DIRECTORATE OF EDUCATION
GNCT of Delhi, Delhi Government

SUPPORT MATERIAL
(2020-2021)
Class : XII

CHEMISTRY

Under the Guidance of

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MANISHA SAXENA
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सत्यमेव जयते

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MESSAGE

The importance of adequate practice during examinations can never be overemphasized. I am happy that support material for classes IX to XII has been developed by the Examination Branch of Directorate of Education. This material is the result of immense hard work, co-ordination and cooperation of teachers and group leaders of various schools. The purpose of the support material is to impart ample practice to the students for preparation of examinations. It will enable the students to think analytically & rationally, and test their own capabilities and level of preparation.

The material is based on latest syllabus prepared by the NCERT and adopted by the CBSE for the academic session 2020-21 and covers different levels of difficulty. I expect that Heads of Schools and Teachers will enable and motivate students to utilize this material during zero periods, extra classes and regular classes best to their advantage.

I would like to compliment the team of Examination Branch for their diligent efforts of which made it possible to accomplish this work in time. I also take this opportunity to convey my best wishes to all the students for success in their endeavours.

(Manisha Saxena)

BINAY BHUSHAN, IAS

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Dear Students,

Directorate of Education is committed to providing qualitative and best education to all its students. The Directorate is continuously engaged in the endeavor to make available the best study material for uplifting the standard of its students and schools.

Every year, the expert faculty of Directorate reviews and updates Support Material. The expert faculty of different subjects incorporates the changes in the material as per the latest amendments made by CBSE to make its students familiar with new approaches and methods so that students do well in the examination.

The book in your hand is the outcome of continuous and consistent efforts of senior teachers of the Directorate. They have prepared and developed this material especially for you. A huge amount of money and time has been spent on it in order to make you updated for 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.

BINAY BHUSHAN
DIRECTOR (EDUCATION)

Dr. (Mrs.) Saroj Bala Sain
Addl. Director of Education
(School / Exam / EVGB/IEB/ VOC.)

सत्यमेव जयते

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Date : 03-10-2019

I am very much pleased to forward the Support Material for classes IX to XII. Every year, the Support Material of most of the subjects is updated/revised as per the most recent changes made by CBSE. The team of subject experts, officers of Exam Branch, members of Core Academic Unit and teachers from various schools of Directorate has made it possible to make available unsurpassed material to students.

Consistence use of Support Material by the students and teachers will make the year long journey seamless and enjoyable. The main purpose to provide the Support Material for the students of government schools of Directorate is not only to help them to avoid purchasing of expensive material available in the market but also to keep them updated and well prepared for exam. The Support Material has always been a ready to use material, which is matchless and most appropriate.

I would like to congratulate all the Team Members for their tireless, unremitting and valuable contributions and wish all the best to teachers and students.

S. Sain

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

DIRECTORATE OF EDUCATION
Govt. of NCT, Delhi

SUPPORT MATERIAL
(2020-2021)

CHEMISTRY
Class : XII
(English Medium)

NOT FOR SALE

PUBLISHED BY : DELHI BUREAU OF TEXTBOOKS

CHEMISTRY
CLASS-XII

LIST OF MEMBERS WHO REVIEWED AND REVISED SUPPORT MATERIAL OF CHEMISTRY AS PER LATEST SYLLABUS PRESCRIBED BY CBSE FOR CLASS XII (2020-21)

S. No.	Name	Designation
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भारत का संविधान

भाग 4क

नागरिकों के मूल कर्तव्य

अनुच्छेद 51क

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

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

CONSTITUTION OF INDIA

Part IV A (Article 51 A)

Fundamental Duties

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

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

भारत का संविधान

उद्देशिका

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

सामाजिक, आर्थिक और राजनैतिक **न्याय,**

विचार, अभिव्यक्ति, विश्वास, धर्म

और उपासना की **स्वतंत्रता,**

प्रतिष्ठा और अवसर की समता

प्राप्त करने के लिए,

तथा उन **सब में,**

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

और अखंडता) सुनिश्चित करने वाली बंधुता

बढ़ाने के लिए

हम दृढ़संकल्प होकर इस संविधान को आत्मार्पित करते हैं।

THE CONSTITUTION OF INDIA

PREAMBLE

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

JUSTICE, social, economic and political,

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

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

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

WE DO HEREBY GIVE TO OURSELVES THIS CONSTITUTION.

CONTENTS

Chemistry (Code No. 043) Question Paper Design

Class XII (2020-21)

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

S. No.	Typology of Questions	Very Short Answer-Objective type (VSA) (1 Mark)	Short Answer-I (SA) (2Marks)	Long Answer-I (LA-I) (3 marks)	Long Answer- II (LA-II) (5 marks)	Total Mark s	% Weigh-tage
1	**Remembering** : Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers.	2	1	1	-	7	10%
2	**Understanding** : Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	6	2	2	1	21	30%
3	**Applying**: Solve problems to new situations by applying acquired knowledge, facts, techniques and rules in a different way.	6	2	2	1	21	30%
4	**Analysing** : Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations.	6	1	2	-	14	20%

	Evaluating: Present and defend opinions by making judgements about information, validity of ideas or quality of work based on a set of criteria. **Creating**: Compile information together in a different way by combining elements in a new pattern or proposing alternative solutions.	-	1	-	1	7	10%
	TOTAL	**20x1=20**	**7x2=14**	**7x3=21**	**3x5=15**	**70(37)**	**100%**

QUESTION WISE BREAK UP

Type of Question	Mark per Question	Total No. of Questions	Total Marks
VSA/ Objective	1	20	20
SA	2	7	14
LA-I	3	7	21
LA-II	5	3	15
Total		37	70

1. No chapter wise weightage.*Care to be taken to cover all the chapters.*
2. *Suitable internal variations may be made for generating various templates keeping the overall weightage to different form of questions and typology of questions same.*

Choice(s):

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

UNIT 1

SOLUTIONS

Points to Remember

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

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

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

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

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

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

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

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

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

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

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

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

Some Important Formulae

1. Mole fraction (X)

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

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

$$X_A + X_B = 1$$

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

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

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

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

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

$$p_A = p_A^0 X_A$$

$$p_B = p_B^0 X_B$$

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

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

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

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

7. Elevation in boiling point (ΔT_b) :

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

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

K_b = molal boiling point elevation constant

m = molality of solution

T_b = Boiling point of solution

T_b^0 = Boiling point of solvent

8. Depression in freezing point (ΔT_f) :

$\Delta T_f = i.K_f m$

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

K_f = molal freezing point depression constant

m = molality of solution

T_f^0 = Freezing point of solvent

T_f = Freezing point of solution

9. Osmotic pressure (π) of a solution :

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

where π = osmotic pressure in bar or atm

V = volume in litres

i = van't Hoff factor

C = molar concentration in moles per litres

n = number of moles of solute

T = Temperature on Kelvin scale

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

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

10. Van't Hoff factor (i)

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

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

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

$i > 1$ For dissociation of solute

$i < 1$ For association of solute

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

MULTIPLE CHOICE QUESTIONS

1. **The molality of 98% H_2SO_4 (density = 1.8 g/mL) by weight is:**

   (a) 6 m (b) 18 m

   (c) 10 m (d) 4 m

2. **Which of the following does not show positive deviation from Raoult's law?**

   (a) benzene + chlorofor (b) benzene + acetone

   (c) benzene + ethanol (d) benzene + CCl_4

3. **Which solution will have least vapour pressure?**

   (a) 0.1 M $BaCl_2$ (b) 0.1 M Uxa

   (c) 0.1 M Na_2SO_4 (d) 0.1 M Na_3PO_4

4. **Which condition is not satisfied by an ideal solution?**

   (a) $\Delta H_{mix} = 0$ (b) $\Delta V_{mix} = 0$

   (c) $\Delta P_{mix} = 0$ (d) $\Delta S_{mix} = 0$

5. **Azeotrope mixture are:**

   (a) mixture of two solids

   (b) those will boil at different temperature

   (c) those which can be fractionally distilled

   (d) constant boiling mixtures

6. **If K_f value of H_2O is 1.86. The value of ΔT_f for 0.1 m solution of non-volatile solute is**

   (a) 18.6 (b) 0.186

   (c) 1.86 (d) 0.0186

7. **Solute when dissolve in water**

   (a) increases the vapour pressure of water

   (b) decreases the boiling point of water

   (c) decrease the freezing point of water

   (d) All of the above

8. **The plant cell will shrink when placed in:**

   (a) water (b) A hypotonic solution

   (c) a hypertonic solution (d) an siotonic solution

9. **The freezing point of 11% aquous solution of calcium nitrate will be:**

   (a) 0°C (b) above 0°C

   (c) 1°C (d) below 0°C

10. The Van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is:

(a) 91.3% (b) 87%

(c) 100% (d) 74%

11. Which of the following solutions would have the highest osmotic pressure:

(a) $\frac{M}{10}$ NaCl (b) $\frac{M}{10}$ Urea

(c) $\frac{M}{10}$ $BaCl_2$ (d) $\frac{M}{10}$ Glucose

12. 0.5 M aquous solution of Glucose is isotonic with:

(a) 0.5 M KCl solution (b) 0.5 M $CaCl_2$ solution

(c) 0.5 M Urea solution (d) 1 M solution of sucrose

13. Which of the following is true for Henry's constant

(a) It decreases with temperature (b) It increases with temperature

(c) Independent on temperature (d) It do not depend on nature of gases.

14. Which one is the best colligative property for determination of molecular mass of polymer?

(a) osmotic pressure (b) elevation in boiling point

(c) depression in freezing point (d) osmosis

15. Which of the following do not depend on temperature?

(a) % W/V (weight/volume) (b) molality

(c) molarity (d) normality

16. Henry's law constant K of CO_2 in water at 25°C is 3×10^{-2} mol/L atm^{-1}. Calculation the mass of CO_2 present in 100 L of soft drink bottled with a partial pressure of CO_2 of 4 atm at the same temperatrue.

(a) 5.28 g (b) 12.0 g

(c) 428 g (d) 528 g

17. Mixing of HNO_3 and HCl is reaction:

(a) endothermic reaction (b) exothermic reaction

(c) both exothermic and endothermic (d) depend on entropy of reaction

18. The most likely on ideal solution is:

(a) $NaCl—H_2O$ (b) $C_2H_5OH—C_6H_6$

(c) $C_7H_{16}—H_2O$ (d) $C_7H_{16}—C_8H_{18}$

19. Van't Hoff factor for a dilute solution of a $K_2[HgI4]$ is:

(a) 2 (b) 1

(c) 3 (d) zero

20. Benzoic acid dissolved in benzene shows a molecular weight of:

(a) 122
(b) 61
(c) 244
(d) 366

21. 6% (W/V) solution of urea will be isotonic with:

(a) 18% (W/V) solution of glucose
(b) 0.5 M solution of NaCl
(c) 1 M solution of CH_3COOH
(d) 6% (W/V) solution of sucrose.

22. Solution showing (+) ve deviation from Raoult's law include:

(a) acetone + CS_2
(b) acetone + C_2H_5OH
(c) acetone + Benzene
(d) acetone + aniline

Fill in the blanks type:

23. The property which depends on number of particles of solute is called ....

24. Azeotrope mixture cannot be separate by ....

25. Match the column and choose correct option

Vant'Hoff factor	**Behaviour of compound**
(A) i = 1	P. Impossible
(B) i > 1	Q. Association is the solution
(C) i < 1	R. Dissociation in the solution
(D) i = 0	S. No dissociation or association

(a) A–S, B–R, C–P, D–Q
(b) A–R, B–S, C–Q, D–P
(c) A–S, B–P, C–R, D–Q
(d) A–S, B–R, C–Q, D–P

Assertion Reason Type

26. Statement 1: Azeotropemixture are formed by only non-ideal solution

Statement 2: Azeotrope mixture can't be separated by fractional distillation.

ANSWERS

1. (b) **2.** (a) **3.** (d) **4.** (d) **5.** (d) **6.** (b) **7.** (d) **8.** (c) **9.** (d) **10.** (b)
11. (c) **12.** (c) **13.** (d) **14.** (a) **15.** (b) **16.** (d) **17.** (b) **18.** (d) **19.** (c) **20.** (c)
21. (a, b, c) **22.** (a, b) **23.** Colligative property **24.** Fractional distillation
25. (d) **26.** (b)

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

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

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

i = normal molecular mass/observed molecular mass

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

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

Ans. 5 and 3

Q. 3. Why the molecular mass becomes abnormal ?

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

Q. 4. What role does the molecular interaction play in the solution of alcohol and water ?

Ans. Positive deviation from ideal behaviour.

Q. 5. 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. 6. Why NaCl is used to clear snow from roads ?

Ans. It lowers freezing point of water.

Q. 7. Why the boiling point of solution is higher than pure liquid ?

Ans. Due to lowering in vapour pressure.

Q. 8. 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.9. Define azeotrope. Give an example of maximum boiling azeotrope.

Q.10. Calculate the volume of 75% of H_2SO_4 by weight (d = 1.8 gm/ml) required to prepare 1 L of 0.2 M solution.

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

$$M_1V_1 = M_2V_2$$

$$= 14.5 \text{ ml}$$

Q.11. Why water cannot be completely separated from aqueous solution of ethyl alcohol ?

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

Q.12. Why anhydrous salts like NaCl or $CaCl_2$ are used to clear snow from roads on hills ?

Hint : They depress freezing point of water.

Q.13. What is the effect on boiling and freezing point of a solution on addition of NaCl ?

Hint : Boiling point increases and freezing point decreases.

Q.14. Why osmotic pressure is considered as colligative property ?

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

Q.15. Liquid A and B on mixing produce a warm solution. Which type of deviation does this solution show ?

Hint : – ve deviations

Q.16. Give an example of a compound in which hydrogen bonding results in the formation of a dimer.

Hint : Carboxylic acids or other example

Q.17. 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. Out of the following three solutions, which has the highest freezing point and why ?

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

Q. 2. Which of the following solutions have highest boiling point and why ?

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

Q. 3. 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. 4. 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. 5. 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. 6. How many grams of KCl should be added to 1 kg of water to lower its freezing point to – 8.0ºC ? (K_f = 1.86 K kg/mol)

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

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

$$m = \frac{\Delta T_f}{i K_f}$$

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

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

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

Q. 7 With the help of diagram, show the elevation in boiling point colligative properties ?

Q. 8. What do you mean by colligative properties ? Which colligative property is used to determine molar mass of polymer and why ?

Q.9. Define reverse osmosis. Write its one use.

Ans. Desalination of water.

Q.10. Why does an azeotropic mixture distills without any change in composition ?

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

Q.11. Under what condition Van't Hoff factor is :

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

Q.12. 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.13. Why is it advised to add ethylene glycol to water in a car radiator in hill station ?

Hint : Anti-freeze.

Q.14. Calculate the molarity of pure water (d = 1 g mL^{-1}).

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

$$\begin{aligned}\text{Mass of 1000 ml of water} &= V \times d \\ &= 1000 \text{ mL} \times 1 \text{ gm}^{-1} \\ &= 1000 \text{ g}\end{aligned}$$

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

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

So, molarity = 55.55M

Q.15. Define Henry's law. Give their two application.

Q.16. The dissolution of ammonium chloride in water is endothermic process. What is the effect of temperature on its solubility ?

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

Q.17. Two liquids A and B boil at 145ºC and 190ºC respectively. Which of them has higher vapour pressure at 80ºC ?

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

Q.18. 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.19. 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.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

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

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

$$\pi = iCRT$$

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

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

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

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

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

$$= 3.418\text{g}$$

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

Ans. If K_2SO_4 is completely dissociated,

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

$$i = 3$$

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

$$\pi = iCRT$$

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

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

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

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

Ans. K_{sp} of CuS = 6×10^{-16}

If S is the solubility, then

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

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

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

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

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

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

Highest molarity = 2.45×10^{-8} M

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

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

(c) $NaClO_4$ and water

Ans. (a) Vander Waals interaction

(b) Vander Waals interaction

(c) Ion-dipole interaction

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

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

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

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

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

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

Ans. Mass of KOH = 30 g

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

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

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

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

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

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

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

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

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

$$= 17.95\text{m}$$

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

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

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

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

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

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

Mass of substance W_B = 6.21 g

Mass of CHCl3 W_A = 24.0 g

K_B = 3.63 ºC/m

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

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

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

Ans. 37.73 g

Q.10. 18 g of glucose ($C_6H_{12}O_6$) (molar mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil ? (Kb for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.1 K)

Ans. 373.202 K

LONG ANSWER TYPE QUESTIONS (5 Marks)

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

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

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

(b)

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

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

Let the molecular formula of sulphur = S_x

Atomic mass of sulphur = 32

Molecular mass = $32 \times x$

$32x = 253$

$x = 7.91 \approx 8$

Molecular formula of sulphur = S_8

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

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

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

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

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

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

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

Temp $= 25 + 273 = 298$ K

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

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

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

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

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

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

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

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

Observed freezing point = 0 – (– 0.320) = 0.320°C

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

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

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

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

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

$i > 1$ when solute is dissociated.

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

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

MgBr$_2$ ionizes as $MgBr_2 \rightarrow Mg^{2+} + 2Br^-$

$$i = 3$$

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

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

$$= 1.59$$

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

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

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

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

$$i = 5$$

(b)

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

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

$$i = 2$$

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

$$= 1.05$$

Boiling point of solution = 100 + 1.05

= 101.05°C

✧✧

UNIT 2

ELECTROCHEMISTRY CONCEPTS

Points to Remember

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

A cell is of two types :

I. Galvanic cell

II. Electrolytic cell

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

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

1. Conductivity (k) :

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

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

2. Relation between k and Λ_m

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

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

Kohlrausch's law :

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

$$\Lambda^\circ_m = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$$

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

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

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

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

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

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

Dry cell :

At anode (Oxidation)

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

At cathode (Reduction)

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

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

Mercury cell :

At anode (Oxidation)

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

At cathode (Reduction)

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

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

Lead storage cell

At anode (Oxidation)

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

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

At cathode (Reduction)

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

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

Overall

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

3. Nernst Equation for electrode reaction :

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

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

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

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

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

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

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

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

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

Corrosion of metals is an electrochemical phenomenon.

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

At anode (Oxidation) :

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

At cathode (Reduction) :

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

Atmospheric oxidation :

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

MULTIPLE CHOICE QUESTIONS (1 Mark)

1. When a lead storage battery is discharged:

(a) SO_2 is evolved

(b) lead is formed

(c) H_2SO_4 is consumed

(d) $PbSO_4$ is consumed

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

(a) 9.65×10^4 C
(b) 93000 C
(c) 1.93×10^5C
(d) 19.3×10^2C

3. KCl is used in salt bridge because:

(a) It forms a good jelly with agar-agar
(b) It is a strong electrolyte
(c) It is a good conductor of electricity
(d) Migration factor of K^+ and Cl^- ions are almost equal

4. The nature of curve of E° cell against log K_C is:

(a) a straight line
(b) parabola
(c) a hyperbola
(d) an elliptical curve

5. For a spontaneous reaction the ΔG, equilibrium constant (K) and $E°_{cell}$ will be respectively.

(a) – ve, < 1, – ve
(b) – ve, > 1, – ve
(c) – ve, > 1, + ve
(d) + ve, > 1, – ve

6. Determine the value of $E°_{cell}$ for the following reaction, $cu^{2+} + Sn^{+2} \longrightarrow Cu + Sn^{+4}$, equilibrium constant is 10^6.

(a) 0.1773
(b) .01773
(c) 0.2153
(d) 1.773

7. Which is the best reducing agent?

(a) F^-
(b) Cl^-
(c) Br^-
(d) I^-

8. If a salt bridge is removed between the half cells, the voltage:

(a) drops to zero
(b) does not change
(c) increase gradually
(d) increases rapidly

9. Faraday's law of electrolysis are related to the:

(a) Atomic number of the cation
(b) atomic number of the anion
(c) equivalent weight of the electrolyte
(d) speed of the cation

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

(a) Ionisation
(b) neutralisation
(c) electrolysis
(d) hydrolysis

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

(a) 1 F (b) 3 F

(c) 5 F (d) 4 F

12. The value of Λ^o_m for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 Ohm^{-1} cm^2 mol^{-1} respectively. Calculate Λ^o_m for NH_4OH solution.

(a) 215.5 (b) 251.5

(c) 244.7 (d) 351.5

13. A current of 9.65 amp flowing for 10 minutes deposits 3.0 g of a metal. The equivalent wt. of the metal is:

(a) 10 g (b) 30 g

(c) 50 g (d) 96.5 g

14. In a Golvenic cell the electrical work done is equal to:

(a) free energy change (b) mechanical work done

(c) thermodynamic work done (d) all of the above

15. When lead storage battery is charged it is:

(a) an electrolyte cell (b) a galvenic cell

(c) a daniel cell (d) a and b both

16. In a galvenic cell the direction of current is:

(a) anode to cathode (b) cathode to anode

(c) Zn rod to Cu rod

(d) Depend on concentration of $ZnSO_4$ and $CuSO_4$

17. Which metal does not give the following reaction M + water $\longrightarrow$ oxide or hydroxide + H_2

(a) Fe (b) Na

(c) Hg (d) Ag

18. Electrolysis of aq. $CuSO_4$ produces:

(a) an increase in pH (b) a decrease in pH

(c) either decrease or increase (d) H_2SO_4 in the solution

19. Zn cannot displace following ions from their aquous solution:

(a) Al^{+3} (b) Cu^{2+}

(c) Fe^{2+} (d) Na^+

20. Which one is not a secondary battery?

(a) laclanche cell (b) Ni-Cd cell

(c) Mercury cell (d) Daniel cell

21. Which of the following decrease with increase in concentration?

(a) conductance (b) specifci conductance

(c) Molar conductance (d) Conductivity

Fill in the blanks type question:

22. To deposite 2 mol of Ca from $CaCl_2$ .... electricity is required.

23. .... gives a constant voltage throughout its life.

24. Match the column and choose correct option:

(A) Conductance P. m^{-1}
(B) Conductivity Q. $5\ cm^{-1}$
(C) Molar conductance R. Siemen
(D) Cell constant S. $5\ cm^2\ mol^{-1}$

(a) A–R, B–Q, C–S, D–P (b) A–R, B–S, C–Q, D–P

(c) A–R, B–Q, C–P, D–S (d) A–R, B–P, C–Q, D–S

25. (A) $MnO_4^- \longrightarrow Mn^{+2}$ (1 mol) P. Required 1F
(B) $CuSO_4 \longrightarrow Cu$ (1 mol) Q. Required 5 F
(C) $Al_2O_3 \longrightarrow Al$ (1 mol) R. Required 3 F
(D) $NaCl \longrightarrow Na$ (1 mol) S. Required 2 F

(a) A–Q, B–P, C–S, D–R (b) A–P, B–Q, C–S, D–R

(c) A–Q, B–S, C–P, D–R (d) A–Q, B–S, C–R, D–P

Assertion-Reason type

26. Statement 1 : Galvanised iron does not rust.

Statement 2 : Zn has more (–) ve electrode potential than Fe.

27. Statement 1 : Conductivity decreases with dilution.

Statement 2 : Number of ions per unit volume decreases on dilution.

ANSWERS

1. (c) **2.** (c) **3.** (d) **4.** (a) **5.** (c) **6.** (a) **7.** (d) **8.** (a) **9.** (c) **10.** (c)
11. (b) **12.** (b) **13.** (c) **14.** (a) **15.** (a) **16.** (b) **17.** (c, d) **18.** (b, d)
19. (a, d) **20.** (a, c, d) **21.** (a, c) **22.** 4 F
23. Mercury cell **24.** (a) **25.** (d) **26.** (a) **27.** (a)

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

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

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

Q. 2. 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

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

Ans. Temperature increases, electrical conductance decreases.

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

Ans. Temperature increases, electrical conductance increases.

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

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

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

Ans. A > D > B > C

Q. 7. Why does a dry cell become dead even if it has not been used for a long time ?

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

Q.8. Why Na cannot be obtained by the electrolysis of aqueous NaCl solution ?

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

Q.9. What is the use of platinum foil in the hydrogen electrode ?

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

Q.10. Why $\Lambda_m{}^o$ for CH_3COOH cannot be determined experimentally ?

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

Q.11. 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.12. 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.13. What is the role of $ZnCl_2$ in a dry cell ?

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

Q.14. 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.15. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methane and methanol.

Q.16. 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.17. Which reference electrode is used to measure the electrode potential of other electrodes.

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

Q.18. 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.19. Define corrosion. What is the chemical formula of rust ?

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

Q.20. What is the electrolyte used in a dry cell ?

Ans. A paste of NH_4Cl.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

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

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

Ans. Nernst equation is :

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

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

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

(b) By increasing the temperature.

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

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

[Given : E^θ_{cell} = 3.17 V]

Ans. $n = 2$

The Nernst equation for the cell is :

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

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

$$= 3.17 - 0.21 = 2.96V$$

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

Ans. $\Lambda^\circ_m (H_2O) = \Lambda^\circ_{m\ H^+} + \Lambda^\circ_{m\ OH^-}$

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

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

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

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

27 gram of Al require electricity = 3F

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

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

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

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

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

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

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

$$Cl^- \rightarrow ½Cl_2 + 1e^-$$

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

Q. 6. Calculate $\overset{\circ}{\Lambda}_m$ for $CaCl_2$ and $MgSO_4$ from the following data :

$\overset{\circ}{\Lambda}_{m\,(Ca^{2+})}$ = 119.0, Mg^{2+} = 106.0, Cl^- = 76.3 and SO_4^{2-} = 160.05 $cm^2\ mol^{-1}$

Ans.
$$\overset{\circ}{\Lambda}_{m(CaCl_2)} = \overset{\circ}{\Lambda}_{m(Ca^{2+})} + 2\overset{\circ}{\Lambda}_{m(Cl^-)}$$
$$= 119 + (2 \times 76.3) = 271.6\ S\ cm^2\ mol^{-1}$$
$$\overset{\circ}{\Lambda}_{m(MgSO_4)} = \overset{\circ}{\Lambda}_{m(Mg^{2+})} + 2\overset{\circ}{\Lambda}_{m(SO_4^{2-})}$$
$$= 106 + 160 = 266\ S\ cm^2\ mol^{-1}$$

Q. 7. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. $H^+ + e^- \rightarrow ½H_2\ n = 1$

$$E = E'' - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$
$$E = 0 - \frac{0.0591}{1} \times pH$$
$$E = -\,0.0591 \times 10\ v$$
$$E = -\,0.591/V$$

Q. 8. If a current of 0.5 amp flows through a metallic wire for 2 hours, how many electrons would flow through the wire ?

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

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

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

Q.9. How much electricity is required in Coulomb for the oxidation of 1 mole of FeO to Fe_2O_3 ?

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

So, 1F = 1 × 96500 C = 96500 C

Q.10. The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm^{-1}. Calculate molar conductivity.

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

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

Q.11. 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.12. The resistance of conductivity cell containing 0.001M KCl solution at 298K is 1500Ω. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3} S cm^{-1}.

Ans. Cell constant = Conductivity × Resistance

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

Q.13. 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.14. Explain Kohlrausch's law of independent migration of ions.

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

$$\Lambda^{\infty}_{m(Na_2SO_4)} = 2\Lambda^{\circ}_{m(Na^+)} + \Lambda^{\infty}_{m(SO_4^{2-})}$$

Q.15. The standard reduction potential for the Zn^{2+} (aq)/Zn (s) half cell is – 0.76V. Write the reactions occurring at the electrodes when coupled with standard hydrogen electrode (SHE).

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

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

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

Q.16. Calculate the electrode potential of a copper wire dipped in 0.1M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 Volt.

Ans. The electrode reaction written as reduction potential is

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

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

Q.17. Two metals A and B have reduction potential values – 0.76 V and + 0.34 V respectively. Which of these will liberate H_2 from dil. H_2SO_4 ?

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

Q.18. How does conc. of sulphuric acid change in lead storage battery when current is drawn from it ?

Ans. Concentration of sulphuric acid decreases.

Q.19. What type of a battery is lead storage cell ? Write the anode and cathode reaction and overall reaction occurring in a lead storage battery during discharging and recharging of cell.

Ans. It is a secondary cell.

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

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

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

Q.20. Why is alternating current used for measuring resistance of an electrolytic solution ?

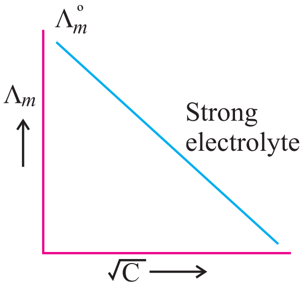
Ans. The alternating current is used to prevent electrolysis so that the concentration of ions in the solution remains constant.

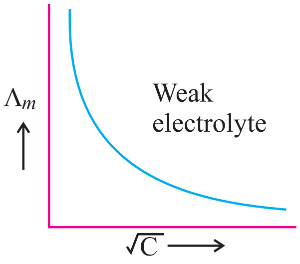
Q.21. E^θ values of MnO_4^-, Ce^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidizing agent.

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

Q.22. Draw a graph between $\overset{\circ}{\Lambda}_m$ and $\sqrt{C}$ for strong and weak electrolyte.

Ans.





Q.23. The conductivity of 0.02M solution of NaCl is 2.6 × 10^{-2} S cm^{-1}. What is its molar conductivity ?

Ans.

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

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

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

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

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

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

Q.24. Give products of electrolysis of an aqueous solution of $AgNO_3$ with silver electrode.

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

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

SHORT ANSWER-II TYPE QUESTIONS

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

Ans.

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

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

$$Q = I \times t$$

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

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

2F amount of electricity deposit copper = 63.5 g

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

$$= 0.296 \text{ g}$$

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

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

takes place. Further show :

(a) Which of the electrode is negatively charged ?

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

(c) Individual reaction at each electrode.

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

(a) Zn electrode (anode)

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

(c) At anode :

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

At cathode :

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

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

Ans.

$$\begin{aligned} \text{Cell constant} &= k \times R \\ &= 0.146 \times 10^{-3} \times 1500 \\ &= 0.219\ \text{cm}^{-1} \end{aligned}$$

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

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

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

Ans. (a) At anode (Oxidation)

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

At cathode (Reduction)

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

(b) At anode (Oxidation)

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

$$Cl + Cl \rightarrow Cl_2$$

At cathode (Reduction)

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

Q. 5. Determine the values of equilibrium constant K_c and ΔG^{θ} for the following reaction :

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

Ans.

$$\Delta G^{\theta} = -\,nFE^{\theta}_{cell}$$

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

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

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

$$= -202.650 \text{ kJ}$$

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

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

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

Q. 6. The K_{sp} for AgCl at 298 K is 1.0×10^{-10}. Calculate the electrode potential for Ag^+/Ag electrode immersed in 1.0M KCl solution. Given $E^\theta_{Ag^+/Ag} = 0.80$ V.

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

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

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

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

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

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

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

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

Q. 7. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500ºC. The free energy change for the decomposition reaction :

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

Ans.

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

$$n = \frac{6 \times 2}{3} = 4e^-$$

$$\Delta G = -nFE$$

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

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

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

Minimum potential difference needed to reduce Al_2O_3 = – 2.487 V.

Q. 8. 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. $$w = z \times i \times t$$

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

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

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

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

Q.9. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 amp for 20 minutes. What mass of the nickel will be deposited at the cathode ? (Ni = 58.7 u)

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

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

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

Q.10. The cell in which the following reaction occurs :

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

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

Ans. $$n = 2$$

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

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

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

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

Q.11. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given Λ^o (H^+) = 349.6 S cm^2 mol^{-1}, Λ^o ($HCOO^-$) = 54.6 S cm^2 mol^{-1}.

Ans. $\Lambda^o_m (HCOOH) = \Lambda^o_m (H^+) + \Lambda^o_m (HCOO^-)$

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

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

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

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

Initial conc.	C mol L^{-1}	0	0
At equil.	C(1 − α)	Cα	Cα

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

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

Q.12. Calculate the standard cell potentials of galvanic cells in which the following reaction take place :

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

Also calculate ΔGº and equilibrium constant of the reaction.

Ans. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

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

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

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

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

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

Or $\log K_c = 34.5014$

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

Q.13. Calculate the potential of the following cell Sn^{4+} (1.5 M) + Zn → Sn^{2+} (0.5 M) + Zn^{2+} (2M).

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

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

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

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

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

$$= 0.895 \text{ V}$$

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

Q.14. E° (Cu^{2+}/Cu) and E° (Ag^+/Ag) is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is +ve. If the concentration of Cu2+ is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag^+.

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

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

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

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

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

Q.15. Calculate the potential of the cell at 298 K :

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

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

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

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

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

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

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

Q.16. The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Ans. Diameter = 1 cm, radius = 0.5 cm

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

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

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

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

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

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

Q.17. Conductivity of saturated solution of $BaSO_4$ at 315 K is 3.648×10^{-6} ohm^{-1} cm^{-1} and that of water is 1.25×10^{-6} ohm^{-1} cm^{-1}. Ionic conductance of Ba^{2+} and SO_4^{2-} are 110 and 136.6 ohm^{-1} cm^2 mol^{-1} respectively. Calculate the solubility of $BaSO_4$ in g/L.

Ans.

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

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

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

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

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

LONG ANSWER TYPE QUESTIONS (5 Marks)

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

Ans.

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

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

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

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

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241\times\left(8.39\times10^{-2}\right)^3}{1-8.39\times10^{-2}}$$

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

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

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

108 g of silver is deposited by 96500 C.

$$1.45 \text{ g silver is deposited by} = \frac{96500\times1.45}{108}$$

$$= 1295.6 \text{ C}$$

$$Q = I \times t$$

$$1295.6 = 1.5 \times t$$

$$t = \frac{12956}{1.5} = 863 \text{ s}$$

In cell A, the electrode reaction is

5.6

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

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

$$\text{1295.6 of electricity deposit Zn} = \frac{65.3\times1295.6}{2\times96500}$$

$$= 0.438 \text{ g}$$

In cell C, the electrode reaction is

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

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

$$\text{1295.6 of electricity deposit Cu} = \frac{63.5\times1295.6}{2\times96500}$$

$$= 0.426 \text{ g}$$

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

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

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

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

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

$$\Lambda^o \, CH_3COO^- + \Lambda^o \, H^+ = \Lambda^o \, CH_3COO^- + \Lambda^o \, Na^+ + \Lambda^o \, H^+$$

$$+ \Lambda^o \, Cl^- - \Lambda^o \, Na^+ - \Lambda^o \, Cl^- \qquad \text{...(i)}$$

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

(c)

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

$$= 91.0 + 425.9 - 126.4$$

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

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

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

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

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

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

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

(b)

$$Cu^+ + e^- \rightarrow Cu$$

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

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

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

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

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

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

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

UNIT 3

CHEMICAL KINETICS

CONCEPT

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

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

Types of Rate of Reaction :

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

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

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

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

Factors affecting Rate of Reaction

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

Rate constant (k) : It is equal to the rate of reaction when 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, $aA + bB \rightarrow cC + dD$

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

where powers p and q are determined experimentally.

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

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

For above case, Order = P + Q

Orders of reaction is determined experimentally.

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

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

Activation energy = Threshold energy – Kinetic energy

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

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

Arhenius Equation :

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

where, K = Rate constant

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

E_a = Activation energy

R = Rate constant

T = Temperature

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

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

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

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

Where R = 8.314 JM^{-1} mol^{-1}

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

1. Integrated rate law equation for zero order reaction is given as below :

(a) $k=\dfrac{[R]_0-[R]_t}{t}$

Where k is rate constant and $[R]_0$ is initial molar concentration.

(b) $t_{1/2}=\dfrac{[R]_o}{2k}$, $t_{1/2}$ is half-life period of zero order reaction.

2. Integrated rate law equation for first order reaction :

(a) $k=\dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]_t}$

where k is rate constant, $[R]_0$ is initial molar concentration and [R], is final concentration at time 't'.

(b) Half-life period ($t_{1/2}$) for first order reaction :

$$t_{½}=\frac{0.693}{k}$$

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

$$CH_3COOC_2H_5+H_2O\rightarrow CH_3COOH+C_2H_5OH$$

$$\text{Rate}=k[CH_3COOC_2H_5]^1$$

$$\boxed{\text{Order} = 1}$$

MULTIPLE CHOICE QUESTIONS (1 Mark)

1. **The half life period of a first order reaction is 100° seconds. Its rate constant is:**

(a) 0.693 sec^{-1} (b) 6.93×10^{-3} sec^{-1}

(c) 6.93×10^{-2} sec^{-1} (d) None of these

2. **In Arrehenius equation if a graph is plotted between 10 gK and 1/T, the slope of the curve will be:**

(a) $\dfrac{-E_a}{R}$ (b) $\dfrac{-E_a}{2.303R}$

(c) $\dfrac{E_a}{R}$ (d) $\dfrac{E_a}{2.303R}$

3. The rate low for a reaction $2C + D \longrightarrow A + E$ is

$$\frac{-d[D]}{dt} = K[C]^2[D]$$

if C is present in large excess, the order of the reaction will be:

(a) zero (b) first
(c) second (d) third

4. What is the activation energy for the reverse of this reaction?

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$$

Data for the given reaction is $\Delta H = 54$ KJ/mol and $\varepsilon_a = 57.2$ KJ.

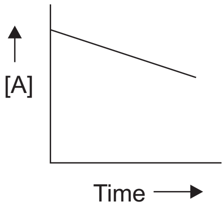
(a) – 54 KJ (b) 3.2 KJ
(c) 60.2 KJ (d) 111.2 KJ

5. The rate constant of a reaction becomes equal to the pre exponential factor when:

(a) the absolute temperature is zero
(b) the activation energy is infinity
(c) the absolute temperature is infinity
(d) the activation energy is zero

6. The following graph show that the reaction is:

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



7. A second order reaction between A and B is elementary reaction:

$$A + B \longrightarrow \text{Product}$$

rate law expression of this reaction will be:

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

8. The order and molecularity of the chain reaction, $H_{2(g)} + Cl_{2(g)} \xrightarrow{h\nu} HCl$

(a) 2, 0 (b) 0, 2
(c) 1, 1 (d) 3, 0

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

(a) $2H_2O_2 \longrightarrow 2H_2O + O_2$
(b) $2O_3 \longrightarrow 3O_2$
(c) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
(d) $CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH + C_2H_5OH$

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

(a) Increase in the number of collisions

(b) Increase in the number of activated molecules

(c) Lowering of activation energy

(d) Shortening of the mean free path.

11. For a creactionj, the following data were obtained:

Concentration (mol/L)	0.1	0.05	0.025	0.0125
Half life in (sec)	30	29.9	30.1	30

the order of reaction is:

(a) 2 (b) 1

(c) 0 (d) fractional

12. For the formation of SO_3 in the following reaction, it is given that

$2SO_2 + O_2 \longrightarrow 2SO_3$ E_a = Activation energy

$SO_2 + 1/2\ O_2 \longrightarrow SO_3$ E'_a = Activation energy

(a) $E_a > E^1_a$ (b) $E_a < E_a^1$

(c) $E_a^1 = E_a^{1/2}$ (d) $E_a = E_a^1$

13. A first order reaction is 20% complete in one hour. At the end of 3 hrs the extent of the reaction is:

(a) 60% (b) 52.2%

(c) 48.8% (d) 44.4%

14. Radioactive decay is an example of:

(a) first order (b) second order

(c) zero order (d) 0.5 order

15. At 227°C, the presence of catalyst causes the activation energy of a reaction to decrease by 4.606 KCal, the rate of the reaction will be increased by:

(a) 2 times (b) 10 times

(c) 100 times (d) 1000 times

16. The decomposition of N_2O_5 occurs as, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ and follows first order kinetics, hence:

(a) the reaction is bimolecular (b) the reaction is unimolecular

(c) $t_{yz} \propto a^\circ$ (d) unit of $K = \frac{mol}{L} sec^{-1}$

17. Rate of which reactions increases with temperature:

(a) of any reactionj (b) of exothermic reaction

(c) of endothermic reaction (d) of none

18. For the reaction, $N_2O_5 \longrightarrow 2NO_2 + O_2$; Given

$$\frac{-d}{dt}[N_2O_5] = K_1[N_2O_5]$$

$$\frac{d}{dt}[NO_2] = K_2[N_2O_5]$$

$$\frac{d}{dt}[O_2] = K_3[N_2O_5]$$, the relation in between of K_1 K_2 K_3 is

(a) $2K_1 = K_2 = 4\,K_3$
(b) $K_1 = K_2 = K_3$
(c) $2K_1 = 4K_2 = K_3$
(d) $2K_1 = 2K_2 = 3K_3$

19. Which of the following statement is/are correct about order of reaction:

(a) order of reaction is determined experimentally
(b) order of reaction can not have fractional value
(c) it does not necessarily depend on stoichiometric coefficients.
(d) it is the sum of power of concentration terms in rate low expression

20. Which one is correct for first order reaction.

(a) $\frac{t_{75\%}}{t_{50\%}} = 1.5$
(b) $\frac{t_{75\%}}{t_{50\%}} = 3$
(c) $\frac{t_{99.9\%}}{t_{50\%}} = 10$
(d) $\frac{t_{87.5\%}}{50\%} = 3$

21. Match the column and found out correct option.

(A) zero order reaction	P. unit of K is $\frac{L}{mol}.sec^{-1}$
(B) first order reaction	Q. unit of K is $\frac{mol}{L}.sec^{-1}$
(C) second order reaction	R. unit of K is sec^{-1}

(a) A–R, B–Q, C–P
(b) A–P, B–Q, C–R
(c) A–Q, B–R, C–P
(d) A–R, B–P, C–Q

Assertion and Reasoning:

22. (a) Statement 1: is true, Statement 2 is true, and Statement 2 is a correct explanation of statement 1

(b) Both statement are true but statement 2 is not a correct explanation for statement 1

(c) Statement 1 is true and statement 2 is false

(d) Statement 1 is false and Statement 2 is true

(e) Statement 1 the rate of reaction is accelerated by the presence of catalyst.

(f) Statement 2 The presence of catalyst makes the value of ΔG° more negative.

23. **Statement 1: Lower the activation energy, faster is the reaction.**

Statement 2 : Catalyst does not affect activation energy of the reaction.

24. Integer type Question:

For first order reaction: $\frac{t_{99.9}}{t_{50}} = x$, Here x is

(a) 3 (b) 5

(c) 7 (d) 10

Fill in the blanks type Questions

25. The reactions taking place in one step is called .... reactions.

26. The order of reaction is .... determined.

Answers

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

11. (b) **12.** (d) **13.** (c) **14.** (a) **15.** (c) **16.** (c) **17.** (a) **18.** (a)

19. (a, c, d) **20.** (c, d) **21.** (c) **22.** (c) **23.** (c) **24.** (d)

25. elementary **26.** experimentally

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. The rate law for a reaction is

$$\textbf{Rate} = \mathbf{K\,[A]\,[B]^{3/2}}$$

Can the reaction be an elementary process ? Explain.

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

Q. 2. For the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expressions $-\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ inter-related ?

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

Q. 3. Identify the order of a reaction from the following rate constant :

$$k = 2.3 \times 10^{-5}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

Ans. Second order

Q. 4. After five half-life periods for a first order reaction, what fraction of reactant remains ?

Ans. $\frac{1}{32}$

Q. 5. What is the effect of adding catalyst on the free energy of a reaction ?

Ans. No change in ΔG.

Q.6. What value of k is predicted for the rate constant by Arrhenius equation is T → ∞ ? Is this value physically reasonable ?

Ans. From the equation $k = Ae^{-E_a/RT}$ if $T \to \infty$ $k \to A$ so that Ea = 0. This is not feasible.

Q.7. Determine the order of reaction :

Step 1. $\mathbf{2NO + H_2 \rightarrow N_2 + H_2O_2}$ **Slow**

Step 2. $\mathbf{H_2O_2 + H_2 \rightarrow 2H_2O}$ **Fast**

Ans.

$$\text{Rate} = k\,[NO]^2\,[H_2]$$

$$\text{Order} = 2 + 1$$

$$= 3$$

Q.8. What is the order of reaction whose rate constant has the same units as the rate of reaction ?

Ans. Zero order

Q.9. 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.10. 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^{o}.

Q.11. 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.12. 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.13. The rate constant of a reaction is 3×10^2 min^{-1}. What is its order of reaction ? (On the basis of units of rate constant)

Ans. First order reaction.

Q.14. Three-fourth of a reaction is completed in 32 minutes. What is the half life period of this reaction ?

Ans. 16 minutes.

Q.15. What is meant by an elementary reaction ?

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

Q.16. Give one example of a reaction where order and molecularity are equal ?

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

Q.17. For a reaction R → P, the rate becomes 2 times when the concentration of the reactant A is increased 4 times. What is the order of reaction ?

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

Q.18. 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. $t = \dfrac{[A]_0 - [A]}{k} = \dfrac{0.10 - 0.075}{0.003} = 8.3 \text{ sec}$

Q.19. In a reaction 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Average rate = $\dfrac{-\Delta[A]}{2\Delta t} = -\dfrac{1}{2}\left(\dfrac{0.4 - 0.5}{10}\right) = 5 \times 10^{-3} \text{M min}^{-1}$

Q.20. 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.21. Give an example of a reaction having fractional order.

Ans. Decomposition of acetaldehyde (order = 1.5).

$$CH_3CHO \xrightarrow{723K} CH_4 + CO$$

Q.22. Decomposition reaction of ammonia on Pt surface has rate constant = 2.5 × 10^{-1} mol L^{-1} sec^{-1}. What is order of reaction ?

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

Q.23. What is order of radioactive decay ?

Ans. First order

Q.24. For a reaction A + B → Product, the rate law is given by $r = k[A]^{1/2}[B]^2$. What is the order of the reaction ?

Ans. Order of reaction = ½ + 2 = 2.5

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

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

Ans. $K_2/K_1 = 4$

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

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

Thus, on calculating and substituting values, we get :

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

Q. 2. If the decomposition of nitrogen oxide as

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

follows a first order kinetics.

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

Ans. Rate $= K[N_2O_5]$

$$K = \frac{\text{Rate}}{[N_2O_5]}$$

$$= \frac{1.5\times10^{-6}}{0.05}$$

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

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

Ans. Rate $= 2.45 \times 10^{-5}$ mol L^{-1} s^{-1}

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

$$= 0.82 \text{ M}$$

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

Ans.

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

Q. 4. Consider the decomposition reaction :

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

This reaction takes place in two steps as given below :

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

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

(a) Determine rate law expression.

(b) Determine the order of reaction.

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

(b) Order = 1 + 1 = 2

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

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

Comparing the equation with Arrhenius equation,

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

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

$$E_a = 28000 \times 8.314$$

$$= 232192\ J\ mol^{-1}$$

Q. 6. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the conc. of the reactant is reduced to half. What is the unit of rate constant for such a reaction ?

Ans. $$\text{Rate} = k[\text{A}]^2$$

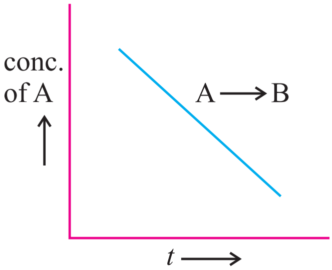
$$\text{Unit of } k = \frac{\text{mol L}^{-1}}{\text{S}} = k(\text{mol}^{-1})^2$$

$$k = \text{mol}^{-1}\ \text{L S}^{-1}$$

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

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

Q. 8.



(a) What is the order of the reaction ?

