define the following:
   (i) Anionic detergents
   (ii) Broad spectrum antibiotics
   (iii) Antiseptic

21. Give reasons:
   (i) Thermal stability decreases from $\text{H}_2\text{O}$ to $\text{H}_2\text{Te}$.
   (ii) Fluoride ion has higher hydration enthalpy than chloride ion.
   (iii) Nitrogen does not form pentahalide.

22. Give reasons:
   (i) Acetylation of aniline reduces its activation effect.
   (ii) $\text{CH}_3\text{NH}_2$ is more basic than $\text{C}_6\text{H}_5\text{NH}_2$.
   (iii) Although $–\text{NH}_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

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, Ritu a class XII student decided 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.

24. (a) Account for the following:
   (i) Transition 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$_2$O$_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.

25. (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 Al = 27 g mol$^{-1}$)

(b) Give reasons:

(i) In stoichiometric defects, NaCl 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.

26. (a) (i) $\text{OH} \quad \text{COOH}$

\[ (\text{CH}_3\text{CO}_2\text{O}) \xrightarrow{\text{H}^+} \] $\text{?}$

(ii) $\text{CH}_3\text{CH}^{-}\text{O}^{-}\text{CH}_2\text{CH}_3$ $\xrightarrow{\text{H}I} \text{?}$

(iii) $\text{CH}_3\quad \text{CH} = \text{CH} \xrightarrow{\text{PCC}} \text{?}$
(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) Write the formula of reagents used in the following reactions:
   (i) Bromination of phenol 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:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{Cu}} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{O-CH}_2\text{CH}_3 + \text{H}_2\text{O} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad }
<table>
<thead>
<tr>
<th>Q.No.</th>
<th>Value Points</th>
<th>Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\text{MnO}_4^- / \text{KMnO}_4$</td>
<td>1</td>
</tr>
<tr>
<td>2.</td>
<td>$\text{N-Ethyl-N-methylethanamine}$</td>
<td>1</td>
</tr>
<tr>
<td>3.</td>
<td>First order</td>
<td>1</td>
</tr>
<tr>
<td>4.</td>
<td>$\text{BrCH}_2\text{CH} = \text{CHCH}_2\text{Cl}$</td>
<td>1</td>
</tr>
<tr>
<td>5.</td>
<td>Both are surface phenomenon / both increase with increase in surface area (or a other correct similarity)</td>
<td>1</td>
</tr>
<tr>
<td>6.</td>
<td>(i) $\text{NH}_3 +3 \text{Cl}_2 \text{(excess)} \rightarrow \text{NCl}_3 + 3\text{HCl}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(ii) $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>OR</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i)$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(ii)$4\text{H}_3\text{PO}_3 \rightarrow 3\text{H}_3\text{PO}_4 + \text{PH}_3$</td>
<td>1</td>
</tr>
<tr>
<td>7.</td>
<td>(i) Properties that are independent of nature of solute and depend on number of moles of solute only.</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(ii) Number of moles of solute dissolved per kg of the solvent.</td>
<td>1</td>
</tr>
<tr>
<td>8.</td>
<td>(i)</td>
<td>1, 1</td>
</tr>
<tr>
<td></td>
<td>![Diagram of Sulfur-Containing Compound]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Diagram of XeF₆]</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>$\Lambda^{\circ}_{\text{CH}<em>2\text{COOH}} = \Lambda^{\circ}</em>{\text{CH}<em>2\text{COO}^-} + \Lambda^{\circ}</em>{\text{H}^-}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$40.9 + 349.6 = 390.5 \text{ S cm}^2/\text{mol}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>Now, $\alpha = \Lambda^m / \Lambda^m'$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td>$= 39.05 / 39.5 = 0.1$</td>
<td>$\frac{1}{2}$</td>
</tr>
</tbody>
</table>
10. (i) \[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{= O} & \quad \text{= O} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{NH}_2\text{NH}_2 & \quad \text{KOH/ethylene glycol, heat} \\
\text{CH}_2 + \text{N}_2
\end{align*}
\]

or

(ii) \[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{= O} & \quad \text{= O} \\
\text{NH}_2\text{NH}_2 & \quad \text{KOH/ethylene glycol, heat} \\
\text{CH}_2 + \text{N}_2
\end{align*}
\]

(iii) \[
\begin{align*}
\text{CH}_3
\end{align*}
\]

Toluenes + CrO\textsubscript{2}Cl\textsubscript{2} + CS\textsubscript{2} \rightarrow

Chromate complex + H\textsubscript{2}O\textsuperscript{+} \rightarrow

Benzaldehyde

11. \[
\Delta T_f = K_f m
\]

Here, \( m = \frac{w_2}{M_2} \times \frac{1}{x} \times \frac{1}{w_2} \times \frac{1}{342} = 90 \)

\( K_f = 12.3 \text{ K} \text{ kg/mol} \)

\( \Delta T_f = K_f m \)

\( = 12.3 \times 10 	imes 1000/180 \times 90 \)

\( = 7.6 \text{ K} \)

\( T_f = 273.15 - 7.6 = 265.55 \text{ K} \) (or any other correct method)

12. (i) \( m = Z \times \text{lt} \)

\[
\begin{align*}
&= \frac{108 \times 2 \times 15 \times 60}{1 \times 96500} \text{ (or any other correct method)} \\
&= 2.01 \text{ g}
\end{align*}
\]

(ii) Cells that converts the energy of combustion of fuels directly into electrical energy.