(b) What is the slope of the curve ?

Ans. (a) Zero order reaction.

(b) $[\text{R}] = [\text{R}_0] - kt$ $\therefore$ Slope $= -k$

Q.9. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction,

$$\text{R} = [\text{R}]_0 - kt$$

For completion of the reaction [R] =0

$$\therefore \quad kt = [\text{R}]_0$$

Or $$t = \frac{[\text{R}]_0}{k}$$

Q.10. For the reaction $\text{N}_2\,(g) + 3\text{H}_2\,(g) \rightarrow 2\text{NH}_3\,(g)$

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

Ans. Rate of reaction $= -\frac{1}{3}\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{NH}_3]}{\Delta t}$ Or $\frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[\text{H}_2]}{\Delta t}$

Q.11. The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

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

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

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

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

Dividing equation (i) by equation (ii),

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

Or $$n = 1$$

Q.12. A reaction which is first order with respect to A has rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 ML^{-1} ?

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

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

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

Q.13. 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.14. A first order reaction has a rate constant 1.15 × 10^{-3} s^{-1}. How long will 5 gram of this reactant take to reduce to 3 grams ?

Ans. $t = 444$ seconds

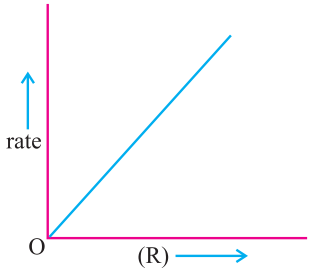
Q.17. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. If rate of formation of NO is 6 × 10^{-4} atm min^{-1}, calculate the rate of formation of H_2O.

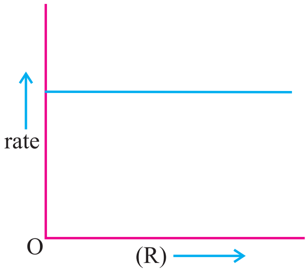
Ans. 9.0×10^{-4} atm min^{-1}

Q.18. Consider a certain reaction A → Product with K = 2.0 × 10^{-2} s^{-1}. Calculate the concentration of A remaining after 100 s, if the initial concentration of A is 1.0 mol L^{-1}.

Ans. [A] = 0.135 M

Q.19. Explain with an example, what is a pseudo first order raction ? The graphs (A and B) given below are plots of rate of reaction Vs concentration of the reactant. Predict the order from the graphs.





Q.20. Differentiate between :

(a) Average rate and instantaneous rate of a chemical reaction.

(b) Molecularity and order of reaction.

Q.21. 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.22. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimentally determined rate expression below 400 K is rate = $k[NO_2]^2$. What mechanism can be proposed for this reaction ?

Q.23. The half life period of a first order reaction is 60 min. What % will be left after 240 mins. ?

Ans. 6.25%

Q.24. Time for half change for a first order reaction is 25 min. What time will be required for 99% reaction ?

Ans. 166.16 mins.

SHORT ANSWER TYPE-II QUESTIONS

Q. 1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value ?

Ans.

$$t = \frac{2.303}{K}\log\frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{\frac{1}{10}}\log\frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{60}\log 10$$

$$t = \frac{2.303}{60}$$

$$= 3.38 \times 10^{-2}\ s^{-1}$$

Q. 2. The rate of most of reaction double when their temperature is raised from 298 K to 308 K. Calculate the activation energy of such a reaction.

Ans.

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

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89\ KJ/mol$$

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.

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3}\ min$$

$$= 10^{-2}\ min^{-1}$$

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

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

$$= 160.9\ min$$

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 × 10^{-1} sec^{-1}. Calculate the frequency factor A.

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

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

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

Or $$\log\left(1.8 \times 10^{-1}\right) + \frac{94.19 \times 10^3}{2.303 \times 8.314 \times 313} = \log A$$

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

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. 2.824×10^{10}

Q. 7. **The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.**

Ans.

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

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

$$= 0.0304 \text{ min}^{-1}$$

Q. 8. **The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :**

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

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

Calculate rate constant.

Ans. 4.98×10^{-4} sec^{-1}

Q. 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 ¾ 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 :**

$$2A + B \rightarrow C + D$$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of formation of D mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-1}

Determine the rate law and the rate constant for the reaction.

Ans. Rate = $K[A][B]^2$

Q. 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 4.5×10^3 sec^{-1} at 10° C and energy of activation 60 kJ/mol. At what temperature would K be 1.5×10^4 sec^{-1}.

Ans. 24° C

Q. 14. (a) Write rate law and order of the following reaction :

$$AB + C_2 \rightarrow AB_2C + C \text{ (slow)}$$

$$AB_2 + C \rightarrow AB_2C \text{ (fast)}$$

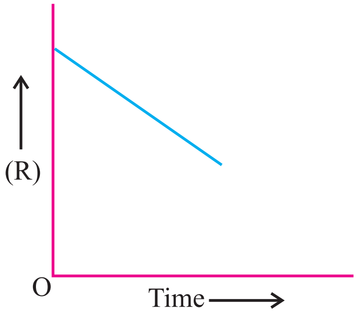
(b) Define energy of activation of a reaction.

(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 → 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_2O, the following results were obtained :

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

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

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

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

(b)

$$K_{30} = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

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

$$K_{90} = \frac{2.303}{90} \log \frac{0.55}{0.085}$$

Average K = 1.98×10^{-2} sec^{-1}

Q. 19. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2 ? [K = 2.5×10^{-4}]

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

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

$$\frac{d[NH_3]}{dt} = \text{rate} = k \times [NH_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$= \frac{1}{2} \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$d[\mathrm{H_2}] = -\frac{3}{2}\frac{d[\mathrm{NH_3}]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-44} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{Rate} = -\frac{d[\mathrm{NH_3}]}{dt} = k \times [\mathrm{NH_3}]^0$$

$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

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

LONG ANSWER TYPE QUESTIONS

Q. 1. (a) Define order of reaction.

(b) Rates of reaction double with every 10° rise in temperature. If this generalization holds for a reaction in the temperature ranges 298 K to 308 K, what would be the value of activation energy for their reaction ? $R = 8.314$ J K^{-1} mol^{-1}.

Ans. (a) **Order of Reaction :** It is the sum of powers to which the conc. terms are raised in rate law expression.

(b)

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

Here, $T_1 = 298$ K, $T_2 = 308$ K, R = K^{-1} mol^{-1}

$$\frac{K_2}{K_1} = 2$$

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

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

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 52898 \text{ J mol}^{-1}$$

$$= 52.898 \text{ KJ mol}^{-1}$$

Q. 2. (a) What are pseudo order reaction ? Give example.

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

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

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

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

For example,

$$\underset{\text{excess}}{CH_3COOC_2H_5 + H_2O} \xrightarrow{H^+} CH_5COOH + C_2H_5OH$$

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

$$\text{Order} = 1$$

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

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

For zero order, $n = 0$

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

For first order, $n = 1$

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

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

$$= S^{-1}$$

(b) For a first order reaction,

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

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

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

$$= \frac{2.303}{K} \log 100$$

$$= \frac{2.303}{K} \times 2 \qquad \text{...(i)}$$

For 90% completion of reaction,

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

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

$$= \frac{2.303}{K} \times 1 \qquad \text{...(ii)}$$

Dividing equation (i) by equation (ii), we get

$$t(99\%) = 2 \times t(90\%)$$

Q. 4. (a) Define rate constant of reaction.

(b) A first order reaction takes 40 mins for 30% decomposition. Calculate $t_{½}$.

Ans. (a) **Rate constant :** It is the rate of chemical reaction when the concentration of reactant taken as unity at a given temperature.

(b) Let initial conc. = a

$$\text{Conc. after 40 mins.} = a - \frac{a \times 30}{100}$$

$$= 0.70\ a$$

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

$$= \frac{2.303}{40} \log \frac{a}{0.70a}$$

$$= \frac{2.303}{40} \log \frac{1}{0.70}$$

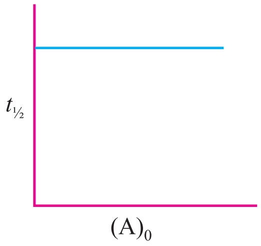
$$= \frac{2.303}{40} \times 0.1549$$

$$= 8.92 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K}$$

$$= \frac{0.693}{8.92 \times 10^{-3}} = 77.7 \text{ min}$$

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 SO_2Cl_2 at a constant volume :

$$SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$$

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

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

Ans. (a) First order reaction

$$K = \text{mol}^{1-n}\, L^{n-1}\, S^{-1}$$

$$n = 1$$

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

$$= S^{-1}$$

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

$$= \frac{2.303}{100}\log\frac{0.5}{\left(2\times 0.5 - 0.6\right)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{0..4}$$

$$= \frac{2.303}{100}\times 0.969 = 2.23\times 10^{-3}\ \mathrm{s}^{-1}$$

Now, Rate = $P_{SO_2Cl_2}$

Pressure of SO_2Cl_2 when total pressure = 0.65 atm

$$P_{SO_2Cl_2} = 2P_i - P_t$$
$$= 2 \times 0.5 - 0.65$$
$$= 0.35 \text{ atm}$$

$$\text{Rate} = 2.23 \times 10^{-3} \times 0.35$$
$$= 7.8 \times 10^{-4} \text{ atm S}^{-1}$$

Q. 6. (a) The activation energy of a reaction is 100 kJ/mol. In the presence of catalyst the activation energy is decreased by 75%. What is the effect on rate constant of the reaction at 20° C ?

(b) $A + 2B \rightarrow 3C + 2D$

The rate of disappearance of B is 1×10^{-2} mol L^{-1} sec^{-1}. What will be (i) rate of reaction (ii) rate of change in the concentration of A and C ?

Ans. (a) 2.35×10^{13} times

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

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

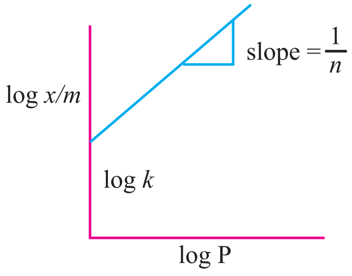
UNIT 4

SURFACE CHEMISTRY

Points to Remember

1. Adsorption occurs because of unbalanced forces acting inwards on the surface of the solid or a liquid.
2. The substance adsorbed is called **adsorbate** and substance on which adsorption takes place is **adsorbent.**
3. In physical adsorption, adsorbate is held to adsorbent by weak van der Waals forces. In chemisorptions, adsorbate is held to adsorbent by strong chemical bond type of foces.
4. Water vapours are adsorbed in silica gel but absorbed in $CaCl_2$.
5. If the concentration of adsorbate is more on the surface with respect to bulk, it is called **positive adsorption.** If it is less on the surface with respect to bulk, it is called **negative adsorption**.
6. Greater the surface area of the adsorbent, the more is the extent of adsorption.
7. Higher the critical temperature of a gas, greater is its extent of adsorption.
8. Physical adsorption is due to van der Waals forces and is reversible. Chemisorption involves the formation of compounds on the surface and is irreversible.
9. At constant temperature, adsorption generally increases with pressure. The lower the temperature, the greater is the effect of pressure.
10. Freundlich adsorption isotherm is

$$\frac{x}{m} = kP^{1/n}\,(n > 1) \qquad i.e., \qquad \log\frac{x}{m} = \log k + \frac{1}{n}\log P$$



The plot of log x/m vs log P gives a straight line with slope = $1/n$ and y-intercept = log k.

11. Adsorption is generally temperature dependent. Generally adsorption is **exothermic** and, therefore, adsorption decreases with the increase in temperature.

12. For adsorption from solution, pressure (P) is replaced by equilibrium concentration (C).

13. A catalyst is a substance that increases the rate of reaction without being consumed in the reaction. In general, a catalyst functions by lowering the energy of activation which in turn makes the rate constant larger and, hence, the rate of reaction higher. (The catalysts take part in reaction but get regenerated during course of reaction.)

14. In **homogeneous catalysis,** the catalyst is in the same phase as that of reactants and in **heterogeneous catalysis,** the catalyst is in the different phase from the reactants.

15. **Enzymes** are biological catalysts. Their main characteristics are their high *specificity,* efficiency (even in traces) and activity at physiological temperature of 37° C and pH of 7.4.

16. Enzyme catalysed reaction takes place in two steps :

    $E+S \rightarrow [ES]$ (fast and reversible)

    $[ES] \rightarrow E + P$ (slow and rate determining)

    (E is enzyme, S is substrate and P is product.)

17. **Colloidal solutions** are intermediate between true solutions and suspensions. Their size ranges in the order 1 nm to 1000 nm.

18. A colloidal system consists of two phases : the dispersed phase and dispersion phase.

19. **Lyophilic sols :** There is strong attraction between dispersed phase and dispersion medium. These are formed by organic substances like gum, starch, protein etc. These are reversible and more stable.

20. **Lyophobic sols :** There is very little interaction between dispersed phase and dispersion medium and are formed by inorganic substances like metals, their sulphides etc. These are irreversible and less stable.

21. The stability of lyophilic sols is due to their greater hydration in the solution.

22. The colloidal systems show Brownian movement, Tyndall effect and electrophoresis.

23. Aggregate of ions in an associated colloidal sol is called **ionic micelle.** The concentration above which these are formed is called **critical micelle concentration** (CMC) and the temperature above which these are formed is called **Kraft temperature** (T_k).

24. Conversion of a freshly precipitated substance into colloidal sol by shaking with a suitable electrolyte is called **peptization.**

25. The movement of colloidal particles under the influence of an electric field is called **electrophoresis.**

26. The process of changing the colloidal particles in a sol into the insoluble precipitate by the addition of some suitable electrolytes is known as **coagulation.**

27. According to Hardy Schulze rule, greater the valency of the flocculating ion of the electrolyte, the faster is the coagulation.

28. The minimum number of millimoles of the electrolyte required for complete coagulation of one litre of a colloidal sol is called its **coagulation or flocculation value.**

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.

MULTIPLE CHOICE QUESTIONS (1 Mark)

1. Rate of physisorption increases with:

(a) decrease in temperature
(b) increase in temperature
(c) decrease in pressure
(d) decrease in surface area

2. The colloidal system consisting of a liquid adsorbate in a solid adsorbent is termed as:

(a) aerosol
(b) foam
(c) emulsion
(d) Gel

3. Which of the following has least coagluating value for positive sol?

(a) Cl^{-}
(b) SO_4^{2-}
(c) PO_4^{-3}
(d) $[Fe(CN)_6]^{-4}$

4. Which can adsorb larger volume of hydrogen gas?

(a) Colloidal solution of platinum
(b) finely divided nickel
(c) finely divided platinum
(d) colloidal $Fe(OH)_3$

5. **What is the emulsifer in milk?**
   (a) albumin (b) soap
   (c) gelatin (d) caesin

6. **Which one of the following gases will be adsorbed most easily?**
   (a) N_2 (b) H_2
   (c) O_2 (d) CO_2

7. **Cottrell precipitator works on the principle of:**
   (a) distribution law (b) addition of electrolate
   (c) Le-chattelier principle (d) Neutralisation of charge on collids

8. **The formation of micelles takes place only above:**
   (a) inversion temperature (b) Boyle temperature
   (c) critical temperature (d) Kraft temperature

9. **A colloidal solutions show:**
   (a) very high osmotic pressure (b) high osmotic pressure
   (c) low asmotic pressure (d) no osmotic pressure

10. **Alums purify muddy water by:**
    (a) dialysis (b) adsorption
    (c) absorption (d) coagulation

11. **Which of the following is an example of associated colloid?**
    (a) soap in water (b) protein in water
    (c) rubber in benzene (d) $AgNO_3$ in water

12. **The coagulating power of an electrolyte for blood decrease in the order.**
    (a) Na^+, Al^{+3}, Ba^{+2} (b) PO_4^{-3}, SO_4^{-2}, Cl^-
    (c) Al^{+3}, Ba^{+2}, Na^+ (d) Cl^-, SO_4^{2-}, PO_4^{-3}

13. **A catalyst do not change:**
    (a) gibbs energy of reaction (b) enthalpy of reaction
    (c) equilibrium constant (d) Activation energy of reaction

14. **Bredig's are method can not be used for the preparation of colloidal sol of**
    (a) Cu (b) Mg
    (c) Ag (d) Na

15. **Which is method of purification of colloidal solution?**
    (a) ultrafiltration (b) electrodialysis
    (c) bredig's arc method (d) dialysis

16. Match the column and choose correct option:

(A) Smoke	P. foam
(B) Butter	Q. emulsion
(C) Hair cream	R. aerosol
(D) Whipped cream	S. gel

(a) A–P, B–S, C–Q, D–R
(b) A–R, B–Q, C–S, D–P
(c) A–R, B–S, C–Q, D–P
(d) A–S, B–P, C–R, D–Q

Matching Column Type

17.

Column 1	**Column 2**
(A) Soap in water	P. Associated colloid
(B) Starch gelatin	Q. Lyoptrilic colloid
(C) Gold sol	R. Collodion
(D) Cellulose nitrate in alcohol	S. Lyophobic colloid

(a) A–R, B–S, C–Q, D–P
(b) A–P, B–Q, C–S, D–R
(c) A–R, B–S, C–P, D–Q
(d) A–P, B–Q, C–R, D–S

Fill in the blanks take question

18. Collodion is a 4% solution of .... in a alcohol or ether.

19. Starch is an example of .... colloids.

Assertion and Reason Type Question

20. **Statement 1 :** Lyophilic sols are more stable than Lyophobic sols.
Statement 2 : Lyophilic sols are highly hydrated in the solution.

(a) both statement are correct and statement 2 is correct explanation of statement 1
(b) both are correct explanation but statement 2 is not explain statement 1.
(c) statement 1 is true both statement 2 is false
(d) statement 2 is false but statement 2 is true

ANSWERS

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

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Why does a gas mixed with another gas not form a colloidal system ?

[*Hint :* Gaseous mixture is homogeneous.]

Q. 2. Why are adsorbate particles attracted and retained on the surface of adsorbent ?

[*Hint :* The unbalanced forces of the adsorbent are responsible for attracting adsorbate particles at adsorbent surface.]

Q. 3. Explain the terms sorption and desorption.

[*Hint :* Sorption is used to describe the process when adsorption and absorption take place simultaneously.

Desorption : Removal of adsorbate from the surface of adsorbent.]

Q. 4. "Chemisorption is highly specific." Illustrate with an example.

[*Hint :* As it involves chemical bonding between adsorbent and adsorbate.]

Q. 5. "Adsorbents in finely divided form are more effective." Why ?

[*Hint :* Due to their more surface area in finely divided form.]

Q. 6. Name two compounds used as adsorbent for controlling humidity.

Ans. Silica gel, Alumina gel

Q. 7. Mention one shape selective catalyst used to convert alcohol directly into gasoline.

[*Hint :* ZSM-5]

Q. 8. 'Generally high temperature is favourable for chemisorption.' Why ?

[*Hint :* To provide energy of activation.]

Q. 9. Name the catalyst used in the following process :

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

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

[*Hint :* (a) Finely divided Fe/FeO, MO as promoter.

(b) Pt (Platinised asbestos)]

Q. 10. Which group elements show maximum catalytic activity for hydrogenation reactions ?

[*Hint :* 7-9 group elements.]

Q. 11. Why gas masks are used by miners in coal mines while working ?

[*Hint :* To absorb poisonous gases.]

Q. 12. Write the chemical reaction involved in the preparation of sulphur sol.

[*Hint :* $SO_2 + 2H_2S \xrightarrow{\text{oxidation}} 3S_{(sol)} + 2H_2O$]

Q. 13. What are the optimum temperature and pH at which enzymes are highly active ?

[*Hint :* Temperature 298-310 K and pH 5 to 7]

Q. 14. What are the physical states of dispersed phase and dispersion medium in foam rubber ?

[*Hint :* Dispersed phase : Gas; Dispersion medium : Solid]

Q. 15. What is the composition of colloidion solution ?

[*Hint :* 4% solution of nitrocellulose in a mixture of alcohol and ether.]

Q. 16. 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. 17. State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface.

[*Hint :* $\Delta S = -$ ve]

Q. 18. Why does sky appear blue to us ?

[*Hint :* Due to scattering of blue light by dust particles and water suspended in air.]

Q. 19. What happens when hydrated ferric oxide and arsenious sulphide sols are mixed in almost equal proportions ?

[*Hint :* Mutual precipitation/coagulation took place.]

Q. 20. Gelatin is generally added to ice-cream. Why ?

[*Hint :* Ice-cream is water in oil type emulsion and gelatin acts as emulsifier.]

Q. 21. How is lake test for aluminium ion based upon adsorption ?

[*Hint :* $Al_2O_3.xH_2O$ has the capacity to adsorb the colour of blue litmus from the solution.]

Q. 22. Mention the two conditions for the formation of micelles.

[*Hint :* CMC and T_k.]

Q. 23. 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. 24. Which of the following is more effective in coagulating positively charged hydrated ferric oxide sol : (i) KCl, (ii) $CaSO_4$, (iii) $K_3[Fe(CN)_6]$?

[*Hint :* $K_3[Fe(CN)_6]$]

Q. 25. 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. 26. Mention one use of ZSM-5 catalyst.

[*Hint :* In dehydration of alcohols in formation of synthetic gasoline.]

Q. 27. 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. 28. Explain the terms : (i) CMC, (ii) Kraft temperature (T_k).

[*Hint :* CMC : Concentration above which micelle formation took place.

Kraft Temperature : It is the temperature above the micelle formation took place.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

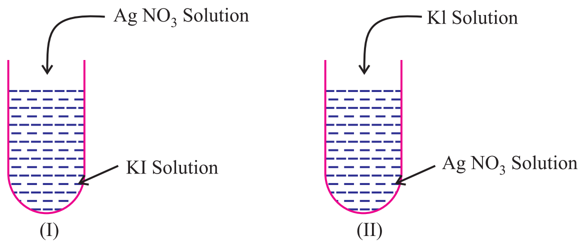
Q. 1. Explain the effect of temperature on the extent of physical and chemical adsorption.

[*Hint :* Physical adsorption decreases with increase of temperature, while chemical adsorption increases with increase of temperature.]

Q. 2. Define the term peptization and mention its cause.

[*Hint :* It is the process of converting a ppts into a colloidal sol by shaking it with small amount of electrolyte with dispersion medium. Ppts adsorb one of the ions of the electrolyte on its surface.]

Q. 3. What will be the charge on colloidal solutions in the following cases ?



Give reasons for the origin of charge.

Ans. (i) 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.

[*Hint :* For o/w emulsions : Proteins, gums, soaps.

For w/o emulsions : Fatty acids, long chain alcohols, lampblack.]

Q. 6. A small amount of silica gel and a small amount of anhydrous calcium chloride are placed separately in two beakers containing water vapour. Name the phenomenon that takes place in both the beakers.

[*Hint :* Silica gel : Adsorption, Anhydrous $CaCl_2$: Absorption, as it forms $CaCl_2.2H_2O$]

Q. 7. Write the differences between adsorption and absorption.

[*Hint :* Adsorption is surface, while absorption is bulk phenomenon.]

Q. 8. 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. 9. Classify the following reactions as homogeneous and heterogeneous catalysis :

(a) $\text{Vegetable oil }(l) + H_2\text{ (g)} \xrightarrow{\text{Ni (s)}} \text{Vegetable ghee (s)}$

(b) $C_{12}H_{22}O_{11}\text{ (aq)} + H_2O\ (l) \xrightarrow{H_2SO_4\text{ (aq)}} C_6H_{12}O_6\text{ (aq)} + C_6H_{12}O_6\text{ (aq)}$

[*Hint :* (a) : Heterogeneous catalysis

(b) : Homogeneous catalysis

Q. 10. 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. 11. 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. 12. 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. 13. 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. 14. 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. 15. Account for the following :

(a) Artificial rain can be caused by spraying electrified sand on the clouds.

(b) Electrical precipitation of smoke.

Q. 16. Write chemical equations for the preparation of sols :

(a) Gold sol by reduction

(b) Hydrated ferric oxide sol by hydrolysis.

[*Hint :* (a) $2AuCl_3 + 3SnCl_2 \xrightarrow{\text{Reduction}} 2Au\ (sol) + 3SnCl_4$

(b) $FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol)\ (Or\ Fe_2O_3.xH_2O) + 3HCl$]

Q. 17. 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. 18. 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. 19. 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. 20. What happens when dialysis is prolonged ?

Ans. When dialysis is prolonged the traces of electrolyte which stabilies the colloids are removed completely. This makes the colloid unstable and therefore coagulation takes place.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Write the difference between :

(a) catalysts and enzymes

(b) promoters and poisons

[*Hint :* (a) Catalyst is a substance that alters the rate of reaction without consuming itself in the reaction. Ezymes are biocatalysts, they are highly specific than catalysts.

(b) Promoters enhance the activity of a catalyst while poisons decrease the activity of catalysts.]

Q. 2. Write the steps of 'Modern Adsorption Theory of Heterogenous Catalysis'.

[*Hint :* (a) Diffusion and adsorption of reactant molecules on the surface of catalyst.

(b) Formation of intermediate on the surface of catalyst.

(c) Desorption of the products from catalysts surface.

(d) Diffusion of products away from the catalyst surface.]

Q. 3. Mention two important features of solid catalysts and explain them with the help of suitable examples.

[*Hint :* Heterogeneous catalyst, activity and selectivity of catalysts. Example, Hydrogenation of unsaturated hydrocarbons in presence of Raney Ni or any other example.]

Q. 4. How are the following colloids different from each other in respect of dispersion medium and dispersed medium ? Give one example of each type.

(a) An aerosol (b) A hydrosol (c) An emulsion

[*Hint :*	D.P.	D.M.	Example
(a)	Solid/liquid	Gas	Smoke, dust, fog, cloud
(b)	Solid	Water	Muddy water
(c)	Liquid	Liquid	Milk, hair cream]

Q. 5. What happens :

(a) By persistent dialysis of a sol.

(b) When river water meets the sea water.

(c) When alum is applied on cuts during bleeding.

[*Hint :* (a) Coagulation of sol takes place.

(b) Delta formation takes place due to coagulation of river water.

(c) Clot is formed due to coagulation of blood which stops further bleeding.]

Q. 6. Distinguish between multimolecular, macromolecular and associated colloids with the help of one example of each.

[*Hint :* (i) Multimolecular colloids formed by aggregation of small atoms or molecules. Example, gold sol, sulphur sol.

(ii) Macromolecular colloids formed by dispersing macromolecules having colloidal size in proper dispersion medium. Example, protein, starch colloid.

(iii) Associated colloids are formed by aggregation of particles at higher concentration to colloidal range. Example, micelles.]

Q. 7. (a) Which property of colloids is responsible for the sun to look red at the time of setting ?

(b) C_2H_2 on addition with H_2 forms ethane in presence of palladium catalyst but if reaction is carried in the presence of barium sulphate and quinoline, the product is 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) $CH \equiv CH + H_2 \xrightarrow{Pd} CH_2 = CH_2 \xrightarrow{Pd} CH_3 - CH_3$

$CH \equiv CH + H_2 \xrightarrow[BaSO_4,\ quinoline]{Pd} CH_2 = CH_2$

($BaSO_4$ in presence of quinoline act as poison. The catalyst in this case is not effective in further reduction.)

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. 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. 2. Write short notes on the following :

(a) Tyndall Effect

(b) Brownian Movement

(c) Hardy Schulze Rule

Ans. (a) **Tyndall Effect :** Scattering of light by colloidal particles by which part of beam becomes clearly visible. This effect is known as tyndall effect.

(b) **Brownian Movement :** Zig-zag motion of colloidal particles.

(c) **Hardy Schulze Rule :** Coagulating value of a coagulating ion is directly proportional to the charge on the ion.

E.g., $Na^+ < Ca^{++} < Al^{3+}$ For negatively charged sol

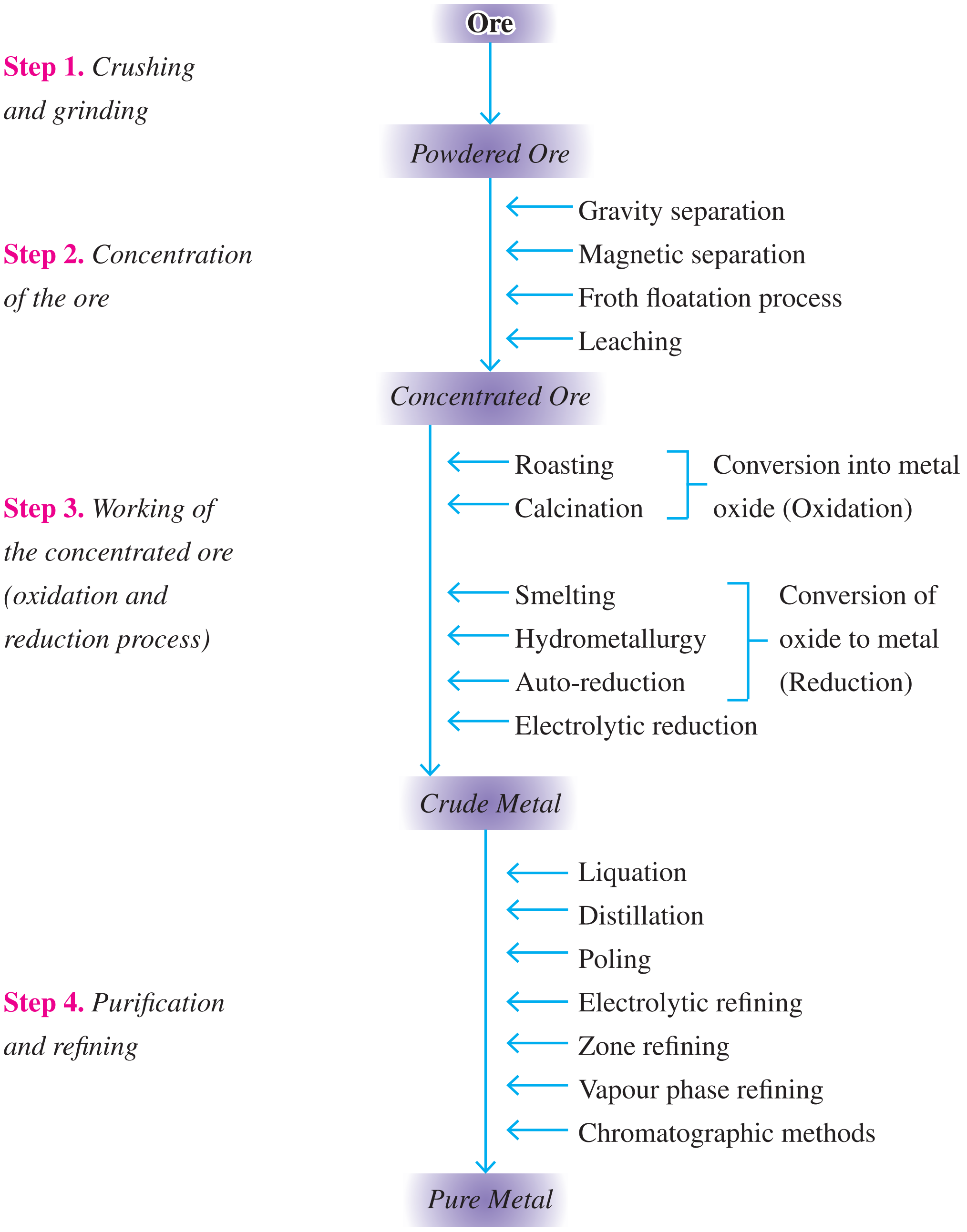
$Cl^- < CO_3^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$ For positive sol

◆

UNIT-5

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Flow-sheet diagram of metallurgical process is given below :



General Types of Ores of Metals

Type of Ore	Metal	Name of ore
1. Oxides	Iron	Haematite, Fe_2O_3
	Aluminium	Bauxite, $Al_2O_3.2H_2O$
	Copper	Cuprite, Cu_2O
	Zinc	Zincite, ZnO
	Manganese	Pyrolusite, MnO_2
2. Sulphides	Copper	Copper pyrites, $CuFeS_2$
	Lead	Galena, PbS
	Zinc	Zinc blende, ZnS
	Mercury	Cinnabar, HgS
3. Carbonates	Iron	Siderite, $FeCO_3$
	Copper	Malachite, $CuCO_3.Cu(OH)_2$
	Calcium	Limestone, $CaCO_3$
	Magnesium	Dolomite, $MgCO_3.CaCO_3$
4. Chloride	Sodium	Rock salt, NaCl
	Magnesium	Carnallite, KCl, $MgCl_2.6H_2O$
	Silver	Horn silver, AgCl
5. Sulphates	Calcium	Gypsum, $CaSO_4.2H_2O$
	Lead	Anglesite, $PbSO_4$
6. Silicates	Magnesium	Calcium magnesium silicate, $CaSiO_2.3MgSiO_2$ (Asbestos)

MULTIPLE CHOICE QUESTIONS

1. **The main function of roasting is:**
   (a) oxidation (b) reduction
   (c) to remove volatile matter (d) to make slag

2. **Which is not a mineral of Al?**
   (a) diaspore (b) bauxite
   (c) corundum (d) galena

3. **Brass contains:**
   (a) Cu + Sn (b) Cu + Ni
   (c) Cu + Zn (d) Mg + Al

4. **Flux used in the smelting of copper arc is:**
   (a) coke (b) magnesia
   (c) silica (d) lime stone

5. **The type of iron obtained from blast furnace is:**
   (a) pig iron (b) cast iron
   (c) wrought iron (d) mild steel

6. **Which one is leached with cyanide process?**
   (a) Cu (b) Al
   (c) Ag (d) Zn

7. **Which one is not a process of purification of metals:**
   (a) chromatrography (b) zone refining
   (c) froth floatation (d) distillation

8. **Which is a copper matte?**
   (a) $Cu_2O + FeS$ (b) $Cu_2S + FeO$
   (c) $Cu_2S + FeS$ (d) $Cu_2O + FeO$

9. **In metallurgical process of Al, cryolite is mixed in its molten state, because it**
   (a) decreases the amount of alumina (b) oxidises the alumina
   (c) increases the melting point of alumina (d) decreases the melting point of alumina

10. **Froth floatation process is used for:**
    (a) cuprite (b) zincite
    (c) copper pyrites (d) bauxite

11. **The anode mud obtained during electro refining of Cu contains:**
    (a) Ag (b) Fe

(c) Au (d) Zn

12. SiO_2 is a :

(a) flux (b) gangue

(c) slag (d) catalyst

Fill in the blanks type questions

13. Cresols and aniline are used as .... in froth floatation process:

14. Haematite is an ore of ....

Match the following type questions

15. Match the column

Column 1	Column 2
(A) cyanide process	P. ultrapure Ge
(B) zone refining	Q. extraction of Cu
(C) Froth floatation process	R. pine oil
(D) electrolytic refining	S. extraction of Au

(a) A–S, B–P, C–R, D–Q (b) A–R, B–S, C–Q, D–P

(c) A–P, B–Q, C–R, D–S (d) A–S, B–R, C–P, D–Q

ANSWERS

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

11. (a, c) **12.** (a, b) **13.** Froth stabilizer **14.** Iron **15.** (a)

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

Q. 1. Name three metals which occur in native state in nature.

Ans. Au, Ag and Pt.

Q. 2. Give the names and formulae of three ores which are concentrated by froth floatation process.

Ans. Galena (PbS), Zinc blende (ZnS), Cinnabar (HgS).

Q. 3. Among Fe, Cu, Al and Pb, which metal(s) cannot be obtained by smelting ?

Ans. Al.

Q. 4. What is the thermodynamic criteria for the feasibility of a reaction ?

Ans. ΔG should be –ve or log K = + ve.

Q. 5. Why can't aluminium be reduced by carbon ?

[*Hint :* Al is stronger reducing agent than carbon.]

Q. 6. 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. 7. What is the composition of copper matte ?

[*Hint :* Cu_2S and FeS]

Q. 8. Which form of copper is called blister copper ?

[*Hint :* The solidified copper obtained has blistered appearance due to the evolution of SO_2, so it is called blistered copper.]

Q. 9. What are froth stabilizers ? Give two examples.

[*Hint :* Examples are cresol and aniline.]

Q. 10. A sample of galena is contaminated with zinc blende. Name one chemical which can be used to concentrate galena selectively by froth floatation method.

Ans. NaCN

Q. 11. What are the constituents of German silver ?

Ans. Cu = 25-30%, Zn = 25-30%, Ni = 40-50%]

Q. 12. 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. 13. Write the reaction involved in the extraction of copper from low grade ores.

Ans. First step is leaching of ore with acid or bacteria then,

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

Q. 14. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Why ?

[*Hint :* Due to formation of inert oxide Al_2O_3.]

Q. 15. Which method of purification is represented by the following reaction :

$$\underset{\text{impure}}{\mathbf{Ti_{(s)}}} + \mathbf{2I_{2(g)}} \rightarrow \mathbf{TiI_{4(g)}} \xrightarrow{\Delta} \underset{\text{pure}}{\mathbf{Ti_{(s)}}} + \mathbf{2I_{2(g)}}$$

[*Hint :* Van Arkel method]

Q. 16. 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. 17. **Write the composition of moleten mixture which is electrolysed to extract aluminium.**

[*Hint :* Molten $Al_2O_3 + Na_3AlF_6$ or CaF_2]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. **What is hydrometallurgy ? Give one example where it is used for metal extraction.**

Ans. Leaching followed by reduction is called hydrometallurgy. It is used in extraction of copper.

Q. 2. **Name the process for the benefaction/concentration of (i) an ore having lighter impurities, (ii) sulphide ore.**

[*Hint :* (i) Gravity separation

(ii) Froth floatation]

Q. 3. **Mention the role of cryolite in the extraction of aluminium.**

[*Hint :* It lowers the melting point of the mixture and brings conductivity.]

Q. 4. **Mention the role of following :**

(a) **SiO_2 in the metallurgy of Cu.**

(b) **$CaCO_3$ in the metallurgy of Fe.**

(c) **CO in the metallurgy of iron.**

(d) **I_2 in the purification of zirconium.**

[*Hint :* (a) Flux

(b) $CaCO_3$ decomposed to CaO, which acts as flux.

(c) Reducing agent

(d) To form a volatile complex with Zr.]

Q. 5. **Extraction of copper directly from sulphide ore is less favourable than from its oxide through reduction. Explain.**

Ans. $2CuS\,(s) + C\,(s) \rightarrow CS_2\,(l) + 2Cu\,(s)$

$CuO\,(s) + C\,(s) \rightarrow CO\,(g) + Cu\,(s)$

G value is more –ve in second case as compared with first case.

Q. 6. **The graphite electrodes in the extraction of 'aluminium' by Hall-Heroult process need to be changed frequently. Why ?**

Q. 7. Write the chemical formulae of the following ores :

(a) Haematite **(b) Magnetite**

(c) Limonite **(d) Siderite**

Ans. (a) Fe_2O_3 (b) Fe_3O_4

(c) $Fe_2O_3.2H_2O$ (d) $FeCO_3$

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

Ans. $ZnCO_3 \rightarrow ZnO + CO_2$ (Calcination)

$ZnO + C \rightarrow Zn + CO$ (Reduction)

Q. 9. Name the elements present in anode mud during refining of copper. Why does it contain such elements ?

Ans. Au and Ag. They are not oxidized at anode. They are less electropositive than copper.

Q. 10. How are impurities separated from bauxite ore to get pure alumina ?

[*Hint :* By leaching.

(i) $Al_2O_3\ (s) + 2NaOH\ (aq) + 3H_2O\ (l) \rightarrow 2Na[Al(OH)_4]\ (aq)$

(ii) $2Na[Al(OH)_4]\ (aq) + CO_2\ (g) \rightarrow Al_2O_3.xH_2O\ (s) + 2NaHCO_3\ (aq)$

(iii) $Al_2O_3.xH_2O \rightarrow \underset{\text{(alumina)}}{Al_2O_3\ (s)} + xH_2O\ (g)$

Q. 11. 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. 12. 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.

$$ZnO + C \xrightarrow{975\ K} Zn + CO$$

Q. 13. Write the method to produce copper matte from copper pyrites.

[*Hint :* Froth floatation.]

Q. 14. Copper can be extracted by hydrometallurgy but not zinc. Explain why ?

[*Hint :* $E^o_{2n^{2+}} / 2n$ = – ve, $E^o_{cu^{+2}} /cu$ = + ve

Q. 15. Gibbs energy of formation ΔG_f^G of MgO (s) and CO (g) at 1273 K and 2273 K are given below :

ΔG_f [MgO (s)] = – 941 kJ mol^{-1} at 1273 K
ΔG_f [CO (g)] = – 439 kJ mol^{-1} at 1273 K
ΔG_f [MgO (s)] = – 314 kJ mol^{-1} at 2273 K
ΔG_f [CO (g)] = – 628 kJ mol^{-1} at 2273 K

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO (s).

Ans. For the reaction, MgO (s) + C (s) → Mg (s) + CO (g)

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

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

The temperature is 2273 K.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. State the principle of refining of metal by the following methods :

(a) Zone refining

(b) Electrolytic refining

(c) Vapour phase refining

[*Hint :*(a) The impurities are more soluble in the melt than in the solid state of the metal.

(b) Impure metal is made to act as anode, while the strip of same metal in pure form as cathode.]

Q. 2. How is pure copper obtained from its principle ore ? Write the chemical reactions occurring during the extraction.

[*Hint :* (i) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + O_2$

(ii) $Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(iii) $Cu_2O + C \rightarrow 2Cu + CO$

(iv) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$]

Q. 3. Name the method of refining of the following metals :

(a) Hg (b) Sn (c) Cu (d) Ge (e) Ni (f) Zr

Ans. (a) Distillation, (b) Liquation, (c) Electrolytic refining, (d) Zone refining, (e) Mond process, (f) Van Arkel process]

Q. 4. The native silver forms a water soluble compound (B) with dilute aqueous solution of NaCN in the presence of a gas (A). The silver metal is obtained by the addition of a metal (C) to (B) and complex (D) is formed as a byproduct. Write the structures of (C) and (D) and identify (A) and (B) in the following sequence :

$Ag + NaCN + [A] + H_2O\ [B] + OH^- + Na^+\ [C] + [B][D] + Ag$

Ans. $[A] = O_2$

$[B] = Na[Ag(CN)_2]$

$[C] = Zn$

$[D] = Na_2[Zn(CN)_4]$

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

[*Hint :* $4Ag + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Ag(CN)_2] + 4NaOH$

$2[Ag(CN)_2]^-\ (aq) + Zn\ (s) \rightarrow [Zn(CN)_4]^{2-}\ (aq) + 2Ag\ (s)$

(i) Oxidising agent – O_2 (ii) Reducing agent = Zn

UNIT 6

p-Block Elements

Anomalous behavior of first element in the p-block elements is attributed to small size, large (charge/radius) ratio, high ionization enthalpy, high electronegativity and unavailability of d-orbitals in its valence shell.

Consequences :

1. The first element in p-block element has four valence orbitals *i.e.,* one 2s and three 2p. Hence maximum covalency of the first element is limited to four. The other elements of the p-block have vacant d-orbitals in their valence shell, *e.g.,* three 3p and five three 3d orbitals. Hence, these elements show maximum covalence greater than four. Following questions can be answered :
   - (i) Nitrogen (N) does not form pentahalide while P forms PCl_5, PF_5 and PF_6^-. Why ?
   - (ii) Sulphur (S) forms SF_6 but oxygen does not form OF_6. Why ?
   - (iii) Though nitrogen forms pentoxide but it does not form pentachloride. Why ?
   - (iv) Fluorine forms only one oxoacid while other halogens form a number of oxoacids. Why ?
2. The first member of p-block elements displays greater ability to form pπ-pπ bond(s) with itself, (*e.g.,* C=C, C≡C, N=N, N≡N) and with the other elements of second period, for example, C=O, C≡N, N=O compared to the subsequent members of the group.

   This is because p-orbitals of the heavier members are so large and diffuse that they cannot have effective sideways overlapping. Heavier members can form p π-dπ bonds with oxygen.

Now, the following questions can be explained using the above mentioned reasoning :

(i) Oxygen exists as O_2 but sulphur as S_8. Why ?

3. Due to small size and high electronegativity and presence of lone pair(s) of electrons, elements N, O, F when bonded to hydrogen atom, forms hydrogen bonds which are stronger than other intermolecular forces. This results in exceptionally high m.p. and b.p. of the compounds having N–H/O–H/F–H bonds.

Isostructural species have same number of bond pairs and lone pairs if present around the central atom in a molecule/ion. Thus, they have the same geometry/shape/structure and the same hybridisation scheme. For example, ICl_4^-/XeF_4, BrO_3^-/XeO_3, BH_4^-/NH_4^+ are the pairs of isostructural species.

Inert pair effect : Due to poor shielding effect of intervening d and/or f-electrons, the effective nuclear charge increases. This increased nuclear charge holds the ns^2 electrons of heavier elements strongly and the tendency of ns^2 electrons to take part in bonding is more and more restricted down the group. Consequently, more stable lower oxidation state which is two units less than higher oxidation state, becomes more and more stable than the higher oxidation state. Following questions can be explained with the help of inert pair effect :

(i) For N and P, + 5 oxidation state is more stable than + 3 oxidation state but for Bi + 3 oxidation state is more stable than + 5. Explain why ?

(ii) $NaBiO_3$ is a strong oxidizing agent. Why ? [*Hint :* Bi (V) is least stable.]

(iii) In group 16, stability of +6 oxidation state decreases and the stability of + 4 oxidation state increases down the group. Why ?

(iv) SO_2 acts as reducing agent. Explain why ?

(v) Why is BrO_4^- a stronger oxidizing agent than ClO_4^- ?

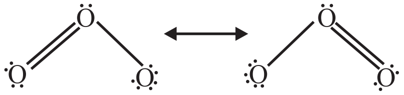
[*Hint :* It is because + 7 oxidation state is less stable in BrO_4^- due to which Br – O bond becomes weaker.]

(vi) $AsCl_5$ is less stable than $SbCl_5$.

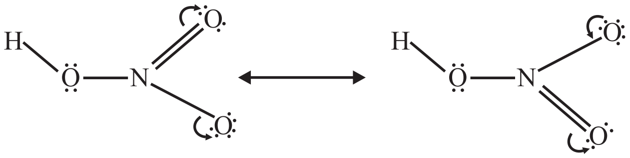
[*Hint :* More effective nuclear charge in As than Sb.]

(vii) The stability of highest oxidation state of 4p element is less than those of 3p and 5p elements of the same group. Why ?

Bond length : Resonance averages bond lengths. The two oxygen-oxygen bond lengths are identical in the O_3 molecule because it is resonance hybrid of following two canonical forms.



In case of HNO_3, two nitrogen-oxygen bonds are identical and smaller than the third nitrogen-oxygen bond. This is because the third N– OH bond is not involved in resonance.

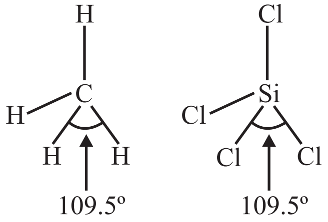


Now the following questions can be explained on the basis of this concept :

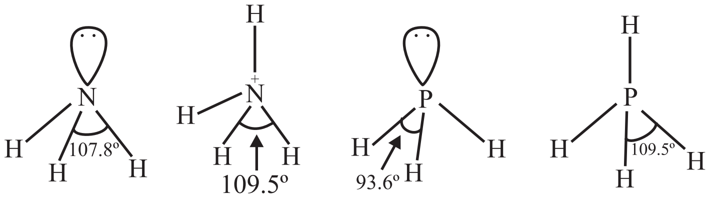
(i) In SO_2, the two sulphur-oxygen bonds are identical. Explain why ?

(ii) In NO_3^- ion, all the three N– O bonds are identical. Why ?

Bond angle : In regular structures (where no lone pairs are present in the valence shell of the central atom in a molecule/ion), the bond angle does not depend upon the size/electronegativity of the central or terminal atoms.



In presence of lone pair(s) on the central tom, the geometry is distorted and the bond angle is changed.



Comparison of HNH and HPH bond angles

Since N is more electronegative than P, the bonding electron pair of N– H bond will shift more towards N atom than the bonding electron pair of P– H bond would shift towards P atom. This results in more bond pair-bond pair repulsion in NH_3 molecule than PH_3 molecule. Because of more Ip-bp repulsion, the N– H bonds are pushed closer to a lesser extent than in PH_3. Consequently, HNH bond angle is greater than HPH angle.

Now, the following questions can be explained using the above mentioned concept :

(i) Bond angle in PH_4^+ ion is higher than in PH_3. Why ?

(ii) H– O– H bond in H_2O is greater than H– S– H angle in H_2S. Why ?

Boiling and melting points of hydrides depends upon the molar mass (or surface area) of molecules. More the molar mass, the higher is the m.p. and b.p. Hydrides forming intermolecular hydrogen bonds have exceptionally high m.p. and b.p. since intermolecular hydrogen bonds are stronger than the van der Waals forces.

Increasing order of melting point and boiling point of hydrides is as given below :

$PH_3 < AsH_3 < SbH_3 < NH_3$	Melting point
$PH_3 < AsH_3 < NH_3 < SbH_3$	Boiling point
$H_2S < H_2Se < H_2Te < H_2O$	Melting point and boiling point
$HCl < HBr < HI < HF$	Boiling point
$HCl < HBr < HF < HI$	Melting point

(i) NH_3 has higher boiling point than PH_3.

(ii) H_2O is liquid and H_2S is gas or H_2S is more volatile than H_2O.

Thermal stability, reducing power and acid strength of hydrides depend upon bond dissociation enthalpy of E– H bond (E = group 15, group 16, and group 17 element). Due to the increase in size down the group, bond dissociation enthalpy of E– H bond decreases. Consequently, while thermal stability decreases down the group, reducing power and acid strength of hydrides increases down the group.

The following questions can be explained using the above concepts.

Explain why :

(i) HF is weaker acid than HCl.

(ii) Among hydrogen halides, HI is the strongest reducing agent.

(iii) H_2Te is more acidic than H_2S.

(iv) NH_3 is mild reducing agent while BiH_3 is the strongest reducing agent among the group-15 hydrides.

(v) H_2S is weaker reducing agent than H_2Te.

Basic nature of hydrides EH_3 of group 15 elements

All the hydrides EH_3 of group 15 elements has one lone pair of electrons. In ammonia, the lone pair of electrons is present in sp^3 hybrid orbital of the N-atom. The sp^3 hybrid orbital is directional and further N is more electronegative than H, the bond pair of N – H is shifted towards N atom which further increases the electron density on N atom. In PH_3, the lone pair of electrons is present in large and more diffuse 3s orbital which is non-directional. As a result, PH_3 is less basic than NH_3 and basic character decreases down the group. NH_3 donates electron pair more readily than PH_3. $(SiH_3)_3N$ has less Lewis basic nature than that of $(CH_3)_3N$ because lone pair of electrons in p-orbital of N atom in $(SiH_3)_3N$ is transferred to the vacant d-orbital of Si atom forming $d\pi$-$p\pi$ bond.

Covalent/Ionic Character of Halides

Pentahalides are more covalent than trihalides since the element (E) in higher oxidation state (+ 5) in pentahalides has more polarizing power than element (E) in lower oxidation state (+ 3) in trihalides, similarly, $SnCl_4$, $PbCl_2$, $SbCl_3$ and UF_4 respectively. Compounds having more ionic character have more m.p. and b.p. than the compounds having more covalent character.

Following questions can be explained by using this concept.

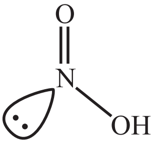
Explain why :

(i) $SnCl_2$ has more b.p. than $SnCl_4$.

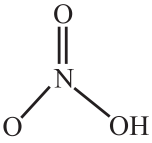
(ii) $SbCl_5$ is more covalent than $SbCl_3$.

(iii) PCl_5 has lower boiling point than that of PCl_3.

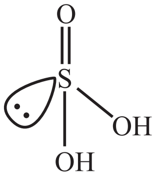
Oxoacids of N, P and halogens :



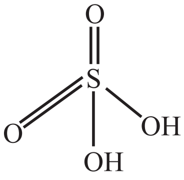
HNO_3



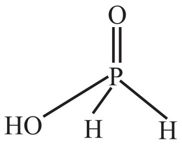
HNO_3

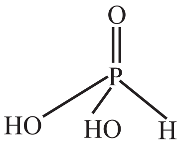


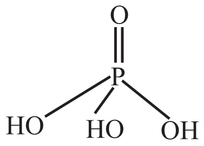
H_2SO_3

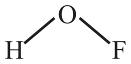


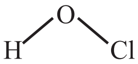
H_2SO_4

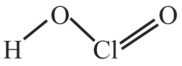

(Monophonic)
(H_3PO_2)

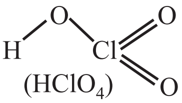

(Diprotic)
(H_3PO_3)

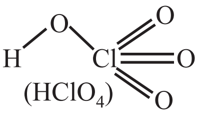

(Triprotic)
(H_3PO_4)


(HOF)


(HClO)


($HClO_3$)


($HClO_4$)


($HClO_4$)

Strength of Oxo Acids

Strength of oxoacids depends upon the polarity of O–H bond which in turn, depends on the electron withdrawing power (or electronegativity) of the element E. Strength of oxoacids increases if the number of oxygen atoms bonded with E increases.

Strength of oxoacids of halogens in the same oxidation state depends on the electronegativity of the halogen. The more the electronegativity, stronger is the oxoacid.

Strength of oxoacid of a halogen in different oxidation state increases with the increase in oxidation state. This is because the stabilization of the oxoanion increases with the number of the oxygen atoms bonded to the halogen atom. More the number of oxygen atoms, the more the dispersal of –ve charge present on the oxoanion and stronger will be the oxoacid.

Oxidising Power of Halogens

$$\begin{tikzcd}
X(g) \arrow[r, "-\Delta_{eg} H"] & X(g) \arrow[d, "\text{aq}"', "-\Delta_{hyd} H^{\theta}"] \\
\frac{1}{2} X_2(g) \arrow[u, "+\frac{1}{2}\Delta_{diss} H^{\theta}"'] \arrow[r, "\Delta_r H^{\theta}"] & X(aq)
\end{tikzcd}$$

The more negative the value of $\Delta_r H^{\theta} = \frac{1}{2}\Delta_{diss} H^{\theta} - \Delta_{eg} H^{\theta} - \Delta_{hyd} H^{\theta}$ the higher will be oxidizing property of the halogen and more positive will be standard reduction potential E^{θ}_{red} of the halogen.

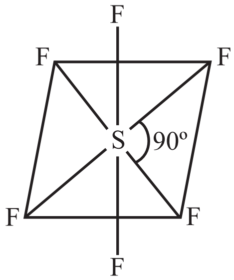
Following questions can be explained on the basis of parameters, like $\Delta_{diss} H^\theta$, $\Delta_{eg} H^\theta$ and $\Delta_{hyd} H^\theta$.

(i) Why does F_2 have exceptionally low bond dissociation enthalpy ?

(ii) Although electron gain enthalpy of fluorine (F) is less negative as compared to chlorine (Cl), Fluorine gas (F_2) is a stronger oxidizing agent than Cl_2 gas. Why ?

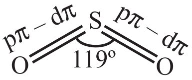
Some Important Reactions

1. $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
2. $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$
3. $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$
4. $2F_2\ (g) + 2H_2O\ (l) \rightarrow 4H^+\ (aq) + 4F^-\ (aq) + O_2\ (g)$
5. $X_2\ (g) + H_2O\ (l) \rightarrow HX\ (aq) + HXO\ (aq)$ (X = Cl, Br)
6. $4I^-\ (aq) + 4H^+\ (aq) + O_2 \rightarrow 2I_2\ (s) + 2H_2O\ (l)$
7. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
8. $2NaOH\ (dil) + X_2 \xrightarrow{\text{Cold}} NaX + NaOX + H_2O$
9. $6NaOH\ (conc) + 3X_2 \xrightarrow{\text{heat}} 5NaX + NaXO_3 + 3H_2O$ $(X_2 = Cl_2, Br_2, I_2)$
10. $2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
11. $NaCl + H_2SO_4 \xrightarrow{\text{heat}} NaHSO_4 + HCl$
12. $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$
13. $XeF_6 + MF \rightarrow M^+[XeF_7]^-$ (M = Na, K, Rb or Cs)
14. $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
15. $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$
16. $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$
17. $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

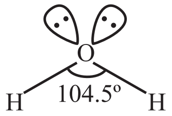


SF_6

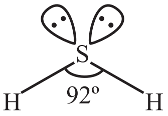
Sp^3d^2 (octahedral)



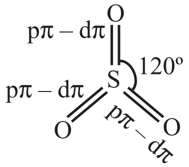
sp^3
Bent molecules



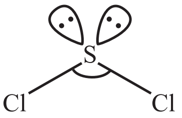
H_2S (sp^3)
V-shape

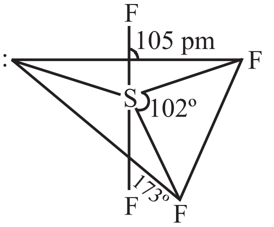


H_2O (sp^3)
V-shape

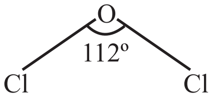


Planer Sp^2

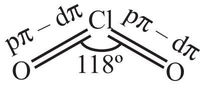




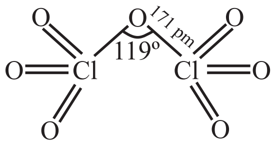
SF_4
Trigonal pyramidal sp3d



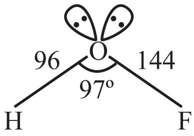
Cl_2O



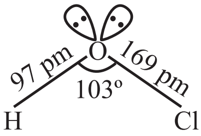
ClO_2



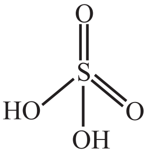
Cl_2O_7



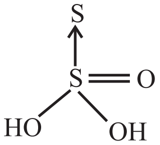
HOF



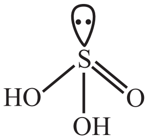
HOCl



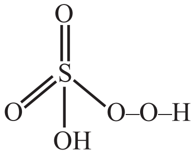
(H_2SO_4)
Sulphuric acid



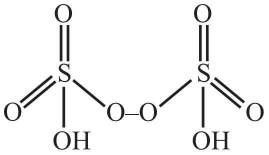
($H_2S_2O_3$)
(Thiosulphuric acid)



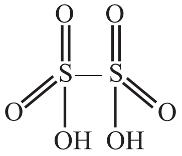
(H_2SO_3)
(Sulphurous acid)



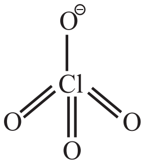
Peroxomonosulphuric acid
(H_2SO_5) (Caro's acid)

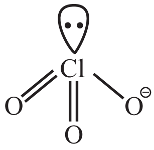


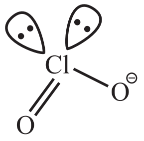
Peroxodisulphuric acid
($H_2S_2O_8$) Marshall's acid

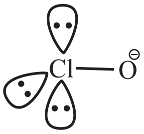


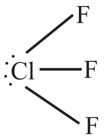
Dithionic acid ($H_2S_2O_6$)



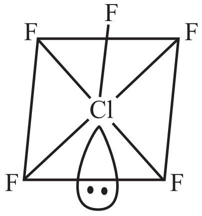




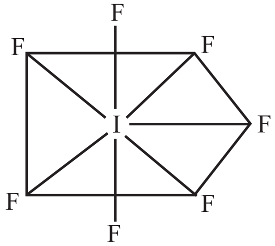




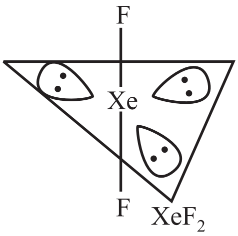
Bent- T-shaped (sp^{3}d) ClF$_3$



Square pyramidal
ClF$_5$ (sp$_3$d^2)

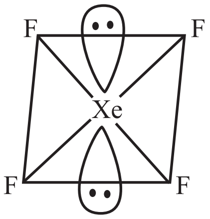


Pentagonal bipyramidal
IF$_5$ (sp^{3}d^3)

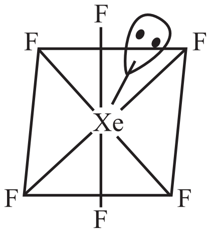


XeF$_2$

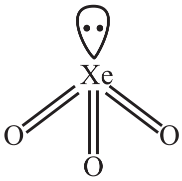
XeF$_2$ Linear (sp^{3}d)



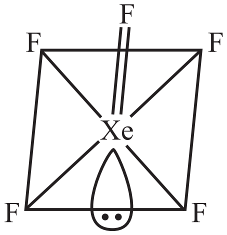
XeF$_4$ Square Planer
(sp^{3}d^2)



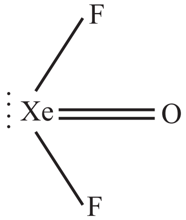
XeF$_6$ (sp^{3}d^2)
Distorted octahedral



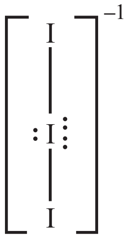
sp^3 Pyramidal
XeO$_3$



Square pyramidal
XeOF$_4$ (sp^{3}d^2)



XeOF$_2$ Linear (sp^{3}d)
Bent-T-shaped



[I$_3^{-1}$ sp^{3}d, Linear]

MULTIPLE CHOICE QUESTIONS

1. On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodise salt, violet fumes come out. This is because

(a) H_2SO_4 reduces HI to I_2	(b) HI is of violet colour
(c) HI gets oxidised to I_2	(d) HI changes to HIO_3

2. Affinity for hydrogen decreases in the group from flourine to iodine which of the halogen acids should have highest bond dissociation enthalpy?

(a) HF	(b) HCl
(c) HBr	(d) HI

3. Which of the following are permonoacids of sulphur?

(a) H_2SO_5 and $H_2S_2O_8$
(b) H_2SO_5 and $H_2S_2O_7$
(c) $H_2S_2O_7$ and $H_2S_2O_8$
(d) $H_2S_2O_6$ and $H_2S_2O_7$

4. In the preparation of compounds of Xe, Bartlett had taken $O_2^+ PtF_6^-$ as a base compound. This is because

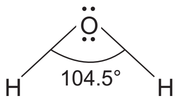
(a) both O_2 and Xe have same size
(b) both O_2 and Xe have same electron gain enthalpy
(c) both O_2 and Xe have almost same ionisation enthalpy
(d) both Xe and O_2 are gases.

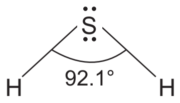
5. Reduction potentials of same ions are given below. Arrange them in decreasing order of oxidising power.

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential E°/V	$E^- = 1.19$ V	$E^- = 1.65$ V	$E^- = 1.74$ V

(a) $ClO_4^- > IO_4^- > BrO_4^-$
(b) $1O_4^- > BrO_4^- > ClO_4^-$
(c) $BrO_4^- > IO_4^- > ClO_4^-$
(d) $BrO_4^- > ClO_4^- > IO_4^-$

6. Bond angle in H_2O (104.5°) is higher than the bond angle of H_2S (921.1°). The difference is due to





(a) O is diatomic and S is titra-atomic
(b) difference in electronegatively of S and O
(c) difference in oxidation states of S and O
(d) difference in shapes of hybrid orbitals of S and O

7. Arrange the following hydrides of group 16 elements in order of increasing stalility.

(a) $H_2S < H_2O < H_2Te > H_2Se$
(b) $H_2O < H_2Te < H_2S_e < H_2S$
(c) $H_2O < H_2S < H_2Se < H_2Te$
(d) $H_2Te < H_2Se < H_2S < H_2O$

8. The hybridisation of sulphur in sulphur tetrafluroide is

(a) sp^3d
(b) sp^3d^2
(c) sp^3d^3
(d) sp^3

9. On heating $KClO_3$, we get

(a) $KClO_2 + O_2$
(b) $KCl + O_2$
(c) $KCl + O_3$
(d) $KCl + O_2 + O_3$

10. The correct order of acidic strength is:

(a) $K_2O > CaO > MgO$
(b) $CO_2 > N_2O_5 > SO_3$
(c) $Na_2O > Mgo > Al_2O_3$
(d) $Cl_2O_7 > SO_2 > P_4O_{10}$

11. Which one is not a property of ozone?

(a) it acts an oxidising agent in dry state

(b) oxidation of K1 into KlO_2

(c) PbS is oxidised to $PbSO_4$ (d) Hg is oxidised to Hg_2O

12. The oxyacid of sulphur that contains a lone pair of electrons on sulphur is:

(a) sulphurous acid (b) sulphuric acid

(c) peroxodisulphuric acid (d) pyrosulphuric acid

13. The oxidation state of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follows the order:

(a) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$ (b) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

(c) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$ (d) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

14. The correct order of increasing electron affinity of halogens is:

(a) 1 < Br < Cl (b) Br < 1 < u

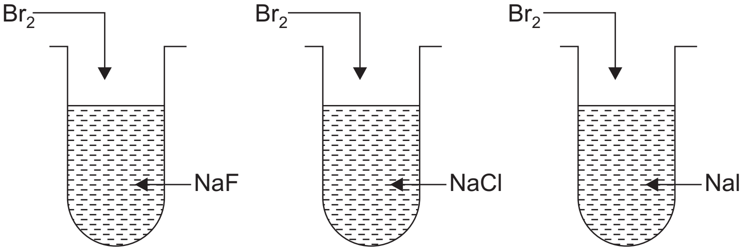
(c) Cl < Br < 1 (d) 1 < Cl < Br

15. Which is the correct arrangement of the compounds based on their bond strength?

(a) HF > HCl > HBr > Hl (b) Hl > HBr > HCl > HF

(c) HCl > HF > HBr > H1 (d) HF > HBr > HCl > H1

16. What is the correct operation when Br_2 is treated with NaF, NaCl and Nal taken in three test tukes lavelled (X), (Y) and (Z)?



(a) F_2 is liberated in (X) and Cl_2 in (Y)

(b) Only l_2 is liberated in (Z).

(c) Only Cl_2 is liberated in (Y)

(d) Only F_2 is liberated in (X)

17. Which of the following increasing order is not correct as mentioned in the property with it?

(a) $HClO < HClO_2 < HClO_3 < HClO_4$ (thermal stalrlity)

(b) $HClO_4 < HClO_3 < HClO_2 < HClO$ (oxidising power)

(c) $F^- < Cl^- < Br^- < 1^-$ (reducing nature)

(d) $HlO_4 < lCl < l_2 < Hl$ (oxidation number of iodine)

18. Complete the following reactions by filling the appropriate choice:

(A) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + \textbf{(i)} + \textbf{(ii)}$

(B) $XeF_6 + 3H_2O \longrightarrow \textbf{(iii)} + 6HF$

	(i)	*(ii)*	*(iii)*
(a)	F_2	H_2O	$XeOF_4$
(b)	24 HF	$3O_2$	XeO_3
(c)	2 HF	$2H_2O$	XeO
(d)	HF	H_2O	Xe_2O_3

19. Among the following molecules (i) XeO_3, (ii) $XeOF_4$, (iii) XeF_6 those having same number of lone pairs on Xe are

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

20. Compound with the geometry square pyramidal and sp^3d^2 hybridisation is

(a) $XeOF_2$
(b) $XeOF_4$
(c) XeO_4
(d) XeO_2F_2

More than one correct Response

21. Which of the following statements are correct?

(a) Among halogens, radius ratio between iodine and fluorine is maximum

(b) Leaving F–F bond, all halogens have weaker X—X bond than X—X' bond in interhalogens

(c) Among interhalogen compounds maximum number of atoms are present in iodine fluoride.

(d) Interhalogen compounds are more reactive than halogen compounds.

22. Which of the following statements are correct for SO_2 gas?

(a) It act as bleaching agent in moist conditions

(b) It's molecule has linear geometry

(c) It's dilute solution is used as disinfectant.

(d) It can be prepared by the reaction of dilute H_2SO_4 with metal sulphide.

23. Which of the following statements are correct?

(a) All the three N—O bond lengths in HNO_3 are equal.

(b) All P–C*l* bond lengths in PCl_5 molecule in gaseous state are equal.

(c) P_4 molecule in white phosphorous have angular strain therefore white phosphours is very reactive.

(d) PCl_5 is ionic in solid state in which cation is tetrahedral and anion is octahedral.

24. Which of the following orders are correct as per the properties mentioned against each?

(a)	$As_2O_3 < SiO_2 < P_2O_3 < SO_2$	Acid strength
(b)	$AsH_3 < PH_3 < NH_3$	Enthalpy of vapourisation
(c)	$S < O < Cl < F$	More negative electron gain enthalpy
(d)	$H_2O > H_2S > H_2Se > H_2Te$	Thermal stability

25. Which of the following statements are true?

(a) Only type of interactions between particles of noble gases are due to weak dispersion forces.

(b) Ionisation enthalpy of molecular oxygen is very close to that of numon.

(c) Hydrolysis of XeF_6 is a redox reaction.

(d) Xenon fluorides are not reactive.

26. Match the items of column 1 and column 2 and mark the correct option

Column 1	Column 2
(A) H_2SO_4	(1) Highest electron gain enthalpy
(B) CCl_3NO_2	(2) Chalcogen
(C) Cl_2	(3) Tear gas
(D) Sulphur	(4) Storage batteries

(a) A–4, B–3, C–1, D–2

(b) A–3, B–4, C–1, D–2

(c) A–4, B–1, C–2, D–3

(d) A–2, B–1, C–3, D–4

27. Match the items of column 1 and column 2 and mark the correct option.

Column 1	Column 2
(A) Its partial hydrolysis does not change oxidation state of central atom	(1) He
(B) It is used in modern diving apparatus	(2) XeF_6
(C) It is used to provide inert atmosphere for filling electrical bulbs	(3) XeF_4
(D) Its central atom is in sp^3d^2 hybridisation	(4) Ar

(a) A–1, B–4, C–2, D–3

(b) A–1, B–2, C–3, D–4

(c) A–2, B–1, C–4, D–3

(d) A–1, B–3, C–2, D–4

Assertion and Reason Type

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

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

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

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

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

(e) Both assertion and reason are wrong statements.

28. **Assertion:** HI cannot be prepared by the reaction of KI with concentrated H_2SO_4.

Reason : HI has lowest H—X bond strength among halogen acids.

29. **Assertion:** Both rhombic and monollinic sulphur exist as S_8 but oxygen exist as O_2.

Reason: Oxygen forms $P_\pi – P_\pi$ multiple bond due to small size and small bond length but $P_\pi – P_\pi$ bonding is not possible is sulphur.

30. The difference in the oxidisation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is

0	1	2	3	4	5	6	7	8	9

ANSWERS

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

11. (b) **12.** (a) **13.** (b) **14.** (a) **15.** (a) **16.** (b) **17.** (d) **18.** (b) **19.** (d) **20.** (b)

21. (a, c, d) **22.** (a, c) **23.** (c, d) **24.** (a), (d) **25.** (a, b)

26. (a) **27.** (c) **28.** (b) **29.** (a) **30.** 5

GROUP 16 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why SF_4 is easily hydrolysed, whereas SF_6 is resistant to hydrolysis ?

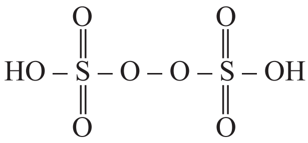
[*Hint :* Water molecule cannot attack 'S' atom due to steric hinderance and 'S' atom is also coordinately saturated in SF_6 molecule.]

Q. 2. In group 16, the stability of + 6 oxidation state decreases and that of + 4 oxidation state increases down the group. Why ?

[*Hint :* Due to inert pair effect.]

Q. 3. Draw the structure of $H_2S_2O_8$ and find the number of S – S bond, if any.

[*Hint :*



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

Number of S – S bond ⇒ 0.]

Q. 4. What happens when sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt ?

[*Hint :* It converts Fe^{3+} ions to Fe^{2+} ions.

$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$]

Q. 5. All the bonds in SF_4 are not equivalent. Why ?

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

Q. 6. O_3 acts as a powerful oxidizing agent. Why ?

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

$O_3 \rightarrow O_2 + [O]$

Q. 7. Which one of the following is not oxidized by O_3 ? State the reason :

KI, $FeSO_4$, K_2MnO_4, $KMnO_4$

[*Hint :* $KMnO_4$, since Mn is showing maximum oxidation state of + 7.]

Q. 8. Why does oxygen not show an oxidation state of + 4 and + 6 ?

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

Q. 9. Oxygen and sulphur in vapour phases are paramagnetic in nature. Explain why ?

[*Hint :* Due to presence of unpaired electrons in anti-bonding molecular orbitals in them.]

Q. 10. Thermal stability of hydrides of group 16 elements decreases down the group. Why ?

[*Hint :* Because down the group E – H bond dissociation enthalpy decreases.]

Q. 11. Why are the two S – O bonds in SO_2 molecule have equal strength ?

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

Q. 12. $Ka_2 << Ka_1$ for H_2SO_4 in water, why ?

[*Hint :* $H_2SO_4\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + HSO_4^-\,(aq);\ Ka_1 > 10$

$HSO_4\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + SO_4^{-2}\,(aq);\ Ka_2 = 10^{-2}$

Ka_2 is less than Ka_1 because HSO_4^- ion has much less tendency to donate a proton.]

Q. 13. H_2O is a liquid while inspite of a higher molecular mass, H_2S is a gas. Explain.

[*Hint :* H_2O molecules are stabilized by intermolecular hydrogen bonding, while H_2S by weak van der Waal's forces.]

Q. 14. The electron gain enthalpy with negative sign for oxygen (– 141 KJ mol^{-1}) is numerically less than that for sulphur (– 200 KJ mol^{-1}). Give reason.

[*Hint :* Due to smaller size of oxygen than sulphur electron-electron repulsion is more in oxygen than sulphur.]

Q. 15. Dioxygen O_2 is a gas while sulphur (S_8) is a solid. Why ?

[*Hint :* Because oxygen is smaller in size hence have capacity to form $p\pi–p\pi$ 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 ANWER-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) $C_{12}H_{22}O_{11} \xrightarrow[H_2SO_4]{\text{conc.}} 12C + 11H_2O$

(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 (V_2O_5).

$2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)\ \Delta H^\theta = -\ 196.6\ KJ\ mol^{-1}$]

Q. 3. Complete the following reactions :

(a) $PbS + O_3 \rightarrow$

(b) $KI + H_2O + O_3 \rightarrow$

(c) $MnO_4^- + SO_2 + H_2O \rightarrow$

(d) $S_8 + H_2SO_4$ **(conc.)** $\rightarrow$

Q. 4. Explain why :

(a) **H_2S is more acidic than H_2O.**

(b) **Two S – O bonds in SO_2 are identical.**

(c) **SF_6 is inert and stable but SF_4 is reactive.**

(d) **Sulphur has greater tendency for catenation than oxygen.**

[*Hint :* (iii) Because six F atoms protect the sulphur atom from attack by any reagent due to steric hindrance but four F atoms in SF_4 cannot offer much steric hindrance, hence reactive.]

Q. 5. How is O_3 estimated quantitatively ?

[*Hint :* O_3 reacts with an excess of KI solution buffered with a borate buffer, I_2 is liberated which is titrated against standard solution of sodium thiosulphate.]

$2I^-\ (aq) + H_2O\ (l) + O_2\ (g) \rightarrow I_2\ (s) + O_2\ (g) + 2OH^-\ (aq)$

Q. 6. Explain why O_3 is thermodynamically less stable than O_2 ?

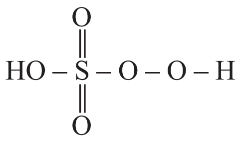
[*Hint :* Because O_3 is endothermic compound/decomposition of O_3 is exothermic and ΔG is negative/decomposition of O_3 is spontaneous.]

Q. 7. Draw the structure of :

(i) **H_2SO_5**

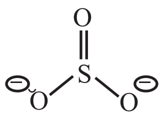
(ii) **SO_3^{2-}**

[*Hint :* (i)



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-H$$

(ii)



SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. **(i)** **How does O_3 react with lead sulphide ? Write chemical equation.**

(ii) **What happens when SO_2 is passed in acidified $KMnO_4$ solution ?**

(iii) **SO_2 behaves with lime water similar to CO_2. Explain why ?**

[*Hint :* (i) $PbS\ (s) + 4O_3\ (g) \rightarrow PbSO_4\ (s) + 4O_2\ (g)$

(ii) It decolourises acidified $KMnO_4$ solution.

$SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

(iii) It turns lime water milky due to the formation of insoluble $CaSO_3$.

$$\underset{\text{(milkiness)}}{Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O}$$

Q. 2. **Complete the reactions :**

(i) $CaF_2 + H_2SO_4$ **(conc.)** $\rightarrow$

(ii) $C_{12}H_{22}O_{11} + H_2SO_4$ **(conc.)** $\rightarrow$

(iii) $SO_2 + MnO_4^- + H_2O \rightarrow$

Q. 3. **An amorphous solid 'A' burns in air to form a gas 'B' which turns lime water milky. The gas is also produced as a by-product during roasting of sulphide ore. This gas decolourises acidified aq. $KMnO_4$ solution. Identify the solid 'A' and the gas 'B' and write the reaction involved.**

[*Hint :* $A = S_8$; $B = SO_2$ (g)]

(i) **How is SO_2 prepared in laboratory ?**

(ii) **What happens when SO_2 is passed through water and reacts with NaOH ? Write balanced equation.**

(iii) **Write its any two uses.**

Hint :(i) $Na_2SO_3\ (s) + H_2SO_4\ (aq) \rightarrow SO_2\ (g) + Na_2SO_4\ (aq) + H_2O\ (l)$

(ii) $2NaOH + SO_2\ (g) \rightarrow Na_2SO_3\ (aq) + H_2O$

$Na_2SO_3\ (aq) + SO_2 + H_2O \rightarrow 2NaHSO_3\ (aq)$

(iii) It is used as bleaching agent and disinfectant.

Q. 4. **Assign reason for the following :**

(i) **Sulphur in vapour state exhibits paramagnetism.**

(ii) **H_2O is less acidic than H_2Te.**

(iii) **In spite of having same electronegativity, oxygen forms hydrogen bond while chlorine does not.**

[*Hint :* (iii) Due to bigger size of Cl.]

Q. 5. Write contact process for the manufacture of king of chemicals.

[*Hint :* (i) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

(ii) $2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$

(iii) $SO_3 + H_2SO_4\ (98\%) \rightarrow H_2S_2O_7$ (oleum)

(iv) $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$]

GROUP 17 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Explain why fluorine forms only one oxoacid, HOF.

[*Hint :* Because of unavailability of d-orbitals in its valence shell.]

Q. 2. Why HF is the weakest acid and HI is the strongest ?

[*Hint :* $K_a\ (HF) = 7 \times 10^{-4}$ $K_a\ (HI) = 7 \times 10^{11}$

Intermolecular H-bonds in H – F and high bond dissociation enthalpy of H – F makes it weakest and weak bond in H – I makes it strongest.]

Q. 3. Explain why halogens are strong oxidizing agents.

[*Hint :* High electronegativity and more negative electron gain enthalpies of halogens.]

Q. 4. I_2 is more soluble in KI than in water. Why ?

[*Hint :* $KI + I_2 \rightarrow KI_3$]

Q. 5. What is cause of bleaching action of chlorine water ? Explain it with chemical equation.

[*Hint :* Formation of nascent oxygen.]

Q. 6. Electron gain enthalpy of fluorine (F) is less negative than that of chlorine (Cl). Why ?

[*Hint :* Due to small size of F atom and compact 2p orbitals there are strong interelectronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience more repulsion in F than in Cl.]

Q. 7. Why can't we prepare HBr by heating KBr with sulphuric acid ?

[*Hint :* As HBr readily reduces H_2SO_4 forming Br_2.]

Q. 8. Explain why : ICl is more reactive than I_2 ?

[*Hint :* Because I – Cl bond is weaker than I – I bond.]

Q. 9. Which oxide of iodine is used for the estimation of carbon mono oxide ?

[*Hint :* I_2O_5]

Q. 10. **Arrange the following oxoacids of chlorine in increasing order of acid strength :**

$HOCl, HOClO, HOClO_2, HOClO_3$

[*Hint :* $HOCl < HOClO < HOClO_2 < HOClO_3$]

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

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

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

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

Q. 13. **ClF_3 exists but FCl_3 does not. Why ?**

[*Hint :* Because F does not show oxidation state other than – 1.]

Q. 14. **Despite lower value of its electron enthalpy with negative sign, fluorine is a stronger oxidizing agent than chlorine. Explain.**

[*Hint :* Due to its low bond dissociation enthalpy (F –F bond) and high hydration enthalpy of F^-.]

Q. 15. **ClF_3 molecule has a bent T-shaped structure and not a trigonal planar structure. Explain.**

[*Hint :* Due to presence of 2LP and 3BP.]

Q. 16. **What happens when NaCl is heated with H_2SO_4 in the presence of MnO_2 ?**

[*Hint :* $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$]

Q. 17. **With what neutral molecule ClO^- is isoelectronic ?**

[*Hint :* ClF or OF_2.]

Q. 18. **Why HF acid is stored in wax coated glass bottle ?**

[*Hint :* HF is corrosive, hence HF attacks glass surface.]

Q. 19. **Bond dissociation enthalpy of F_2 is less than that of Cl_2. Explain why ?**

[*Hint :* F_2 is having higher electron-electron repulsion due to its smaller size, as compared to Cl_2.]

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. (i) **Interhalogen compounds are more reactive than halogens except F_2. Why ?**

(ii) **Give one important use of ClF_3.**

[*Hint :* (i) Because X – X bond in interhalogens is weaker than X – X bond in halogens except F – F bond.

(ii) ClF_3 is used for the production of UF_6.]

Q. 2. (i) Write the composition of bleaching powder.

(ii) What happens when NaCl is heated with conc. H_2SO_4 in the presence of MnO_2. Write the chemical equation.

[*Hint :* (i) $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$]

Q. 3. A colourless pungent smelling gas, which easily liquefies to a colourless liquid and freezes to a white crystalline solid, gives dense white fumes with ammonia. Identify the gas and write the chemical equation for its laboratory preparation.

[*Hint :* $NaCl + H_2SO_4$ (conc.) $\rightarrow NaHSO_4 + HCl$]

Q. 4. NO_2 readily dimenise, whereas ClO_2 does not. Why ?

[*Hint :* Due to bigger size of Cl than N.]

Q. 5. Compare the oxidizing powers of F_2 and Cl_2 on the basis of bond dissociation enthalpy, electron gain enthalpy of halogens and hydration enthalpy of halide ions.

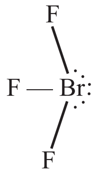
[*Hint :* It is due to low enthalpy of dissociation of F – F bond and high hydration enthalpy of F^-.]

Q. 6. Which fluorinating agent are oftenly used instead of F_2 ? Write chemical equation showing their use as flurorinating agents.

[*Hint :* $U (s) + 3ClF_3 (l) \rightarrow UF_6 (g) + 3ClF (g)$]

Q. 7. Draw the structure of BrF_3.

Hint :



Bent T - shaped

Complete the following reactions :

8. (i) $Al_2O_3 (s) + NaOH (aq) + H_2O (l) \rightarrow$

(ii) $HCl + O_2 \rightarrow$

9. (i) $Ca(OH)_2 + Cl_2 \rightarrow$

(ii) N_2 (excess) $+ Cl_2 \rightarrow$

10. (i) $Na_2SO_3 + Cl_2 + H_2O \rightarrow$

(ii) $N_2 + Cl_2$ (excess) $\rightarrow$

11. (i) $Cl_2 + NaOH$ (cold & dil.) $\rightarrow$

(ii) $Cl_2 + NaOH$ (hot & conc.) $\rightarrow$

12. (i) $Fe + HCl \rightarrow$

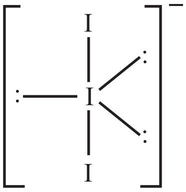
(ii) $Cl_2 + F_2$ (excess) $\rightarrow$

13. (i) $U + ClF_3 \rightarrow$

(ii) $FeSO_4 + H_2SO_4 + Cl_2 \rightarrow$

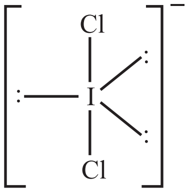
14. **Draw the structure of : (a) I_3^- (b) ICl_2^-.**

Hint :



Linear

$[I - I \leftarrow I^-]$



Linear

$[Cl - I \leftarrow Cl^-]$

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. **Give appropriate reason for each of the following :**

(i) **Metal fluorides are more ionic than metal chlorides.**

(ii) **Perchloric acid is stronger than sulphuric acid.**

(iii) **Addition of chlorine to KI solution gives it a brown colour but excess of Cl_2 makes it colourless.**

[*Hint :* (i) According to Fajan's Rule, bigger ions are more polarized than the smaller ions by a particular cation.

(ii) ClO_4^- is more resonance stabilized than SO_4^{2-} since dispersal of negative charge is more effective in ClO_4^- as compared with SO_4^{2-}.

(iii) $2KI + Cl_2 \rightarrow 2KCl + I_2$

$5Cl_2 \text{ (excess)} + I_2 + 6H_2O \rightarrow \underset{\text{(colourless)}}{2HIO_3} + 10HCl$

Q. 2. **X_2 is a greenish yellow gas with pungent offensive smell used in purification of water. It partially dissolves in H_2O to give a solution which turns blue litmus red. When X_2 is passed through NaBr solution, Br_2 is obtained.**

(i) **Identify X_2, name the group to which it belongs.**

(ii) **What are the products obtained when X_2 reacts with H_2O ? Write chemical equation.**

(iii) What happens when X_2 reacts with hot and conc. NaOH ? Give equation.

[*Hint :* (i) Cl_2, 17 group.

(ii) $Cl_2 (g) + 2H_2O (l) \longrightarrow HCl (aq) + HOCl (aq)$

(iii) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

Q. 3. Arrange the following in the order of the property indicated for each set :

(i) F_2, Cl_2, Br_2, I_2 (Increasing bond dissocation energy)

(ii) HF, HCl, HBr, HI (decreasing acid strength)

[*Hint :* (i) F_2 has exceptionally low bond dissociation enthalpy. Lone pairs in F_2 molecule are much closer to each other than in Cl_2 molecule. Stronger electron-electron repulsions among the lone pairs in F_2 molecule make its bond dissociation enthalpy exceptionally low, $I_2 < F_2 < Br_2 < Cl_2$

(ii) Acid strength depends upon H – X bond dissociation enthalpy. As the size of 'X' atom increases, bond dissociation enthalpy of H – X decreases. HI > HBr > HCl > HF

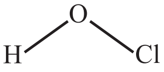
Q. 4. Draw the structure of :

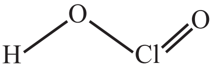
(i) Hypochlorous acid

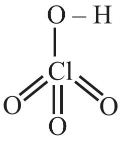
(ii) Chlorous acid

(iii) Perchloric acid

Hint :

(a) 

(b) 

(c) 

Q. 5. Which is more acidic among $HClO_4$ and HIO_4 ? Why ?

[*Hint :* $HClO_4$ is more acidic than HIO_4. Because Cl is more electronegative than Br, due to which ClO_3 group have more tendency to withdraw electrons of O – H bond towards itself as compared to BrO_3 group.]

GROUP 18 ELEMENTS

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What inspired N. Barlett for carrying out reaction between Xe and PtF_6 ?

[*Hint :* Almost same ionization enthalpy of oxygen and Xe.]

Q. 2. **Predict the shape and the bond angle (90º or more or less) in the following case :**

XeF_2 and the angle $\mathbf{F - \underset{\cdot\cdot}{\overset{\cdot\cdot\cdot\cdot}{Xe}} - F}$

[*Hint :* Linear, 180º]

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) $2XeF_2\ (s) + 2H_2O\ (l) \rightarrow 2Xe\ (g) + 4HF\ (aq) + O_2\ (g)$

(ii) $Xe + PtF_6 \rightarrow Xe^+[PtF_6]^-$]

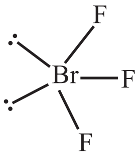
Q. 4. **Complete the reactions :**

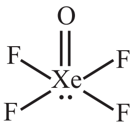
(i) $XeF_6 + H_2O \rightarrow$

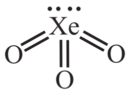
(ii) $XeF_6 + H_2O \rightarrow$

Q. 5. **Draw the structure of BrF_3, $XeOF_4$, XeO_3 using VSEPR theory.**

[*Hint :*







Q. 6. **Account for the following :**

(i) **XeF_2 has linear structure and not a bent structure.**

(ii) **The majority of known noble gas compounds are those of Xenon. Why ?**

[*Hint :* (ii) Xe has low ionization enthalpy as compared to other noble gases.]

Q. 7. **Write the chemical reactions :**

(i) $XeF_2\ (s) + H_2O\ (l) \rightarrow$

(ii) $XeF_4 + O_2F_2 \rightarrow$

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. **Assign reason to the following :**

(i) **Noble gases have large positive values of electron gain enthalpy.**

(ii) **Helium is used by scuba divers.**

(iii) **No chemical compound of helium is known.**

[*Hint :* (i) Due to their electron configuration.

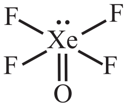
(ii) Due to its less solubility in blood.

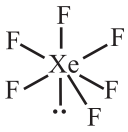
(iii) Due to its high ionization enthalpy.]

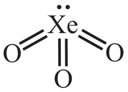
Q. 2. **Draw the structure of :**

(i) **$XeOF_4$** **(ii)** **XeF_6** **(iii)** **XeO_3**

[*Hint :*







Q. 3. Complete the reactions :

(i) $XeF_2 + NaF \rightarrow$

(ii) $XeF_4 + SbF_5 \rightarrow$

(iii) $XeF_4 + H_2O \rightarrow$

Q. 4. (i) How is XeO_3 prepared from XeF_6 ? Write the chemical equation for the reaction.

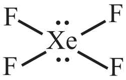
(ii) Draw the structure of XeF_4.

[*Hint :* (i) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

Or

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(ii)



LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (a) How is XeF_6 prepared from the XeF_4 ? Write the chemical equation for the reaction.

(b) Deduce the structure of XeF_6 using VSEPR theory.

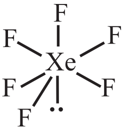
(c) How does XeF_2 reacts with PF_5 ?

(d) Give one use each of helium and neon.

(e) Write the chemical equation for the hydrolysis of XeF_4.

[*Hint :* (a) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

(b) Distorted octahedral (6BP + 1LP)



(c) $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$

(d) He is used in filling balloons/used by scuba divers.

Ne is used in discharge tubes, advertisement display purposes.

(e) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$]

Q.2. A greenish yellow gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate solution gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with the evolution of a colourless gas 'Y'. Identify gases 'X' and 'Y'.

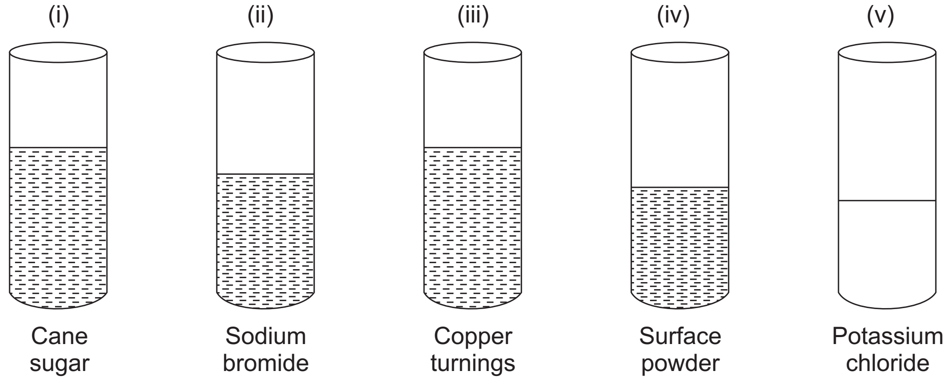
[Hint:]

$$\underset{X}{Cl_2} + H_2O \longrightarrow HCl + HClO$$

$$AgNO_3 + HCl \longrightarrow \underset{\text{(whiteppt.)}}{AgCl} + HNO_3$$

$$Mg + 2HCl \longrightarrow MgCl_2 + \underset{(Y)}{H_2}$$

Q.3. Concentrated sulphuric acid is added followed by heating in each of the following test types labelled (i) to (v)



Identify in which of the above test tubes, the following changes will be observed. Support your answer with the help of a chemical equation.

(a) formation of black substance

(b) evolution of brown gas

(c) evolution of colourless gas

(d) formation of brown substance which on dilution becomes blue.

(e) disappearance of yellow powder along with the evolution of a colourless gas.

[*Hint*]

(a) $C_{12}H_{22}O_{11} \xrightarrow{\text{Conc.} H_2SO_4} \underset{\text{(Black mass)}}{12C + 11H_2O}$

(b) $2NaBr + 3H_2SO_4 \xrightarrow{\text{heat}} 2NaHSO_4 + SO_2 + Br_2 + 2H_2O$

(c) $KCl + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HCl(g)$

(d) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(e) $S_8 + 16H_2SO_4 \longrightarrow 24SO_2 + 16H_2O$

Q.4.An aqueous solution of gas 'A' gave the following data (reactions):

(a) It decolourised an acidified $KMnO_4$ solution.

(b) On boiling with H_2O_2 followed by cooling and then adding an aqueous solution of $BaCl_2$, a white precipitate insoluble in dilute HCl was obtained.

(c) On passing H_2S through the solution of the gas, white turbidity was obtained. Identify the gas and give equations for gas steps (i), (ii), and (iii).

Ans. (i) $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow \underset{\text{(Colourless)}}{K_2SO_4} + \underset{\text{(Colourless)}}{2MnSO_4} + 2H_2SO_4$

(ii) $H_2O_2 + SO_2 \xrightarrow{\text{Boil}} H_2SO_4$

$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{(white ppt.)}}{BaSO_4} + 2HCl$

(iii) $\underset{\text{'A'}}{SO_2} + 2H_2S \longrightarrow \underset{\text{(turbidity)}}{3S} + 2H_2O$

Q.5. An element 'A' exist as a yellow solid in standard stae. It forms a voilet hydride 'B' which is a foul smelling gas and is extensively used in qualitative analysis of salts. When reated with oxygen. 'B' forms an oxide 'C' which is a colourless and pungent smelling gas. The gas when passed through acidified $kMnO_4$ solution, decolourises it, 'C' gets oxidised to another oxide 'D' in the presence of heterogenous catalyst. Identifier A, B, C, D and also give the chemical equation of reaction 'C' with acidified $KmnO_4$ solution and for conversion of 'C' into 'D'.