13. (i) Coordination isomerism

(ii) Unpaired electrons in [Ni(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+} / d-d transition

(iii) Pentaamminecarbonatocobalt(III) Chloride
14. (i) Lyophobic are liquidf (dispersion medium)-hating and lyophillic are liquid(dispersion medium)-loving colloids.
(ii) Solution is a Homogenous mixture while colloid is heterogenous mixture / does not show Tyndall effect -shows Tyndall effect.
(iii) Homogenous catalysis : reactants and catalyst are in same phase -
Heterogeneous catalysis: reactants and catalyst are not in same phase.
(or any other correct difference)

15. (a) \[ k = \frac{2.303}{t} \log \frac{[A]^o}{[A]} \]
    \[ = \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} \]
    \[ = \frac{2.303}{300} \log 2 = 2.31 \times 10^{-3} \text{ s}^{-1} \]
At 600s, \[ k = \frac{2.303}{t} \log \frac{[A]^o}{[A]} \]
    \[ = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} \]
    \[ = 2.31 \times 10^{-3} \text{ s}^{-1} \]
k is constant when using first order equation therefore it follows first order kinetics.

or

In equal tiem interal, half of the reactant gets converted into product and the rate of reaction is independent of concentration of reactant, so it is a first order reaction.

(b) \[ t_{1/2} = \frac{0.693}{k} \]
    \[ = \frac{0.693}{2.31} = 10^{-3} \]
    \[ = 300 \text{ s} \]
(If student writes directly that half life is 300 s, award full marks)
16. (i) 1-Bromopentane  
(ii) 2-Bromopentane  
(iii) 2-Bromo-2-methylbutane

17. (i) The impurities are more soluble in the melt than in the solid state of the metal.  
(ii) PbS  
(iii) Impurities like $\text{SiO}_2$ etc are removed by using NaOH solution and pure alumina is obtained.

18. (i) $\text{C}_6\text{H}_5\text{MgBr}$  $\text{B : C}_6\text{H}_5\text{COOH}$  $\text{C : C}_6\text{H}_5\text{COCl}$  
(ii) $\text{A : CH}_3\text{CHO}$  $\text{B : CH}_3\text{CH(OH)}\text{CH}_2\text{CHO}$  $\text{C : CH}_3\text{CH = CHCHO}$

OR

18.  
(i) $\text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{SOCl}_2} \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{H}_2\text{Pd-BaSO}_4} \text{C}_6\text{H}_5\text{CHO}$  
(ii) $\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{C}_6\text{H}_5\text{COOH}$  
(iii) $\text{CH}_3\text{COCH}_3 \xrightarrow{\text{NaBH}_4} \text{CH}_3\text{CH(OH)}\text{CH}_3$  
$\xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CH}_3\text{CH = CH}_2$ (or any other correct method)

19. (i) $\text{HOCH}_2\text{CH}_2\text{OH} + \text{HOOC} \xrightarrow{\text{O}} \text{COOH}$  
(ii) $\text{H}_2\text{N} \begin{array}{c} \text{N} \\ \text{N} \\ \text{N} \end{array} \text{NH}_2 + \text{HCHO}$  
(iii) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + \text{CH}_2 = \text{CHCN}$

$\frac{1}{2} + \frac{1}{2}$  
$\frac{1}{2} + \frac{1}{2}$  
$\frac{1}{2} + \frac{1}{2}$

20. (i) Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons / alkylbenzene sulphonate or detergents whose anionic part is involved in cleansing action.  
(ii) Broad spectrum antibiotics: Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria.  
(iii) Antiseptics are the chemicals which either kill or prevent growth of microbes on living tissues.
21.  (i) Due to the decrease in bond dissociation enthalpy / due to increase in atomic size from O to Te.  
    (ii) Due to small size of fluoride ion / high charge density of fluoride ion / high charge size ratio of fluoride ion.  
    (iii) Absence of d-orbitals.

22.  (i) Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group /ating structures.  
    (ii) Because of +1 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

23.  (i) concerned , caring, socially alert, leadership ( or any other 2 values)  
    (ii) starch  
    (iii) a -Helix and B-pleated sheets  
    (iv) Vitamin B / B₁ / B₂ / B₆ / C (any two )

24.  (a)(i) Due to small size and high ionic charge / availability of d orbitals.  
    (ii) Higher is the oxidation state higher is the acidic character / as the oxidation state of a metal increases, ionic character decreases  
    (iii) Because Mn²⁺ has d⁵ as a stable configuration whereas Cr³⁺ is more stable due to stable t³₂g  
    (b) Similarity-both are stable in +3 oxidation state/ both show contraction/irregular electronic configuration (or any other suitable similarity) Difference- actinoids are radioactive and lanthanoids are not / actinoids show wide range of oxidation states but lanthanoids don’t (or any other correct difference)

OR

(a) i) In p block elements the difference in oxidation state is 2 and in transition metals the difference is 1
(ii) Cu\(^{2+}\), due to disproportionation reaction / low hydration enthalpy

(iii) Due to formation of chromate ion / CrO\(_4^{2-}\) ion, which is yellow in colour

(b) Actinoids are radioactive, actinoids show wide range of oxidation states

---

25. (a) \( \rho = (zM)/a^3 \) \( \text{Na} \)

\[ 11.5 = z \times 93 / [(300 \times 10^{-10})^3 \times 6.02 \times 10^{23}] \]

\( Z = 2.0 \)

Body centred cubic (bcc)

(b)

<table>
<thead>
<tr>
<th>Amorphous solids</th>
<th>Crystalline solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short range order</td>
<td>Long range order</td>
</tr>
<tr>
<td>Isotropic</td>
<td>Anisotropic</td>
</tr>
</tbody>
</table>

1 + 1

(or any other correct difference)

---

OR

25. (a) \( n = \text{given mass} / \text{molar mass} \)

\[ = 8.1 \times 10^2 \text{ mol} \]