Solution:

(iii) $\underset{(A)}{S_8(s)} + 8H_2(g) \xrightarrow{\text{heat}} \underset{(B)}{8H_2S(g)}$

$$\underset{(B)}{2H_2S(g)} + 3O_2(g) \xrightarrow{\Delta} \underset{(C)}{2SO_2(g)} + 2H_2O(g)$$

$$\underset{(C)}{2SO_2(g)} + O_2(g) \xrightarrow{\text{Pt.}} \underset{(D)}{2SO_3(g)}$$

Overall : $\underset{(\text{voilet})}{2KMnO_4} + 5SO_2 + 2H_2O \longrightarrow \underset{(\text{colourless})}{K_2SO_4} + \underset{(\text{colourless})}{2MnSO_4} + 2H_2SO_4$

UNIT 7

THE *d*- AND *f*-BLOCK ELEMENTS

1. Introduction

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals – 3*d* series (Sc to Zn), 4*d* series (Y to Cd) and 5*d* series (La to Hg, omitting Ce to Lu).

d-block elements are known as transition elements because their position in the periodic table is between the s-block and p-block elements. Electronic configuration of the *d*-block elements is $(n-1)d^{1\text{-}10}ns^{o-2}$ but Cu^+, Zn, Cd, Hg etc. $[(n-1)d^{10}]$ are *d*-block elements, but not transition metals because these have completely filled *d*-orbitals.

Transition Metals of *d*-block Elements

3rd group ns^2	**4th group** $d^1\ ns^2d^2$	**5th group** ns^2d^3	**6th group** ns^2d^5	**7th group** ns^2d^5	**8th group** ns^2d^6	**9th group** ns^2d^7	**10th group** ns^2d^8	**11th group** ns^2d^{10}	**12th group** ns^2d^{10}
$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

2. General Properties of the Transition Elements

(i) Atomic and Ionic Radii

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements of the series.

(ii) Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms. They have stronger interatomic interaction and hence, stronger bond.

(iii) Ionisation Enthalpies

- In a series from left to right, ionization enthalpy increases due to increase in nuclear charge.

- The irregular trend in the first ionization enthalpy of the 3*d* metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals.

(iv) Oxidation States

- Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are

Sc(+ 3), Ti(+ 4), V(+ 5), Cr(+ 3, + 6), Mn(+ 2, + 7), Fe(+ 2, + 3), Co(+ 2, + 3), Ni(+ 2), Cu)+ 2), Zn(+ 2)

- The transition elements in their lower oxidation states (+ 2 and + 3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.
- Only Os and Ru show + 8 oxidation states in their compounds.
- Ni and Fe in $Ni(CO)_4$ and $Fe(CO)_5$ show zero oxidation state.

(v) Trends in the Standard Electrode Potentials

- Transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials.
- If sum of the first and second ionization enthalpies is greater than hydration enthalpy standard potential ($E^{o}_{M^{2+}/M}$) will be positive and reactivity will be lower and vice-versa.

(vi) Trends in Stability of Higher Oxidation States

The higher oxidation numbers are achieved in TiX_4, VF_5 and CrF_6. The + 7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3 and increasing order of oxidizing power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.

(vii) Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.
- The magnetic moment is determined by the number of unpaired electrons.

$$\text{Magnetic moment} = \sqrt{n(n+2)}$$

where, n = number of unpaired electrons.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

(viii) Formation of Coloured Ions

- The *d*-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.

- In V_2O_5, V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.

(ix) Formation of Complex Compounds

- Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of electron from ligands.

- They have vacant *d*-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

(x) Catalytic Properties

- Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.

- Transition metals also provide larger surface area for the reactant to be adsorbed.

(xi) Formation of Interstitial Compounds

- Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.

- The principal physical and chemical characteristics of these compounds are as follows :

  (i) They have high melting points, higher than those of pure metals.
  (ii) They are very hard, some borides approach diamond in hardness.
  (iii) They retain metallic conductivity.
  (iv) They are chemically inert.

(xii) Alloy Formation

Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogeneous mixture and form the alloy.

E.g., Brass (copper-zinc) and bronze (copper-tin) etc.

3. Some Important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

(i) Ore

Ferrochrome or chromate ($FeO.Cr_2O_3$) or ($FeCr_2O_4$)

(ii) Preparation

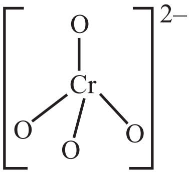
$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow \underset{\text{(yellow)}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \rightarrow \underset{\text{(orange)}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

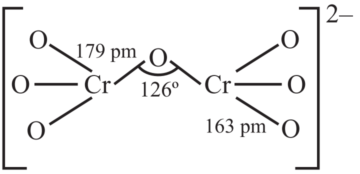
$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium dichromate is more soluble than potassium dichromate.

- Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.



chromate ion sp^3



dichromate ion sp^3

(iii) Properties

Sodium and potassium dichromates are strong oxidizing agents, thus, acidified $K_2Cr_2O_7$ will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin (IV) and iron (II) salts to iron (III).

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$

(iv) Uses

(a) $K_2Cr_2O_7$ is used as oxidizing agent in volumetric analysis.

(b) It is used in mordant dyes, leather industry, photography (for hardening of film).

(c) It is used in chromyl chloride test.

(d) It is used in cleaning glassware.

Potassium Permanganate ($KMnO_4$)

(i) Ore

Pyrolusite (MnO_2)

(ii) Preparation

$$2MnO_2 + 4KOH + O_2 \rightarrow \underset{\text{(green)}}{2K_2MnO_4} + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

(iii) Commercial preparation

$$\underset{}{MnO_2} \xrightarrow[\text{with air or } KNO_3]{\text{Fused with KOH oxidised}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{(alkaline medium)}]{\text{Electrolytic oxidation}} \underset{\substack{\text{Permanganate ion} \\ \text{(purple)}}}{MnO_4^{-}}$$

(iv) Properties

$KMnO_4$ acts as strong oxidizing agent.

(a) In presence of dilute H_2SO_4, $KMnO_4$ is reduced to manganous salt.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Acidic $KMnO_4$ solution oxidizes oxalates to CO_2, iron (II) and iron (III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

$$C_2O_4^{2-} \rightarrow CO_2 + 2e^-$$

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

$$NO_2^- \rightarrow NO_3^- + 2e^-$$

$$2I^- \rightarrow I_2 + 2e^-$$

To acidify $KMnO_4$, only H_2SO_4 is used and not HCl or HNO_3 because HCl reacts with $KMnO_4$ and produce Cl_2 while HNO_3, itself acts as oxidizing agent.

(b) In alkaline medium, $KMnO_4$ is reduced to insoluble MnO_2.

$$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

Alkaline or neutral $KMnO_4$ solution oxidizes I^- to IO_3^-, $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2 etc.

(v) Uses

(a) In laboratory preparation of Cl_2.

(b) $KMnO_4$ is used as an oxidizing agent, disinfectant.

(c) In making Baeyer's reagent.

4. The Inner Transition Elements (*f*-Block)

The *f*-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

Lanthanoids

General characteristics

- General configuration [Xe] $4f^{1\text{-}14}$, $5d^{0\text{-}1}$, $6s^2$.
- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.

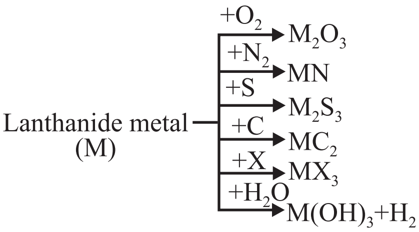
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.

- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.

- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodymium.

- Oxidation states → Ce^{4+}; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common + 3 state. The E^o_{value} for Ce^{4+}/Ce^{3+} is + 1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu^{2+} is formed by losing the two s-electrons and its f^7 configuration accounts for the formation of this ion. However, Eu2+ is a strong reducing agent changing to the common + 3 state. Similarly, Yb^{2+} which has f^{14} configuration is a reductant, Tb^{4+} has half-filled *f*-orbitals and is an oxidant.

- Lanthanoid are very reactive metals like alkaline earth metals.



- Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigarette and gas lighters, toys, tank and tracer bullets.

Actinoids

- Genral configuration [Rn] $5f^{1-14}$, $6d^{0-2}$, $7s^2$.

- Actinoids exhibit a range of oxidation states due to comparable energies of 5*f*, 6*d* and 7*s* orbitals. The genral oxidation state of actinoids is + 3.

- All the actinoids are strong reducing agents and very reactive.

- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc. like lanthanoids.

- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.

MULTIPLE CHOICE TYPE QUESTIONS

1. **One of the characteristics of transition metals to form the complex ion is:**
   (a) Having unpaired electron in *d*-subshell
   (b) Having paired electrons in *d*-subshells
   (c) Providing empty *d*-orbitals
   (d) Having small charge/size ratio

2. **The correct electronic configuration of copper atom is:**
   (a) $3d^{10}4s^1$ (b) $3d^{10}4s^2$
   (c) $3d^9 4s^2$ (d) $3d^5 4s^2 4p^4$

3. **The equivalent wight of $K_2Cr_2O_7$ in acid medium is equal to**
   (a) molecule weight (b) 1/2 molecular weight
   (c) 1/6 molecular weight (d) 1/5 molecular weight

4. **Manganese exhibits maximum oxidation state in:**
   (a) K_2MnO_4 (b) $KMnO_4$
   (c) MnO_2 (d) Mn_3O4

5. **The equivalent weight of $KMnO_4$ (formula weight M) when it is used as an oxidant in neural medium is**
   (a) M (b) M/2
   (c) M/3 (d) M/5

6. **Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions is**
   (a) 1/3 (b) 3
   (c) 1/6 (d) 6

7. **CrO_3 dissolves in aqueous NaOH to give:**
   (a) CrO_4^{2-} (b) $Cr(OH)_3$
   (c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

8. **The electronic configuration of gadolinium (At. No 64) is:**
   (a) [Xe] $4f^8\, 5d^0\, 6s^2$ (b) [Xe] $4f^7\, 5d^2\, 6s^2$
   (c) [Xe] $4f^3\, 5d^5\, 6s^2$ (d) [Xe] $4f^6\, 5d^2\, 6s^2$

9. **Electronic configuration of a transition element in + 3 oxidation state is [Al] $3d^5$. What is is atomic number?**
   (a) 25 (b) 26
   (c) 27 (d) 24

10. **On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.**

(a) Mn_2O_7 (b) MnO_2
(c) $MnSO_4$ (d) Mn_2O_3

11. Which of the following oxidation state is common for all lanthanoids?

(a) + 2 (b) + 3
(c) + 4 (d) + 5

12. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because:

(a) CO_2 is formed as the products (b) Reaction is exothermic
(c) MnO_4^- catalysis the reaction (d) Mn^{2+} acts as autocatalyst

13. $KMnO_4$ acts as an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is:

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$

(c) $\frac{4}{5}$ (d) $\frac{1}{5}$

14. Which of the following is amphotric oxide?

Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4.

(a) V_2O_5, Cr_2O_3 (b) Mn_2O_7, CrO_3
(c) CrO, V_2O_5 (d) V_2O_5, V_2O_4

15. The magnetic moment is associated with its spin angular momentum. Spin only magnetic moment value of Cr^{3+} ion is ....

(a) 2.87 B.M (b) 3.87 B.M
(c) 3.47 B.M (d) 3.57 B.M

16. Generally transition elements and their salts are coloured due to the product of unpaired electrons in metal ions. Which of the following compounds are coloured?

(a) $KMnO_4$ (b) $Ce(SO_4)_2$
(c) $TiCl_4$ (d) Cu_2Cl_2

17. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?

(a) CO^{2+} (b) Cr^{2+}
(c) Mn^{2+} (d) Cr^{3+}

18. Which of the following actionoids show oxidation states upto + 7?

(a) Am (b) Pu
(c) U (d) Np

19. Which of the following ions show higher spin only magnetic moment value?

(a) Ti^{3+}
(b) Mn^{2+}
(c) Fe^{2+}
(d) Co^{3+}

20. Which of the following will not act as oxidising agents?

(a) CrO_3
(b) MnO_3
(c) WO_3
(d) CrO_4^{2-}

21. Match the components/elements given in column I with uses given in column II.

Column 1	**Column 2**
(A) Lanthanoid oxide	(1) Production of iron alloy
(B) Lanthanoid	(2) Television screen
(C) Misch metal	(3) Petroleum cracking
(D) Magnesium based alloy	(4) Lanthanoid metal + iron
(E) Mixed oxides of lanthanoids are employed	(5) bullets
	(6) In X-ray screen

(a) A–4, B–3, C–1, D–2
(b) A–3, B–4, C–1, D–2
(c) A–4, B–1, C–2, D–3
(d) A–2, B–1, C–3, D–4

22. Match the solutions given in Column 1 and the colours given in column II.

Column 1	**Column 2**
(i) $FeSO_4.7H_2O$	(a) green
(ii) $NiCl_2.4H_2O$	(b) light pink
(iii) $MnCl_2.4H_2O$	(c) Blue
(iv) $COCl_2.6H_2O$	(d) Pale green
(v) Cu_2Cl_2	(e) pink
	(f) colourless

Assertion and Reason Type

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.*

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

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

(c) Assertion is not True, but reason is True.

(d) Both assertion and reason are False.

23. Assertion: Cu^{2+} iodide is not known.

Reason: Cu^{2+} oxidises I^- to iodine.

24. **Assertion:** Separation of Zr and Hf is difficult.

Reason : Because Zr and Hf lie in the same graph of the periodic table.

25. **The magnetic moment of a transition metal ion is found to be 4.90 BM. The number of unpaired electrons present in the ion is**

3	4	5	6	5.5	2

ANSWERS

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

11. (b) **12.** (d) **13.** (a) **14.** (a) **15.** (b) **16.** (a, b) **17.** (a, d)

18. (b, d) **19.** (b, c) **20.** (b, c)

21. (i)—(b), (ii)—(a), (iii)—(d), (iv)—(e), (v)—(c)

22. (i)—(d), (ii)—(a), (iii)—(b), (iv)—(e), (v)—(f) **23.** (a) **24.** (b) **25.** 4

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. **Explain $CuSO_4.5H_2O$ is blue while $CuSO_4$ is colourless ?**

Ans. Because water molecules act as ligands and results in crystal field splitting of *d*-orbitals of Cu^{2+} ion.

Q. 2. **Which element among 3*d* series exhibit highest oxidation state ?**

Ans. Mn

Q. 3. **In 3*d* series (Sc to Zn), the enthalpy of atomization of Zn is low. Why ?**

Ans. Due to absence of unpaired electrons.

Q. 4. **Which element among 3*d* series exhibit only one oxidation state ?**

Ans. SC

Q. 5. **Why is the 3rd ionization energy of Mn (Z = 25) is unexpectedly high ?**

Ans. Due to half-filled electronic configuration.

Q. 6. **Define alloy.**

Ans. Alloys are homogeneous solid solutions of two or more metals.

Q. 7. **Transition metals show zero oxidation state with ligands like CO. Explain.**

Ans. Co form synergic bonding with metal ion.

Q. 8. **Why can't HCl acid be used to acidify $KMnO_4$ solution ?**

Ans. Because $KMnO_4$ oxidize HCl into Cl_2.

Q. 9. **Name one ore of Mn and Cr.**

Ans. Mn : MnO_2

Cr : $FeCr_2O_4$

Q. 10. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their + 3 state ?

Ans. Mn^{+2} has half-filled electronic configuration.

Q. 11. Why do transition metal (elements) show variable oxidation states ?

Ans. Due to presence of vacant *d*-orbitals.

Q. 12. Write any uses of pyrophoric alloy.

Ans. Making bullets, shells and ligher flints.

Q. 13. Which is more basic – $La(OH)_3$ or $Lu(OH)_3$? Why ?

Ans. $La(OH)_3$, due to lanthanide contraction, lower size, more covalent character, least basic.

Q. 14. Find out number of Cr – O – Cr bond/bonds in $Cr_2O_7^{2-}$ ion.

Ans. 1

Q. 15. What is effect of increasing pH on $K_2Cr_2O_7$ solution ?

Ans. It changes into K_2CrO_4 solution/orange colour change into yellow colour.

Q. 16. Why is Ce^{4+} in aqueous solution a good oxidizing agent ?

Ans. Because Ce^{4+} is most stable in Ce^{+3} state in aqueous solution.

Q. 17. Why do Zr and Hf exhibit similar properties ?

Ans. Due to lanthanide contraction.

Q. 18. What is lanthanoid contraction ?

Ans. The regular slow decrease in the atomic or ionic radii of lanthanoids with increasing atomic number.

Q. 19. Why is Cu (Z = 29) considered a transition metal ?

Ans. Due to its partially filled *d*-orbital in Cu^{2+} state.

Q. 20. Arrange the given in increasing order of acidic character :

CrO_3, CrO, Cr_2O_3.

Ans. $CrO < Cr_2O_3 < CrO_3$

Q. 21. Why $KMnO_4$ or MnO_4^- ion is coloured ?

Ans. Due to charge transfer complex formation.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Chromium is typical hard metal while mercury is a liquid. Explain why ?

Ans. Cr has five unpaired *d*-electrons. Hence metallic bonds are strong. In Hg, there is absence of unpaired electrons and size is larger.

Q. 2. Why $KMnO_4$ is used in cleaning surgical instruments in hospitals ?

Ans. This is because $KMnO_4$ has a germicidal action.

Q. 3. Most of the transition metals do not displace hydrogen from dilute acids, why ?

Ans. Due to their –ve reduction potential.

Q. 4. Explain why Cu^+ is not stable in aqueous solution ?

Ans. Due to less –ve $\Delta_{hyd}H^\theta$ of Cu^+/it cannot compensate 2nd ionization potential of Cu.

Q. 5. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

Ans. Oxygen and fluoride have small size and high electronegativity. They can oxidise the metal.

Q. 6. Write electronic configuration of Cu^{+2} and Co^{+2}.

Ans. $Cu^{+2} = [Ar]\ 3d^9\ 4s^0$

$Co^{+2} = [Ar]\ 3d^7$

Q. 7. Balance the following equations :

(a) $MnO_4^- + Fe^{2+} + H^+ \rightarrow$

(b) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \rightarrow$

Ans. (a) $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{+2} + Fe^{+3}$

(b) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \rightarrow Cr^{+3} + Sn^{+4}$

Q. 8. Briefly explain why electronic configuration of lanthanoids are not known with certainty ?

Ans. 4*f*/5*d* subshells are very close in energy. +ve electrons can jump from 4*f* to 5*d* or vice-versa.

Q. 9. Why Zn, Cd, Hg are soft and have low melting point ?

Ans. Due to weak interatomic attraction/absence of unpaired electrons.

Q. 10. What is the effect of pH on the solution of $K_2Cr_2O_4$ solution ?

Ans. $K_2Cr_2O_4$ solution changes into $K_2Cr_2O_7$/yellow colour changes into orange colour.

Q. 11. Which of the following is/are transition element and why ?

Zn, Cd, Ag, Fe, Ni

Ans. Fe, Ni, Ag

Q. 12. What are interstitial compounds ? Give example.

Ans. When small atoms like C, H, B and N occupy interstitial site in their lattice. Example, TiC, Fe_3H,

Q. 13. Why are Zn, Cd, Hg volatile metals ? Explain.

Ans. Due to weak interatomic attraction/low boiling point.

Q. 14. Why is first ionization energy of 5*d* elements higher than those of 3*d* and 4*d* elements ?

Q. 15. Explain 'Misch metal' and write its use.

Ans. It is an alloy of 95% lanthanoid and 5% iron and traces of S, C, Ca and Al. Used in lighter flint, bullet tips etc.

Q. 16. The following two reactions of HNO_3 with Zn are given :

(a) $Zn + \text{conc. } HNO_3 \rightarrow Zn(NO_3)_2 + X + H_2O$

(b) $Zn + \text{dil. } HNO_3 \rightarrow Zn(NO_3)_2 + Y + H_2O$

Identify X and Y.

Ans. $X = NO_2$

$Y = N_2O$

Q. 17. Complete the equations :

(a) $KMnO_4 \xrightarrow{\Delta}$

(b) $3K_2MnO_4 \xrightarrow[\substack{\text{for long time} \\ \text{acidic medium}}]{\text{on standing}}$

Ans. (a) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(b) $3K_2MnO_4 \rightarrow MnO_4^- + MnO_2 + 2H_2O$

Q. 18. Out of Fe and Cu, which one would exhibit higher melting point ?

Ans. Fe, due to large number of unpaired *d*-electrons/more interatomic attraction.

Q. 19. Sc, the first member of first transition series does not exhibit variable oxidation state. Why ?

Ans. Due to noble gas electronic configuration in + 3 oxidation state no other oxidation state is stable.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. (a) Deduce the number of 3*d* electrons in the following ions :

Cu^{2+}, Sc^{+3}

(b) Why do transition metals form alloy ?

(c) Why Zn^{+2} salts are white ?

Ans. (a) Cu^{+2} : 9 electrons

Sc^{+3} : 0 electron

(b) Transition metals have similar atomic radii.

(c) Absence of unpaired electron.

Q. 2. Complete and balance the following equations :

(a) $MnO_4^{2-} + H^+ \rightarrow$

(b) $KMnO_4 \xrightarrow{heat}$

(c) $MnO_4^- + FeC_2O_4 \xrightarrow{H^+}$

Ans. (a) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(b) $2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$

(c) $MnO_4^- + FeC_2O_4 + H^+ \rightarrow Mn^{+2} + Fe^{+3} + CO_2$

Q. 3. Describe the oxidizing action of $K_2Cr_2O_7$ with the following. Write ionic equations for its reaction (acidic medium) with :

(a) I^- **(b)** **Iron(II)** **(c)** H_2S

Ans. (a) It liberates I_2 form I^-.

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{+3} + 7H_2O + 3I_2$

(b) It oxidizes Fe^{+2} to Fe^{+3}.

$Cr_2O_7^{2-} + 6Fe^{+2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 6Fe^{+3}$

(b) It oxidizes H_2S to sulphur.

$Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3S$

Q. 4. Write any four differences between lanthanoids and actinoids.

Ans.

	Lanthanoids	**Actinoids**
(a)	They are generally non-radioactive.	They are radioactive.
(b)	Most of their ions are colourless.	Coloured ions.
(c)	Show + 3, + 4 and + 2 oxidation state.	Beside + 3, show higher oxidation state.
(d)	Less tendency of complex formation.	Higher tendency.

Q. 5. (a) Why is separation of lanthanoid elements difficult ?

(b) Transition metal exhibit higher enthalpies of atomization. Explain why ?

(c) Why have the transition metal high enthalpy of hydration ?

Ans. (a) Due to lanthanide contraction, the size of these elements is nearly same.

(b) Transition metal contain large number of unpaired electrons, and they have strong interatomic attractions.

(c) Due to their small size and large nuclear charge.

Q. 6. (a) Use Hund's rule to derive the electronic configuration of Ce^{+3} ions and calculate its magnitude moment.

(b) Is lanthanum a *f*-block element ?

Ans. (a) $_{58}Ce = [Xe]\ 4f^1\ 5d^1\ 6s^2$

$Ce^{+3} = 4f^1$ one unpaired electron

$$= \sqrt{n(n+2)} = 1.73 \text{ BM}$$

(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 NH_3.

$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

(b) $Cu^+ : 3d^{10}\ 4s^0$ – All electrons are paired.

$Cu^{+2} : 3d^9$ – Here, one unpaired electron is present.

(c) Due to resonance.

Q. 8. The E° values in respect of electrodes of Cr, Mn and iron are :

$Cr^{+3}/Cr^{+2} = -0.4$ V

$Mn^{+3}/Mn^{+2} = +1.5$ V

$Fe^{+3}/Fe^{+2} = +0.8$ V

Compare the feasibilities of further oxidation of these ions.

Ans. Cr^{+3} is more stable than Cr^{2+}.

Mn^{+2} is more stable than Mn^{+3}.

Fe^{3+} is more stable than Fe^{2+}.

Order of feasibility of + 2 oxidation state is :

$Mn^{+2} > Fe^{+2} > Cr^{+2}$

Q. 9. Write any three properties of interstitial compounds.

Ans. (a) They are chemically inert.

(b) They retain metallic conductivity.

(c) They have high melting point than their pure metals.

(d) These are harder and more corrosion resistant.

Q. 10. Account for the following :

(a) All Scandium salts are white.

(b) The Ist ionization energy of the 5*d* series are higher than 3*d* and 4*d* transition elements in respective groups.

(c) Ce^{+3} can be easily oxidized to Ce^{+4}.

Ans. (a) Sc has only + 3 oxidation state, there is no unpaired electron.

(b) Due to lanthanide contraction, effective nuclear charge increase.

(c) Due to gain noble gas electron configuration.

Q. 11. A green chromium compound (A) on fusion with alkali gives a yellow compound (B) which on acidification gives a orange coloured compound (C). Identify A, B, C. Write equations for reactions.

Ans. A : $FeCr_2O_4$ B : Na_2CrO_4 C. $Na_2Cr_2O_7$

$$\underset{(A)}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \rightarrow \underset{(B)}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$Na_2CrO_4 + H_2SO_4 \rightarrow \underset{(C)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

Q. 12. When an oxide of Mn (A) is fused with KOH in the presence of an oxidizing agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionate in neutral or acidic solution to give purple compound (C). Identify A, B, C.

Ans. A : MnO_2 B : K_2MnO_4 C : $KMnO_4$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. A violet compound of manganes (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of KNO_3 to give compound (B). On heating compound (C) with conc. H_2SO_4 and NaCl, Cl_2 gas is liberated and compound (D) of manganese is formed. Identify A, B, C, D alongwith reactions involved.

Ans. A : $KMnO_4$ B : K_2MnO_4 C : MnO_2 D : $MnCl_2$

$$\underset{(A)}{KMnO_4} \xrightarrow{\Delta} \underset{(B)}{K_2MnO_4} + MnO_2 + O_2$$

$$MnO_2 + KOH + KNO_3 \rightarrow K_2MnO_4$$

(C) (B)

$MnO_2 + NaCl + \text{conc. } H_2SO_4 \rightarrow MnCl_2$

(C) (D)

Q. 2. (a) What is meant by disproportionation of an oxidation state ? Give one example.

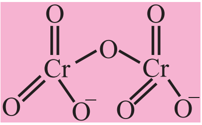
(b) Draw the structures of $Cr_2O_7^{2-}$, CrO_4^{-2}, MnO_4^{-}.

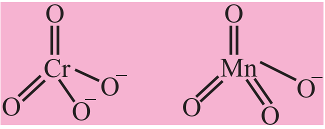
(c) What is the effect of lanthoids contraction beyond lanthanoid ?

Ans. (a) When any atom or ion undergo oxidation and reduction simultaneously it is called disproportionation.

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

(b)





(c) Size of respective 4*d* and 5*d* series elements becomes comparable from fourth group onwards (*e.g.,* Zr and Hf).

UNIT 8

Coordination Compounds

1. Introduction

Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in solution are known as complex compounds.

Example,

$$K_4\ [Fe(CN)_6] + H_2O \rightarrow 4K(aq)^+ + [Fe(CN)_6]^{4-}(aq)$$

2. Types of Complex

(i) Anionic complex

$$K_3[Fe(C_2O_4)_3] \rightarrow 3K^+ + \underset{\text{anionic complex}}{[Fe(C_2O_4)_3]^{3-}}$$

(ii) Cationic complex

$$[CoCl_2(en)_2]Cl \rightarrow \underset{\text{cationic complex}}{[CoCl_2(en)_2]^+} + Cl^-$$

(iii) Neutral complex

$[Ni(CO)_4]$

neutral complex

3. Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Types of Ligands

(i) Unidentate, a ligand which is bound to a metal ion through a single donor atom.

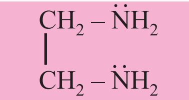
e.g., H_2O, NH_3, CO, Cl^-, NH_2^- etc.

(ii) Didentate, a ligand which is bound to a metal ion through a two donor atoms.

e.g.,

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array}$$

Oxalate ion



$$\begin{array}{l} CH_2-\ddot{N}H_2 \\ | \\ CH_2-\ddot{N}H_2 \end{array}$$

ethylene diamine

(iii) Polydentate, a ligand which is bound to a metal ion through a several donor atoms.

e.g., ethylene diamine tetraacetate ion $[EDTA]^{4-}$.

(iv) Ambidentate ligands, which can ligate through two different atoms.

e.g., $-NO_2$ – ONO, – SCN – NCS etc.

(v) Chelate ligands, these may be a di- or polydentate ligand which form closed ring with central metal ion. Closed ring is known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

4. Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups *e.g.,* $Co(NH_3)_6]^{3+}$ are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups *e.g.,* $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

5. Nomenclature of Coordination Compounds

Cationic Complex

$[Cr(NH_3)_3(H_2O)_3]Cl_2$

triamminetriaquachromium (III) chloride

(i) Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.

(ii) Central metal atom and oxidation state indicated by Roman numeral in parenthesis.

(iii) Name of ionisable anion.

Anionic Complex

$K_3[Fe(CN)_6]$

Potassium hexacyanoferrate (III)

(i) Name of ionisable metal and oxidation state

(ii) Name of ligand in an alphabetical order

(iii) Central metal atom + ate and oxidation state

Neutral Complex

$[Pt(NH_3)_2Cl(NO_2)]$

Diammine chloronitrito-N-platinum (II)

(i) Name of ligands in an alphabetical order

(ii) Central metal atom and oxidation state

6. Isomerism in Coordination Compounds

Stereo isomerism and structural isomerism are the two principal types of isomerisms which are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is of two types : geometrical isomerism and optical isomerism.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

(i) **Square planar complex of formula $[MX_2L_2]$ (X and L are unidentate),** the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer.

e.g., $[Pt(NH_3)_2Cl_2]$

(ii) **Square planar complex of the type $[MABXL]$ (where A, B, X, L are unidentates)** shows three isomers – **two *cis* and one *trans*.** Such isomerism is not possible for tetrahedral geometry.

e.g., $[Pt(NH_3)(Br)(Cl)(Py)]$

(iii) **Octahedral complexes of formula $[MX_2L_4]_1$** in which the two ligands X may be oriented *cis* or *trans* to each other.

e.g., $[Co(NH_3)_4Cl_2]^+$

(iv) **Octahedral complexes of formula $[MX_2A_2]$** where X are unidentates and A are didentate and form *cis* and *trans* isomers.

e.g., $[CoCl_2(en)_2]$

(v) **Octahedral coordination entities of the type $[Ma_3b_3]$** like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meriodional (mer) isomer.

Optical Isomerism

- It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called *dextro* (*d*) and *laevo* (*l*).
- Optical isomerism is common in octahedral complexes but at least one didentate ligand should be present.

  e.g., $[Co(en)_3]^{3+}$, $[PtCl_2(en)_2]^{2+}$ etc.

Structural Isomerism

In structural isomerism, isomers have different bonding pattern. Different types of structural isomerism is as follows :

(i) Linkage isomerism, arises in a coordination compound containing ambidentate ligand.

e.g., $[Co(NH_3)_5(NO_2)]Cl_2$

$[Co(NH_3)_5(ONO)]Cl_2$

(ii) Coordination isomerism, arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

e.g., $[Co(NH_3)_6][Cr(CN)_6]$

$[Cr(NH_3)_6][Co(CN)_6]$

(iii) Ionisation isomerism, when the ionisable anion exchange with anion ligand.

e.g., $[CO(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

(iv) Solvate isomerism, is also known as 'hydrate isomerism'. In this case water is involved as a solvent.

e.g., $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl_2.H_2O$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

7. Bonding in Coordination Compounds

Werner's Theory

(i) In complex compounds, metal atom exhibit two types of valencies – primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.

Valence Bond Theory

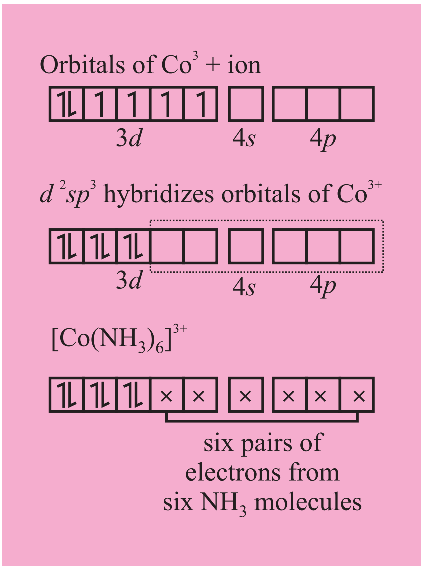
According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

(i) Six ligands (unidentate) (octahedral entity) Generally central atom belongs 3*d* series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

(a) Inner orbital complexes, which are formed due to participation of (n –1)d orbitals in hybridisation is (d^2sp^3) and shape of complex will be octahedral.

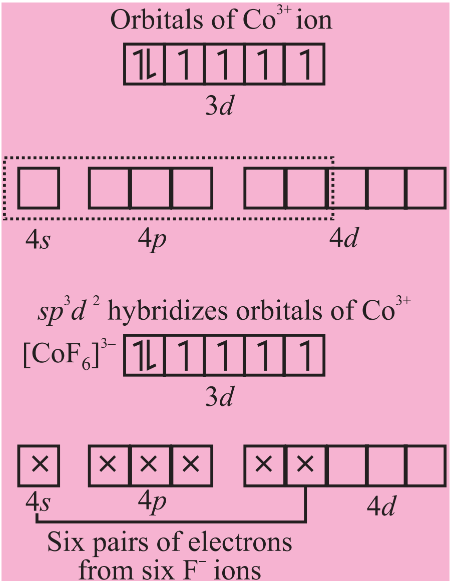
(b) Outer orbital complexes, which are formed due to participation of nd orbitals in hybridisation is (sp^3d^2). Generally halides (F^-, Cl^-, Br^-, I^-), SCN^-, S^{2-} form outer orbital complexes and other ligands form inner orbital complexes.

e.g., **Inner orbital complex,** $[Co(NH_3)_6]^{3+}$



All electrons are paired therefore, complex will be diamagnetic in nature.

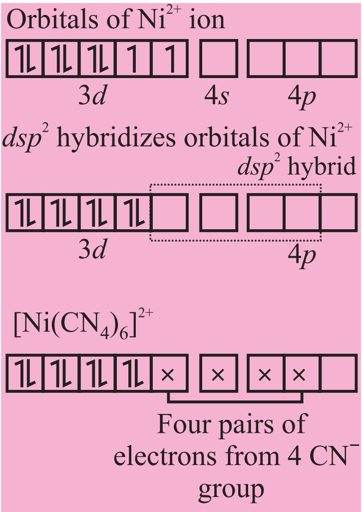
e.g., **Outer orbital complex,** $[CoF_6]^{3-}$



Complex has unpaired electrons, therefore, complex will be paramagnetic in nature.

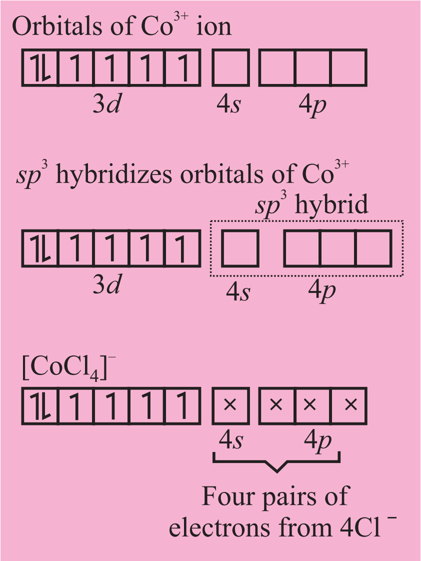
Complexes with coordination number : 4

1. $[Ni(CN)_4]^{2-}$



All electrons are paired. Complex will be diamagnetic in nature.

2. $[CoCl_4]^-$

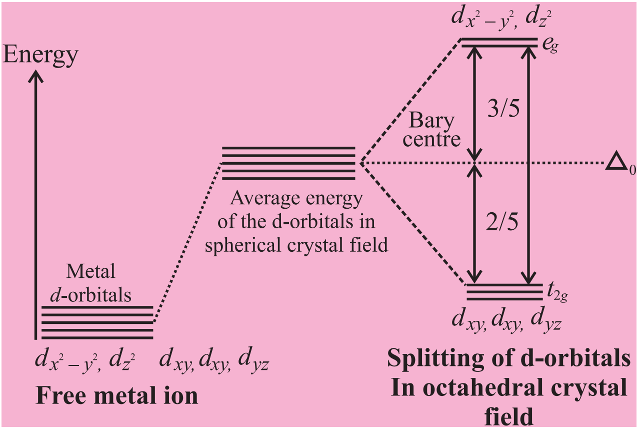


Complex has unpaired electrons. Complex will be paramagnetic in nature.

Crystal Field Theory

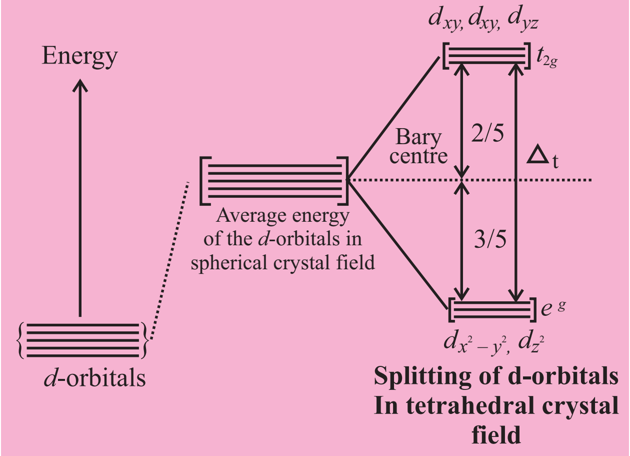
The five *d*-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory. The five *d*-orbitals in a gaseous metal atom/ion have same energy.

(i) Crystal field splitting in octahedral coordination entities.



- Energy separation is denoted by Δ_o (the subscript o is for octahedral).
- The energy of the two e_g orbitals (higher energy orbitals) will increase by $(3/5)\Delta_o$ and that of the three t_{2g} (lower energy orbitals) will decrease by $(2/5)\Delta_o$.
- If $\Delta_o < p$, the fourth electron enters one of the e_g, orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < p$ are known as weak field ligands and form high spin complexes.
- If $\Delta_o > p$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g$. Ligands which produce this effect are known as strong field ligands and form low spin complexes, where p represents the energy required for electron pairing in a single orbital.

(ii) Crystal field splitting in tetrahedral coordination entities.



- In tetrahedral coordination entities, $\Delta_t = (4/9)\Delta_o$. Consequently the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

- Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

8. Colour in Coordination Compounds

- In complex compounds *d*-orbitals split in two sets t_{2g} and e_g. These have different energies. The difference in energies lies in visible region and electron jump from ground state t_{2g} level to higher state e_g level. This is known as *d-d* transition and it is responsible for colour of coordination compounds.

- *d-d* transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configuration are coloured. On the other hand, the ions d^0 and d^{10} configuration do not show *d-d* transition.

9. Importance and Applications of Coordination Compounds

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

- Some important extraction processes of metals, like those of silver and gold make use of complex formation.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

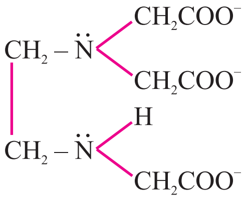
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

Supplementary List of Ligands

Ligand	F^-	Cl^-	Br^-	I^-	OH^-	CN^-	O^{2-}	O_2^{2-}	O_2^-	CO_3^{2-}	PH_3
Name	fluoro	chloro	bromo	iodo	hydroxo	cyano	oxo	peroxo	super-oxo	car-bon-ato	phosphine
Ligand	SO_4^{2-}	NO_2^-	ONO^-	SCN^{-1}	NCS	CH_3COO^-	C_5H_5N	S^{2-}	$S_2O_3^{2-}$	NO_3^-	SO_3^{2-}
Name	sulphato	nitro	nitrito	thiocyanato	isothiocyanato	acetate	pyridine (Py)	sulphido	thiosulphato	nitrato	sulphito
Ligand	NC^-	$(C_6H_5)_3P$	CS	NH_2^-	NH^{2-}	H_2NCSNH_2	$C_2O_4^{2-}$	H_2O	NH_3	CO	NO
Name	isocyano	triphenyl phosphine	thiocarbonyl	amido	imido	thiourea (tu)	oxalate (ox)	aqua	ammine	carbonyl	nitrosyl

$H_2N–CH_2–CH_2–NH_2$

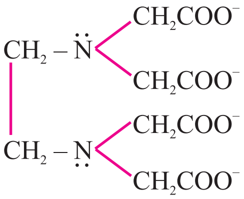
Ethylene diamine (en)



Ethylene diamine triacetate ion $EDTA^{3-}$

$H_2NCH_2CH_2NHCH_2CH_2NH_2$

Diethylenetriamine (diene)



Ethylene diamine triacetate ion $EDTA^{3-}$

MULTIPLE CHOICE QUESTIONS

1. Which of the following compounds formed by Cu^{2+} ions is most stable?

(a) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$; Log K = 11.6

(b) $Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}$; Log K = 27.3

(c) $Cu^{2+} + 2\ en \longrightarrow [Cu(en)_2]^{2+}$; Log K = 15.4

(d) $Cu^{2+} + 4H_2O \longrightarrow [Cu(H_2O)_4]^{2+}$; Log K = 8.9

2. The colour of the coordination compounds depends on the crystals field splitting. What will be the correct order of absorption of warleinth of light in the visible region. for the complenes $[CO(NH_3)_6]^{3+}$; $[CO(CN)_0]^{3-}$; $[CO(H_2O)_6]^{3+}$.

(a) $[CO\ (CN)_6]^{3-} > [CO(NH_3)_6]^{3+} > [CO(H_2O)_6]^{3+}$

(b) $[CO\ (NH_3)_6]^{3+} > [CO(H_2O)_6]^{3+} > [CO(CN)_6]^{3-}$

(c) $[CO\ (H_2O)_6]^{3+} > [CO(NH_3)_6]^{3+} > [CO(CN)_6]^{3-}$

(d) $[CO\ (CN)_6]^{3-} > [CO(NH_3)_6]^{3+} > [CO(H_2O)_6]^{3+}$

3. When 0.1 mol $COCl_3\ (NH_3)_5$ is treated with excess of $AgNO_3$; 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to.

(a) 1 : 3 electrolyte (b) 1 : 2 electrolyte

(c) 1 : 1 electrolyte (d) 3 : 1 electrolyte

4. The correct IUPAC name of $[Pt(NH_3)_2\ Cl_2]$ is

(a) Diamminedichloridoplatinum (II)

(b) Diamminedichlorideplatinum (IV)

(c) Diamminedichlorideplatinum (0)

(d) Dimminedichlorideplatinum (IV)

5. This stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complen species?

(a) $[Fe\ (CO)_5]$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(C_2O_4)_3]^{3+}$ (d) $[Fe(H_2O)_6]^{3+}$

6. Indicate the complen ion which shows geometrical isomerism.

(a) $[Cr(H_2O)_4\ Cl_2]^+$ (b) $[Pt(NH_3)_3Cl]$

(c) $[Pt(NH_3)_6]^{3+}$ (d) $[CO(CN)_5(NC)]^{3-}$

7. The CFSE for octahedral $[CaCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[COCl_4]^{2-}$ will be:

(a) 18,000 cm^{-1} (b) 16,000 cm^{-1}

(c) 8,000 cm^{-1} (d) 20,000 cm^{-1}

8. **Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complens of the type [Pd (C_6H_5)$_2$(SCN)$_2$] and [Pd(C_6H_5)$_2$ (NCS)$_2$] are:**

(a) Linkage isomers.	(b) Coordination isomers
(c) Ionisation isomers	(d) Geometrical isomers

9. **The compounds [CO(SO_4)(NH_3)$_5$ Br and [CO(SO_4) (NH_3)$_5$] Cl represent.**

(a) Linkage isomerism	(b) Ionisation isomerism
(c) Coordination isomerism	(d) No isomerism

10. **Which of the following species is not impected to be a ligand?**

(a) NO	(b) NH_4^+
(c) $NH_2CH_2NH_2$	(d) CO

11. **What kind of isomerism exist between [Cr (H_2O)$_6$] Cl_3 (violet) and [Cr(H_2O)$_5$Cl] Cl_2 . H_2O (greyish green)?**

(a) Linkage isomerism	(b) Saluate isomerism
(c) Ionisation isomerism	(d) Coordination isomerism

12. **IUPAC name of [Pt(NH_3)$_2$Cl(NO_2)] is:**

(a) Platinum diaminechloritrite

(b) Chloronitrito-N-ammine platinum(II)

(c) Diamminechloridonitrite-N-platinum (II)

(d) Diamminechlornitrite-N-platinate(II)

13. **Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complen ions are diamagnetic?**

(a) $[CO(NH_3)_6]^{3+}$	(b) $[Mn(CN)_6]^{3-}$
(c) $[Fe(CN)_6]^{4-}$	(d) $[Fe(CN)_6]^{3-}$

14. **Which of the following options are correct for $[Fe(CN)_6]^{3-}$ complen?**

(a) d^2sp^3 hybridisation	(b) sp^3d^2 hybridisation
(c) paramagnetic	(d) diamagnetic

15. **Identify the optically acive compounds from the following:**

(a) $[CO(en)_3]^{3+}$	(b) trans $[CO(en)_2Cl_2]^+$
(c) Cis $[CO[en)_2Cl_2]^+$	(d) $[Cr(NH_3)_5Cl]$

16. **Match the complen ions given in column 1 with the hybridisation and number of unpaired electrons given in column 2 and assign the correct code.**

Column 1	**Column 2**
(A) $[Cr(H_2O)_6]^{3+}$	(1) dsp^2; 1
(B) $[CO(CN)_4]^{2-}$	(2) sp^3d^2; 5

(C) $[Ni(NH_3)_6]^{2+}$	(3) d^2sp^3; 3
(D) $[Mn\ F_6]^{4-}$	(4) sp^3; 4
(5) sp^3d^2; 2	

(a) A–3, B–1, C–5, D–2
(b) A–4, B–3, C–2, D–1
(c) A–3, B–2, C–4, D–1
(d) A–4, B–1, C–2, D–3

17. **Match the complen species given in column 1 with the possible isomerism given in column 1 and assign the correct code:**

Column 1	Column 2
(A) $[CO(NCS)\ (NH_3)_5]\ (SO_3)$	(1) + 4
(B) $[CO(NH_3)_4\ Cl_2]\ SO_4$	(2) 0
(C) $[CO\ (S_2O_3)_3]\ Na_4$	(3) + 1
(D) $[CO_2(CO)_8]$	(4) + 2
	(5) + 3

(a) A–1, B–2, C–4, D–5
(b) A–4, B–3, C–2, D–1
(c) A–5, B–1, C–4, D–2
(d) A–4, B–2, C–2, D–3

Note: *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.*

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

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

(c) Assertion is True, but reason is False.

(d) Both assertion and reason are False.

18. **Assertion:** Toxic metal ions are removed by the chelating ligands.

Reason: Chelate complens tend to be move stable.