Numbers of atoms = \( \frac{8.1}{27} \times 6.022 \times 10^{23} \)

\( Z = 2.0 \times \frac{8.1}{27} \times 6.022 \times 10^{23} / 4 \)

\( = 4.5 \times 10^{22} \)

Or

27g of Al contains = \( 6.022 \times 10^{23} \) atoms

8.1g of Al contains = \( (6.022 \times 10^{23} / 27) \) \( \times 8.1 \)

No of unit cells = total no of atoms / 4

\[ = \frac{8.1}{27} \times 6.022 \times 10^{23} / 4 \]

\[ = 4.5 \times 10^{22} \]

1

(b) (i) Due to comparable size of cation and anion / large size of sodium ion

(ii) P has 5 valence e\(^-\), an extra electron results in the formation of n-type semiconductor.
(iii) In ferrimagnetism domains/magnetic moments are aligned in opposite direction in unequal numbers while in antiferromagnetic the domains align in opposite direction in equal numbers so they cancel magnetic moments completely, net magnetism is zero/diagrammatic representation.

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>26.</td>
<td>(a) (i) ( \text{COOH} ) ( \text{OCOCH}_3 )</td>
</tr>
<tr>
<td></td>
<td>(ii) ((\text{CH}_2)_2\text{CHOH}) and (\text{CH}_3\text{CH}_2\text{I})</td>
</tr>
<tr>
<td></td>
<td>(iii) (\text{CH}_3\text{CH} = \text{CHCHO})</td>
</tr>
<tr>
<td></td>
<td>(i) Add neutral (\text{FeCl}_3) to both the compounds, phenol gives violet complex,</td>
</tr>
<tr>
<td></td>
<td>(ii) Add anhy (\text{ZnCl}_2) and cone. (\text{HCl}) to both the compounds,</td>
</tr>
<tr>
<td></td>
<td>(or any other correct test)</td>
</tr>
<tr>
<td></td>
<td>2-methyl propan-2-ol gives turbidity immediately.</td>
</tr>
</tbody>
</table>

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<tr>
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<tbody>
<tr>
<td>(a)</td>
<td>(i) Aq. (\text{Br}_3)</td>
</tr>
<tr>
<td></td>
<td>(ii) (\text{B}_2\text{H}_6), (\text{H}_2\text{O}_2) and(\text{OH}^-)</td>
</tr>
<tr>
<td>(b)</td>
<td>(i) ethanol &lt; phenol &lt; Nitrophenol</td>
</tr>
<tr>
<td></td>
<td>(ii) propane &lt; propanal &lt; propanol</td>
</tr>
<tr>
<td>(c)</td>
<td>(\text{CH}_3\text{CH}_2\text{O}^+ + \text{CH}_3\text{CH} = \text{O}^-)</td>
</tr>
</tbody>
</table>
General Instructions:
(i) All questions are compulsory.
(ii) Questions number 1 to 5 are very short-answer questions and carry 1 mark each.
(iii) Questions number 6 to 10 are short-answer questions and carry 2 marks each.
(iv) Questions number 11 to 22 are also short-answer questions and carry 3 marks each.
(v) Questions number 23 is a value based question and carry 4 marks.
(vi) Questions number 24 to 26 are long-answer questions and carry 5 marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Write the IUPAC name of the following: 1

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{C} \quad \text{CH} \quad \text{CH}_3 \\
\text{C}_2\text{H}_5 \quad \text{OH}
\]

2. Out of chlorobenzene and benzyl chioroide which one gets easily hydrolysed by aqueous NaOH and why? 1

3. CO (g) and H\(_2\) (g) react to give different products in the presence of different catalysts. Which ability of the catalyst is shown by these reactions? 1

4. Write the coordination number and oxidation state of Platinum in the complex [Pt(en)\(_2\)Cl\(_2\)]. 1

5. Analysis shows that FeO has a non-stoichiometric composition with formula Fe\(_{0.95}\)O. Give reason. 1

6. Complete and balance the following chemtecel 2

(a) \(\text{Fe}^{2+} + \text{MnO}_4^- + \text{H}^+ \rightarrow\)

(b) \(\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \rightarrow\)

7. How do you convert the following? 2

(a) Ethanal to Propanone

(b) Toluene to Benzoic acid
OR

Account for the following:

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
(b) \( pK_a \) value of 4-nitrobenzoic acid is lower than that of benzoic acid.

8. For the reaction

\[
2\text{N}_2\text{O}_2(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}),
\]

the rate of fromation of \( \text{NO}_2(\text{g}) \) is \( 2.8 \times 10^{-3} \text{ M S}^{-1} \). Calculate the rate of disappearance of \( \text{N}_2\text{O}_5(\text{g}) \).

9. Among the hydrides of Group-15 elements, which have the

(a) lowest boiling point?
(b) maximum basic character?
(c) highest bond character?
(d) maximum reducing character?

10. Calculate the freezing point of a containing 60 g of glucose (Molar mass = 180 g mol\(^{-1}\)) in 250 g of water.

\( (K_f \text{ of water} = 1.86 \text{ K kg mol}^{-1}) \)

11. An element ‘\( X \)’ (At mass = 40 g mol\(^{-1}\)) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of ‘\( X \)’ and the number of unit cells in 4 g of ‘\( X \)’ (\( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \))

12. Given reasons for the following:

(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
(b) Aquatic animals are comfortable in colt water than in warm water.
(c) Elavation of boiling point 1 M KCl solution is nearly doubtle than that of 1 M sugar solution.

13. Write the structures of the main products in the following reactions.

(i)

\[
\begin{array}{c}
\text{O} \\
\text{CH}_2-\text{C-CH}_3 \\
\text{O}
\end{array}
\xrightarrow{\text{NaBH}_4}
\]
14. (a) Write the formula of the following coordination compound.
Iron (III) hexacyanoferrate (II)
(b) What type of isomerism is exhibited by the complex
[Co(NH₃)₅Cl]SO₄?
(c) Write the hybridisation and number of unpaired electrons in the
complex [CoF₆]³⁻ (Atomic No. of Co = 27)

15. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl
compound with molecular formula C₄H₈O. Isomery (A) and (C) give
positive. Tollens’ test whereas isomer (B) does not give Tollens’ test
but gives positive iodoform test. Isomers (A) and (B) on reduction with
Zn/Hg – Conc. HCl give the same product (D).
(a) Write the structure of (A), (B), (C) and (D).
(b) Out of (A), (B) and (C) isomers, which one least reactive towards
addition of HCN?

16. (a) Identify the chiral molecule in following pair:

(b) Write the structure of the product when chlorobenzene is treated
with methyl chloride in the presence of sodium metal and bry ether.
(c) Write the structure of the alkene formed by dehydrohalogenation of
1-bromo-methyl cyclohexane with alcoholic KOH.

17. Give reasons:
(a) E° value for Mn³⁺/Mn²⁺ couple is much more positive than that for
Fe³⁺/Fe²⁺.
(b) Iron has higher enthalpy of atomisation than of copper.
(c) Sc³⁺ is colourless in aqueous solution whereas Ti³⁺ is coloured.
18. Write the chemical reactions involved in the process of extraction of Gold. Explain the role of dilute NaCN and Zn in this process. 3

19. Define the following with, an example each. 3
   (a) Polysaccharides
   (b) Denatured protein
   (c) Essential amino acids

   OR

   (a) Write the product when D glucose reacts with conc. HNO₃.
   (b) Amino acids show amphoteric behaviour. Why?
   (c) Write one difference between α-helix and β-pleated structure of protein.

20. A first order reaction is 50% complete in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction (Given: log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK⁻¹ mol⁻¹) 3

21. (a) Why is bithional added to soap?
   (b) What is tincture of iodine? Write its one use.
   (c) Among the following, which one acts as a food preservative? Aspartame, Aspirin, Sodium Benzoate, Paracetamol. 3

22. What happens when
   (a) a freshly prepared precipitate of Fe(OH)₃ is shaken with a small amount of FeCl₃ solution?
   (b) persistent dialysis of a colloidal solution is carried out?
   (c) an emulsion is centrifuged? 3

23. Shyam went to a grocery shop to purchase some food items. The shopkeeper packed all the items in polythene bags and gave them to Shyam. But Shyam refused to accept the polythene bags and asked the shopkeeper to pack the items in paper bags. He informed the shopkeeper about the heavy penalty imposed by the government for using polythene bags. The shopkeeper promised that he would use paper bags in future in place of polythene bags. 4

   Answer the following:
   (a) Write the values (at least two) shown by Shyam.
(b) Write one one structural difference between low-density polythene and high-density polythene.

(c) Why did Shyam refuse to accept the items in polythene bags?

(d) What is a biodegradable polymer? Give an example.

24. (a) Write the cell reaction and calculate the e.m.f of the following cell at 298 K:

\[ \text{Sn (s) / [Sn}^{2+} \text{(0.004 M) || H}^+ \text{(0.020 M) || H}_2 \text{ (g) (1 bar) || Pt (s)}} \]

(b) Give reasons:

(i) On the basis of E values, O\(_2\) gas should be liberated at anode but it is Cl\(_2\) gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH\(_3\)COOH decreases on dilution.

OR

(a) For the reaction

\[ 2\text{AgCl (s) + H}_2 \text{ (g) (1 atm) \longrightarrow 2Ag (s) + 2H}^+ \text{ (0.1 M) + 2Cl}^- \text{ (0.1 M).} \]

\[ \Delta G = -43600 \text{ J at 25 C.} \]

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

[log 10\(^{-n}\) = \(n\)]

(b) Define fuel cell and write its two advantages.

25. (a) Write the reactions involved in the following:

(i) Hofmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

(b) Give reasons:

(i) (CH\(_3\))\(_2\)NH is more basic than (CH\(_3\))\(_3\)N in an aqueous solution.

(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

OR

(a) Write the structures of the main products of the following reaction:

\[ \text{NH}_2 \]

(i) \[ \text{Pyridine} \rightarrow (\text{CH}_3\text{CO})_2\text{O} \]
(ii) \( \text{SO}_2\text{Cl} \rightarrow (\text{CH}_3)\text{NH} \)

(iii) \( \text{Cl}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} \)

(b) Give a simple chemical test to distinguish between Aniline and \( \text{N,N-} \)dimethylamline.

(c) Arrange the following in the increasing order \( \text{pK}_a \) values:
\[ \text{C}_6\text{H}_5\text{NH}_2, \text{C}_2\text{H}_5\text{NH}_2, \text{C}_5\text{H}_5\text{NHCH}_3 \]

26. (a) Give reasons:

(i) \( \text{H}_3\text{PO}_3 \) undergoes disproportionstion reaction but \( \text{H}_3\text{PO}_4 \) does not.

(ii) When \( \text{Cl}_2 \) reacts with excess of \( \text{F}_2 \), \( \text{ClF}_3 \) is formed and not \( \text{FCl}_3 \).

(iii) Dioxygen is a gas while Sulphur is a solid at room temperature.