19. **Assertion:** $[(Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

Reason: Because it has d^2sp^3 type hybridisation.

20. **The coordination number of metal M in the complen $[M(en)\ (C_2O_4)\ ClBr]^-$ is**

5	6	8	4	2	0

ANSWERS

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

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What is ambidentate ligand ? Give one example.

Ans. Monodentate ligands contain more than one coordinating atoms. Example, CN^-.

Q. 2. Write the IUPAC name of $[PtCl_2(en)_2(NO_3)_2]$.

Ans. Dichloridobis(ethylenediammine)nitratoplatinum(IV)

Q. 3. What is a chelate ligand ? Give one example.

Ans. The ligand which contain from two or more donar sites simutaneously to form cyclic complaces. Example, ethane-1-2 diammine.

Q. 4. How many geometrical isomers are possible for the $[Ni(NH_3)_4]^{+2}$?

Ans. Not possible because all 4 ligands are same.

Q. 5. Define coordination polyhedron.

Ans. The spatial arrangement of the ligand with the central metal ion.

Q. 10. Give the chemical formula of potassium hexacyano ferrate (II).

Ans. $K_4[Fe(CN)_6]$

Q. 11. Give one use of Ziegler Natta catalyst.

Ans. Heterogeneous catalysis or in high density polymerisation.

Q. 12. 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. 13. The chemical formula of Wilkinson's catalyst is :

Ans. $[(Ph_3P)_3RhCl]$

Q. 14. Which of the two is more stable – $K_4[Fe(CN)_6]$ Or $K_3[Fe(CN)_6]$?

Ans. $K_4[Fe(CN)_6]$ because Fe has d^6 configuration in this case.

Q. 15. Arrange the following complexes in order of increasing electrical conductivity :

$[CO(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4]Cl_3$

Ans. $[CO(NH_3)_3Cl_3] < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_4Cl]Cl_3$

More number of ions < more electrical conductivity

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Calculate the magnetic moments of the following complexes :

(i) $[Fe(CN)_6]^{-4}$ **(ii) $[FeF_6]^{-3}$**

Ans. (i) $Fe^{+2} \rightarrow 3d^6$. CN^- is a strong ligand so e^- pair $4p$, no unpaired e^- then magnetic moment is zero

(ii) $$\mu_{BH} = \sqrt{n(n+2)} = 0$$

$n = 5$, So $$\mu = \sqrt{n(n+2)}$$

$$\mu = \sqrt{5(5+2)}$$

$$\mu = \sqrt{35} = 5.96 \text{ BM}$$

Q. 2. Explain the following :

(i) NH_3 act as a ligand but NH_4^+ does not.

(ii) CN^- is a ambidentate ligand.

Ans. (i) NH_3 has one lone pair while NH_4^+ does not.

(ii) Because it has two donor atoms in a monodentate ligand.

Q. 3. Mention the main postulates of Werner theory.

Ans. (i) Metal ion has two types of valency.

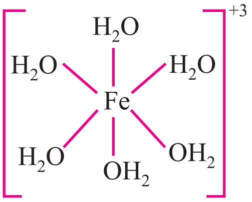
(ii) Primary valency and secondary valency.

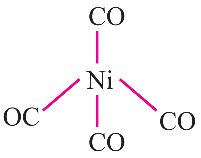
(iii) Secondary valency is equal to coordination number.

Q. 4. Draw the structure of :

(i) $[Ni(CO)_4]$ (ii) $[Fe(H_2O)_6]^{+3}$

Ans.





Q. 5. How does EDTA help as a cure for lead poisoning ?

Ans. Calcium in Ca-EDTA complex is replaced by lead in the body. The more soluble compled lead-EDTA is eliminated in urine.

Q. 6. Define homoleptic and heteroleptic complexes.

Ans. **Homoleptic :** When metal atom/ion is linked with one type of ligands. Example, $[Ni(CO)_4]$.

Heteroleptic : With the more than one kind of ligands. Example, $[Co(NH_3)_4Cl_2]^+$.

Q. 7. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why ?

Ans. In $[NiCl_4]^{-2}$, Ni has $3d^8 4s^0$ configuration, Cl^- can't pair up while in $[Ni(CO)_4]$, Ni has $3d^8 4s^2$ configuration, CO pair up electrons

Q. 8. The oxidation number of cobalt in the complex :

(i) $K[Co(CO)_4]$ (ii) $[Co(C_2O_4)_3]^{-3}$

Ans. (i) – 1 (ii) + 3

Q. 9. What are t_{2g} and e_g orbitals ?

Ans. In a free transition metal ion, the *d*-orbitals are degenerate. When it form complex, the degeneracy is split and *d*-orbitals split into t_{2g} and e_g orbitals.

Q. 10. What is the solution in which photographic film is washed ? What reaction takes place ?

Ans. Hypo solution.

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Q. 11. What is spectrochemical series ?

Ans. The arrangement of ligands in order of their increasing crystal field splitting field strength.

Q. 12. What are the assumptions of Crystal Field theory.

Ans. (i) Ligand act as a point charge.

(ii) Metal ion has electrostatic attraction force with the ligand.

(Or any other)

Q. 13. $CuSO_4$ is colourless while $CuSO_4.5H_2O$ is coloured. Why ?

Ans. $CuSO_4$ does not has any ligand, so splitting of *d*-orbital take place while $CuSO_4.5H_2O$ has water ligand.

Q. 14. What is the difference between inner and outer orbital complexes ?

Ans. **Inner sphere complex :** When *d*-orbital of inner shell take part in hybridisation.

Outer sphere complex : When *d*-orbital of outermost shell take part in hybridisation.

Q. 15. How is stability of coordination compound determined in aqueous solution ?

Ans. By using stability constant.

More stability constant, more stability.

Q. 16. In a complex ion $[Co(NH_3)_5NO_2]Cl_2$,

(i) Identify the ligand.

(ii) Oxidation number of metal ion.

Ans. (i) NH_3, NO_2.

(ii) + 3

Q. 17. Explain how the nature of ligand affects the stability of complex ion.

Ans. Strong ligand : More stability

Weak ligand : Less stability

Q. 18. What is meant by denticity of a ligand ? Find out denticity of :

(i) $C_2O_4^{-2}$ (ii) EDTA

Ans. The number of ligand group/coordinating group.

(i) 2 (ii) 6

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. **A coordination compound has the formula $CoCl_3.4NH_3$. It does not liberate NH_3 but forms a precipitate with $AgNO_3$. Write the structure and IUPAC name of the complex compound. Does it show geometrical isomerism ?**

Ans. Formula : $[Co(NH_3)_4Cl_2]Cl$

Name : Tetraaminedichloridocobalt(III) chloride

Yes, it show geometrical isomerism.

Q. 2. **Why does a tetrahedral complex of the type $[MA_2B_2]$ not show geometrical isomerism ?**

Ans. Because all position of tetrahedral is same in orientation.

Q. 3. **The molar conductivity of the complex $CoCl_3.4NH_3.2H_2O$ is found to be same as that of 3 : 1 electrolyte. What is the structural formula. Name and number of geometrical isomer of the complex.**

Ans. As coordination number of Co is 6 and complex should be A_3B or AB_3 type, formula is $[Co(NH_3)_4(H_2O)_2]Cl_3$.

Name : Tetraaminediaqua cobalt (III) chloride

Geometrical isomer : 2 (cis and trans)

Q. 4. **$[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. Why ?**

Ans. $[Ti(H_2O)_6]^{3+}$: In this core Ti^{+3} has one unpaired e^- while Sc^{+3} does not has any unpaired electron.

Q. 5. **Describe with an example of each, the role of coordination compounds in :**

(i) Biological system

(ii) Analytical chemistry

(iii) Medicinal chemistry

Ans. (i) Vit. B-12, it is a antipernicious anemia factor.

(ii) Determining and estimation of metal.

(iii) EDTA is used in lead poisoning.

Q. 6. **Write the type of isomerism exhibited by the following complexes :**

(i) $[Co(NH_3)_5Cl]SO_4$

(ii) $[Co(en)_3]^{+3}$

(iii) $[Co(NH_3)_6][Cr(CN)_6]$

Ans. (i) Ionization

(ii) Optical

(iii) Coordination isomerism

Q. 7. Explain the following :

(i) CO is stronger ligand than NH_3.

(ii) Low spin octahedral complexes of nickel are not known.

(iii) Aqueous solution of $[Ti(H_2O)_6]^{+3}$ is coloured.

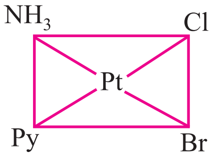
Ans. (i) CO has high value of crystal field splitting energy than Cl.

(ii) Ni has d^8 configuration which does not affect by field strength of ligand.

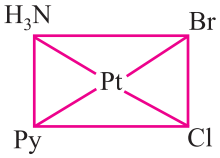
(iii) In this case, Ti^{+3} has $t_{2g}^{\ 1}\ e_g^{\ 0}$ configuration. It can perform *d*-*d* transition.

Q. 8. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(Py)]$ and how many of these will exhibit optical isomerism ? Here, Py = Pyridine.

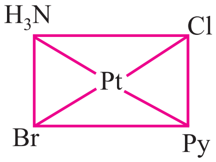
Ans. 3 isomers are possible.



Cis-



Cis-



Trans-

Monodentate ligand in square planar complex do not show optical isomerism.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. A metal ion M^{n+} having d^4 valence electronic configuration combines with three didentate ligands to form a complex compound. Assuming $\Delta_o > p$:

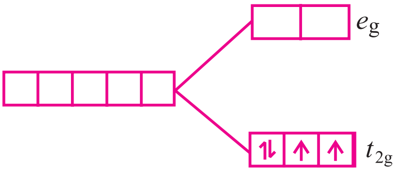
(i) Draw the diagram showing *d*-orbital splitting during this complex formation.

(ii) What type of hybridisation will M^{n+} have ?

(iii) Name the type of isomerism exhibited by this complex.

(iv) Write the electronic configuration of metal M^{n+}.

Ans. (i) If $\Delta_o > p$ then



(ii) d^2sp^3

(iii) $[M(AA)_3]$ type complex show optical isomerism.

(iv) $t_{2g}^{\ 4}\ e_g^{\ 0}$

Q. 2. (i) Discuss the nature of bonding in metal carbonyls.

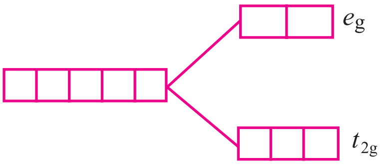
(ii) Draw figure to show the splitting of *d*-orbitals in an octahedral crystal field and write electronic configuration of M^{2+} ion when :

(a) $\mathbf{p > \Delta_o}$

(b) $\mathbf{\Delta_o > p}$

Ans. (i) The metal carbon bond in metal carbonyls possess both σ and π character. The M – C σ bond if formed by the $M \leftarrow C \equiv O$ while M – C π bond if formed by the donation of a pair of electron from filled *d*-orbital of metal to antibonding π^* orbital of CO.

(ii)



(a) $t_{2g}^{3}\,e_{g}^{2}$ (b) $t_{2g}^{5}\,e_{g}^{0}$

Q. 3. (i) $\mathbf{[Fe(CN)_6]^{4-}}$ **and** $\mathbf{[Fe(H_2O)_6]^{2+}}$ **are of different colours in dilute solution. Why ?**

(ii) A complex is prepared by mixing $\mathbf{CoCl_3}$ **and** $\mathbf{NH_3}$ **in the molar ratio of 1 : 4. 0.1M solution of this complex was found to be freeze at – 0.372º C. What is the formula of the complex ?** $\mathbf{K_f = 1.86^{o}C/M}$

Ans. (i) In both the cases Fe is in + 2 state, it has 4 unpaired electrons but CN^- and H_2O has different crystal field splitting energy.

(ii) $\Delta T_f = i.K_f.m$

i = 2 means complex dissociate into two ions.

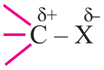
Hence the formula is $[Co(NH_3)_4Cl_2]Cl$

UNIT 9

HALOALKANES AND HALOARENES

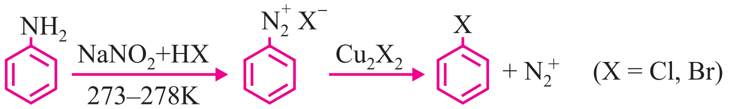
Points to Remember

1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I)
2. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula Ar – X.
3. Since halogen is more electronegative than C, hence C – X bond is polar.



4. **Named Reactions :**

(a) Sandmeyer Reaction :



(b) Finkelstein Reaction :

$$R - X + NaI \xrightarrow{\text{dry acetone}} R - I + NaX \quad (X = Cl, Br)$$

(c) Swartz Reaction :

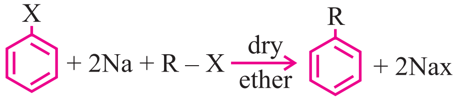
$$CH_3 - Br + AgF \rightarrow CH_3 - F + AgBr$$

Instead of Ag – F, other metallic fluoride like Hg_2F_2, CoF_2 or SbF_3 can also be used.

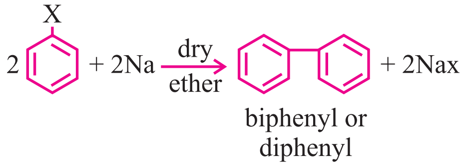
(d) Wurtz Reaction :

$$2R - X + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

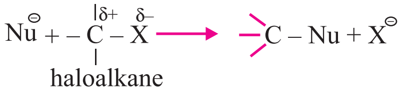
(e) Wurtz-Fittig Reaction :



(f) Fittig Reaction :

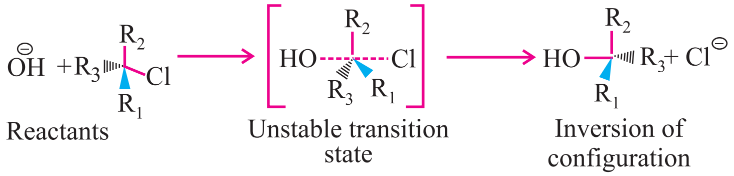


5. Nucleophilic Substitution Reactions :



$$\overset{\ominus}{Nu} + -\overset{|\,\delta+}{\underset{|}{C}} - \overset{\delta-}{X} \longrightarrow\ >C - Nu + X^{\ominus}$$

(a) Substitution nucleophilic bimolecular ($S_N{}^2$) :

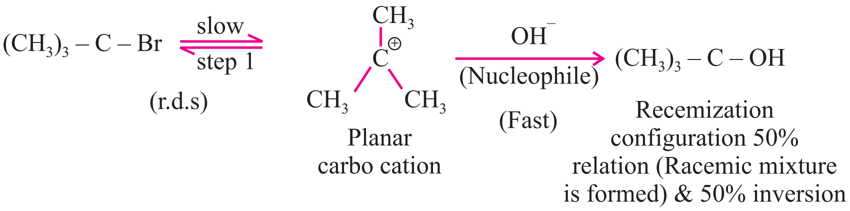


1. 1° haloalkane
2. Bimolecular, 2nd order
3. One step

Order of reactivity : 1° > 2° > 3°

Deciding factor : Steric hindrance

(a) Substitution nucleophilic unimolecular ($S_N{}^1$) :



1. 3° haloalkane
2. Unimolecular, 1st order
3. Two steps

Order of reactivity : 3° > 2° > 1°

Deciding factor : Stability of carbo cation

* Allylic $\left[CH_2 = CH - \overset{\oplus}{C}H_2\right]$ and benzylic $\left[C_6H_5\overset{\oplus}{C}H_2\right]$ halides undergo reaction via SN^1 mechanism as the corresponding carbo cations are resonance stabilized.

6. Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

7. Halogen is deactivating but *o, p*-directing in electrophilic substitution reaction of haloarenes.

8. $CHCl_3$ is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

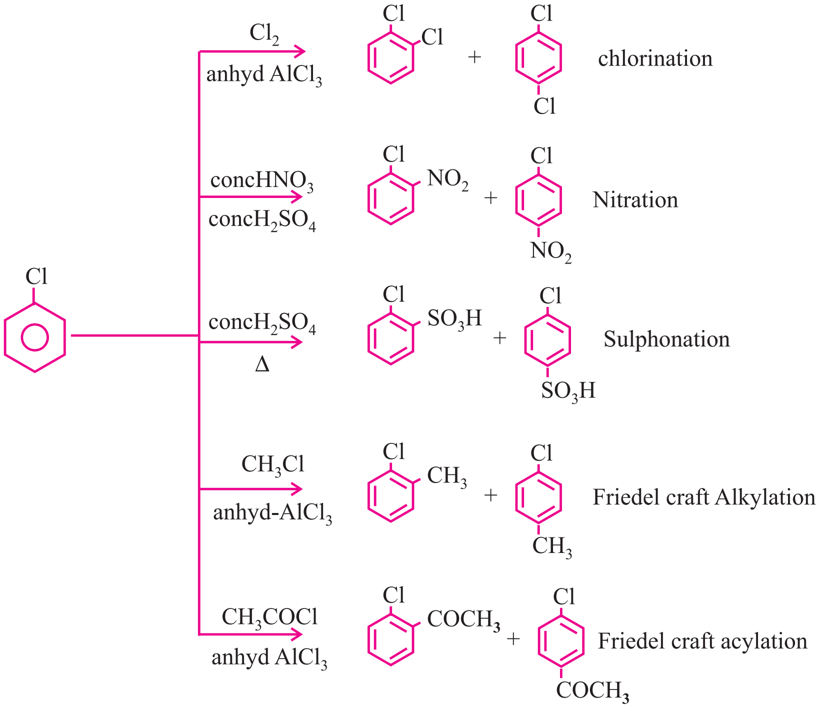
$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Chloroform Carbonyl chloride (phosgene)

9. Reaction of Haloalkanes :

$$R\text{–}X \xrightarrow{NaOH \text{ or } KOH} R\text{–}OH$$
$$R\text{–}X \xrightarrow{NaI} R\text{–}I$$
$$R\text{–}X \xrightarrow{KCN} RCN$$
$$R\text{–}X \xrightarrow{AgCN} RNC$$
$$R\text{–}X \xrightarrow{KNO_2} R\text{–}O\text{–}N = O$$
$$R\text{–}X \xrightarrow{AgNO_2} R\text{–}NO_2$$
$$R\text{–}X \xrightarrow{LAH} RH$$
$$R\text{–}X \xrightarrow{NH_3} R\text{–}NH_2$$
$$R\text{–}X \xrightarrow{Mg} R\text{–}MgX$$
$$R\text{–}X \xrightarrow{Na,\ D.E.} R\text{–}R$$
$$R\text{–}X \xrightarrow{NaOR} R\text{–}O\text{–}R'$$
$$R\text{–}X \xrightarrow{R'COOAg} R'COOR$$

10. Electrophilic Substitution Reaction of Haloarenes :

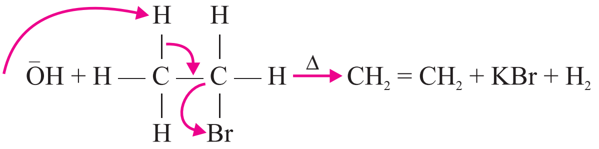


11. Elimination reaction: Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atom. [Reverse of addition]

Two types (*i*) β-Elimination ⟶ ($E_1 \rightarrow$ Two step eliminate; $E_2 \rightarrow$ One step eliminate)

(*ii*) α-elimination

Saytzaff's Rule



$$CH_3-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow{\text{Aloc.KOH}} CH_2 = CH_2 + KBr + H_2$$

(81% More highly substituted Alkenes,
More stable)

12. Distinguishing test for alkyl chlorides, bromides and iodide : Alkyl chlorides react with $AgNO_3$ to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with $AgNO_3$ to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with $AgNO_3$ to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.

E.g., $$CH_3-Cl \xrightarrow[AgNO_3]{HNO_3} AgCl\downarrow$$

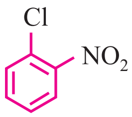
White ppt.

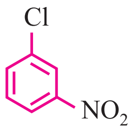
Vinyl and aryl halides do not yield silver halide under these conditions.

MULTIPLE CHOICE QUESTIONS

1. Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:

(a) 

(b) 

(c) 

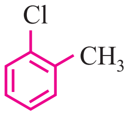
(a) a < b < c

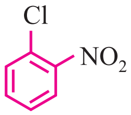
(b) a < b < a

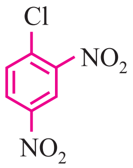
(c) a < c < b

(d) c < a < b

2. Arrange the following compound in increasing order of rate of reaction towards nucleophilic substitution.

(i) 

(ii) 

(iii) 

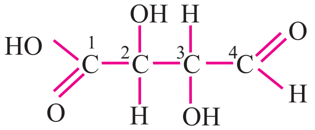
(a) i < ii < iii

(b) i < iii < ii

(c) ii < i < iii

(d) iii < ii < i

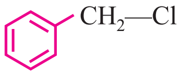
3. Which of the carbon atom present in the molecule given below are asymmetric.

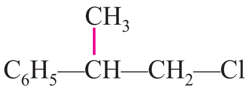
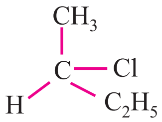


(a) 1, 2 , 3, 4 (b) 2, 3

(c) 1, 4 (d) 1, 2, 3

4. Which of the following compound will undergo recevisation when solution of KOH hydrolyses?

(i)  (ii) $CH_3CH_2—CH_2—Cl$

(iii)  $C_6H_5—\overset{CH_3}{\overset{|}{C}H}—CH_2—Cl$ (iv) 

(a) i and iv (b) ii and iv

(c) iii and iv (d) iv

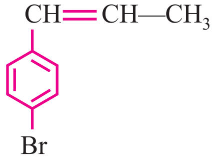
5. In a $S_N{}^1$ reaction on chiral centres, there is

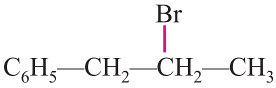
(a) 100 % retention (b) 100 % inversion

(c) 100 % recenisation

(d) inversion is more than retention leading to recenisation

6. The reaction of $C_6H_5—CH{=}CH—CH_3$ with HBr produces

(a) $C_6H_5—CH_2\ CH_2—CH_2—Br$ (b) 

(c)  $C_6H_5—\overset{Br}{\overset{|}{C}H}—CH_2—CH_3$ (d)  $C_6H_5—CH_2—\overset{Br}{\overset{|}{C}H_2}—CH_3$

7. In $S_N{}^2$ reactions, the correct order of reactivity fo the following compounds:

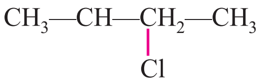
(i) CH_3Cl (ii) $(CH_3)_3CCl$

(iii) $(CH_3)_2CHCl$ (iv) $CH_3CH_2—Cl$

(a) i > ii > iii > iv (b) iv > iii > ii > i

(c) i > iv > iii > ii (d) iv > i > ii > iii

8. The increasing order of reactivity of the following halides for the $S_N{}^1$ reaction is

(i)  $CH_3—CH—\underset{Cl}{\underset{|}{C}H_2}—CH_3$ (ii) $CH_3—CH_2—CH_2—Cl$

(iii) $P—H_3CO—C_6H_4—CH_2—Cl$

(a) iii < ii < i (b) ii < i < iii

(c) i < iii < ii (d) ii < iii < i

9. Arrange the following compounds in increasing order of their boiling point

(i) $(CH_3)_2CH_2CH_2—Br$ (ii) $CH_3—(CH_2)_3—Br$ (iii) $(CH_3)_3C—Br$

(a) ii < i < iii (b) i < ii < iii

(c) iii < i < ii (d) iii < ii < i

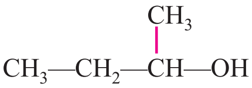
10. Toluene reacts with halogen in thepresence of $FeCl_3$ giving ortho and parabola compound. The reactions is

(a) electrophilic elimination reaction (b) electrophilic substitution

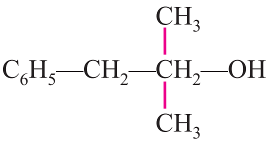
(c) free radical addition reaction (d) nucleophilic substitution

11. The order of reactivity of following alcohols with halogen acid (HX) is

(i) $CH_3—CH_2—CH_2—OH$

(ii) 

$CH_3—CH_2—\overset{\displaystyle CH_3}{\overset{|}{C}H}—OH$

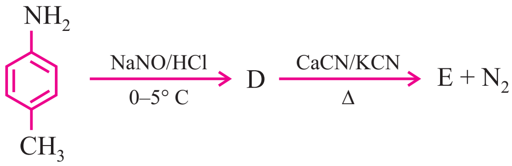
(iii) 

$C_6H_5—CH_2—\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}H_2}}}—OH$

(a) i > ii > iii (b) iii > ii > i

(c) ii > i > iii (d) i > iii > ii

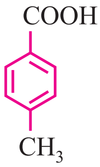
12. In the reaction



the product is:

(a) 

(b) 

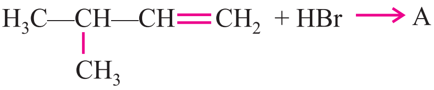
(c) 

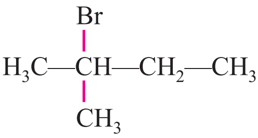
(d) 

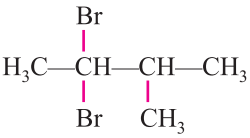
13. Chlorobenzene is formed by reactionj of chlorine with benzene in presence of $AlCl_3$. Which of the following species attacks the beneze ring in this reaction.

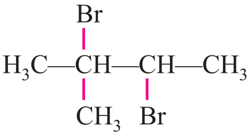
(a) Cl^- (b) Cl^+

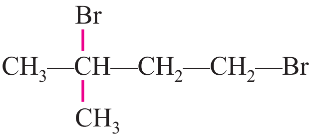
(c) $AlCl_3$ (d) $AlCl_4^-$

14. 
$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 + HBr \longrightarrow A$

(a) 
$H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}H-CH_2-CH_3$

(b) 
$H_3C-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}H-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(c) 
$H_3C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}H-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$

(d) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}H-CH_2-CH_2-Br$

15. The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives 'X' and the reaction with Cl_2 in presence of light gives 'Y'. Thus 'X' and 'Y' are:

(a) 'X' = benzyl chloride and 'Y' = m-chlorotoluene

(b) 'X' = benzyl chloride and 'Y' = o-chlorotoluene

(c) 'X' = m-chlorotoluene and 'Y' = p-cholorotoluene

(d) 'X' = p-chlorotoluene and 'Y' = benzyl chloride.

16. Anyl halides are less reactive toward nucleophilic substitution reaction than alkyl halides due to

(a) the formation of stable carbonimion

(b) resonance stabilization

(c) longer carbon-halogen bond

(d) sp^2 hybridised carbon attached to halogen

17. A new carbon carbon bond is possible in the following reaction reactions:

(a) $C_6H_6 + CH_3Cl \xrightarrow{\text{anhy. AlCl}_3}$

(b) $CH_3CH_2Br + CH_3CH_2NH_2 \longrightarrow$

(c) $CH_3-Br + CH_3CH_2-ONa \longrightarrow$

(d) $CH_3CH_2-Br + kCN(alc) \longrightarrow$

18. Which of the following state are correct

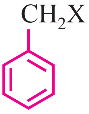
(a) Benzyl halides are more reactive than vinyl and anyl halides

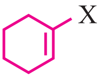
(b) Vinyl/halides are more reactive than alkyl halides

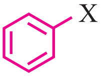
(c) Aryl halides are less reactive than alkylhalide

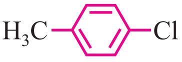
(d) Aryl halides are more reactive than benzyl halides

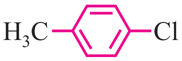
19. Which of the following contain sp^2 hybridised carbon bonded to X?

(a) 

(b) 

(c) 

(d) 

20. The IUPAC name of the following compound are 

(a) 1-chloro-4-methyl benzene (b) 4-chlorotoluene

(c) 1-methyl-4-chlorobenzene (d) 4-methylchlorobenzene

Note : *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.*

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

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

(c) Assertion is Incorrect, but reason is Correct.

(d) Both assertion and reason are Incorrect.

Assertion and Reasoning

21. Assertion : S_N^2 reaction proceeds with inversion of configuration.

Reason : S_N^2 reactionoccurs in one step

22. Assertion : Treatment of chloroethane with saturated solution of AgCN give ethyl isocyanide as major product.

Reason : Cyanide ion (CN^-) is an ambident nucleophile.

Matching Column Type

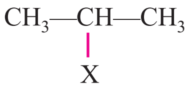
23. Match the items of column 1 and column 2

Column1	**Column 2**
(A) CH_2Cl_2	P. Antiseptic
(B) CCl_4	Q. Insecticide
(C) (p-Cl C_6H_4)$CHCCl_3$	R. Pyrene
(D) CHI_3	S. Refrigerend

(a) A–R, B–Q, C–S, D–P (b) A–S, B–R, C–Q, D–P

(c) A–Q, B–P, C–S, D–R (d) A–P, B–S, C–R, D–Q

24. Match the items of column 1 and column 2

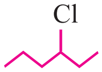
(A)  $CH_3—\underset{X}{\underset{\mid}{C}H}—CH_3$	P. Anyl halide
(B) $CH_2=CH—CH_2—X$	Q. Alkyl halide
(C) 	R. Vinyl halide
(D) $CH_2=CH—X$	S. Allyl halide

(a) A–P, B–Q, C–S, D–P (b) A–S, B–R, C–Q, D–P

(c) A–Q, B–P, C–S, D–R (d) A–P, B–S, C–R, D–Q

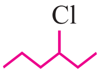
Integer Type Question

25. In how many pairs, the second compound reacts faster than the first in S_N1 reaction with OH^-?

(i)  , 

(ii) CH_3I, CH_3Br

(iii) $(CH_3)_3CBr$, $(CH_3)_2HBr$

(iv)  , 

(v) CH_3Cl, $(CH_3)_2CHCl$

(vi) $(CH_2)_2CHBr$, CH_3CH_2Br

0	1	2	3	4	5	6	7	8	9

ANSWERS

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

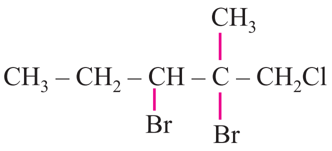
11. (b) **12.** (a) **13.** (b) **14.** (a) **15.** (d)

16. (b, d) **17.** (a, d) **18.** (a, c) **19.** (b, d) **20.** (a, b)

21. (b) **22.** (b) **23.** (b) **24.** (b)

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Give IUPAC name of :



$$CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2Cl$$

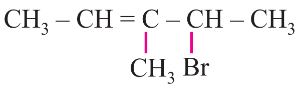
[*Hint :* 1-chloro-2, 3-dibromo-2-methyl pentane]

Q. 2. Identify A and B in each of the following processes :

$$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{Reduction} B$$

[*Hint :* A : CH_3-CH_2-CN; B : $CH_3CH_2CH_2NH_2$]

Q. 3. Draw the structure of 4-bromo-3-methylpent-2-ene.

[*Hint :* 

$$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-\underset{Br}{\underset{|}{CH}}-CH_3$$

Q. 4. Why Grignard reagent should be prepared under anhydrous conditions ?

Q. 5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Q. 6. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure ?

[*Hint* 

$$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_3$$

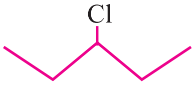
Q.7. An organic compound 'A' on treatment with KCN gave B which on hydrolysis with dil. HCl gave acetic acid. Identify A.

[*Hint :* A : CH_3Cl]

Q. 8. Write IUPAC name of iodoform.

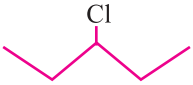
[*Hint :* Triiodomethane]

Q. 9. Which one of the following two substances undergo SN^1 reaction faster and why ?



Or

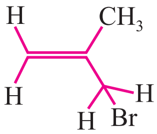
(Hint :



(2°)

Q. 10. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanides as the chief product. Explain.

Q. 11. Write the IUPAC name of the following compound :



[*Hint :* 3-bromo-2-methylprop-1-ene]

Q. 12. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions :

$$CH_3F, CH_3I, CH_3Br, CH_3Cl$$

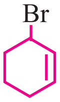
[*Hint :* $CH_3F < CH_3Cl < CH_3Br < CH_3I$]

Q. 13. Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution reaction. Explain why ?

Q. 14. Complete the reaction :

$+ Br_2 \xrightarrow[\text{Uv light}]{\text{heat or}}$

(Hint :



)

Q. 15. How will you convert 2-bromo propane into 1-bromo propane ?

Q. 16. Give one chemical test to distinguish between chlorobenzene and benzyl chloride ?

[*Hint :* $AgNO_3$ test]

Q. 17. Why iodoform show antiseptic properties ?

[*Hint :* Due to free liberated iodine.]

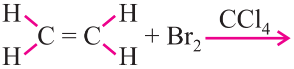
Q. 18. The presence of nitro group ($-NO_2$) at ortho or para positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. Explain.

Q. 19. For the preparation of alkyl chlorides from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following reactions :

(i) $C_6H_5N_2Cl + KI \rightarrow$

(ii) 

$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4}$

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 :

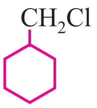
(i) Boiling point of alkyl bromide is higher than alkyl chloride.

(ii) Alkyl halides are better solvents than aryl halides.

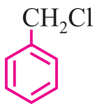
[*Hint :* (i) High magnitude of van der Waal's forces in alkyl bromides.

(ii) C – X is more polar in haloalkanes.]

Q. 4. Which of the following compounds would undergo S_N^1 reaction faster and why ?



(A)



(B)

Hint : B

Q. 5. Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre :

(i) 1, 2-dichloropropane

(ii) 3-bromopent-1-ene

Q. 6. Convert :

(i) Benzene to m-nitrochlorobenzene

(ii) Benzene to diphenyl

Q. 7. What happens when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

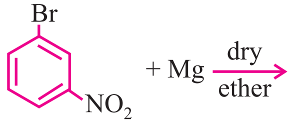
Q. 8. (i) Alkyl iodides develop colouration on long standing particularly in light. Explain.

[*Hint :* (i) Due to decomposition by light and produce I_2.]

Q. 9. Tert-butyl bromide reacts with aq. NaOH by S_N^1 mechanism while n-butylbromide reacts with S_N^2 mechanism. Why ?

Q. 10. Although chlorine is an electron withdrawing group, yet it is o, p-directing in electrophilic aromatic substitution reactions. Explain, why is it so ?

Q. 11. Identify the products :

(i) 

(ii) 

$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{alc.KOH}} A \xrightarrow[H_2O_2]{HBr} B$$

Q. 12. (i) Arrange the following halides in order of increasing $S_N{}^1$ reactivity :

CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

(ii) Which out of 1-bromobutane & 2-bromobutane would react faster by $S_N{}^2$ pathway and why ?

Q. 13. Identify the products :

$$C_6H_6 \xrightarrow[\text{anhy.}AlCl_3]{CH_3Cl} A \xrightarrow[hv]{Cl_2\,(1\text{ mole})} B \xrightarrow{\text{aq.KOH}} C \xrightarrow{HBr} D$$

Q. 14. Carry out the following conversions :

(i) But-1-ene to n-butyliodide

(ii) Isopropyl alcohol to iodoform

Q. 15. An organic compound A reacts with PCl_5 to give compound B. Compound B reacts with Na/ether to give n-butane. What are compounds A and B ?

[*Hint :* A = C_2H_5OH, B = C_2H_5Cl]

Q. 16. Write short note on :

(i) Sandmeyer reaction

(ii) Finkelstein reaction

Q. 17. Name the reagents used to convert :

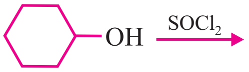
(i) 2-chloropropane to 2-nitropropane

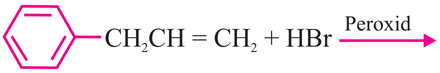
(ii) Chloroethane to n-butane

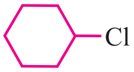
[*Hint :* (i) $AgNO_2$

(ii) Na/dry ether]

Q. 18. Draw structure of monohalo product in each of the following :

(i) 

(ii) 

Ans. (i) 

(ii) 

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Rearrange the compounds of each of the following sets in order of reactivity towards S_N^2 displacement :

(i) 2-bromo-2-methyl butane, 1-bromopentane, 2-bromopentane

(ii) 1-bromo-3-methylbutane, 2-bromo-2-methyl butane, 2-bromo-3-methyl butane

(iii) 1-bromobutane, 1-bromo-2, 2-dimethyl propane, 1-bromo-2-methyl butane

Q. 2. Answer the following :

(i) Haloalkanes easily dissolve in organic solvents, why ?

(ii) What is known as racemic mixture ? Give example.

(iii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N^1 substitution reaction and why ?

Q. 3. Answer the following :

(i) What is meant by chirality of a compound ? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why ?

$$CH_3CHClCH_2CH_3 \text{ or } CH_3CH_2CH_2Cl$$

(iii) Which one undergo S_N^2 substitution reaction faster and why ?

or

Q. 4. Complete the following reactions :

(i) $CH_3CH_2OH \xrightarrow{SOCl_2} A \xrightarrow{KCN} B$

(ii) $(CH_3)_2CHBr + Na \rightarrow$

(iii) $CH_3CH_2Cl \xrightarrow{AgNO_3}$

Q. 5. How the following conversions can be carried out ?

(i) But-1-ene to n-butyl iodide

(ii) Tert-butyl bromide to isobutyl bromide

(iii) Ethanol to but-1-yne

Q. 6. Write short notes on :

(i) Wurtz-Fittig reaction

(ii) Fittig reaction

(iii) Dehydrohalogenation reaction

Q. 7. An organic compound 'A' having molecular formula C_4H_8 on treatment with dil. H_2SO_4 give another compound 'B'. B on treatment with conc. HCl and anhy. $ZnCl_2$ gives 'C'. C on treatment with sodium ethoxide gives back 'A'. Identify the compound. Write the equations involved.

Q. 8. What happens when :

(i) 1-bromopropane reacts with metallic sodium.

(ii) Bromoethane is treated with caustic potash.

(iii) Iodomethane is treated with ammonia.

Q. 9. Identify A, B and C :

$$\text{2-propanol} \xrightarrow{SOCl_2} A \xrightarrow{Mg} B \xrightarrow{H_2O} C$$

Q. 10. Account for the following :

(i) A small amount of ethyl alcohol is added to $CHCl_3$ stored for use as an anaesthetic.

(ii) After using CCl_4 as a fire extinguisher inside a closed space, the space is thoroughly ventilated.

(iii) When 2-chloro-3-methylbutane is treated with alcoholic potash, 2-methyl-2-butene is the main product.

[*Hint :* (i) To convert harmful $COCl_2$ to ethyl carbonate.

(ii) To sweep out $COCl_2$ formed by CCl_4 vapour and H_2O vapour.

(iii) Saytzeff rule.

Q. 11. How will you distinguish between :

(i) Vinyl chloride and ethyl chloride

(ii) Chlorobenzene and cyclohexyl chloride

(iii) Ethyl chloride and ethyl bromide

Q. 12. Explain the following :

(i) The dipole moment of chloroethane is higher than that of chlorobenzene.

(ii) Although haloalkane are polar in character yet they are insoluble in water.

(iii) Vinyl chloride is unreactive in nucleophilic substitution reactions.

Q. 13. (i) Which will have a higher boiling point ?

1-chloroethane or 2-chloro-2-methyl butane. Give reason.

(ii) p-chloronitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving resonating structure as well.

Q. 14. (i) What are ambident nucleophiles ? Explain with an example.

(ii) Convert ethyl bromide to diethyl ether.

(iii) What are freons ?

Q. 15. A hydrocarbon 'A' (C_4H_8) is added with HBr in accordance with Markonikov's rule to give compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ($C_4H_{10}O$). Identify A, B and C.

Q. 16. (i) Which isomer of C_4H_9Cl will have the lowest boiling point ?

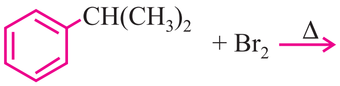
(ii) Predict the alkenes that would be formed by dehydrohalogenation with sodium ethoxide and ethanol. Predict major alkenes :

(a) 2-chloro-2-methylbutane

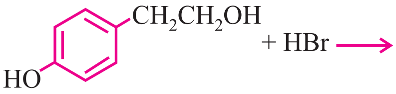
(b) 3-bromo-2, 2, 3-trimethylpentane

Q. 17. Write the structure of major product in each of the following :

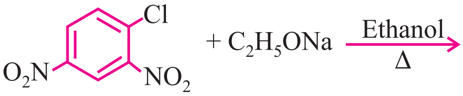
(i)



(ii)



(iii)



Q. 18. Write the main products when :

(i) n-butyl chloride is treated with alcoholic KOH

(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.

(iii) Methyl chloride is treated with AgCN.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How would you bring about the following conversions :

(i) Propene to 2-bromopropane

(ii) Bromoethane to propanoic acid

(iii) 1-chloropropane to 1-propanol

(iv) Ethanol to chloroethane

(v) 1-iodopropane to propene

Q. 2. What happens when : (Give chemical reactions)

(i) Cyclohexanol is treated with thionyl chloride

(ii) p-hydroxybenzyl alcohol is heated with HCl.

(iii) Ethyl bromide is refluxed with NaI in acetone.

(iv) Ethyl bromide is treated with mercurous fluoride.

(v) Chlorobenzene is subjected to hydrolysis.

Q. 3. Complete the following reactions :

(i) $C_6H_6 \xrightarrow{Cl_2/Fe} X \xrightarrow[\text{Pyridine}]{CuCN} Y \xrightarrow{H^+,H_2O}$

(ii) $C_2H_4 \xrightarrow{HBr} X \xrightarrow{\text{aq. KOH}} Y \xrightarrow{I_2,NaOH} Z$

(iii) $CH_3CH_2Br \xrightarrow{AgCN} A$

(iv) 3-ethylpent-2-ene $\xrightarrow{Br_2/H_2O} B$

Q. 4. Account for the following :

(i) Sulphuric acid is not used during the reaction of alcohols with KI.

(ii) p-methoxybenzyl bromide reacts faster than p-nitrobenzyl bromide with sodium ethoxide to form an ether product.

(iii) Organic halogen compounds used as solvents in industry are chlorides rather than bromides and iodides.

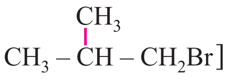
(iv) Wurtz reaction fails in case of tert-alkyl halides.

(v) Alkyl halides are insoluble in water though they contain a polar C – X bond.

(vi) Use of $CHCl_3$ as anaesthetic is not preferred.

Q. 5. (i) A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

(ii) Iodoform gives a precipitate with $AgNO_3$ on heating while $CHCl_3$ does not. Why ?



[*Hint :* A : $\Rightarrow CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2Br$]

CONCEPTUAL QUESTIONS

Q. 1. Why haloalkanes are more reactive than haloarenes?

Ans. In haloarenes, there is partial double bond character b/w carbon and halogen due to resonance effect which makes him less reactive.

(ii) In benzene, carbon being sp^2 hybridised which is smaller in size than sp^3 present in haloalkanes. So C–Cl bond in aryl halides is shorter and stronger.

Q. 2. Why do haloalkenes under go nucleophillic substitution whereas haloarenes under go electophillic substitution?

Ans. Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophillic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophillic reagents.

Q. 3. When an alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide where as if alkyl halide is treated with AgCN,the major product is alkyl isocyanide?

Ans. Refer NCERT

Q. 4 The treatment of alkyl chlorides with aqueous KOH lead to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain?

Ans. In aqueous KOH,OH^- is nucleophile which replaces another nucleophile.

$R\text{-}X + KOH \longrightarrow R\text{-}OH + KX$

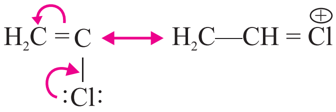
Where as in alcoholic KOH, $C_2H_5O^-$ ion is produced which is a strong base hence β-elimination took place to form alkane

$C_2H_5OH + KOH \longrightarrow C_2H_5O\text{-} + K^+$

$CH_3CH_2\text{-}Cl + \text{alcoholic KOH} \longrightarrow CH_2 = CH_2 + C_2H_5OH$

Q. 5 Explain why vinyl chloride is unreactive in nucleophillic substitution reaction?

Ans. Vinyl chloride is unreactive in nucleophillic substitution reaction because of double bond character between C–Cl bond which is difficult to break.



$$H_2C=\underset{\displaystyle :Cl:}{\underset{|}{C}} \longleftrightarrow H_2C-CH=\overset{\oplus}{Cl}$$

Q. 6 Arrange the following compounds according to reactivity towards nucleophillic substitution reaction with reagents mentioned :-

(i) 4-nitrochlorobenzene> 2,4 dinitrochlorobemzene > 2,4,6, trinitrochlorobenzene with CH_3ONa

Ans. 2,4,6, trinitrochlorobenzene > 2,4 dinitrochlorobemzene > 4- nitrochlorobenzene

Q. 7 Why Grignard reagent should be prepared under an hydrous conditions?

Ans. Grignard reagent react with H_2O to form alkanes, therefore they are prepared under anhydrous condition.

Q. 8 Why is Sulphuric acid not used during the reaction of alcohols wiht KI?

Ans. It is because HI formed will get oxidized to I_2 by concentrated Sulphuric acid which is an oxidizing agent.

Q. 9 p-dichlorobenzene has highest m.p. than those of ortho and m-isomers?

Ans. p-dichlorobenzene is symmetrical, fits into crystal lattice more readily and has higher melting point.

Q. 10. Give reasons:

(i) C–Cl bond length in chlorobenzene is shorter than C–Cl bond in CH_3Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_N1 reactions are accompained by racemization in optically active alkyl halides.

Ans. (i) In chlorobenzene, each carbon atom is sp^2 hybridised/ resonating structures / partial donable bond character.

(ii) Due to + R effect in chlorobenzene / difference in hybridization i.e., sp^2 and sp^3 respectively.

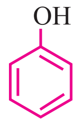
(iii) Due to formation of planer carbocation.

UNIT-10

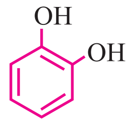
ALCOHOLS, PHENOLS AND ETHERS

Quick Concepts to Remember

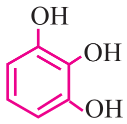
1. Hydroxyl (– OH) derivatives of alkane are called alcohols.
2. Alcohols are classified as 1°, 2° and 3°.
3. –OH group is attached to sp^3 hybridized carbon. Alcohols further may be monohydric, dihydric and polyhydric on the basis of OH group.
4. **Phenols :** Compounds containing – OH group bound directly to benzene ring.



Phenol

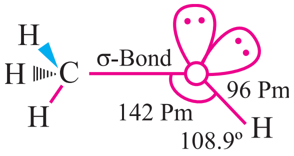


Catechol



Pyrogallol

5. **Structure :** Oxygen atom is sp^3 hybridised and tetrahedral geometry of hybrid atomic orbitals ROH bond angle depends upon the R group. R – O – H angle for $CH_3 – OH$ is 108.9°.