(b) Draw the structures of the following:

(i) \( \text{XeF}_4 \)

(ii) \( \text{HClO}_3 \)

OR

(a) When concentrated sulphuric acid was added to an unknown salt present in test tube a brown gas (A) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, the gas (A) changed into a colourless solid (B).

(i) Identify (A) and (B)

(ii) Write the structures of (A) and (B)

(iii) Why does gas (A) Change to solid on cooling?

(b) Arrange the following in the decreasing order of their reducing character:
\[ \text{HF, HCl, HBr, HI} \]

(c) Complete the following reaction:
\[ \text{XeF}_4 + \text{SbF}_5 \rightarrow \]
<table>
<thead>
<tr>
<th>Q.No.</th>
<th>Value Points</th>
<th>Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3,3 - Dimethylpentan-2-ol</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Benzyl chloride; Due to resonance, stable benzyl carbocation is formed.</td>
<td>½, ½</td>
</tr>
<tr>
<td>3</td>
<td>Selectivity of a catalyst</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Coordination Number = 6, Oxidation State = +2</td>
<td>½, ½</td>
</tr>
<tr>
<td>5</td>
<td>Shows metal deficiency defect / It is a mixture of Fe²⁺ and Fe²⁺/Some Fe²⁺ ions are replaced by Fe³⁺ / Some of the ferrous ions get oxidised to ferric ions.</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>(a) $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(b) $2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \rightarrow 2 \text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(Half mark to be deducted in each equation for not balancing)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(a) $\text{CH}_3\text{CHO} \xrightarrow{\text{(i) CH}_3\text{MgBr, Dry ether}} \xrightarrow{\text{(ii) H}_2\text{O/H}^+} \text{CH}_3\text{CH(OH)CH}_3 \xrightarrow{\text{CrO}_3} \text{CH}_3\text{COCH}_3$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(b) <img src="image.png" alt="image" /></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(or any other correct method)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(a) because the carboxyl group is deactivating and the catalyst aluminiumchloride (Lewis acid) gets bonded to the carboxyl group</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(b) Nitro group is an electron withdrawing group (-I effect) so it stabilises the carboxylate anion and strengthens the acid / Due to the presence of an electron withdrawing Nitro group (-I effect).</td>
<td>1</td>
</tr>
</tbody>
</table>
### Question 8

Rate of reaction:
\[
\text{Rate} = \frac{1}{4} \frac{\Delta (\text{NO}_2)}{\Delta (t)} = \frac{1}{2} \frac{\Delta (\text{N}_2\text{O}_5)}{\Delta (t)} \\
\frac{1}{4} (2.8 \times 10^{-3}) = \frac{1}{2} \frac{\Delta (\text{N}_2\text{O}_5)}{\Delta (t)}
\]

Rate of disappearance of \(\text{N}_2\text{O}_5\):
\[
\left( -\frac{\Delta (\text{N}_2\text{O}_5)}{\Delta (t)} \right) = 1.4 \times 10^{-3} \text{ M/S}
\]

(Deduct half mark if unit is wrong or not written)

### Question 9

(a) \(\text{PH}_3\)
(b) \(\text{NH}_3\)
(c) \(\text{NH}_3\)
(d) \(\text{BiH}_3\)

### Question 10

\[
\Delta T_r = K_m \\
= K_f \frac{w_2 \times 1000}{M_2 \times w_1} \\
= \frac{1.86 \times 60 \times 1000}{180 \times 250} \\
= 2.48 \text{ K}
\]

\[
\Delta T_r = T_f - T_i \\
2.48 = 273.15 - T_i \\
T_i = 270.67 \text{ K} \div 270.52 \text{ K} - 2.48 \text{ C}
\]

### Question 11

\[
d = \frac{2M}{a^3 N_A} \\
= \frac{4 \times 40}{(4 \times 10^{-8}) \times 6.022 \times 10^{-23}} \\
= 4.15 \text{ g/cm}^3
\]

No of unit cells = total no of atoms/4
\[
= \left[ \frac{4}{40} \times 6.022 \times 10^{23} \right] / 4 \\
= 1.5 \times 10^{22}
\]

(Or any other correct method)
12. (a) As compared to other colligative properties, its magnitude is large even for very dilute solutions/macromolecules are generally not stable at higher temperatures and polymers have poor solubility / pressure measurement is around the room temperature and the molarity of the solution is used instead of molality.

(b) Because oxygen is more soluble in cold water or at low temperature.

(c) Due to dissociation of KCl / KCl (aq) → K⁺ + Cl⁻, i is nearly equal to 2

13. (ii) C₆H₅CH(OH)CH₃

![Chemical Structure](image)

(iii) C₂H₅I + C₆H₅OH (No splitting of marks)

14. (a) Fe[Fe (CN)₆]₃

(b) Ionisation isometism

(c) sp³ d⁵, 4

15. (a) A = CH₃CH₂CH₂CHO

B = CH₃COCH₂CH

C = (CH₃)₂CHCHO

D = CH₃CH₂CH₂CH₃

(b) B

16. (a) 

(b) 

(c) CH₃ or CH₂CH₂
17. (a) The comparatively high value for Mn Shows that Mn$^{2+}$ (d$^5$) is particularly stable / Much larger third ionisation energy of Mn (where the required change is from ds to (f)
(b) Due to higher number of unpaired electrons.
(c) Absence of unpaired d- electron in Sc$^{3+}$ whereas in Ti$^{3+}$ there is one unpaired electron or Ti$^{3+}$ shows d-d transition.