6. **Isomerism :**
   - (i) Functional isomerism
   - (ii) Chain isomerism
   - (iii) Positional isomerism
7. **General Methods of Preparation :**

(i) Acid catalysed hydration of alkenes :

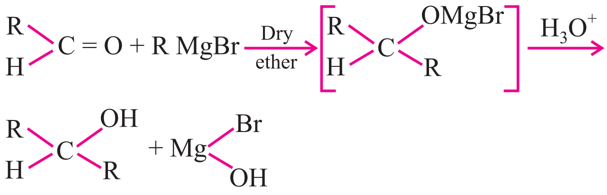
$$CH_3 - CH = CH_2 + H_2O \xrightarrow{dil.H_2SO_4} CH_3 - \overset{\overset{\displaystyle OH}{|}}{CH} - CH_3$$

(ii) Hydroboration oxidation :

$$3CH_3 - CH = CH_2 + \tfrac{1}{2}B_2H_6 \xrightarrow{D.E} (CH_3 - CH_2 - CH_2)_3B \xrightarrow[H_2O_2]{OH^-}$$

$$CH_3 - CH_2 - CH_2OH + H_3BO_3$$

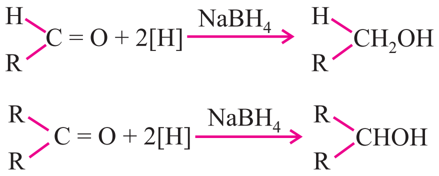
(iii) From carbonyl compounds with Grignard's reagent :



Formaldehyde gives 1° alcohol and ketones gives tertiary alcohol.

(iv) By reduction of carbonyl compounds :

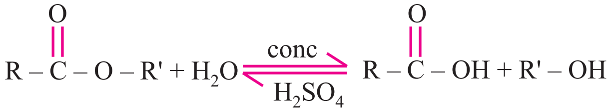
$$RCHO + 2[H] \xrightarrow{Pd} RCH_2OH$$



(v) By reduction of esters with $LiAlH_4$ or Na/C_2H_5OH :

$$R-\overset{\overset{O}{\|}}{C}-OR' + 4[H] \xrightarrow{LiAlH_4} R-CH_2OH + R'-OH$$

(vi) By hydrolysis of esters :



$$R-\overset{\overset{O}{\|}}{C}-O-R' + H_2O \underset{H_2SO_4}{\overset{conc}{\rightleftharpoons}} R-\overset{\overset{O}{\|}}{C}-OH + R'-OH$$

(vii) From alkyl halides :

$$R-X + KOH\ (aq) \rightarrow R-OH + KX$$

(viii) By reduction of acids and their derivatives :

$$R-COOH \xrightarrow{LiAlH_4} RCH_2OH$$

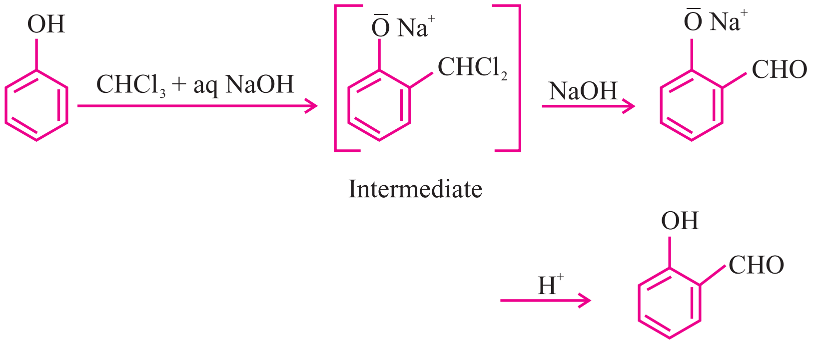
$$R-COCl + 2H_2 \xrightarrow{Ni} R.CH_2OH + HCl$$

(ix) From 1° amines :

$$R-NH_2 \xrightarrow{NaNO_2+HCl} ROH + H_2O + N_2$$

NAME REACTIONS

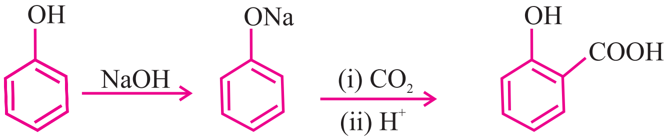
1. Reimer Tiemann Reaction x



Intermediate

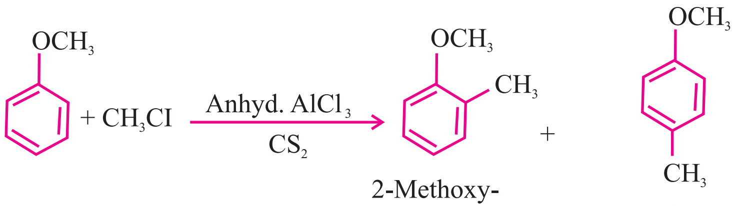
Salicyaldehyde

2. Kolbe reaction



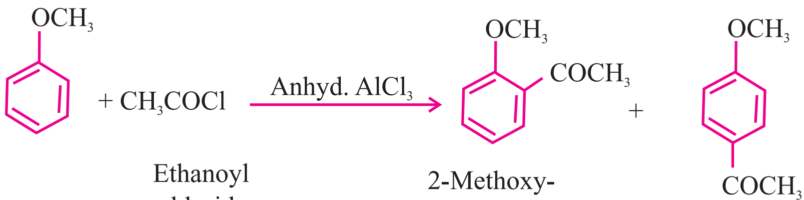
2-Hydroxybenzoic acid
(Salicylic acid)

3. Friedel craft reaction



2-Methoxy-
toluen
(Minor)

4-Methoxy
toluen
(Major)



Ethanoyl
chloride

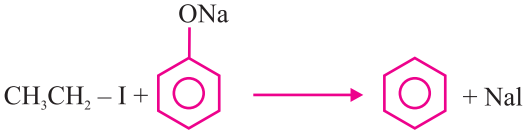
2-Methoxy-
acetophenone
(Minor)

4-Methoxy-
acetophenone
(Maior)

4. Williamson synthesis: Reaction with alkyl halide with sodium alkoxide or sod. Phenoxide is called Williamson synthesis.

$$R-X+R^1-O-Na \longrightarrow R-O-R^1+NaX$$

$$CH_3I + CH_3CH_2ONa \longrightarrow CH_3O.CH_2-CH_3 + Nal$$

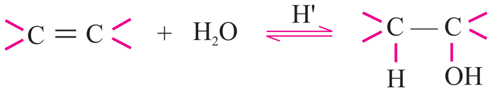


Both simple and mixed ether can be produced.

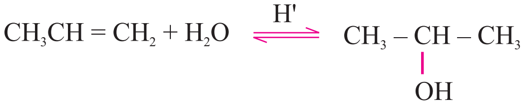
Depending upon structure and cleavage of unsymmetrical ethers by halogen acid may occur either by SN^2 or SN^1 mechanism.

MECHANISMS

1. Hydration of Alkene :



$$>C=C< + H_2O \overset{H'}{\rightleftharpoons} >\underset{H}{C}-\underset{OH}{C}<$$



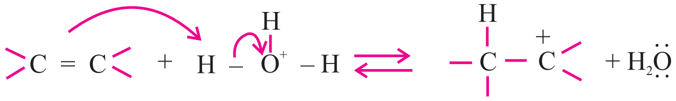
$$CH_3CH=CH_2+H_2O \overset{H'}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

Mechanism

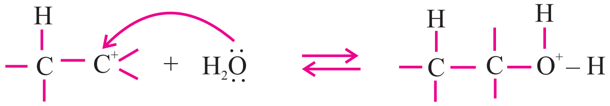
The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

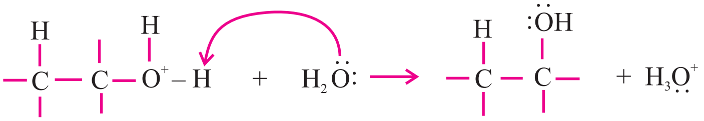
$$H_2O + H^+ \rightarrow H_3O^+$$



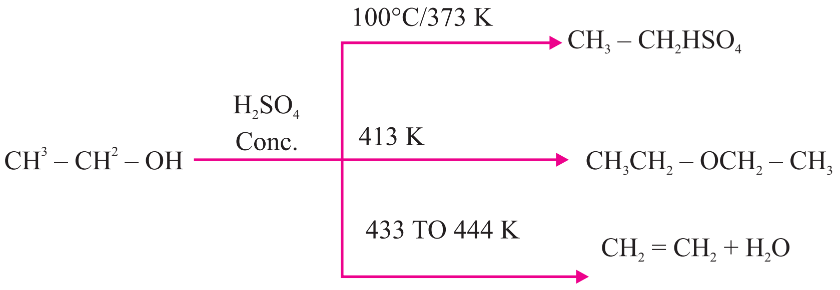
Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.

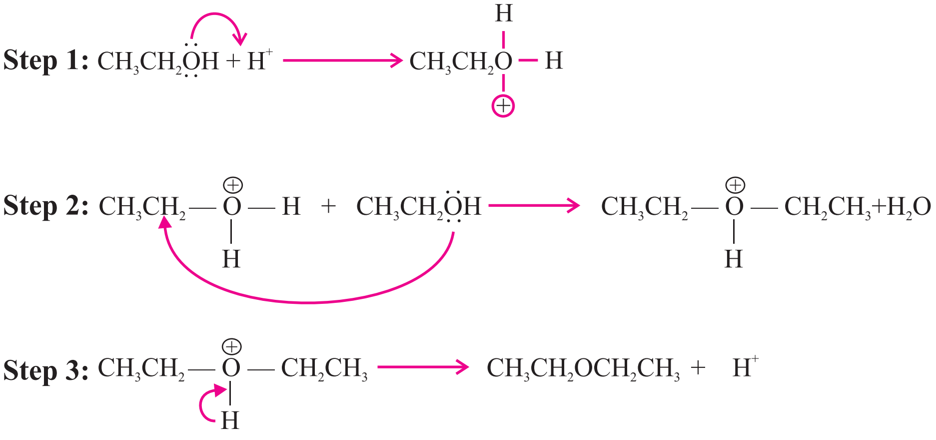


2. Dehydration Reaction



(1) $2CH_3CH_2OH \xrightarrow[\text{H}_2\text{SO}_4\ 413\ \text{k}]{\text{Conc.}} CH_3CH_2OCH_2CH_3$

Mechanism:

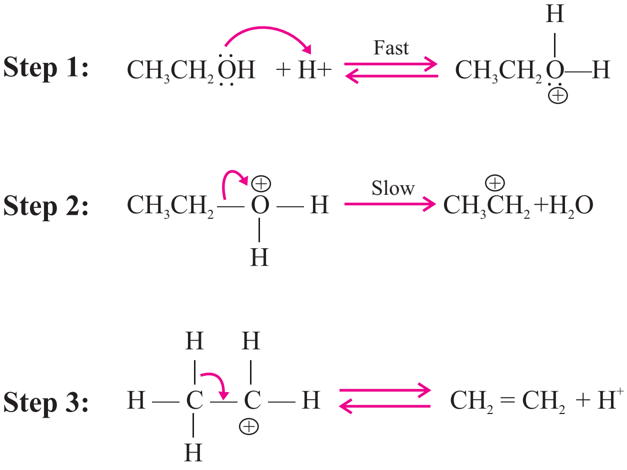


Step 1: $CH_3CH_2\ddot{\underset{..}{O}}H + H^+ \longrightarrow CH_3CH_2\overset{H}{\underset{\oplus}{O}}-H$

Step 2: $CH_3CH_2-\overset{\oplus}{\underset{H}{O}}-H + CH_3CH_2\ddot{\underset{..}{O}}H \longrightarrow CH_3CH_2-\overset{\oplus}{\underset{H}{O}}-CH_2CH_3+H_2O$

Step 3: $CH_3CH_2-\overset{\oplus}{\underset{H}{O}}-CH_2CH_3 \longrightarrow CH_3CH_2OCH_2CH_3 + H^+$

(2) $CH_3CH_2OH \xrightarrow[443\ \text{K}]{\text{Conc. } H_2SO_4} H_2C=CH_2 + H_2O$



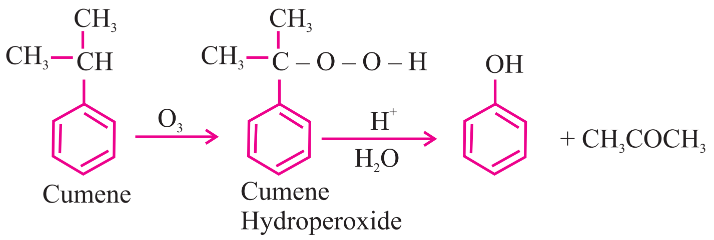
Step 1: $CH_3CH_2\ddot{\underset{..}{O}}H + H+ \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} CH_3CH_2\overset{H}{\underset{\oplus}{O}}-H$

Step 2: $CH_3CH_2-\overset{\oplus}{\underset{H}{O}}-H \xrightarrow{\text{Slow}} CH_3\overset{\oplus}{C}H_2+H_2O$

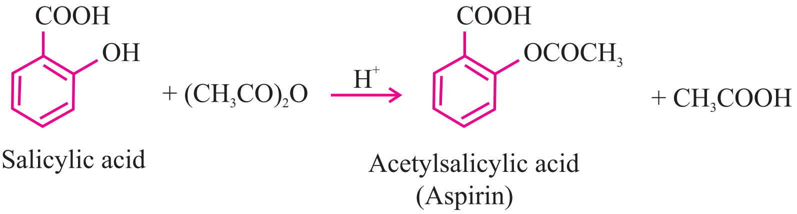
Step 3: $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\oplus}{C}}-H \rightleftharpoons CH_2=CH_2 + H^+$

IMPORTANT PREPARATIONS

(1) Preparation of phenol from Cumene



(2) Prepation os spirin



8. Ethers are dialkyl derivatives of water or monoalkyl derivatives of alcohols with formula R – O – R'

9. Lucas test can be used to distinguish primary, secondary and tertiary alcohols ($ZnCl_2$ + HCl).

   (3° turbidity – instant, 2° - 5 minutes, 1° - heating for 60 minutes)

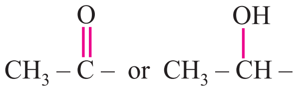
10. Ethers are relatively inert and hence are used as solvents.

11. 100% ethanol is known as absolute alcohol.

12. 95% ethanol is called rectified spirit.

13. A mixture of 20% ethanol and 80% gasoline is known as power alcohol.

14. Iodoform test is used for distinguishing compounds having the groups



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}- \quad \text{or} \quad CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-$$

15. Presence of EWGs increase the acid strength of phenols while EDG decrease the acid strength.

    EWG : $-NO_2$, – X, – CN, – COOH etc.

    EDG : – R, – OR, – OH, $-NH_2$ etc.

16. 3° alcohols are resistant to oxidation due to lack of α-hydrogen.

17. Intermolecular H-bonds of *p*- and *m*-nitrophenol increases water solubility/acid strength while intramolecular H-bonds in *o*-nitrophenol decreases these properties.

18. In the reaction of alkyl aryl ether (anisole) with HI, the products are always alkyl halide and phenol because O – R bond is weak than O – Ar bond which has partial double character due to resonance.

19. C – O – C bond in ether is bent and hence the ether is always polar molecule even if both alkyl groups are identical.

MULTIPLE CHOICE QUESTIONS

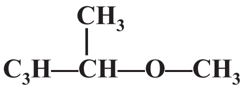
1. **Arrange the following compound in decreasing order of boiling point**

(i) propan-1-ol (ii) butane-1-ol
(iii) butan-2-ol (iv) pentan-1-ol
(a) i > iii > ii > iv (b) i > ii > iii > iv
(c) iv > iii > ii > i (d) iv > ii > iii > i

2. **What is the correct order of reactivity of alcohols in the following reaction?**

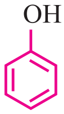
$$R-OH + CHl \xrightarrow{Zn,dust} R-Cl + H_2O$$

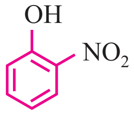
(a) 1° > 2° > 3° (b) 1° < 2° > 3°
(c) 3° > 2° > 1° (d) 3° > 1° > 2°

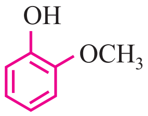
3. **IUPAC name of the compound** 
$\mathbf{C_3H-\overset{\overset{CH_3}{|}}{CH}-O-CH_3}$ **is:**

(a) 1-methoxy-1-methyl ethane (b) 2-methoxy-2-methyl ethane
(c) 2-methoxy propane (d) isopropylmethyl ether

4. **The correct order of decreasing acid strength of the following compound is:**

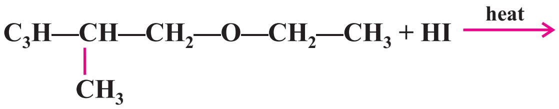
(i) 

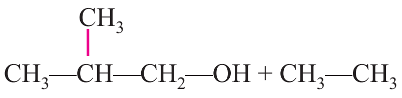
(ii) 

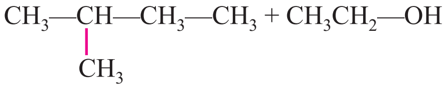
(ii) 

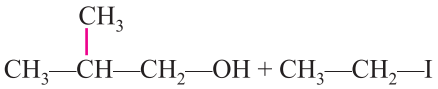
(a) i > ii > iii (b) iii > ii > i
(c) ii > i > iii (d) ii > iii > i

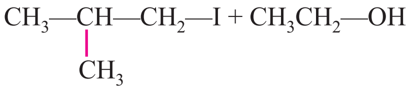
5. **In the reaction :**


$$\mathbf{C_3H-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{heat}}$$

(a) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-OH + CH_3-CH_3$

(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3-CH_3 + CH_3CH_2-OH$

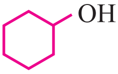
(c) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-OH + CH_3-CH_2-I$

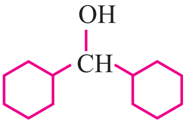
(d) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-I + CH_3CH_2-OH$

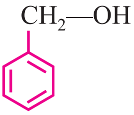
6. Phenol $\xrightarrow[\text{anhydrous AlCl}_3]{CH_3Cl}$ X $\xrightarrow{\text{alkaline KMnO}_4}$ Y $\xrightarrow{\text{alkaline KMnO}_4}$ Z, The product Z is

(a) Benzaldehyde
(b) Benzoicacid
(c) Benzene
(d) Toluene

7. Which is most acidic

(a)


(b)


(c)


(d)


8. The electrophile involved in the given reaction is:

(a) $:CCl_2$
(b) $^-CCl_3$
(c) ^+CHO
(d) $^+CHCl_2$

9. The major product obtained on interactionof phenol with NaOH and CO_2 is

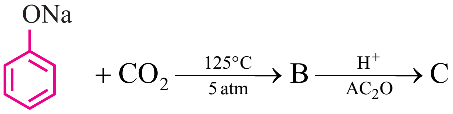
(a) Benzoic acid
(b) Salicaldehyde
(c) Salicylic acid
(d) Pthalic acid

10. In the following sequence of reaction

$CH_3—CH_2—OH \xrightarrow{PI_v} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$

The product D is:

(a) n-butylalcohol
(b) n-propylalcohol
(c) propanal
(d) butanal

11.


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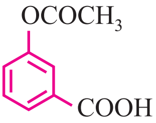

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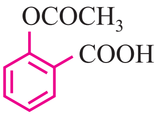

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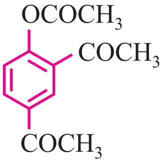

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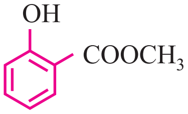
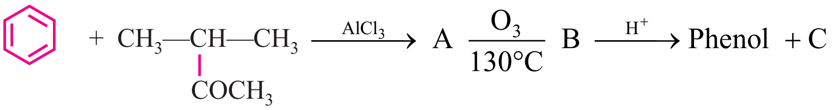


12. 

Identify 'C' in the following is:

(a) Water (b) Ethanol

(c) Cumenehydroperoxide (d) acetone

13. Iodoform canbe prepared from all except

(a) butan-2-one (b) acetophenone

(c) propan-2-ol (d) propan-1-ol

14. The ether  **when treated with HI produces**

(a) 

(b) 

(c) 

(d) 

15.  **the products are:**

(a) 

(b) 

(c) 

(d) d

16. Which of the following alcohol on dehydration with conc H_2SO_4 gives but-2-enc?

(a) 2-methylpropan-2-ol (b) Butan-1-ol

(c) 2-methyl propan-1-ol (d) Butan-2-ol

17. Which of the following alcohol give iodoferm test?

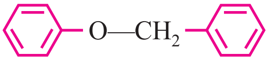
(a) Butan-1-ol (b) Propan-1-ol

(c) Propan-2-ol (d) Ethanol

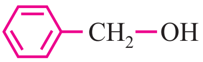
18. Which of the following is a weaker acid than phenol?

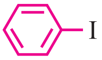
(a) 4-Methoxy phenol (b) 3, 5-dinitrophenol

(c) 4-Methyl phenol (d) 4-Nitrophenol

19. The ether  **when treated with HI produces.**

(a) 

(b) 

(c) 

(d) 

20. Correct statements in case of n-butanol and t-butanol are:

(a) both are having equal solubility in water

(b) t-butanol is more soluble in water than n-butanol

(c) boiling point of t-butanol is lower than n-butanol

(d) boiling point of n-butanol is lower than t-butanol

Assertion Reason Type Questions

The question given below consist of an Assertionand the Reason. Use the following key to choose the appropriate answer.

(a) If both assertion and reasonare CORRECT and reason is the CORRECT explanation of the assertion.

(b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

(c) If assertion is CORRECT but reason is INCORRECT.

(d) If assertion is INCORRECT but reason is CORRECT.

(e) If both assertion and reason are INCORRECT.

21. **Assertion:** The boiling point of alcohol is higher than those of hydrocarbons of comparable moleculal mass.

Reason: Alcohol show intramolecular hydrogen banding.

22. **Assertion:** O and p-nitrophenols can be separated by steam distillation.

Reason: O-isomeris steamvolatile due to chelation and p-isomer is not steam volatile due to intermolecular hydrogen bonding.

Matching Column Type

23. **Match the column**

(A) Methanol and ethanol	P. lucas reagent
(B) Phenol and cyclohexanol	Q. Sodium metal
(C) n-propylalcohol and tertbutyl alcohol	R. Iodoformtest
(D) Methanol and diethylether	S. Ferric chloride

(a) A–Q, B–S, C–P, D–R (b) A–S, B–P, C–Q, D–R

(c) A–P, B–Q, C–R, D–S (d) A–R, B–S, C–P, D–Q

24. **Match the column**

(A) Willionsan synthesis	P. Conversion of phenol to salicylic acid
(B) Conversion of 2° alcohol to ketone	Q. Conversion of phenol to salicaldehyde
(C) Reimer Tiemann reaction	R. Heated with Cu-573k.
(D) Kolbc's reaction	S. reaction of alkyl halide with sodium alkoxide

(a) A–S, B–R, C–Q, D–P

(b) A–R, B–S, C–Q, D–P

(c) A–R, B–Q, C–P, D–S

(d) A–Q, B–P, C–R, D–S

Integer Type Questions

The answer to each of the following question is a single-digit integer ranging from 0 to 9. Darken the correct digit.

25. The number of alcohols giving iodoform test among the following is:

CH_3CH_2OH, CH_3OH, $CH_3CH_2CH_2OH$, $(CH_3)_2$ CHOH, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH(OH)CH_3$, $CH_3CH(OH)CH(CH_3)_2$, $(C_2H_5)_2CHOH$, $(CH_3)_3COH$

0	1	2	3	4	5	6	7	8	9

ANSWERS

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

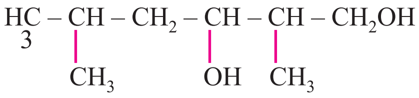
11. (b) **12.** (d) **13.** (d) **14.** (a) **15.** (d)

16. (b, d) **17.** (c, d) **18.** (a, c) **19.** (a, d) **20.**(b, c)

21. (c) **22.** (a) **23.** (d) **24.** (a) **25.** 4

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Write IUPAC name of the following compound :

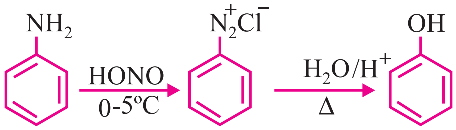


$$\underset{3}{HC} - \underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_2OH$$

Ans. 2,5-Dimethylhexane-1, 3 diol.

Q. 2. How is phenol obtained from aniline ?

Ans.



Q. 3. Why phenol is acidic in nature ?

Ans. Due to stability of phenoxide ion by resonance.

Q. 4. Arrange the following in decreasing order of their acidic character :

(i)

(ii) C_6H_5OH **(iii)**

Ans. (iii) > (ii) > (i)

Q. 5. Among HI, HBr and HCl, HI is most reactive towards alcohols. Why ?

Ans. Due to lowest bond dissociation energy of HI.

Q. 6. Name a compound which is used as antiseptic as well as disinfectant.

Ans. Solution of phenol : 0.2% antiseptic, 2% disinfectant.

Q. 7. What is nitrating mixture ?

Ans. Conc. ($H_2SO_4 + HNO_3$)

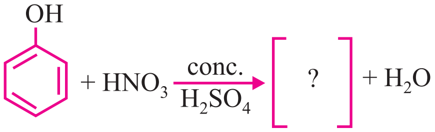
Q. 8. Lower alcohols are soluble in water, higher alcohols are not. Why ?

Ans. Due to formation of hydrogen bonds.

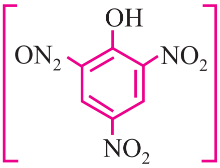
Q. 9. What happens when CH_3CH_2OH heated with red P and HI ?

Ans. $C_2H_5OH + 2HI \xrightarrow{\text{Red P}} C_2H_6 + I_2 + H_2O$

Q. 10. Complete the following reaction :



Ans.



2, 4, 6-Trinitro phenol (Picric acid)

Q. 11. Ethanol has higher boiling point than methoxy methane. Give reason.

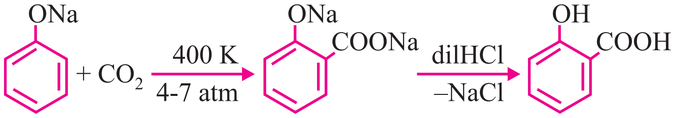
Ans. Because of H-bonds.

Q. 12. How could you convert ethanol to ethene ?

Ans. $C_2H_5OH \xrightarrow[443\text{ K}]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$

Q. 13. Explain Kolbe's reaction with example.

Ans.



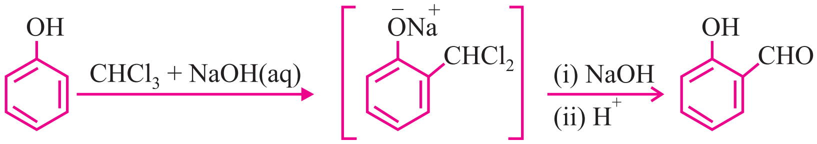
Q. 14. Which of the following isomer is more volatile :
o-nitrophenol or p-nitrophenol

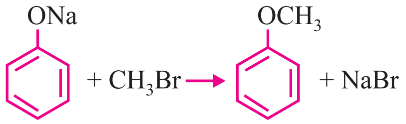
Ans. o-nitrophenol.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Write one chemical reaction to illustrate the following :
(i) Reimer-Teimann reaction
(ii) Williamson's synthesis

Ans. (i)



(ii) 

Q. 2. Account for the following :

(i) Phenol has a smaller dipole moment than methanol.

(ii) Phenol goes electrophilic substitution reactions.

Ans. (i) Due to – ve charge on oxygen in delocalized by resonance.

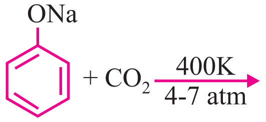
(ii) Due to greater electron density than benzene.

Q. 3. Complete the following equations and name the products :

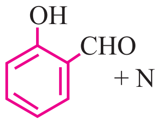
(i) Phenol + $FeCl_3 \rightarrow$

(ii) $C_6H_5OH + CHCl_3 + NaOH \xrightarrow{340\text{ K}}$

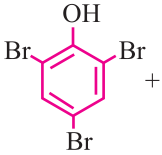
(iii) $C_6H_5OH + Br_2\text{ (aq)} \rightarrow$

(iv) 

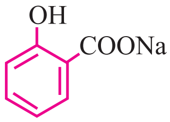
Ans. (i) $[(C_6H_5O)_3Fe] + 3HCl$

(ii) 

$+ NaCl + H_2O$

(iii) 

+ HBr

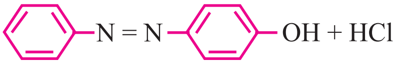
(iv) 

Q. 4. Write :

(i) Friedel-Crafts reaction

(ii) Coupling reaction

Ans. (i) 

(ii) $C_6H_5N_2Cl + C_6H_5OH \xrightarrow{pH=9-10}$ 

Q. 5. Give one reaction of alcohol involving cleavage of :

(i) C – O bond

(ii) O – H bond

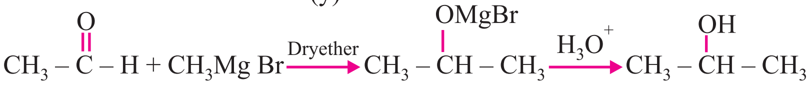
Ans. (i) $CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$

(ii) $CH_3CH_2OH + Na \rightarrow CH_3CH_2ONa + H_2$

Q. 6. Etherial solution of an organic compound 'X' when heated with Mg gave 'Y'. 'Y' on treatment with CH_3CHO followed by acid hydrolysis gave 2-propanol. Identify the compound 'X'. What is 'Y' known as ?

Ans.

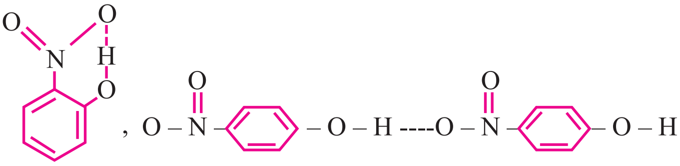
$$\underset{x}{CH_3Br} + Mg \xrightarrow{\text{Dryether}} \underset{(y)}{CH_3MgBr}$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + CH_3MgBr \xrightarrow{\text{Dryether}} CH_3-\overset{\overset{\displaystyle OMgBr}{|}}{CH}-CH_3 \xrightarrow{H_3O^+} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3$$

Q. 7. While separating a mixture of *o*- and *p*-nitrophenols by steam distillation name the isomer which is steam volatile. Give reason.

Ans.



H-bonding and association of molecules.

Q. 8. Account for the following :

(i) Phenol has a smaller dipole moment than CH_3OH.

(ii) Phenol do not give protonation reactions readily.

Ans. (i) Because phenol has electron attracting benzene ring.

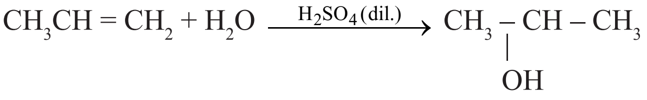
(ii) Resonance and +ve charge oxygen does not have tendency to accept a proton.

Q. 9. Write the reactions and conditions involved in the conversion of :

(i) Propene to propan-2-ol.

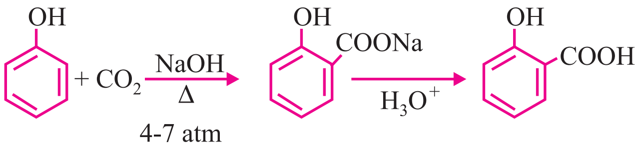
(ii) Phenol to salicylic acid.

Ans. (i)



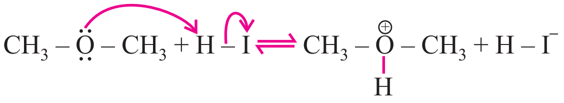
$$CH_3CH=CH_2 + H_2O \xrightarrow{H_2SO_4\text{(dil.)}} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

(ii)

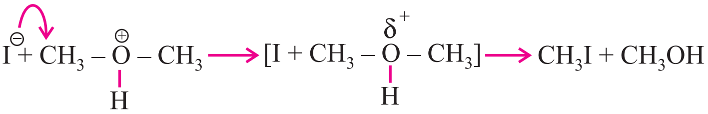


Q. 10. Write mechanism of reaction of HI with methoxymethane.

Ans.



$$CH_3-\ddot{O}-CH_3 + H-I \rightleftharpoons CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{O}}-CH_3 + H-I^-$$



$$\overset{\ominus}{I} + CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{O}}-CH_3 \longrightarrow [I + CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\delta^+}{O}}-CH_3] \longrightarrow CH_3I + CH_3OH$$

Q. 11. **Arrange in order of boiling points :**

(i) $C_2H_5 - O - C_2H_5$, C_4H_9COOH, C_4H_9OH

(ii) C_3H_7CHO, $CH_3COC_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

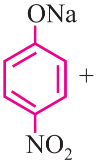
Ans. (i) $C_4H_9COOH > C_4H_9OH > C_2H_5 - O - C_2H_5$

(ii) $(CH_3CO)_2O > C_2H_5COOCH_3 > CH_3COC_2H_5 > C_3H_7CHO$

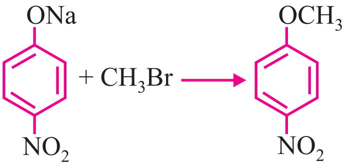
Q. 12. **Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?**

(i) 

+ CH_3ONa

(ii) 

+ CH_3Br

Ans. (ii) 

It is because of double bond character, (C – Br) bond in 

due to resonance it is less reactive towards SN, RXN.

Q. 13. **Ethers are relatively inert. Justify.**

Ans. Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides $\left(C - \underset{\cdot\cdot}{\ddot{O}} - C\right)$.

Q. 14. **How will you distinguish between CH_3OH and C_2H_5OH ?**

Ans. $C_2H_5OH + 4I_2 + 3Na_2CO_3 \xrightarrow[\text{Iodoform (yellow)}]{\text{warm}} CHI_3 + HCOONa + 5NaI + 2H_2O + 3CO_2$

CH_3OH does not give this test.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. **Name the reagents which are used in the following conversions :**

(i) **1° alcohol to an aldehyde**

(ii) **Butan-2-one to butan-2-ol**

(iii) **Phenol to 2, 4, 6 tribromophenol**

Ans. (i) PCC, a complex of chromium trioxide with pyridine and HCl.

(ii) $NaBH_4$, sodium borohydride.

(iii) Br_2 (water)

Q. 2. Write structures of the major products of the following :

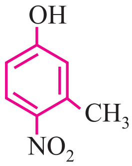
(i) Mononitration of 3-methylphenol

(ii) Dinitration of 3-methylphenol

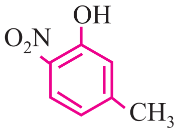
(iii) Mononitration of phenyl ethanoate

Ans. – OH and – CH_3 are *o*- and *p*-directing groups. The products are :

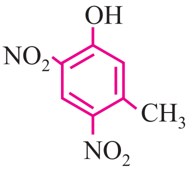
(i)



and



(ii)



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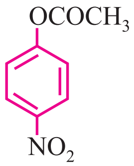


Q. 3. Complete the following reactions :

(i) $CH_3CH_2CH_2CHO \xrightarrow{Pd/H_2/Ni}$

(ii) $CH_3CH = CHCH_2OH \xrightarrow{PCC}$

(iii) $CH_3CH = CH_2 \xrightarrow[(2)\ 3H_2O_2/OH^-]{(1)\ B_2H_6}$

(iv) $C_6H_5OH \xrightarrow[(2)\ CO_2, H^+]{(1)\ Aq.NaOH}$

(v) $CH_2Br - CH_2Br \xrightarrow{KOH}$

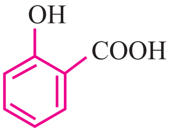
(vi) $C_2H_5NH_2 \xrightarrow{HNO_2}$

Ans. (i) $CH_3CH_2CH_2CH_2OH$

(ii) $CH_3CH = CHCH_2 - OH$

(iii) $CH_3CH_2CH_2OH$

(iv)



(v) $CH_2OH - CH_2OH$

(vi) CH_3CH_2OH

Q. 4. Give equations of the following reactions :

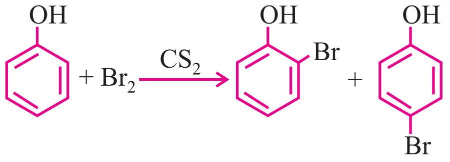
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(ii) Bromine in CS_2 with phenol.

(iii) Treating phenol with chloroform in presence of aqueous NaOH.

Ans. (i) $CH_3-CH_2-CH_2OH + 2[O] \xrightarrow[KMnO_4]{\text{alkaline}} CH_3CH_2COO^-K^+$

(ii)



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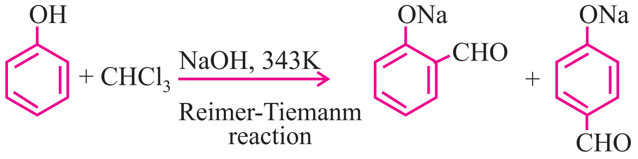


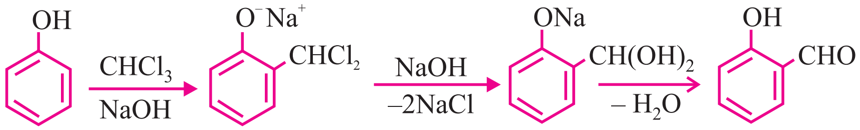
Q. 5. Describe the following reactions with examples :

(i) Reimer-Teimann reaction

(ii) Kolbe's reaction

(iii) Friedel Crafts acylation of anisole

Ans. (i)



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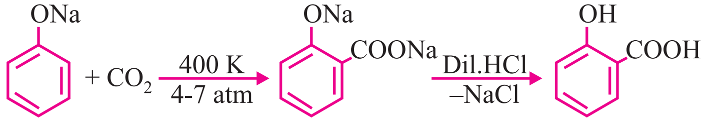
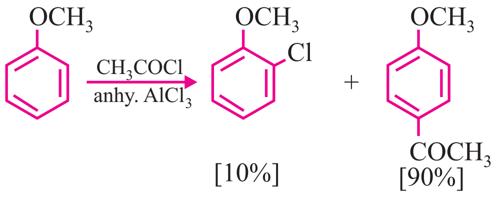


Salicylic acid

(iii)



Q. 6. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3. Explain.

Ans. In acidic medium alcohols protonated then loses H_2O to form a carbo cation. If HCl Cl^- strong nucleophile cause nucleophilic substitution, HNO_3 causes oxidation.

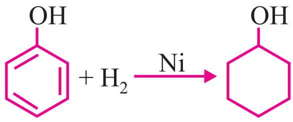
Q. 7. How will you convert :

(i) Phenol to cyclohexanol

(ii) Benzyl chloride to benzyl alcohol

(iii) Anisole to phenol

Ans. (i)



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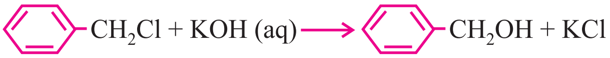

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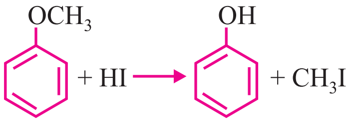


LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. An alcohol A ($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives carboxylic acid 'B' ($C_4H_8O_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443 K gives compound 'C' with aqueous H_2SO_4. 'C' gives compound 'D' ($C_4H_{10}O$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidized. Identify A, B, C and D and write their structure.

Ans. A : $(CH_3)_2CHCH_2OH$ B : $CH_3CH(CH_3)COOH$

C : $(CH_3)_2C = CH_2$ D : $(CH_3)_3 - C - OH$

Q. 2. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

Ans. A :

B : CH_3CH_2OH

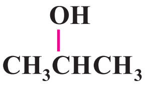
C : $CH_3CHOHCH_3$ D : CH_3COOH

E : CH_3COCH_3

Q. 3. Which of the following compounds gives fastest reaction with HBr and why?

(i) $(CH_3)_3COH$ (ii) $CH_3CH_2CH_2OH$

(iii)



$CH_3\overset{OH}{\overset{|}{C}}HCH_3$

(iv)

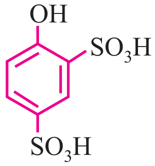
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH$

Ans. (i) **$(CH_3)_3C - OH$**

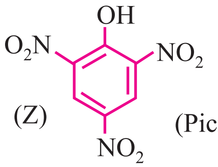
Due to formation of EDG and formation of cation.

Q. 4. Phenol, C_6H_5OH when it first reacts with concentrated sulphuric acid, forms Y. The compound, Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted commercially to Z by reacting it with conc. HNO_3.

Ans. (Y)



(Z)



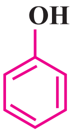
(Picric acid)

Phenol is not reacted directly with conc. HNO_3 because the yield of picric acid is very poor.

Q. 5. Fill in the blanks :

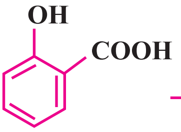
(i) Glucose $\xrightarrow{\text{Zymase}}$

(ii)



$+ Br_2 \xrightarrow[H_2O]{} ?$

(iii)



$\xrightarrow[H^+]{(CH_3CO)_2O} ?$

(iv)

$CH_3\overset{CH_3}{\overset{|}{C}}HOCH_2CH_3 \xrightarrow{HI} ?$

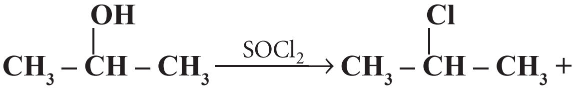
(v) Phenol + Zn (dust) →

(vi) Phenol + Na →

(vii) $R_2CHOH + HCl + \underset{\text{(anhydrous)}}{ZnCl_2} \rightarrow R_2CHCl + \text{..........}$

(viii) $R - CHOH - R \xrightarrow{[O]}$

(ix)

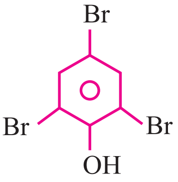


$CH_3 - \overset{OH}{\overset{|}{C}}H - CH_3 \xrightarrow{SOCl_2} CH_3 - \overset{Cl}{\overset{|}{C}}H - CH_3 +$

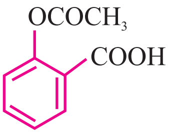
(x) $CH_3 - CH_2 - OH \xrightarrow{\text{Bleaching powder}}$

Ans. (i) C_2H_5OH

(ii)



(iii)



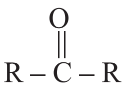
(iv) $(CH_3)_2CHOH$ and CH_3CH_2I

(v) C_6H_6

(vi) C_6H_5ONa

(vii) H_2O

(viii)



$R - \overset{O}{\overset{||}{C}} - R$

(ix) SO_2

(x) $CHCl_3$

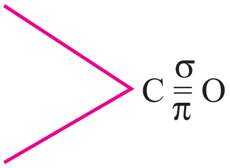
UNIT 11

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Points to Remember

1. Aldehydes and ketones, are commonly called as carbonyl compounds.
2. In Rosenmund's reduction, poisoning of Pd with $BaSO_4$ prevent reduction of $R-CHO$ to $R-CH_2OH$.
3. In the reaction of toluene with CrO_3, acetic anhydride is used to protect benzaldehyde by forming benzylidenediacetate to avoid its oxidation to benzoic acid.
4. Order of reactivity of aldehydes and ketones towards nucleophilic addition is :
   (i) $HCHO > CH_3CHO > CH_3CH_2CHO$.
   (ii) $HCHO > RCHO > R\,CO\,R$.
   (iii) $ArCHO > Ar\,COR > Ar\,CO\,Ar$.
5. Benzaldehyde does not reduce Fehling's reagent.
6. Aldehydes and ketones with atleast one α–H atom get condensed in presence of a base. This is known as Aldol condensation.
7. Aldol condensation involves carbanion as intermediate.
8. Aldehydes with no α–H atoms under Cannizzaro's reaction.
9. Ketones react with dihydric alcohols to form cyclic ketals.
10. Monocarboxylic acids having (C_{12}–C_{18}) carbon atoms, are called fatty acids.
11. Boiling points of carboxylic acids is greater than corresponding alcohols.
12. Presence of EWGs enhances the acidic character of carboxylic acids.
13. –COOH group is *m*-directing in electrophilic substitution reactions.
14. Compounds containing – CHO group are named as carbaldehydes if – CHO groups are three or more.
15. Isomerism : Chain, position and functional.

16. Structure of –CHO group sp^2 hybridised.



17. General Methods of Preparation:

(i) Controlled oxidation of 1° alcohols :

$$RCH_2OH \xrightarrow{PCC/CrO_3} RCHO$$

(Collin's reagent)

(ii) Dehydrogenation of 1° alcohols :

$$RCH_2OH \xrightarrow{Cu/573\ K} RCHO + H_2$$

(iii) From Rosenmund reaction/reduction :

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

(iv) Hydration of alkynes :

$$CH \equiv CH \xrightarrow[40\%\ H_2SO_4]{1\%\ HgSO_4} [CH_2 = CHOH] \xrightarrow{Tautomerism} CH_3CHO$$

(v) Reductive ozonolysis of alkenes :

$$R - CH = CH - R \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} 2RCHO + H_2O_2$$

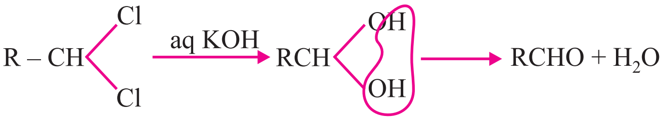
(vi) From salts of fatty acids :

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{D\ Dist.} 2RCHO + 2CaCO_3$$

(vii) Stephen's reduction of nitrile compounds :

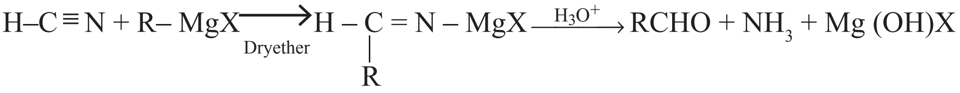
$$R - C \equiv N \xrightarrow{SnCl_2/HCl} [R - CH = NH.HCl] \xrightarrow[H_2O + H^+]{H_3^+O} RCHO + NH_4Cl$$

(viii) Hydrolysis of germinal halides :



$$R - CH\begin{matrix} Cl \\ Cl \end{matrix} \xrightarrow{aq\ KOH} RCH\begin{matrix} OH \\ OH \end{matrix} \longrightarrow RCHO + H_2O$$

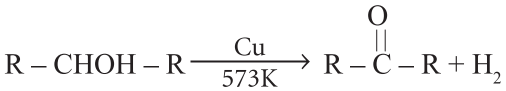
(ix) From Grignard's reagent :



$$H–C \equiv N + R– MgX \xrightarrow[Dryether]{} H - \underset{\displaystyle R}{\underset{|}{C}} = N - MgX \xrightarrow{H_3O^+} RCHO + NH_3 + Mg\ (OH)X$$

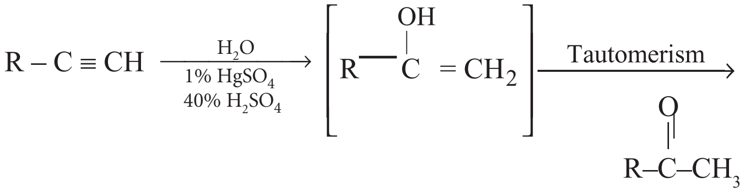
General Methods of Preparation of Ketones only

(i) Dehydrogenation of 2° alcohols :



$$R-CHOH-R \xrightarrow[573K]{Cu} R-\overset{\overset{\displaystyle O}{||}}{C}-R+H_2$$

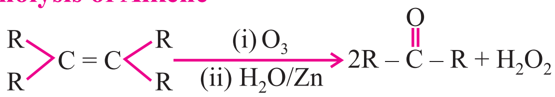
(ii) Hydration of alkynes :



$$R-C\equiv CH \xrightarrow[\substack{1\%\ HgSO_4\\ 40\%\ H_2SO_4}]{H_2O} \left[R-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2\right] \xrightarrow{\text{Tautomerism}} R-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$

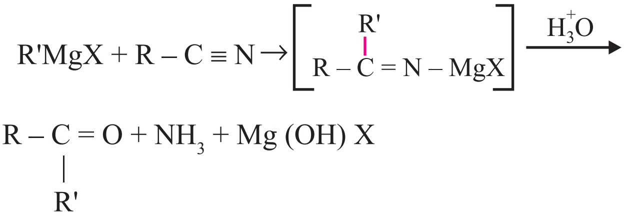
Ozonolysis of Alkene

(iii)



$$\begin{matrix}R\\R\end{matrix}\!\!>C=C<\!\!\begin{matrix}R\\R\end{matrix} \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3} 2R-\overset{\overset{\displaystyle O}{||}}{C}-R+H_2O_2$$

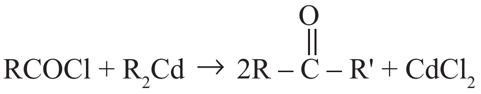
(iv) From Grignard's reagents :



$$R'MgX+R-C\equiv N\rightarrow\left[R-\overset{\overset{\displaystyle R'}{|}}{C}=N-MgX\right]\xrightarrow{H_3\overset{+}{O}}$$

$$\underset{\underset{\displaystyle R'}{|}}{R-C=O}+NH_3+Mg\,(OH)\,X$$

(iv) From acid chlorides :



$$RCOCl+R_2Cd\rightarrow 2R-\overset{\overset{\displaystyle O}{||}}{C}-R'+CdCl_2$$

Physical Properties:

HCHO is a gas at normal temperature. Formalin is 40% as solution of HCHO. Due to polarity they have high values of boiling point. Solubility in water is only for lower members.