18. $4\text{Au}(s) + 8\text{CN}^-\text{(aq)} + 2\text{H}_2\text{O(aq)} + \text{O}_2(g) \rightarrow 4[\text{Au(CN)}_2]^-(\text{aq}) + 4\text{OH}^-\text{(aq)}$
$2[\text{Au(CN)}_2]^-(\text{aq}) + \text{Zn}(s) \rightarrow 2\text{Au}(s) + [\text{Zn(CN)}_4]^{2-} \text{(aq)}$
(No marks will be deducted for not balancing)
NaCN leaches gold/NaCN acts as a leaching agent / complexing agent Zn acts as reducing agent / Zn displaces gold.

19. (a) Carbohydrates that give large number of monosaccharide units on hydrolysis / large number of monosaccharides units joined together by glycosidic linkage Starch/ glycogen/ cellulose (or any other)
(b) Proteins that lose their biological activity / proteins in which secondary and tertiary structures are destroyed Curdling of milk (or any other)
(c) Amino acids which cannot be synthesised, in the body. Valine / Leucine (or any other)

OR

19. (a) Saccharic acid / COOH-(CHOH)$_4$-COOH
(b) Due to the presence of carboxyl and amino group in the same molecule / due to formation of zwitter ion or dipolar ion.
(c) a-helix has intramolecular hydrogen bonding while $\beta$ pleated has intermolecular hydrogen bonding/$\alpha$-helix results due to regular coiling of polypeptide chains while in $\beta$ pleated all polypeptide chains are stretched and arranged side by side.
20. \[ k_2 = \frac{0.693}{20}, \quad k_1 = \frac{0.693}{40} \]
\[ \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \]
\[ k_2/k_1 = 2 \]
\[ \log 2 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{320 - 300}{320 \times 300} \right], \text{Ea} = 27.66 \text{ KJ Mol}^{-1} \]

21. (a) To impart antiseptic properties
(b) 2-3% solution of iodine in alcohol- water mixture/ iodine dissolved in alcohol, used as an antiseptic/ applied on wounds.
(c) Sodium benzoate / Aspartame

22. (a) Peptisation occurs / Colloidal solution of Fe(OH)_3, is formed
(b) Coagulation occurs
(c) Demulsification or breaks into constituent liquids

23. (a) Concerned about environment, caring, socially alert, law abiding citizen (or any other 2 values)
(b) Low density polythene is highly branched while high density polythene is linear.
(c) As it is non-biodegradable.
(d) Which can be degraded by microorganisms, eg PHBV (or any other correct example)

24. (a) (i) \( \text{Sn} + 2 \text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2 \) (Equation must be balanced)
\[ E = E_0 \frac{0.059}{2} \log \left( \frac{[\text{Sn}^{2+}]}{[\text{H}^+]} \right)^2 \]
\[ = [0 \text{ (- 0.14)}] - 0.0295 \log \frac{(0.004)}{(0.02)^2} \]
\[ = 0.14 - 0.0295 \log 10 = 0.11 \text{ V} / 0.1105 \text{V} \]

(b) (i) Due to overpotential/ Overvoltage of O₂
(ii) The number of ions per unit volume decreases.
24. (a) \( \Delta G = -nFE \)
\[-43600 = - 2 \text{ 96500 E} \]
\[E = 0.226 \text{ V} \]
\[E = E - 0.059/2 \log ([H^+]^2 [Cl^-]^2 /[H_2]) \]
\[= 0.226 - 0.059/2 \log[ (0.1)^2 (0.1)^2] / 1 \]
\[= 0.226 -0.059 /2 \log 10^{-4} \]
\[= 0.226 + 0.118 = 0.344 \text{ V} \]
(Deduct half mark if unit is wrong or not written)
(b) Cells that convert the energy of combustion of fuels (like hydrogen, methane, methanol, etc.) directly into electrical energy are called fuel cells. Advantages: High efficiency, non polluting (or any other suitable advantage)

25. (a) (i) \( \text{Ar/ } \text{R-CONNH}_2 + \text{Br}_2 + 4 \text{NaOH} \rightarrow \text{Ar/ } \text{R-NH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 2 \text{H}_2\text{O} \)
(ii) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{273-278K} \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{NaCl} + 2\text{H}_2\text{O} \)
(or any other correct equation)
(iii)
(b) (i) Because of the combined factors of inductive effect and solvation or hydration effect
(ii) Due to resonance stabilisation or structural representation / resonating structures.
25. (a) (i) C₆H₅NHCOCH₃
(ii) C₆H₅SO₂N(CH₃)₂
(iii) C₆H₆

(b) Add chloroform in the presence of KOH and heat, Aniline gives a offensive smel while N,N dimethylaniline does not. (or any other correct test)

(c) C₂H₅NH₂ → C₆H₅NHCH₃ → C₆H₅NH₂

26. (a)(i) In +3 oxidation state of phosphorus tends to disproportionate to higher and lower oxidation states / Oxidation state of P in H₃PO₄ is +3 so it undergoes disproportionation but in H₂PO₄ it is +5 which is the highest oxidation state, so it cannot.

(ii) F cannot show positive oxidation state as it has highest electronegativity. Because Fluorine cannot expand its covalency / As Fluorine is a small sized atom, it cannot pack three large sized Cl atoms around it.

(iii) Oxygen has multiple bonding whereas sulphur shows catenation / Due to σ-π bonding in oxygen whereas sulphur does not / Oxygen is diatomic therefore held by weak intermolecular force while sulphur is polyatomic held by strong intermolecular forces.

(b) (i) (ii)
26. (a) (i) \( A = \text{NO}_2, B = \text{N}_2\text{O}_4 \)

\[ \text{N} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \]

(iii) Because \( \text{NO}_2 \) dimerises to \( \text{N}_2\text{O}_4/\text{NO}_2 \) is an odd electron species.

(b) \( \text{HI} > \text{HBr} > \text{HCl} > \text{HF} \)

(c) \( \text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^− \)

\( \frac{1}{2}, \frac{1}{2} \)

\( \frac{1}{2}, \frac{1}{2} \)

1

1

1

* Note: Value Based Question is not included in new blue print.
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 questions and carry 1 mark each.

(iii) Questions number 6 to 12 are short-answer questions and carry 2 marks each.

(iv) Questions number 13 to 24 are also short-answer questions and carry 3 marks each.

(v) Questions number 25 to 27 are long-answer questions and carry 5 marks each.

(vi) 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 HNO₃, a brown gas is evolved which undergoes dimerization. Identify the gas. 1

4. Write the IUPAC name of [[Co-(NH₃)₅ NO₂] (NO₂)] 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

\[
\text{Rate} = k \ [A]^2 \ [B]
\]

(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:
   (a) \( \text{XeF}_4 + \text{SbF}_5 \rightarrow \) 
   (b) \( \text{XeF}_2 + \text{H}_2\text{O} (l) \rightarrow \)

OR

Give reasons for the following:
   (a) Xenon does not form fluorides such as \( \text{XeF}_3 \) and \( \text{XeF}_5 \).
   (b) Out of noble gases, only Xenon is known to form real chemical compounds.

9. (a) Name the oil soluble vitamin which is a powerful antioxidant.
   (b) Name the product of hydrolysis of sucrose.

10. (a) What change occurs in the nature of egg protein on boiling?
    (b) What is the difference between the structure of starch and cellulose?

11. Differentiate:
    (i) Lyophilic sol and lyophobic sol
    (ii) Homogeneous catalyst and heterogeneous catalyst.

12. Define:
    (i) Emulsion
    (ii) Peptisation.

13. 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\(^{-3}\).

   \[
   \text{[Atomic mass of Fe} = 56 \text{ g mol}^{-1} \text{, } N_A = 6.02 \times 10^{23} \text{ mol}^{-1}] 
   \]

14. 3.9 g benzoic 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).

   \[
   \text{[Given: Molar mass of Benzoic Acid} = 122 \text{ g mol}^{-1}, \text{ } K_f (\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}] 
   \]

15. 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.
OR

The rate constant of a first order reaction increases from $4 \times 10^{-2}$ to $24 \times 10^{-2}$, 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$^{-1}$]

16. (a) Indicate the principle behind the method for the refining of zinc.  
(b) Account for the following:
(i) It is advantageous to roast sulphide ore to oxide before reduction.
(ii) Zinc oxide can be reduced to metal by heating with carbon but not Cr$_2$O$_3$.

17. Account for the following:  
(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$_3$.

18. For the complex [CoF$_6$]$^{3-}$ write the hybridization type, magnetic character and spin nature of the complex.  
(Atomic number of Co = 27)

19. How do you convert the following?  
(a) Propene to propan-2-ol
(b) Bromobenzene to 2-bromoacetophenone
(c) Alkyl halides though polar, are immiscible with water. Why?

20. Write the reactions involved in the following:  
(a) Aldol condensation
(b) Cannizzaro’s reaction
(c) Rosenmund reduction
21. Give reasons for the following:  
   (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.

22. An aromatic compound A on treatment with ammonia followed by heating forms compound B which on heating with Br₂ and KOH forms compound C having molecular formula C₆H₇N. Give the structures of A, B and C.  

23. (a) Identify the monomers in the following polymeric structure:  

   ![Polymer Structure](image)

(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 a polymer, to which class does polyester belong?

24. Give one example for each of the following:  
   (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.

25. Calculate the emf and ΔG for the following cell at 298 K:  
   Mg (s) | Mg²⁺ (0.01 M) || Ag⁺ (0.0001 M) | Ag (s)  
   [Given: E⁰_{Mg²⁺/Mg} = -2.34 V; E⁰_{Ag⁺/Ag} = 0.80 V]  
   OR

   (a) Give reasons for the following:  
      (i) Iron does not rust even if zinc coating is broken in a galvanized 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.

\[\text{Given: } \lambda_0^{H^+} = 349.6 \text{ S cm}^2\text{ mol}^{-1}\text{ and }\lambda_0^{\text{HCOO}^-} = 54.6 \text{ S cm}^2\text{ mol}^{-1}\]

26. (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?

OR

(a) Give reasons for the following:

(i) Transition metals are paramagnetic.

(ii) Transition metals show variable oxidation states.

(iii) Zr and Hf have nearly similar atomic radii.

(b) Write the preparation of KMnO\(_4\) from pyrolusite ore(MnO\(_2\)).

27. (a) How do you convert the following?

(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

\[
\begin{array}{c}
\text{NO}_2 \\
\text{OH} \\
\text{NO}_2
\end{array}
\]

OR

(a) Write the mechanism for the preparation of alcohols from alkenes (acid catalyzed hydration).

(b) Give reasons for the following:

(i) Phenols do not undergo sundergo substitution of the –OH group like alcohols.

(ii) p-nitrophenol is more acidic than p-methylphenol.
UNSOLVED SAMPLE PAPER
Chemistry-XII (Theory)

Time allowed

(i) All questions are compulsory.
(ii) Questions number 1 to 5 are very short-answer questions and carry 1 mark each.
(iii) Questions number 6 to 12 are short-answer questions and carry 2 marks each.
(iv) Questions number 13 to 24 are also short-answer questions and carry 3 mark each.
(v) Questions number 25 to 27 are long-answer questions and carry 5 marks each.
(vi) Use log tables, if necessary. Use of calculators is not allowed.