Reactivity :

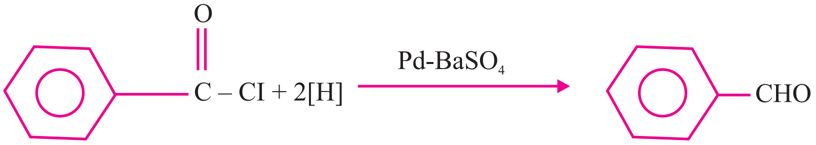
(i) + I effect of alkyl groups decreases the +ve charge on carbonyl carbon.

(ii) Steric hindrance : Bulky group hinder approach of nucleophile.

(iii) α-hydrogen atom is acidic due to resonance.

1. ROSENMUND REDUCTION:

Acyl chlorides when hydrogenated over catalyst, palladium on barium sulphate yield aldehydes



Benzoyl chloride Benzaldehyde

2. STEPHEN REACTION

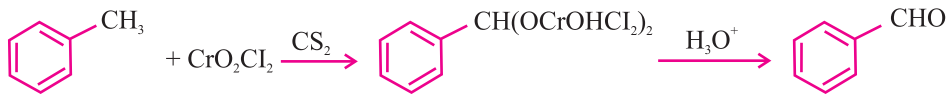
Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$RCN + SnCI_2 + HCI \longrightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

3. ETARD REACTION

On treating toluene with chromyl chloride CrO_2Cl_2, the methyl group is oxidized to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

OR



Toluene Chromium complex Benzaldehyde

This reaction is called Etard reaction

4. CLEMMENSEN REDUCTION

The carbonyl group of aldehydes and ketone is reduced to -CH2 group on treatment with zinc amalgam and cone. Hydrochloric acid.

$$>C=O \xrightarrow[HCl]{Zn - Hg} >CH_2 + H_2O$$

Alkanes

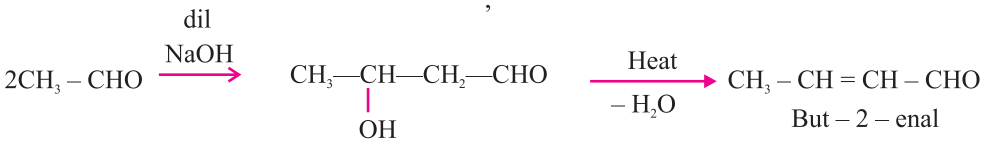
5. WOLFF- KISHNER REDUCTION

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol

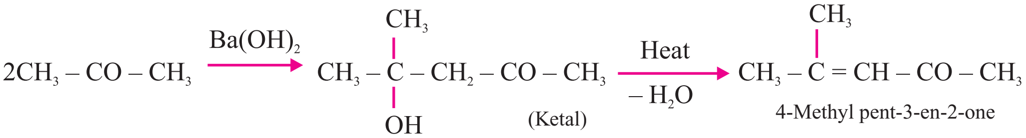
$$>C=O \xrightarrow[\text{KOH/Ethylone glycol heat}]{NH_2 - NH_2} \underset{\text{Alkanes}}{>CH_2 + H_2O}$$

6. ALDOL CONDENSATION

Aldehydes and ketones having at least one a-hydrogen condense in the presence of dilute alkali as catalyst to form p-hydroxy ehydes (aldol) or β-hydroxy ketones (ketol).



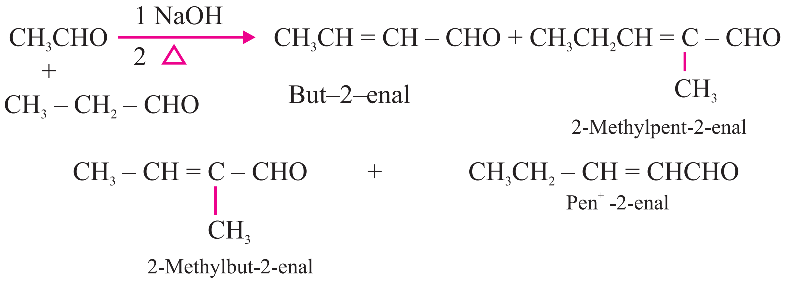
$$2CH_3-CHO \xrightarrow{\text{dil NaOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{But}-2-\text{enal}}{CH_3-CH=CH-CHO}$$



$$2CH_3-CO-CH_3 \xrightarrow{Ba(OH)_2} \underset{\text{(Ketal)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CO-CH_3} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{4-Methyl pent-3-en-2-one}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CO-CH_3}$$

7. CROSS- ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.



$$\begin{matrix} CH_3CHO \\ + \\ CH_3-CH_2-CHO \end{matrix} \xrightarrow[2\ \Delta]{1\ NaOH} \underset{\text{But–2–enal}}{CH_3CH=CH-CHO} + \underset{\text{2-Methylpent-2-enal}}{CH_3CH_2CH=\underset{\underset{CH_3}{|}}{C}-CHO}$$

$$\underset{\text{2-Methylbut-2-enal}}{CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CHO} + \underset{\text{Pen}^{+}\text{ -2-enal}}{CH_3CH_2-CH=CHCHO}$$

8. CANNIZZARO REACTION

Aldehydes which do not have an a-hydrogen atom, undergo self oxidation and reduction (dispropotionation) reaction on treatment with concentrated alkali, to yield carboxylic acid salt and an alcohol respectively.

$$\text{H-CHO} + \text{H-CHO} + \text{Conc.KOH} \longrightarrow CH_3OH + HCOOK$$

$$C_6H_5CHO + NaOH\ (\text{con.}) \xrightarrow{\text{Methanol}} C_6H_5CH_2OH + C_6H_5\ COONa^{+}$$

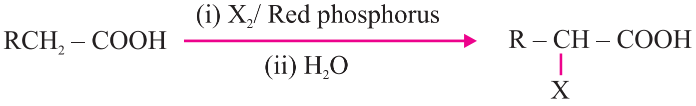
Benzaldehyde

Benzyl alcohol Sodium benzoate

CARBOXYLIC ACID

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)

Carboxylic acids having an a – hydrogen are halogenated at the a -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give a -halocarboxylic acids.



$$RCH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/ Red phosphorus}} R-\underset{\displaystyle X}{\underset{|}{CH}}-COOH$$

X = CI, Br

α – halocarboxylic acids

2. ESTERIFICATION

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc.H_2SO_4 as catalyst to form esters.

$$RCOOH + R'OH \xrightleftharpoons{H^+} RCOOR' + H_2O$$

18. Vinegar is 8 to 10% solution of CH_3COOH.

19. α-hydrogen atoms in carboxylic acid are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction.

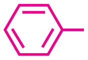
21. Relative acid strength of $RCOOH > HOH > ROH > HC \equiv CH > NH_3$. It is because a strong acid has weak conjugate base.

22. Some dicarboxylic acids bearing general formula $HOOC-(CH_2)_n-COOH$ where n – 0, 1, 2, ...etc.

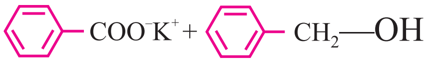
$HOOC-COOH$	Oxalic acid	1, 2 ethanedioic acid
$HOOC-CH_2-COOH$	Malonic acid	1, 3 propanedioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	1, 4 butanedioic acid
$HOOC-(CH_2)_3-COOH$	Glutonic acid	1, 5 pentamdioic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid	1, 6 hexanedioic acid

23. Melting points : Higher : Even carbon atoms than next lower or higher homologues containing even number of carbon atoms due to symmetry and closer packing of molecules in the crystal lattice.

MULTIPLE CHOICE QUESTIONS

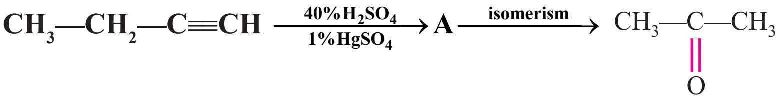
1. **Which product is formed when  is treated with concentrated KOH solution?**

   (a) 

   (b) 

   (c) 

   (d) 

2. 

   $$CH_3—CH_2—C\equiv CH \xrightarrow[1\% HgSO_4]{40\% H_2SO_4} A \xrightarrow{\text{isomerism}} CH_3—\underset{\underset{O}{\|}}{C}—CH_3$$

   Structure of 'A' and type of isomerism in the above reaction are respectively

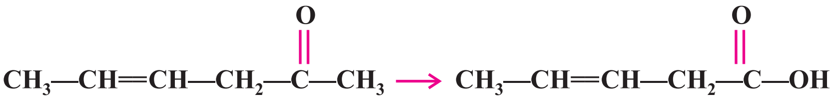
   (a) Prop-1-en-2-ol, metamerism
   (b) prop-1-cn-ol, tautomerism
   (c) prop-2-en-2-ol, geometrical
   (d) prop-1-en-2-ol, tautomerism

3. **Compound A and C in the following reaction are ....**

   $$CH_3CHO \xrightarrow[(ii)H_2O]{(i)CH_3MgBr} A \xrightarrow[\Delta]{H_2SO_4} B \xrightarrow[\text{Oxidation}]{\text{Hydroboration}} C$$

   (a) identical
   (b) position isomer
   (c) functional isomer
   (d) optical isomer

4. **The most suitable reagent for the following conversion?**

   $$CH_3—CH=CH—CH_2—\overset{\overset{O}{\|}}{C}—CH_3 \rightarrow CH_3—CH=CH—CH_2—\overset{\overset{O}{\|}}{C}—OH$$

   (a) Tollen's reagent
   (b) Benzoyl peroxide
   (c) I_2 and NaOH solution
   (d) Sn and NaOH solution

5. **Toluene** $\xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd}$ **the product 'C' is:**

   (a) $C_6H_5\ CH_2—OH$
   (b) C_6H_5CHO
   (c) C_6H_5COOH
   (d) $C_6H_5CH_3$

6. **Increasing order of rate of HCN addition to compound (I-IV) is**

   (i) HCHO
   (ii) CH_3COCH_3
   (iii) $PHCOCH_3$
   (iv) PHCOPH

   (a) iv < ii < iii < i
   (b) iv < iii < ii < i
   (c) iii < iv < ii < i
   (d) i < ii < iii < iv

7. **Among the following which has the lowest pka value:**

   (a) CH_3COOH
   (b) HCOOH
   (c) $(CH_3)_2CHCOOH$
   (d) $CH_3—CH_2—OH$

8. The correct order of acidity in given compounds

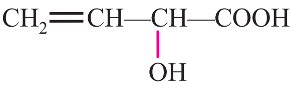
(i) FCH_2COOH (ii) $ClCH_2COOH$

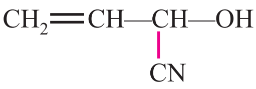
(iii) NO_2CH_2COOH (iv) CH_3COOH

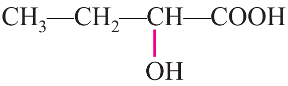
(a) i > ii > iii > iv (b) iv > iii > ii > i

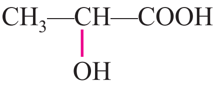
(c) iii > iv > i > ii (d) iii > i > ii > iv

9. $CH_3CHO + HCHO \xrightarrow[\text{Heat}]{\text{dilNaOH}} A \xrightarrow[H_3O]{HCN} B$ the structure of 'B' is:

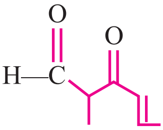
(a) 
$CH_2{=}CH{-}\underset{OH}{CH}{-}COOH$

(b) 
$CH_2{=}CH{-}\underset{CN}{CH}{-}OH$

(c) 
$CH_3{-}CH_2{-}\underset{OH}{CH}{-}COOH$

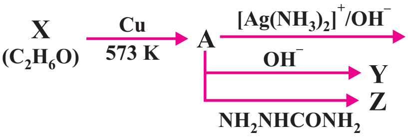
(d) 
$CH_3{-}\underset{OH}{CH}{-}COOH$

10. The IUPAC nameof compound is:



(a) 2-Formylhex-2-ene-3-one (b) 5-methyl-4-oxo-hex-2-en-5-al

(c) 3-keto-2-methylhex-5-enal (d) 3-keto-2-methylhex-4-enal

11. 

Identify X, A, Y, Z.

(a) A-methoxymethane, X-ethanol, Y-ethanoic acid, Z-semicarbazide

(b) A-ethanol, X-ethano, Y-but-z-enal, Z-semicarbazone

(c) A-ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydroazone

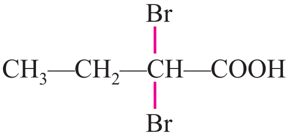
(d) A-Methoxymethane, X-ethanoicacid, Y-acetate ion and Z-Hydrazine

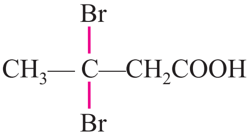
12. Which of the following reactions will not result in the formation of carbon carbon bond?

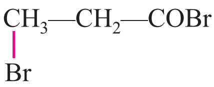
(a) Cannizaro's reaction (b) Wurtz reaction

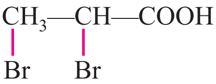
(c) Friedel craft reaction (d) Reimer Tiemann reaction

13. Priopionic acid with Br_2/P yields a dibromo product It's structure will be:

(a) 
$CH_3{-}CH_2{-}\overset{Br}{\underset{Br}{CH}}{-}COOH$

(b) 
$CH_3{-}\overset{Br}{\underset{Br}{C}}{-}CH_2COOH$

(c) 
$\underset{Br}{CH_3}{-}CH_2{-}COBr$

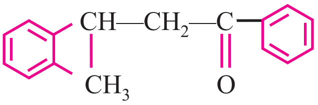
(d) 
$\underset{Br}{CH_3}{-}\underset{Br}{CH}{-}COOH$

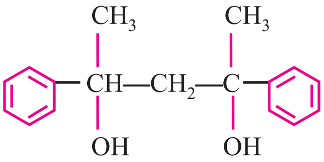
14. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc HCl is called:

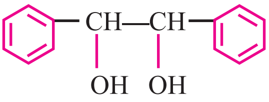
(a) Dow process (b) Cope reduction

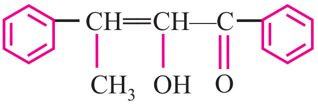
(c) Wolf-kishner reduction (d) Clemmenson's Reduction

15. Acetophenone when reacts with a base, yields a stable compound which has the structure:

(a) 

(b) 

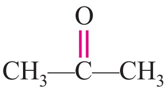
(c) 

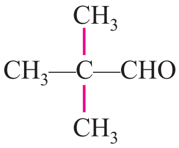
(d) 

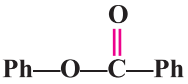
16. Which of the following compound do not undergo aldol condensation

(a) $CH_3—CHO$

(b) $C_6H_5—CHO$

(c) 
$CH_3—\overset{\overset{O}{\|}}{C}—CH_3$

(d) 
$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO$

17. The treatment of compound  $Ph—O—\overset{\overset{O}{\|}}{C}—Ph$ **with NaOH yields.**

(a) Phenol

(b) Sodium phenoxide

(c) Sodium benzoate

(d) Benzophenone

18. Which of the following conversion can be carried out by demmensen reduction

(a) Benzaldehyde to benzyl alcohol

(b) Cyclohexanone to cyclohexane

(c) Benzoylchloride into benzaldehyde

(d) Benzophenone to diphenyl methane

19. Through which of the following reaction number of carbon can be increased in the chair?

(a) Grignard reagent

(b) Cannizaro reaction

(c) Aldol condensation

(d) HVZ reaction

20. Benzophenone can be obtained by ....

(a) Benzoyl chloride + Benzene + anhy. $AlCl_3$

(b) Benzoyl chloride + Diphenylanion

(c) Benzoyl chloride + Phenyl magnesium chloride

(d) Benzene + carbon monoxide + $ZnCl_2$

Assertion Reason Type Questions

The question given below consist of an Assertionand the Reason. Use the following key to choose the appropriate answer.

(a) Assertion and reason both are CORRECT and reason is the CORRECT explanation of the assertion.

(b) Assertion and reason both are wrong statements.

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

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

(e) Assertion and reason both are correct statements but reasson is not correct explanation of assertion.

21. **Assertion :** Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

22. **Assertion :** The α-hydrogen in carbonyl group is less acidic.

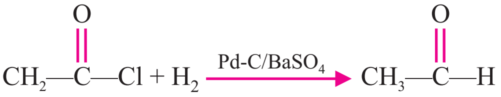
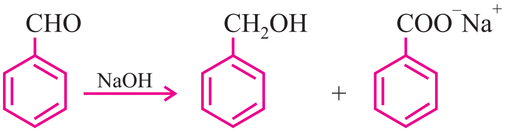
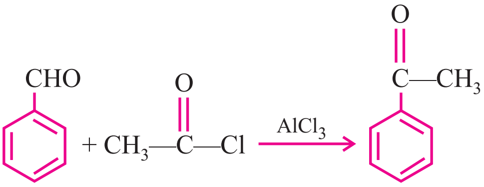
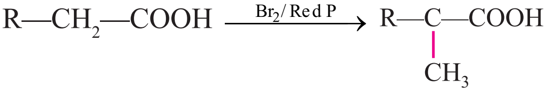
Reason : The anion formed after loss of a—H atom is resonance stabilised.

Matching Column Type

23. **Match the reactions given in Column I withthe suitable reagents given in Column II.**

Column-I		Column-II
(A) Benzophenone → Diphenylmethane	(i)	$LiAlH_4$
(B) Benzaldehyde → 1-Phenylethanol	(ii)	DIBAL—H
(C) Cyclohexanone → Cyclohexanol	(iii)	Zn(Hg)/Conc. HCl
(D) Phenyl benzoate → Benzaldehyde	(iv)	CH_3MgBr

24. **Match the example given in Column I with the suitable reagents given in Column II.**

	Column-I	Column-II
(A)	 $CH_2-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd\text{-}C/BaSO_4} CH_3-\overset{\overset{O}{\|}}{C}-H$	(i) Friedel Craft acylation
(B)		(ii) HVZ reaction
(C)		(iii) Aldol condensation
(D)	 $R-CH_2-COOH \xrightarrow{Br_2/Red\ P} R-\underset{CH_3}{\underset{\|}{C}}-COOH$	(iv) Cannizaro's reaction
(E)	$CH_3-CN \xrightarrow[(ii)\ H_2O/OH^+]{(i)\ SnCl_2/HCl} CH_3CHO$	(v) Rosenmund's reduction
(F)	$2CH_3CHO \xrightarrow{NaOH} CH_3-CH=CHCHO$	(vi) Stephen's reaction

Integer Type Question

25. **How many of following compound undergo aldol condensation Methanol, 2-Methylpentanal, bnzaldehyde, benzophenone cyclohexanone, 1-phenyl propanone, phenylacetaldehyde, butan-1-01, 2, 2-Dimethylbutanal**

0	1	2	3	4	5	6	7	8	9

ANSWERS

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

11. (b) **12.** (a) **13.** (a) **14.** (d) **15.** (d) **16.** (b, d) **17.** (b, c)

18. (b, d) **19.** (a, c) **20.** (a, b) **21.** (a) **22.** (d)

23. (a)—(iii), (b)—(iv), (c)—(i), (d)—(ii)

24. (a)—(v), (b)—(iv), (c)—(i), (d)—(ii), (e)—(vi), (f)—(iii) **25.** 4

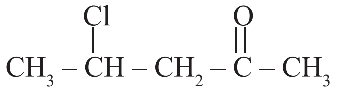
VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Arrange the following compounds in increasing order of their acid strengths : $(CH_3)_2CHCOOH, CH_3CH_2CH(Br)COOH, CH_3CH(Br)CH_2COOH$

Ans. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

Q. 2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.

Ans.



$$CH_3-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$$

Q. 3. Which type of aldehyde can go Cannizzaro reaction ?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogen.

Q. 4. Name the aldehyde which does not give Fehling's solution test.

Ans. Benzaldehyde.

Q. 5. Arrange the following in order of their increasing reactivity towards HCN :

$CH_3CHO, CH_3COCH_3, HCHO, C_2H_5COCH_3$

Ans. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

Q. 6. Mention industrial product obtained from HCHO.

Ans. Bakelite

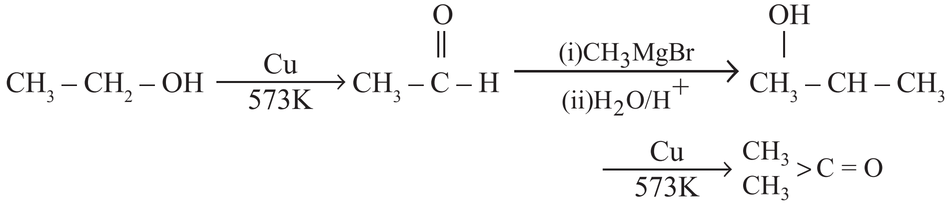
Q. 7. Arrange the following compounds in increasing order of their boiling point :

CH_3CHO, CH_3CH_2OH, CH_3-O-CH_3, $CH_3-CH_2-CH_3$

Ans. $CH_3-CH_2-CH_3 < CH_3-O-CH_3 < CH_3CHO < CH_3CH_2OH$

Q. 8. How is acetone obtained from ethanol ?

Ans.



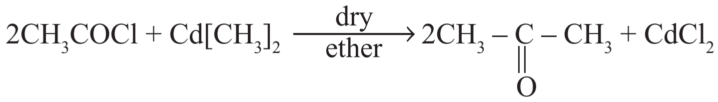
$$CH_3-CH_2-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[(ii)H_2O/H^+]{(i)CH_3MgBr} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow[573K]{Cu} \begin{matrix}CH_3\\CH_3\end{matrix}\!>C=O$$

Q. 9. Why do aldehydes and ketones have lower boiling point than alcohols ?

Ans. Due to presence of associated molecules with H-bonding in alcohols.

Q. 10. Write reaction between acetyl chloride and dimethyl cadmium.

Ans.

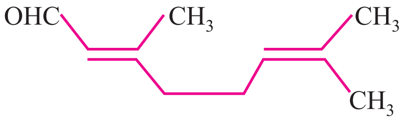


$$2CH_3COCl + Cd[CH_3]_2 \xrightarrow[ether]{dry} 2CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CdCl_2$$

Q. 11. What happens when CH_3CHO is treated with $K_2Cr_2O_7$ in presence of H_2SO_4 ?

Ans. $CH_3CHO + [O] \xrightarrow{K_2Cr_2O_7+H_2SO_4} CH_3COOH$

Q. 12. Write the IUPAC name of



Ans. 3, 7-Dimethylocta-2, 6 dien-1-al

Q. 13. Give balanced equation and name of products when CH_3COOH is treated with PCl_5 ?

Ans. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

Q. 14. What product is obtained when ethyl benzene is oxidized with alkaline $KMnO_4$?

Ans. Benzoic acid (C_6H_5COOH) is obtained.

Q. 15. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Give reason.

Ans. Because the positive charge on carbonyl carbon of CH_3CHO decreases to lesser extent due to one ERG $-CH_3$) andhence more reaction.

Q. 16. What is RDX ?

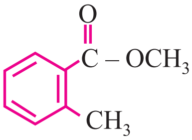
Ans. RDX is Research and Development Explosive which is prepared by the nitration of hexamethylene diamine under controlled conditions.

Q. 17. Write IUPAC names of the following compound :

HOOC – CH = CH - COOH

Ans. But-2-ene-1, 4-dioic acid

Q. 18. Write the IUPAC name of



Ans. Methyl-2-methylbenzoate.

Q. 19. Why does benzoic acid not undergo Friedel-Craft reaction ?

Ans. – COOH group in C_6H_5COOH is an E. W. G. which deactivates the benzene ring. Hence electrophilic substitution becomes difficult.

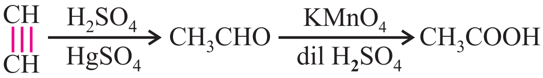
SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. How will you convert :

(i) $C_2H_2 \rightarrow CH_3COOH$

(ii) $C_6H_5CONH_2 \rightarrow C_6H_5COOH$

Ans. (i)

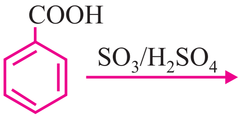


$$CH \equiv CH \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[\text{dil } H_2SO_4]{KMnO_4} CH_3COOH$$

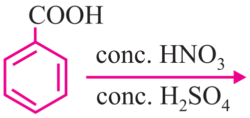
(ii) $C_6H_5CONH_2 + HNO_2 \rightarrow C_6H_5COOH + N_2 + H_2O$

Q. 2. Complete the following :

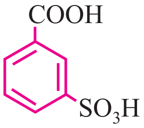
(i)



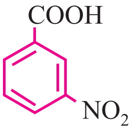
(ii)



Ans. (i)

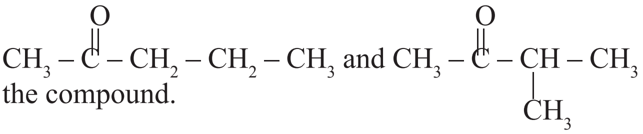


(ii)



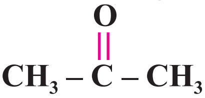
Q. 3. An organic compound X has molecular formula $C_5H_{10}O$. It does not reduce Fehling's solution but forms a bisulphite compound. It also gives positive Iodoform test. What are possible structures of X ? Explain your reasoning relating structure.

Ans. Ketone give +ve test with Iodoform. It is methyl-ketone.



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3$ and $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$ are possible structures of the compound.

Q. 4. Give the chemical test to distinguish between :

(i) CH_3CHO and  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(ii) CH_3CHO and C_6H_5CHO

Ans. (i) CH_3CHO gives Tollen's reagent test.

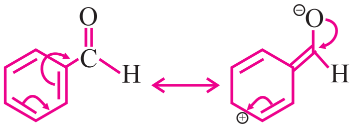
$$CH_3CHO + 2AgNO_3 + 2NH_4OH \rightarrow CH_3COOH + \underset{\text{Silver mirror}}{2Ag} + 2NH_4NO_3 + 2H_2O$$

(ii) CH_3CHO gives brick red ppt.

$$CH_3CHO + 2CuSO_4 + 4NaOH \rightarrow CH_3COOH + \underset{\text{Brick red ppt.}}{Cu_2O} + Na_2SO_4 + 2H_2O$$

Q. 5. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal ? Explain your answer.

Ans. Carbon atom of carbonyl is C_6H_5CHO is less reactive than that of propanal. C_6H_5CHO less polar due to resonance.



Q. 6. Which acid of each pair shown here would you expect to be stronger ?

(i) CH_3CO_2H or CH_2FCO_2H

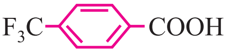
(ii) CH_2FCO_2H or CH_2ClCO_2H

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

(iv)  **or** 

Ans. (i) FCH_2COOH (ii) CH_2FCOOH

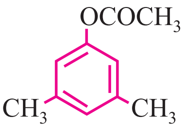
(iii)  $CH_3-\overset{F}{\overset{|}{C}H}-CH_2COOH$

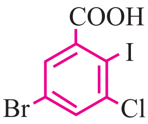
(iv) 

Q. 7. Carboxylic acids do not give reactions of aldehydes and ketones why ?

Ans. It is due to resonance  $R-\overset{O}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{O}}H \longleftrightarrow R-\overset{O^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{O}H$ Position of $>C=O$ group keep changing.

Q. 8. Write IUPAC name of the following :

(i) 

(ii) 

Ans. (i) 3, 5 Dimethylphenylethanoate

(ii) 5 bromo 3-chloro-2-iodobenzoic acid

Q. 9. Account for the following :

(i) Oxidation of toluene to C_6H_5CHO with CrO_3 is carried out in presence of acetic anhydride.

(ii) Melting point of an acid with even number is higher than those of its neighbours with odd number of carbon atoms.

Ans. (i) It is used to prevent oxidation to benzoic acid.
(ii) Acids with even number of carbon atoms fit into crystal lattice.

Q. 10. Distinguish between :

(i) C_2H_5OH and CH_3CHO

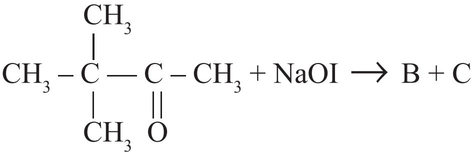
(ii) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$

Ans. (i) C_2H_5OH evolves H_2 gas with Na, CH_3CHO not.

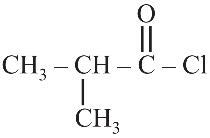
(ii) Acetophenone will give yellow ppt. of iodoform while $C_6H_5CH_2CHO$ will not.

Q. 11. Complete the following reactions by identifying A, B and C :

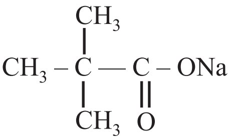
(i) **A + Hydrogen (g) $\xrightarrow{Pd/BaSO_4}$ $(CH_3)_2CH-CHO$**

(ii) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{||}}{C}-CH_3 + NaOI \longrightarrow B + C$$

Ans. (i) 'A' is 

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-Cl$$

(ii) 'B' is CHI_3 and 'C' is 

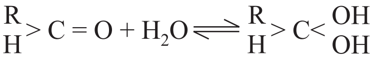
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{||}}{C}-ONa$$

Q. 12. Benzaldehyde gives a positive test with Tollen's reagent but not with Fehling's and Benedict solutions. Why ?

Ans. It is due to stronger oxidizing nature of Tollen's reagent as compared to Fehling and Benedict's solution and cannot oxidise benzaldehyde to benzoic acid. In general, all these three can oxidise aliphatic aldehydes.

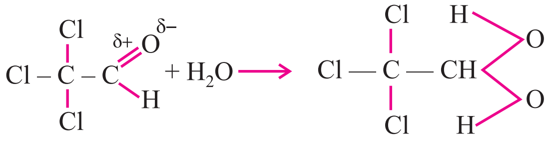
Q. 13. Aldehydes usually do not form stable hydrates but chloral normally exists as chloral hydrate. Give reason.

Ans. In case of aldehyde reaction is reversible.



$$\begin{matrix}R\\H\end{matrix}\!>C=O+H_2O \rightleftharpoons \begin{matrix}R\\H\end{matrix}\!>C<\!\begin{matrix}OH\\OH\end{matrix}$$

In case of CCl_3CHO, Cl atoms increases +ve charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.



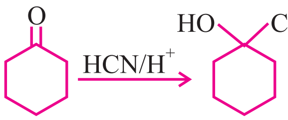
Chloralhydrate

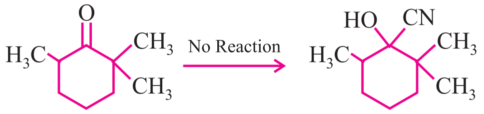
Q. 14. Give possible explanation for the following :

(i) Cyclohexanone forms cyanohydrins in good yield but 2, 2, 6 trimethyl-cyclohexanone does not.

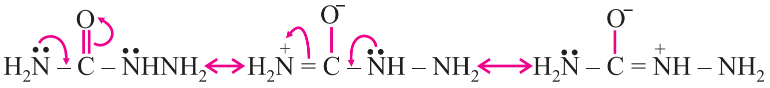
(ii) There are two – NH_2 groups in semicarbazide. However, only one is involved in formation of semi carbozone.

Ans. (i) Due to steric hindrance for CN^- at C = O and not of 3-methyl groups at α-position but in case of





(ii) Only one – NH_2 group attached to C = O is involved in resonance. As result electron density on these NH_2 group decreases and hence does not act as nucleophile.



$$H_2\ddot{N}-\overset{O}{\overset{\|}{C}}-\ddot{N}HNH_2 \leftrightarrow H_2\overset{+}{N}=\overset{O^-}{\overset{|}{C}}-\ddot{N}H-NH_2 \leftrightarrow H_2\ddot{N}-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H-NH_2$$

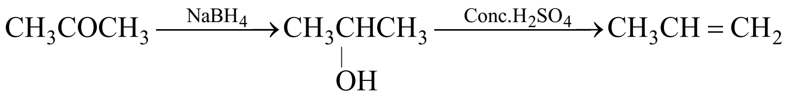
Q. 15. Aldehydes are easily oxidisable yet propanal can conveniently be prepared by the oxidation of propanol by acidic $K_2Cr_2O_7$.

Ans. Aldehydes having boiling points less than 373 K can be removed by distillation therefore propanal can easily be prepared from propanol by distillation from the alcohol acid dichromate solution.

Q. 16. Do the following conversions in not more than two steps

(i) Benzoic acid to Benzalolehyde (ii) Propanone to propene

Ans. (i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[H_2]{Pol-BaSO_4} C_6H_5CHO$



(ii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{Conc.H_2SO_4} CH_3CH = CH_2$

Q. 17. Write the reactions involved in the following reactions:

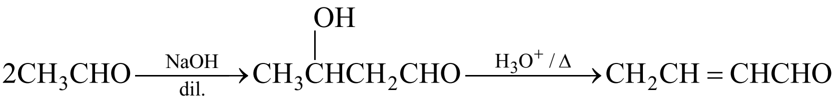
(i) Clemmensen reduction (ii) Cannizzoro reaction

Ans. (i) $>C = O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$

(ii) $\begin{matrix}H\\H\end{matrix}>C = O + \begin{matrix}H\\H\end{matrix}>C = O \xrightarrow[KOH]{Conc.} CH_3OH + HCOO^-K^+$

Q. 18. Convert the following (i) Ethyl benzene to benzoic acid (ii) Ethanal to but-2-enal

Ans. (i) $C_6H_5C_2H_5 \xrightarrow{K_2Cr_2O_7/H^+} C_6H_5COOH$



(ii) $2CH_3CHO \xrightarrow[dil.]{NaOH} CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2CHO \xrightarrow{H_3O^+/\Delta} CH_3CH = CHCHO$

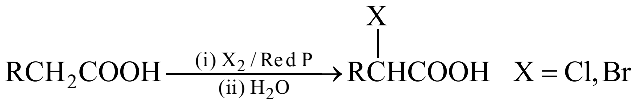
SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Illustrate the following name reactions :

(i) Hell-Volhard Zelinsky reaction

(ii) Wolff kishner reduction

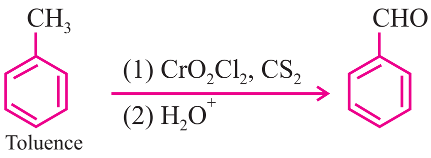
(iii) Etard reaction



Ans. (i) $RCH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/Red\ P} R\overset{\displaystyle X}{\overset{|}{C}}HCOOH \quad X = Cl, Br$

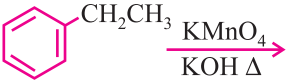
(ii) $>C = O \xrightarrow[(ii)\ KOH/Ethylene\ glycol,\ heat]{(i)\ NH_2NH_2} >CH_2 + N_2$

(iii)



Q. 2. Predict the organic products of the following reactions :

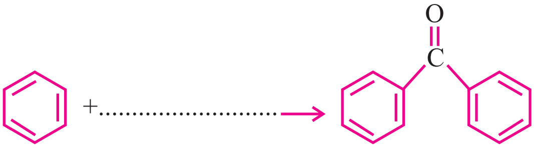
(i)



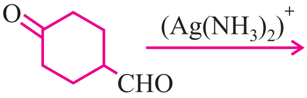
(ii)

(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iv)



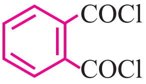
(v)



(vi)

Ans. (i) $C_6H_5 - COOK$

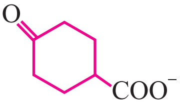
(ii)



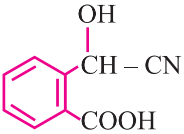
(iii) $C_6H_5CH = N - NHCONH_2$

(iv) $C_6H_5COCl/AlCl_3$

(v)



(vi)



Q. 3. Write chemical reaction to affect the following transformations :

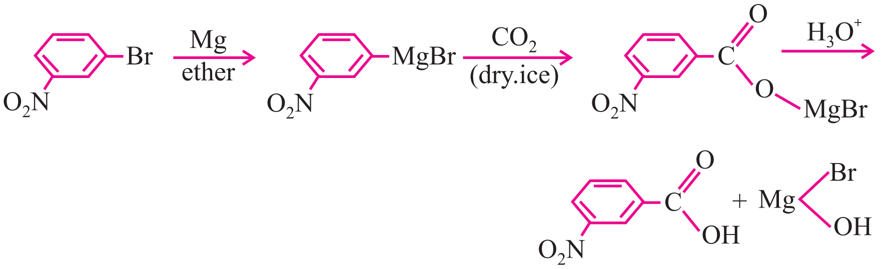
- **(i) Butan-1-ol → Butanoic acid**
- **(ii) Benzyl alcohol to pheynylethanoic acid**
- **(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid**
- **(iv) 4-methylacetophenone to Terephthalic acid**
- **(v) Cyclohexene → Hexane-1, 6 dioic acid**
- **(vi) Butanal → Butanoic acid**

Ans. (i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3+H_2SO_4} CH_3CH_2CH_2COOH$

(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN$

$\xrightarrow[H_3O]{\Delta} C_6H_5CH_2COOH$

(iii)



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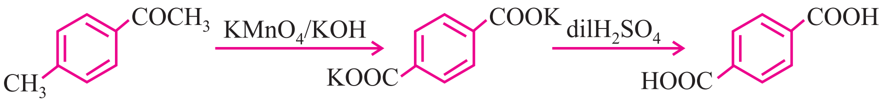


Dipotassium benzene 1, 4 dicarboxylate

Terephthalic acid

(v)

Cyclohexene

Hexane-1, 6 dioicacid (adipic acid)

(vi) $CH_3CH_2CH_2CHO \xrightarrow[\text{Tollen's reagent}]{\text{Amm. } AgNO_3} CH_3CH_2CH_2COOH$

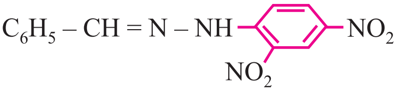
Q. 4. Draw the structure of the following derivatives :

- **(i) 2, 4-dinitrophenylhydrazone of C_6H_5CHO**
- **(ii) Cyclopropanone oxime**
- **(iii) Acetaldehydedimethylacetal**
- **(iv) Semicarbazone to cyclobutanone**

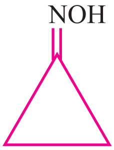
(v) Ethylene ketal of hexan-3-one

(vi) Methylhemiacetal of formaldehyde

Ans. (i)



(ii)



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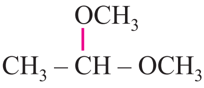
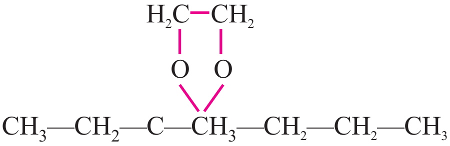


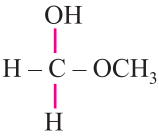
$CH_3-\overset{OCH_3}{CH}-OCH_3$

(iv)

(v)



(vi)



$H-\underset{H}{\overset{OH}{C}}-OCH_3$

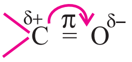
Q. 5. Draw the structure of a carbonyl group and indicate:

(i) hybridized state of carbon

(ii) the σ and π bonds

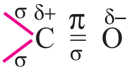
(iii) the electrophilic and nucleophilic centres

Ans. (i)

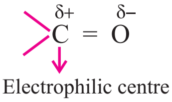


hybridized state of 'C' is sp^2

(ii)

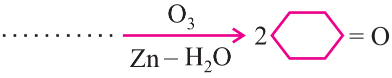


(iii)

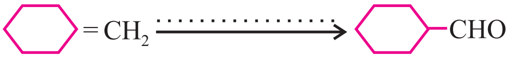


Q. 6. Complete the following as missing starting material, reagent or products :

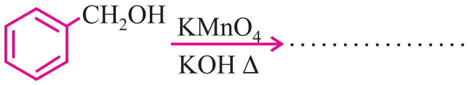
(i)



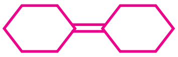
(ii)



(iii)



Ans. (i)

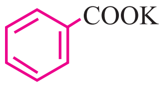


(Ozonolysis)

1, 2 Dicyclohexylethene

(ii) B_2H_6/THF, H_2O_2/OH^-, PCC (Hydroboration)

(iii)



(Oxidation)

Potassium benzoate

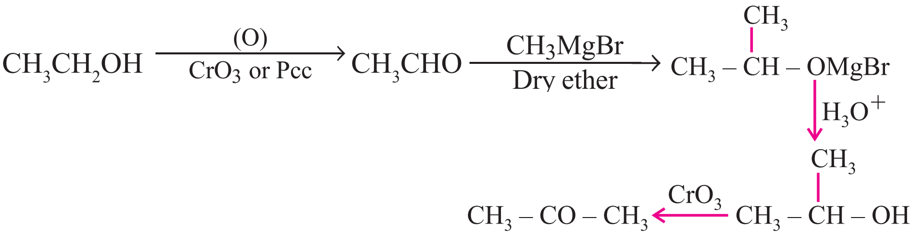
Q. 7. How can the following converted :

(i) Ethanol → Acetone

(ii) Benzene → Acetophenone

(iii) Benzoic acid → Benzaldehyde

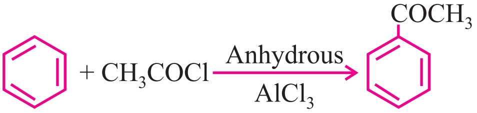
Ans. (i)



$$CH_3CH_2OH \xrightarrow[CrO_3 \text{ or Pcc}]{(O)} CH_3CHO \xrightarrow[\text{Dry ether}]{CH_3MgBr} CH_3-\overset{\overset{CH_3}{|}}{C}H-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{\overset{CH_3}{|}}{C}H-OH$$

$$CH_3-CO-CH_3 \xleftarrow{CrO_3} CH_3-\overset{\overset{CH_3}{|}}{C}H-OH$$

(ii)



(iii) $C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$

Q. 8. Give reasons for the following :

(i) Carboxylic acids do not give characteristic reactions of carbonyl group.

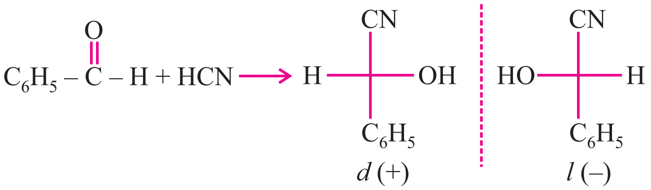
(ii) Treatment of C_6H_5CHO with HCN gives a mixture of two isomers which cannot be separated even by fractional distillation.

(iii) Sodium bisulphite is used for purification of ketones and aldehydes.

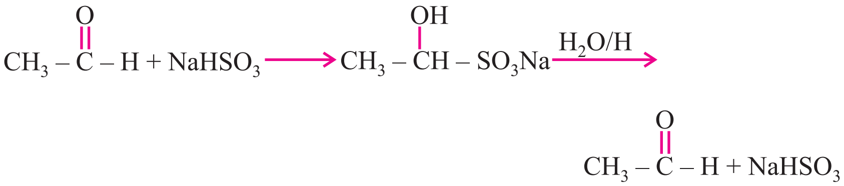
Ans. (i)

$R-\overset{O}{\overset{\|}{C}}-\ddot{O}H \longleftrightarrow R-\overset{O^-}{\overset{|}{C}}=\overset{\oplus}{O}H$ Because of resonance, the position of $>C=O$ group is changing.

(ii) Due to two optical isomers fractional distillation is not possible.



(iii) Due to formation of additional compound with $NaHCO_3$ whereas impurities do not.



$$CH_3-\overset{O}{\overset{\|}{C}}-H + NaHSO_3 \longrightarrow CH_3-\overset{OH}{\overset{|}{C}H}-SO_3Na \xrightarrow{H_2O/H} CH_3-\overset{O}{\overset{\|}{C}}-H + NaHSO_3$$

Q. 9. Write tests to distinguish between :

(i) CH_3CHO and C_6H_5CHO

(ii) C_6H_5-OH and CH_3COOH

(iii) Pentanal and Pentan-2-one

Ans. (i) CH_3CHO gives brick red ppt. with Fehling, C_6H_5CHO not.

(ii) Phenol does not give brisk effervescence but CH_3COOH gives this test with $NaHCO_3$.

(iii) Pentanal forms silver mirror but pentan-2-one does not.