1. What is the effect of catalyst on:
   (i) Gibbs energy (ΔG) and
   (ii) Activation energy of a reaction?
   1

2. Write one similarity between Physisorption and Chemisorption.
   1

3. Write 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.
   (CH₃)₂N – CH₂CH₃
   1

6. Write the reactions involved in the following reactions:
   (i) Clemmensen reduction
   (ii) Cannizzaro reaction
   1+1=2
7. Draw the structures of the following: 1+1=2
   (i) H₄P₂O₇
   (ii) XeOF₄

8. Define the following terms: 1+1=2
   (i) Abnormal molar mass
   (ii) Van’t Hoff factor (i)

9. Calculate the degree of dissociation $\alpha$ of acetic acid if its molar conductivity ($\Lambda_m$) is 39.05 S cm² mol⁻¹. 2
   Given $\lambda$ (H⁺) = 349.6 S cm² mol⁻¹ and $\lambda$ (CH₃COO⁻) = 40.9 S cm² mol⁻¹

10. Complete the following chemical equations: 1+1=2
    (i) F₂ + 2Cl⁻ $\rightarrow$
    (ii) 2XeF₂ + 2H₂O $\rightarrow$

    OR

    What happens when
    (i) HCl is added to MnO₂?
    (ii) PCl₅ is heated?

    Write the equations involved.

11. (i) Which polysaccharide component of carbohydrates is commonly present in based? 2
    (ii) Give two example of water soluble vitamins.

12. (i) Write two types of secondary structure of protein. 2
    (ii) Differentiate DNA and RNA.

13. Given reasons: 1x3=3
    (i) Acetylation of aniline reduces is its activation effect.
    (ii) CH₃NH₂ is more basic than C₆H₅NH₂.
    (iii) Although –NH₂ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.
14. Give reasons: \(1\times 3 = 3\)

(i) Thermal stability decreases from \(\text{H}_2\text{O}\) to \(\text{H}_2\text{Te}\).

(ii) Fluoride ion has higher hydration enthalpy than chloride ion.

(iii) Nitrogen does not form pentahalide.

15. Define the following: \(1\times 3 = 3\)

(i) Anionic detergents

(ii) Limited spectrum antibiotics

(iii) Tranquilizers

16. Write the structures of the monomers used for getting the following polymers: \(1\times 3 = 3\)

(i) Nylon-6

(ii) Melamine-formaldehyde polymer

(iii) Teflon

17. Write structures of compounds A, B and C in each of the following reactions:

(i) \(\text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{Mg/dry ether}} \text{A} \xrightarrow{(a)\text{CO}_2\text{N}_2\text{H}_4}{(b)\text{H}_2\text{O}^+} \rightarrow \text{B} \rightarrow \text{PCl}_3 \rightarrow \text{C}\)

(ii) \(\text{CH}_3\text{CN} \xrightarrow{(a)\text{SnCl}_3/\text{HCl}}{(b)\text{H}_2\text{O}^+} \rightarrow \text{A} \rightarrow \text{B} \rightarrow \text{dil NaOH} \rightarrow \Delta \rightarrow \text{C}\)

OR

Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Prapanone to Propene

18. (a) Write the principle of method used for the refining of germanium. \(1\times 3 = 3\)

(b) Out of \(\text{PbS}\) and \(\text{PbCO}_3\) (ores of lead), which one is concentrated by froth floatation process preferably?

(c) What is the significance of leaching in the extraction of aluminium?
19. Following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards $S_{N2}$ reaction.
(ii) Write the compound which is optically active.
(iv) Write the compound which is most reactive towards $\beta$-elimination reaction.

20. Following data are obtained for the reaction:

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$

<table>
<thead>
<tr>
<th>t/s</th>
<th>0</th>
<th>300</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[N_2O_5]$/mol L$^{-1}$</td>
<td>$1.6 \times 10^{-2}$</td>
<td>$0.8 \times 10^{-2}$</td>
<td>$0.4 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

(a) Show that it follows order reaction.
(b) Calculate the half-life.

(Given $\log 2 = 0.3010$ $\log 4 = 0.6021$)

21. Write one difference between each of the following:

(i) Multimolecular colloid and Macromolecular colloid
(ii) Sol and Gel
(iii) O/W emulsion and W/O emulsion

22. (i) What type of isomerism is shown by the complex $[\text{Co(en)}_3]Cl_3$?
(ii) Write the hybridization and magnetic character $[\text{Co(C}_2\text{O}_4)_3\text{Cl}_3]$ (At. No. of Co = 27)
(iv) Write IUPAC name of the following Complex $[\text{Co(NH}_3)_3]Cl_3$

23. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $\text{AgNO}_3$ for 15 minutes.

(Given: Molar mass of Ag = 108 g mol$^{-1}$ 1F = 96500 C mol$^{-1}$)

24. 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.
Given: (Molar mass of sucrose = 342 g mol\(^{-1}\))
(Molar mass of glucose = 180 g mol\(^{-1}\))

25. (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 Al = 27 g mol\(^{-1}\))

(b) Give reasons:

(i) In stoichiometric defects, NaCl 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

26. (a) Write the product(s) in the following reactions:

(i) \[
\text{OH} \quad \text{COOH} \quad \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} \quad \text{H}^+ \]

(ii) \[
\text{CH}_3 \quad \text{CH}_3 - \text{CH} - \text{O} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{H}} \]

(iii) \[
\text{CH}_3 - \text{CH} = \text{CH}_2 - \text{OH} \xrightarrow{\text{PCC}}
\]

(b) Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol
(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:

$$
\text{CH}_3 - \text{CH}_2 - \text{OH} \quad \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} \quad \text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O} \\
\phantom{\text{CH}_3 - \text{CH}_2 - \text{OH}} \quad \text{H}
$$

27. (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.