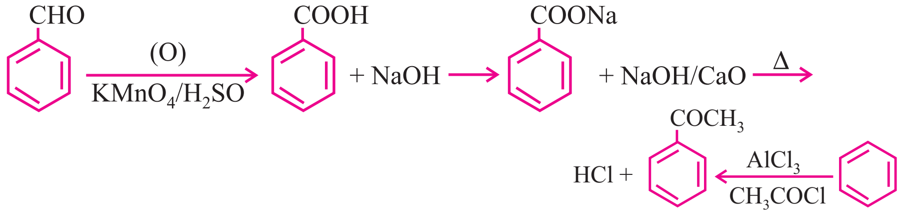
Q. 10. Convert :

(i) Benzaldehyde to acetophenone

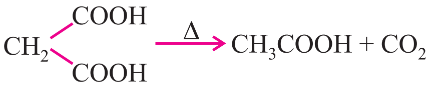
(ii) Malonic acid to acetic acid

(iii) Acetaldehyde to 2-butanol

Ans. (i)

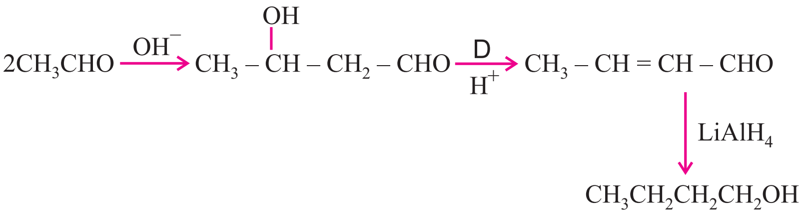


(ii)



Malonic acid

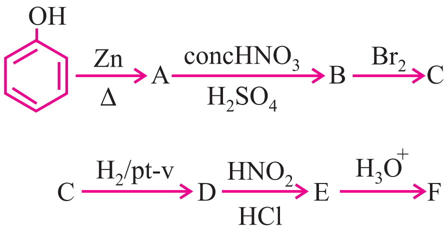
(iii)



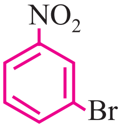
$$2CH_3CHO \xrightarrow{OH^-} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO \xrightarrow[H^+]{D} CH_3-CH=CH-CHO \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

2-Butanol

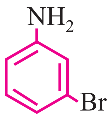
Q. 11. Write the structures of organic compound A to F in the following sequence of reactions :



Ans. $A = C_6H_6$ $B = C_6H_5NO_2$ C =

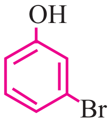


D =



E =

F =

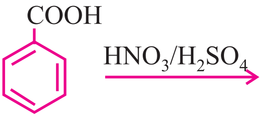


Q. 12. Complete the following :

(i) $CH_3CONH_2 + HNO_2 \rightarrow$

(ii) $CH_3CONH_2 + NaOH + Br_2 \rightarrow$

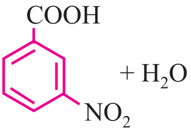
(iii)



Ans. (i) $CH_3COOH + N_2 + H_2O$

(ii) $CH_3NH_2 + Na_2CO_3 + NaBr + H_2O$

(iii)



Q. 13. Write the structures of A, B, C, D and E in the following reactions:

$$\begin{tikzcd}
C_6H_6 \arrow[r, "CH_3COCl", "\text{anhyd. } AlCl_3"'] & A \arrow[r, "Zn\text{–}Hg", "HCl"'] \arrow[d, "NaOI"] & B \arrow[r, "(1)\ KMnO_4 - KOH", "(2)\ H_3O^+"'] & C \\
& D + E & &
\end{tikzcd}$$

Ans. $A = CH_5COCH_3$

B = $C_6H_5CH_2CH_3$

C = C_6H_5COOH

D = C_6H_5COONa

E = CHI_3

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Which of the following compounds would undergo Aldol condensation, which the Cannizzaro reaction and which neither ? Write the structures of the expected products of aldol condensation and Cannizzaro reaction :

(i) Methanal	**(ii) 2-Methylpentanal**
(iii) Benzaldehyde	**(iv) Benzophenone**
(v) Cyclohexanone	**(vi) 1-Phenylpropanone**
(vii) Phenylacetaldehyde	**(viii) Butan-1-ol**
(ix) 2, 2 Dimethylbutanal	

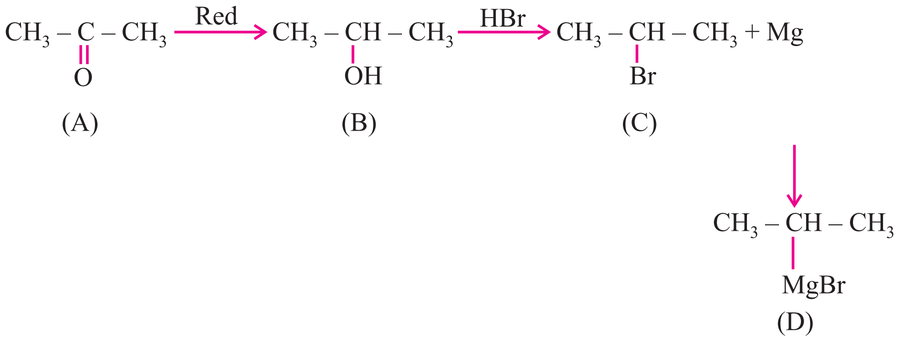
Ans. (i), (iii) and (ix) will give Cannizzaro reaction due to absence of α-hydrogen.

(ii), (v), (vi) and (vii) will give aldol condensation due to presence of α-hydrogen.

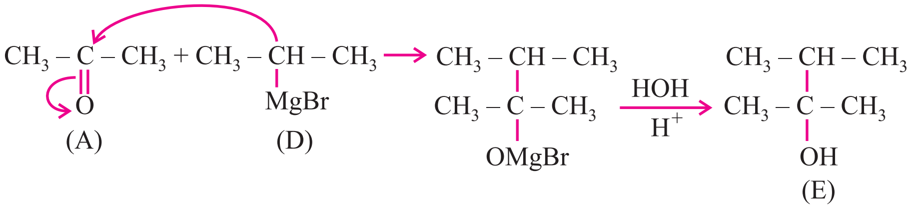
(iv) and (viii) will neither undergo Cannizzaro's reaction nor Aldol condensation because benzophenone does not give α-hydrogen and butanol is alcohol, not aldehyde which cannot undergo aldol condensation.

Q. 2. An organic compound 'A' (C_3H_6O) is resistant to oxidation but forms compound 'B' (C_3H_8O) on reduction. 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D' which reacts with 'A' to form a product which on hydrolysis gives 'E'. Identify 'A' to 'E'.

Ans. 'A' must be ketone.



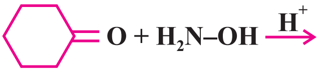
$$\underset{(A)}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow{Red} \underset{(B)}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow{HBr} \underset{(C)}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3} + Mg \longrightarrow \underset{(D)}{CH_3-\underset{\underset{MgBr}{|}}{CH}-CH_3}$$



2, 3 Dimethylbutan-2-ol

Q. 3. (a) Write the products of the following reactions:

(i)



(ii) $2C_6H_5CHO + NaOH \longrightarrow$
Conc.

(iii) $CH_3COOH \xrightarrow{Cl_2/P}$

(b) Give simple tests to distinguish between the following pairs of compounds.

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and propanone

Ans. (a) (i)

(ii)

(ii) $Cl–CH_2COOH$

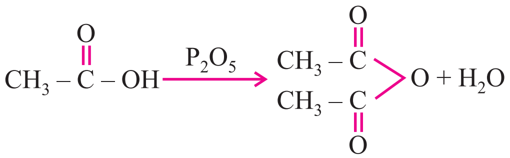
(b) (i) Add $NaHCO_3$, benzoic acid will give brisk ettervscence whereas benzaldehyde will not give this test.

(ii) Refer Q.7(e) of long answer type questions.

Q. 4. (i) How will you prepare (a) acetic anhydride and (b) acetyl chloride from CH_3COOH ? Write the equation involved in each case.

(ii) Why is the boiling point of acid anhydride higher than the acid from which it is obtained ?

Ans. (i) (a)



(b)

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

(ii) Acid anhydride bigger size than corresponding acids and stronger van der Waal's forces of attraction than their corresponding acids.

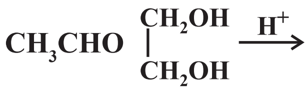
Q. 5. Complete the following reactions and write main products :

(i) $CH_3CONH_2 + HNO_2 \rightarrow$ **(ii)** $CH_3COCl + H_2O$ **(steam)** $\rightarrow$

(iii) $CH_3MgBr \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CO_2/H^+}$ **(iv)** $CH_3COOH + NH_3 \xrightarrow{\Delta}$

(v) $CH_3COOH + C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4}$ **(vi)** $HCHO + NH_3 \rightarrow$

(vii) $CH_3CHO \xrightarrow{LiAlH_4}$ **(viii)**



$$CH_3CHO \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{H^+}$$

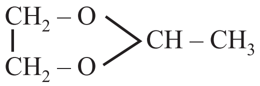
(ix) $CH_3COR + NaOI \rightarrow$ **(x)** $C_6H_5CHO + NH_2 - NH_2 \rightarrow$

Ans. (i) CH_3COOH (ii) CH_3COOH

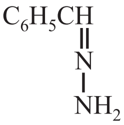
(iii) CH_3COOH (iv) CH_3CONH_2

(v) $CH_3COOC_2H_5$ (vi) $(CH_2)_6N_4$ (Urotropine)

(vii) CH_3CH_2OH (viii)



(ix) CHI_3 (x)



$$\begin{array}{l} C_6H_5CH \\ \quad\;\, \| \\ \quad\;\, N \\ \quad\;\, | \\ \quad\;\, NH_2 \end{array}$$

Q. 6. Give reasons for the following :

(i) C_6H_5COOH is weaker than formic acid.

(ii) HCOOH and CH_3COOH differentiated by Tollen's reagent.

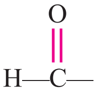
(iii) R – COOH do not give characteristic reaction with > C = O.

(iv) Carboxylic acids are stronger acids than phenols.

(v) Acid amides are weakly basic in nature.

Ans. (i) Due to unstability of carboxylate anion due to conjugation.

(ii) Presence of



$$H - \overset{\overset{\large O}{\|}}{C} -$$

group

(iii) > C = O group is sterically hindered in carboxylic acid.

(iv) Dispersal of –ve charge on carboxylate ions than phenoxide 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-CH_2COOH is lower than that of Cl–CH_2COOH

(d) Write the product in the following reaction

$$CH_3CH = CHCH_2CN \xrightarrow[\text{(2) } H_2O]{\text{(1) DIBAL - H}}$$

(e) How can you distinguish between propanal and propanone?

Ans. (a) $HCHO + HCHO \xrightarrow{\text{Conc. NaOH}} HCOONa + CH_3OH$

(b) $CH_3CH = N–NHCONH_2$

(c) Stronger –I effect of fluorine makes F-CH_2COOH to be stronger acid than Cl–CH_2COOH and less pka

(d) $CH_3CH = CHCH_2CHO$

(e) Silver mirror formed on adding ammonical silver nitrate to propanal and not with propanone.

UNIT 12

AMINES

Points to Remember

1. Amines are alkyl and/or aryl derivatives of $\ddot{N}H_3$.

2. Functional groups of 1°, 2° and 3° amines are respectively as given below :

$$-\ddot{N}H_2, -\ddot{N}H- \text{ and } -\underset{|}{\ddot{N}}-$$

3. Gabriel phthalimide synthesis can't be used for the preparation of 2° and 3° amines. It gives aliphatic primary amine only.

4. Hoffmann's bromamide reaction gives 1° amines having one carbon atom less than parent primary amide.

5. The order of basic strength of aliphatic amines is :

   (i) Aliphatic amines are more basic than $\ddot{N}H_3$.

   (ii) In aqueous solution medium, the order is 2° > 1° > 3° (for–CH_3 group) and 2° > 3° > 1° for – C_2H_5 group.

   (iii) In non-aqueous medium or gaseous phase, the order is 3° > 2° > 1°.

6. Basic strength of aromatic amines :

   (i) Aromatic amines are weaker bases than $\ddot{N}H_3$.

   (ii) ERGs like – CH_3, – OR, – NH_2 etc. increase basic strength while EWGs like – NO_2, – CN etc. decrease the basic strength. The effect of substituents is more at para positions and less at meta position.

7. Basic strength of amines is expressed in terms of K_b or pK_b.

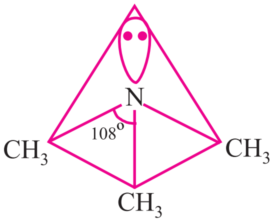
8. 1°, 2° and 3° amines can be distinguished by Hinsberg's test.

9. Hinsberg's reagent is benzenesulphonyl chloride ($C_6H_5SO_2Cl$).

10. 3° amines like trimethylamine are used as insect attractants.

11. Diazonium salts are represented by the general formula $[Ar\,N \equiv N]^+ X^-$.

12. **Structure of amines :** Pyramidal for trimethyl amine $\left(CH_3\right)_3 - \ddot{N}$. They are Lewis bases.



13. Carbylamine test only given by 1° amines.

14. Manich reaction involves the reaction of ketones with HCHO and NH_3 (or amine) in acidic medium to form Manich bases.

15. 1° amines give effervescence with HNO_2.

16. $-NH_2$ group in aniline is *o*- and *p*- directing and is highly activating in nature.

17. Acylation of aniline is done before subjecting it to nitration or halogenation.

18. Aliphatic diazonium salts are very unstable and do not exist while aromatic salts are relatively stable.

19. These salts are prepared from 1° aryl amines by diazotization reactions.

20. Diazotised salts (diazonium salts) are used to prepare a variety of aromatic compounds.

21. $R - C \equiv N$ have generally pleasant odours but alkyl isocyanides have highly unpleasant odours.

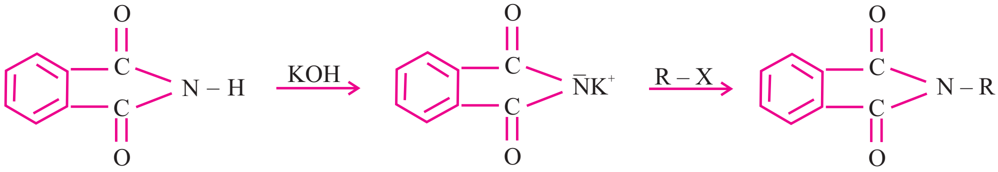
22. Alkyl isocyanides have lower boiling points than that of isomeric alkyl cyanides due to lower dipole moments.

23. Arenediazonium salts are highly reactive compounds and reactivity is due to excellent leaving ability of diazo group as N_2 gas.

NAME REACTIONS

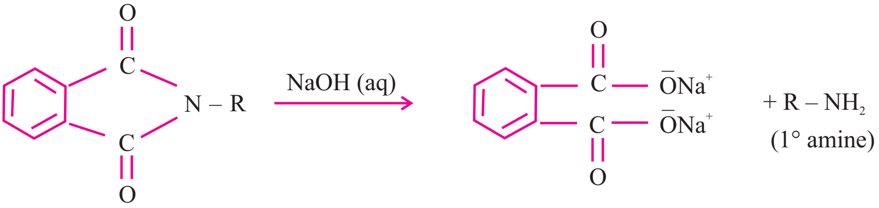
1. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment wi ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



Phthalimide

N–Alkylphthalimide



2. **Hoffmann bromamide degradation reaction**

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amine so formed contains one carbon less than present in the amide.

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

3. **Carbylamine reaction**

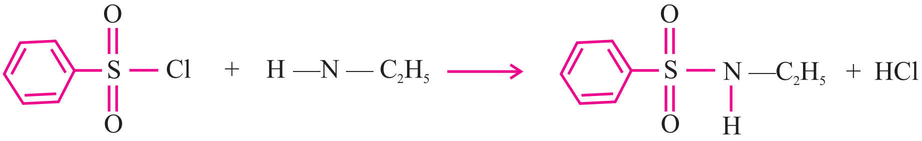
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2O$$

4. **Hinsberg Test:**

Benzenesulphonyl chloride ($C_6H_5SO_2CI$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

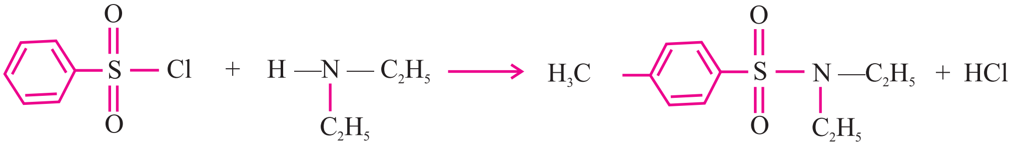
(a) The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzenesulphonyl amide.



N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, N, N-diethylbenzenesulphonamide is formed.



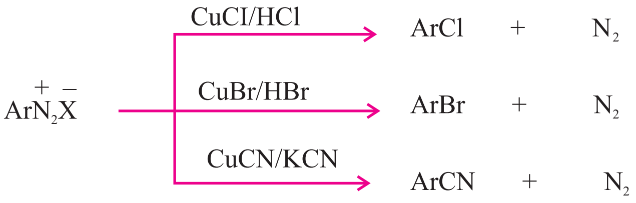
N,N-Diethylbenzenesulphonamide

Since N, N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.

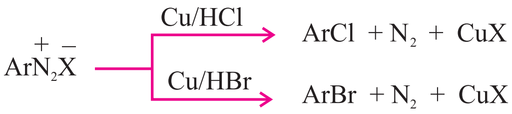
5. Sandmeyer Reaction

The C1-, Br- and CN- nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of Cu(I) ion.



6. Gatterman Reaction

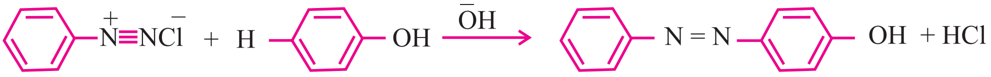
Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



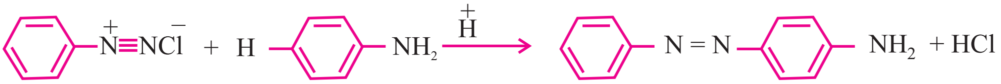
7. Coupling reactions

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the -N=N- bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.



P-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene
(yellow dye)

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine

(ii) Secondary and tertiary amines

(iii) Ethylamine and aniline

MULTIPLE CHOICE QUESTIONS

1. In the nitration of benzene using a moisture of Conc H_2SO_4 and conc. HNO_3 the species which initiates the reaction is:

(a) NO_2 (b) NO^+

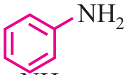
(c) NO_2^+ (d) NO_2^-

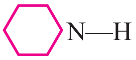
2. The correct IUPAC name of $Cu_2 = CH—CH_2NHCH_3$ is:

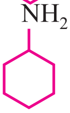
(a) Allymethyl amine (b) 2-amino-4-pentene

(c) 4-aminopent-lene (d) N-methylprop-2-en-anine

3. Which is the weakest base:

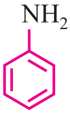
(a) 

(b) 

(c) 

(d) CH_3NH_2

4. The correct order of basic strength for the following compounds is:

(i) 

(ii) 

(iii) 

(a) ii < iii < i (b) iii < i < ii

(c) iii < ii < i (d) ii < i < iii

5. Methylamine reacts with HNO_2 to form

(a) $CH_3-O-N=0$ (b) CH_3OCH_3

(c) CH_3OH (d) CH_3CHO

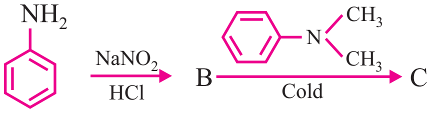
6. CH_3CH_2COOH

The structure of 'c' would be

(a) $CH_3CH_2CO\ NH_2$ (b) $CH_3CH_2NHCH_3$

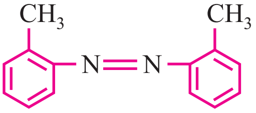
(c) $CH_3CH_2NH_2$ (d) $CH_3CH_2CH_2NH_2$

7.

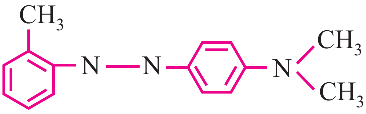


The structure of 'c' would be

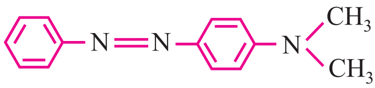
(a)



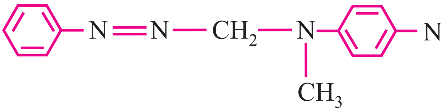
(b)



(c)



(d)



8. Which of the following statement about primary amine is false:

(a) Aryl amines react with nitrous acid to produce phenol

(b) Alkylamines are stronger base than ammonia

(c) Alkyl amines are stronger base than aryl amines

(d) Alkyl amines react with nitrous acid to produce alcohol

9. Which of the following is most stable diazoniom salt?

(a) $CH_3N_2^+ X^-$ (b) $C_6H_5N_2^+ X^-$

(c) $CH_3CH_2N_2^+ X^-$ (d) $C_6H_5CH_2N_2^+ X^-$

10. Method by which aniline can not be prepared is:

(a) reduction of nitrobenzene with H_2/Pd in ethanol.

(b) potassium salt of phthalimide treated with chlorobenzene

(c) hydrolysis of phenyl isocyanide with acidic solution

(d) degradation of benzamide with bromine in alkaline medium solution.

11. In the chemical reaction:

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow A + B + 3H_2O$

The compound A and B are respectively:

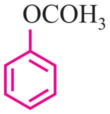
(a) $CH_3CH_2CONH_2$ and 3KCl
(b) $CH_3CH_2NC + K_2CO_3$
(c) CH_3CH_2NC and 3KCl
(d) $CH_3CH_2CNB + 3KCl$

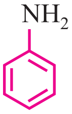
12. Considering the basic strength of amines in aqueous solution which one has the smallest pk_b value?

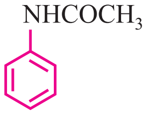
(a) $(CH_3)_2NH$
(b) $C_6H_5NH_2$
(c) CH_3NH_2
(d) $(CH_3)_3N$

13. Which of the following compound will give significant amount of meta product during mono-nitration reaction?

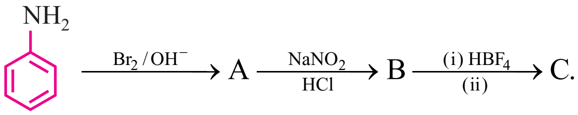
(a) 

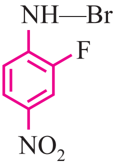
(b) 

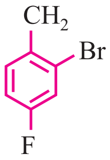
(c) 

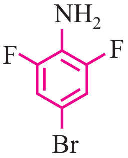
(d) 

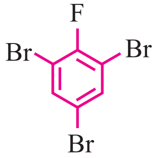
14. The final product (c) in the following sequence of reaction is:

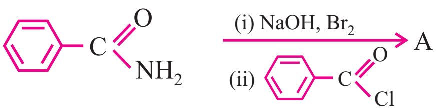


(a) 

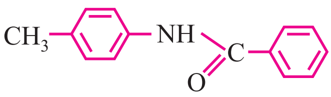
(b) 

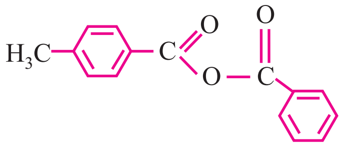
(c) 

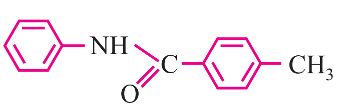
(d) 

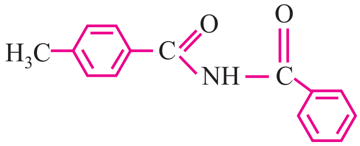
15. In the reaction 

The structure of product A is:

(a) 

(b) 

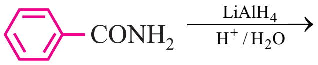
(c) 

(d) 

16. A positive carbylamine test is given by

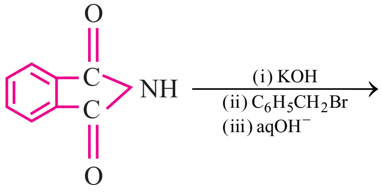
(a) N< N-Dimethylaniline
(b) 2, 4-Dimethylaniline
(c) N-Methyl-0-methylaniline
(d) *p*-methylbenzylamine

17. Which of the following reactions form benzylamine:

(a) 

(b) $C_6H_5CONH_2 \xrightarrow{NaOBr}$

(c) $C_6H_5CN \xrightarrow{H^+/H_2O}$

(d) 

18. Which reagent among the following can affect the conversion?

$CH_3—C\equiv N \longrightarrow CH_3CH_2NH_2$

(a) H_2, Pt
(b) Ammonical $AgNO_3$
(c) LiA/H_4
(d) $NaBH_4$

19. In which of the following amines,the first has lower pk_b value than the second

(a) aniline, m-nitroaniline
(b) m-Toluidine, p-toluidine
(c) aniline, p-chloroaniline
(d) aniline, p-aminophenol

20. Bromobenzene can be prepared from benzene diazonium chloride. When its is treated with

(a) Cu/HBr
(b) Br_2; HBr
(c) CuBr/HBr
(d) Br_2, CCl_4

Assertion Reason Type Questions

The question given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(a) Assertion and reason both are CORRECT and reason is the CORRECT explanation of the assertion.
(b) Assertion and reason both are wrong statements.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
(e) Assertion and reason both are correct statements but reasson is not correct explanation of assertion.

Assertion and Reasoning

21. Assertion : n-Propylamine has higher boiling point than trimethylamine.

Reason : Among n-propylamine molecules, there is hydrogen bonding but there is not hydrogen bonding in trimethylamine.

22. Assertion : Aniline does not undergo Friedel Crafts reaction.

Reason : Friedel Crafts reaction is an electrophilic substitution reaction.

23. Match column 1 and column II

Column-I	**Column-II**
(A) Ammolysis	(p) Amine with lesser no. of carbon atom
(B) Gabriel phthalimide	(q) Detection of primary amine
(C) Hoffmann bromide amide degradation	(r) Reaction of pthalimide with KOH and R—X
(D) Carbylamine reaction	(s) Reaction of alkyl halides with NH_3

(a) A–s, B–r, C–p, D–q (b) A–p, B–q, C–r, D–s

(c) A–r, B–s, C–p, D–q (d) A–s, B–r, C–q, D–p

24. Match column 1 and column II

Column-I	**Column-II**
(A) Benzene sulphonyl chloride	(p) zwitter ion
(B) Sulphanilic acid	(q) Hinsberg reagent
(C) Alkyl diazonium salts	(r) Dyes
(D) Aryl diazonion salts	(s) Conversion to alcohols

(a) A–p, B–q, C–s, D–r (b) A–q, B–p, C–s, D–r

(c) A–q, B–p, C–r, D–s (d) A–s, B–r, C–q, D–p

25. The no. of amines having pkb less than $C_6H_5NH_2$ among the following.

P—CH_3—C_5H_4 NH_2, O—CH_3—$C_6H_4NH_4$, m—$CH_3C_6H_4$—NH_2, $C_6H_5N(CH_3)_2$, $C_6H_5NHCH_3$, p—$NO_2C_6H_4$ NH_2, p—$ClC_6H_4NH_2$, $C_6H_5CH_2NH_2$, $C_6H_5CH_2CH_2NH_2$

0	1	2	3	4	5	6	7	8	9

ANSWERS

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

11. (c) **12.** (a) **13.** (c) **14.** (d) **15.** (a) **16.** (b, d) **17.** (a, d)

18. (a, c) **19.** (a, c) **20.** (a, c) **21.** (a) **22.** (b)

23. (a) **24.** (b) **25.** 7

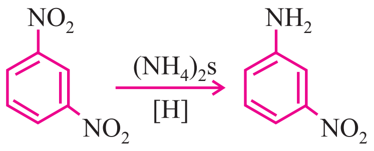
VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Write IUPAC name of CH_3NC.

Ans. Methane carbylamine.

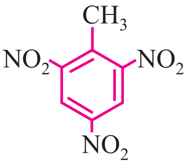
Q. 2. Convert m-dinitrobenzene to m-nitro aniline.

Ans.

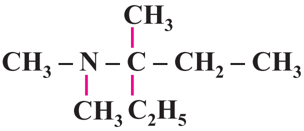


Q. 3. Draw structure of TNT, an explosive.

Ans.



Q. 4. Write IUPAC name of



$CH_3-\underset{CH_3}{N}-\underset{C_2H_5}{\overset{CH_3}{C}}-CH_2-CH_3$

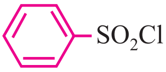
Ans. 3-Methyl-N,N-dimethyl pentanamine

Q. 5. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., $[CH_3(CH_2)_{15}N(CH_3)_2]^+Cl^-$.

Q. 6. What is Hinsberg's reagent ?

Ans. Benzene sulphonyl chloride,



Q. 7. Why aniline dissolves in HCl ?

Ans. $C_6H_5NH_2 + HCl \rightarrow [C_6H_5NH_3]^+Cl^-$.

It dissolves due to its basic nature.

Q. 8. How will you test the presence of primary amine ?

Ans. By carbyl amine test.

$$RNH_2 + CHCl_3 + 3KOH \rightarrow R—NC + 3KCl + 3H_2O$$

Q. 9. What is vapour phase nitration ?

Ans. $CH_4 + HNO_3 \xrightarrow{623\ K} CH_3NO_2$

(High temperature and nitration in vapour phase only)

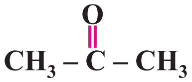
Q. 10. Write one use of dopamine and atropine alkaloid.

Ans. Dopamine : Neurotransmitter

Atropine alkaloid : 0.5-1.0% solution ophthalmic examination.

Q. 11. Direct nitration of aniline is not carried out. Explain.

Ans. ($H_2SO_4 + HNO_3$) easily oxidized aniline into tarry complex product due to high e^- density on the benzene ring of aniline.

Q. 12. Among the compounds as following which will react with  $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ **to give product containing > C = N – ?**

(i) $C_6H_5NH_2$ **(ii)** $(CH_3)_3N$

(iii) $C_6H_5NHC_6H_5$ **(iv)** $C_6H_5NHNH_2$

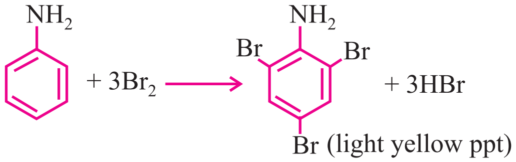
Ans. $C_6H_5NH_2$ and $C_6H_5NHNH_2$.

Q. 13. How will you give expression for K_b to indicate its basic strength ?

Ans. $$K_b = \frac{\left[RNH_3^{+}\right]\left[OH^{-}\right]}{\left[R-NH_2\right]}$$

Q. 14. What happens when aniline is treated with bromine ?

Ans.



Q. 15. Write a chemical equation to illustrate the ammonolysis.

Ans. For alcohols :

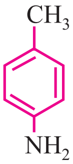
$$C_2H_5OH \xrightarrow[Al_2O_3/620K]{NH_3} C_2H_5\ddot{N}H_2 \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_2\,\ddot{N}H \xrightarrow{C_2H_5OH} (C_2H_5)_3\,\ddot{N}$$

For alkyl halides :

$$C_2H_5I \xrightarrow[-HI]{NH_3/373\,K} C_2H_5\ddot{N}H_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2\,\ddot{N}H \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3\,\ddot{N} \xrightarrow[-HI]{C_2H_5I} \left[(C_2H_5)_4\ddot{N}\right]^{+} I^{-}$$

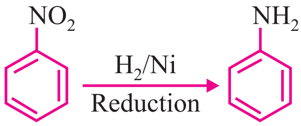
Q. 16. Write the structure of p-toluidine.

Ans.



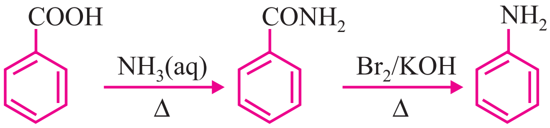
Q. 17. Prepare/convert nitrobenzene into aniline.

Ans.



Q. 18. Convert C_6H_5COOH to $C_6H_5NH_2$.

Ans.



Q. 19. Write isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

Q. 20. Arrange the following compounds in increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

SHORT ANSWER TYPE QUESTIONS (2 Marks)

Q. 1. Complete the following acid-base reactions and name the products :

(i) $CH_3CH_2CH_2NH_2 + HCl \rightarrow$

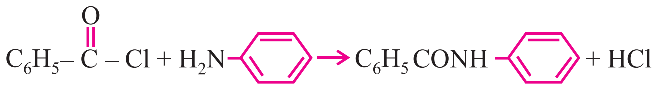
(ii) $(CH_3CH_2)_3N + HCl \rightarrow$

Ans. (i) $CH_3CH_2CH_2N^+H_3Cl^-$ (n-propyl ammonium chloride)

(ii) $(CH_3CH_2)_3 - N^+HCl^-$ (Triethyl ammonium chloride)

Q. 2. Write chemical reaction of $C_6H_5NH_2$ + C_6H_5COCl and name product obtained.

Ans.



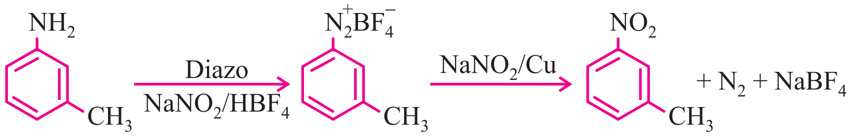
N-phenyl benzamide

Q. 3. How will you convert :

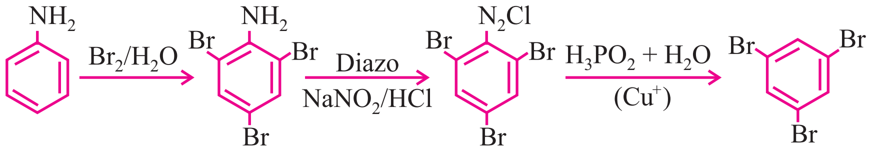
(i) 3-methylaniline → 3-nitrotoluene

(ii) Aniline → 1, 3, 5-tribromobenzene

Ans. (i)



(ii)



Q. 4. How will you convert :

(i) Propanoic acid → Ethanoic acid

(ii) Nitromethane → Dimethylamine

Ans. (i) $C_2H_5COOH \xrightarrow[\Delta]{NH_3} C_2H_5CONH_2 \xrightarrow{Br_2/KOH} C_2H_5NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$

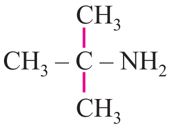
(ii) $CH_3NO_2 \xrightarrow{H_2/Ni} CH_3NH_2 \xrightarrow{CH_3Cl/KOH} CH_3N \equiv C \xrightarrow{H_2/Ni} CH_3 - NH - CH_3$

Q. 5. Draw the structures of the following compounds :

(i) N-isopropylaniline **(ii) t-butylamine**

Ans. (i)

(ii)



$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - NH_2$$

Q. 6. Why $C_6H_5N^+(CH_3)_3OH^-$ a stronger base than NH_4OH ?

Ans. Due to – I effect of phenyl group, it decreases e^- density on nitrogen atom but no such group in NH_4OH.

Q. 7. Explain K_b order : $Et_2NH > Et_3N > EtNH_2$ in aqueous solution.

Ans. Basicity of amines in aqueous solution depends upon :

(i) + I effect of an alkyl group.

(ii) Extent of hydrogen bonding with H_2O.

(iii) Steric effects of alkyl groups.

Q. 8. Distinguish between 1°, 2° and 3° amines by HNO_2 **acid test.**

Ans. 1° gives N_2 gas. 2° gives yellow oily compound. 3° form water soluble salts.

$$CH_3CH_2NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$$

$$R_2NH + HNO_2 \rightarrow R_2N - N = O + H_2O$$

$$(CH_3CH_2)_3N + HNO_2 \longrightarrow [(CH_3CH_2)_3\overset{\oplus}{N}H]\,NO_2^-$$

Soluble in water

Q. 9. A compound 'A' having molecular formula C_3H_7ON reacts with Br_2 in presence of NaOH to give compound 'B'. This compound 'B' reacts with HNO_2 to form alcohol and N_2 gas. Identify compound 'A' and 'B' and write the reaction involved.

Ans. 'A' is $CH_3CH_2CONH_2 \xrightarrow[NaOH]{Br_2} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow{HNO_2} C_2H_5OH + N_2 + H_2$

Q. 10. Write chemical equation for the following conversions :

(i) $CH_3 - CH_2 - Cl \rightarrow CH_2 - CH_2 - CH_2 - NH_2$

(ii) $C_6H_5 - CH_2 - Cl \rightarrow C_6H_5CH_2CH_2 - NH_2$

Ans. (i) With NaCN and reduction.

i.e., $C_2H_5Cl \xrightarrow[\text{NaCN}]{\text{Ethanol}} C_2H_5-C\equiv N \xrightarrow{\text{red n}} CH_3-CH_2-CH_2-NH_2$

(ii) $C_6H_5CH_2Cl \xrightarrow[\text{NaCN}]{\text{Ethanol}} C_6H_5-C\equiv N \xrightarrow{H_2/Ni} C_6H_5CH_2CH_2-NH_2$

Q. 11. Account for :

(i) Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions. Aniline on nitration gives a substantial amount of m-nitroaniline.

(ii) Aniline does not go Friedel Crafts reaction.

Ans. (i) It is because aniline is protonated to form anilinium cation, in which $\overset{\oplus}{N}H_3$ group is meta-directing.

(ii) It is because aniline is basic, can form adduct with $AlCl_3$, electrophile cannot be generated.

Q. 12. Account for the following :

(i) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(ii) Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

Ans. (i) $-NH_2$ is ERG, electrophilic substitution takes place faster.

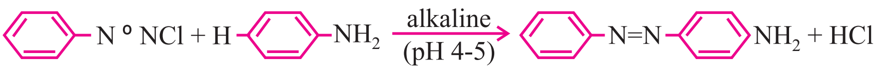
(ii) Nitro compounds are more polar than hydrocarbons therefore have more van der Waal's forces of attraction.

Q. 13. Write short notes on :

(i) Coupling reaction

(ii) Ammonolysis

Ans. (i)



(ii) Ammonolysis : $R-X+NH_3 \rightarrow R-NH_2+HX$

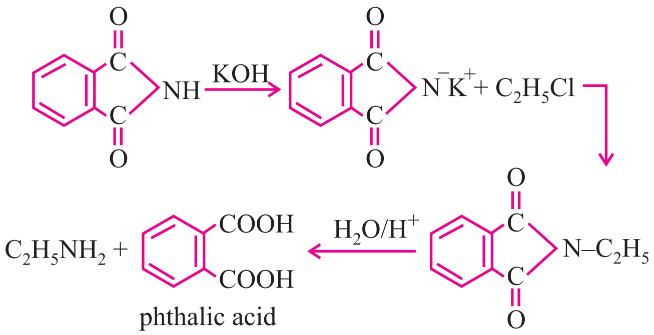
$RNH_2 + R-X \rightarrow (R)_2N + HX$

$(R)_2NH + R-X \rightarrow (R)_3N + HX$

$(R)_3N + R-X \rightarrow [R_4N]^{\oplus}X^{-}$

Q. 14. Prepare pure sample of 1° amine from 1° alkyl halide.

Ans. By Gabriel Phthalimide Reaction



ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. What happens when :

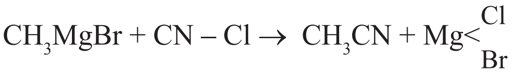
(i) An alkyl halide reacts with $AgNO_2$ and product is reduced.

(ii) An alkyl halide is treated with AgCN and product is hydrolysed.

(iii) Methyl magnesium is treated with cyanogens chloride.

Ans. (i) $R-X+AgNO_2 \xrightarrow[-AgX]{} R-NO_2 \xrightarrow[{[H]}]{Sn/HCl} R-NH_2$

(ii) $R-X+AgCN \xrightarrow[-AgX]{} RNC \xrightarrow{H_2O/H^+} RNH_2 + HCOOH$

(iii) 

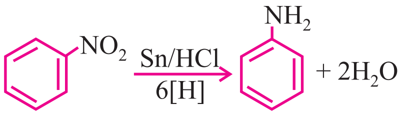
$CH_3MgBr + CN-Cl \rightarrow CH_3CN + Mg<^{Cl}_{Br}$

Q. 2. How would you prepare :

(i) $C_6H_5NH_2$ from $C_6H_5NO_2$

(ii) CH_3NH_2 from $C_2H_5NH_2$

(iii) $C_2H_5NH_2$ from CH_3NH_2

Ans. (i) 

(ii) $C_2H_5NH_2 \xrightarrow{HNO_2} C_2H_5OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{(O)} CH_3COOH \xrightarrow{NH_3}$

$CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$

(iii) $CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{KCN} CH_3CN$

$\xrightarrow{[H]} CH_3CH_2NH_2$

Q. 3. Write the structure of the products in each case :

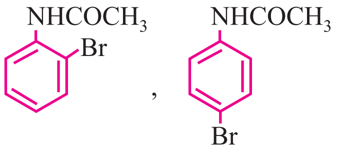
(i) $CH_3CH_2NH_2 \xrightarrow[\Delta]{(CH_3CO)_2O}$

(ii) $CH_3CONHC_6H_5 \xrightarrow{Br_2/Fe}$

(iii) $CH_3CH_2CN \xrightarrow{H_2O/H^+}$

Ans. (i) $CH_3CH_2NHCOCH_3$, CH_3COOH

(ii)



(iii) $CH_3CH_2COOH + NH_4^+$

Q. 4. Write the structures of A, B and C in following

(i) $C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} A \xrightarrow[O\text{-}5°C]{NaNO_2+HCl} B \xrightarrow{KI} C$

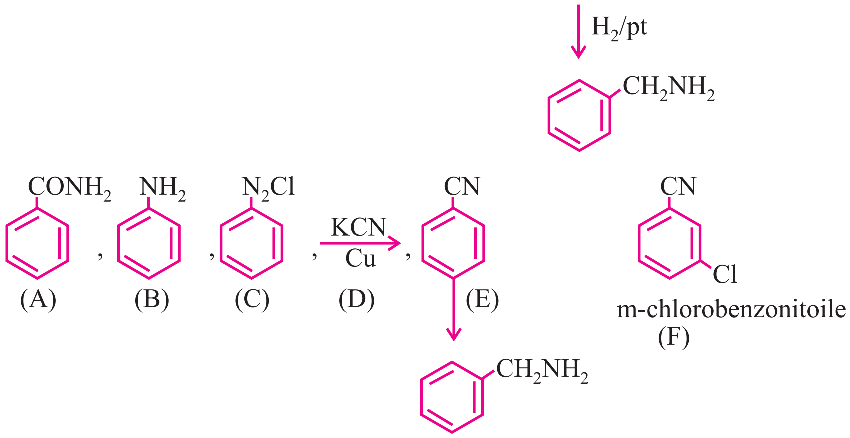
(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{CHCl_3+AlCKOH} C$

Ans. (i) $C_6H_5NH_2, C_6H_5N_2^+Cl^-, C_6H_5I$

(ii) CH_3CN, $CH_3CH_2NH_2$, CH_3CH_2NC

Q. 5. Write the structure of reagents/organic compounds 'A' to 'F' :

Ans. $A \xrightarrow[H_2O]{NaOH/Br_2} B \xrightarrow[O'C]{NaNO_2/HCl} C \xrightarrow{D} E \xrightarrow{Cl_2/Fe} F$



Benzylamine

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Arrange the following :

(i) In decreasing order of pKb values :

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength :

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(iii) In decreasing order of basic strength :

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$, CH_3NH_2

(iv) Decreasing order of basic strength in gas phase :

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) Increasing order of boiling point :

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Ans. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) (a) p-nitroaniline < aniline < p-toluidine

(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(iii) $(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$

(iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

Q. 2. How will you convert :

(i) Ethanoic acid into methanamine

(ii) Hexane nitrile into 1-aminopentane

(iii) Methanol into ethanoic acid

(iv) Ethanamine into methanamine

Ans. (i)

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\substack{\text{Hydrazoic}\\\text{acid}}}{HN_3} \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} \underset{\text{Methylamine}}{CH_3NH_2} + N_2 + CO_2$$

(ii) $$\underset{\text{Hexane nitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{partial hydrolysis}]{\text{Conc. HCl}} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{1-Aminopentane}}{CH_3(CH_2)_4NH_2}$$

(iii) $$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{SOCl_2} CH_3Cl \xrightarrow{\text{KCN (alc)}} CH_3CN \xrightarrow{H^+/H_2O} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

(iv) $$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[(NaNO_2+HCl)]{HNO_3} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3COOH \xrightarrow{NH_4OH} CH_3COONH_4$$
$$\xrightarrow{\text{heat}} CH_3CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

Q. 3. Write short note on the following :

(i) Carbylamine reaction

(ii) Diazotization

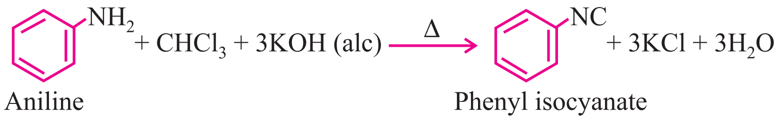
(iii) Hoffmann's bromide reaction

(iv) Coupling reaction

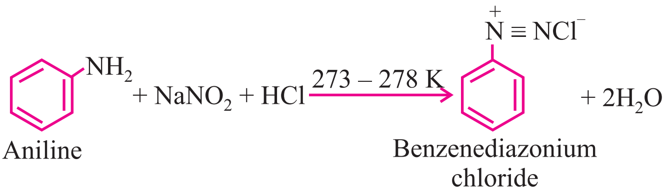
(v) Ammonolysis

Ans. (i) **Carbylamine reaction :** When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identify the presence of primary amine or chloroform.

$$RCH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} RCH_2NC + 3KCl + 3H_2O$$



(b) **Diazotization :** When primary aromatic amine is treated with $NaNO_2$ and HCl at 273-278 K, diazonium salt is obtained. This reaction is known as diazotization.



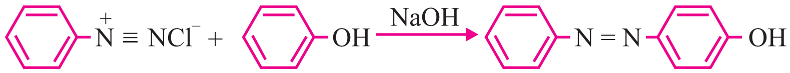
Benzenediazonium chloride is a very important synthetic compound, which can be changed into heloarenes, phenol, cyanobenzene, benzene etc.

(c) **Hoffmann's bromide reaction :** When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

This reaction is used to reduce one carbon atom from a compound.

(d) **Coupling reaction :** When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes are produced in which diazo (– N = N –) group is retained. Coupling reactions generally take place at p-position of phenol or aromatic amines.



Benzenediazonium chloride

Phenol

p-Hydroxyazobenzene (Azo dye)

(e) **Ammonolysis :** Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1º, 2º, 3º amines and quaternary ammonium salt.

$$\begin{tikzcd}
RCH_2Cl + NH_3 \arrow[r, "-HCl"'] & RCH_2NH_2 \arrow[r, "RCH_2Cl", "-HCl"'] & (RCH_2)NH \arrow[r, "-HCl"'] & (RCH_2)_3N \arrow[d, "-HCl"', "RCH_2Cl"] \\
 & & & (RCH_2)_3\overset{+}{N}\overset{-}{Cl}
\end{tikzcd}$$

Q. 4. Complete the following reactions :

(i) $C_6H_5NH_2 + H_2SO_4$ **(conc.)** $\rightarrow$

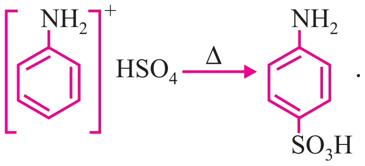
(ii) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(iii) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(iv) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(v) $C_6H_5NH_2 + CHCl_3 + 3KOH$ **(alc.)** $\rightarrow$

Ans. (i)



(ii) $C_6H_6 + N_2 + HCl + CH_3CHO$

(iii) $C_6H_5NHCOCH_3 + CH_3COOH$

(iv) $C_6H_6 + H_3PO_3 + HCl + N_2$

(v) $C_6H_5NC + 3KCl + 3H_2O$

Q. 5. Write A, B and C in the given reactions :

(i) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$

(iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{HNO_2} B \xrightarrow[2\Delta]{H_2O/H^+} C$

(iv) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

(v) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{partial hydrolysis}]{OH^-} B \xrightarrow{NaOH/Br_2} C$

Ans. (i) C_6H_5CN, C_6H_5COOH, $C_6H_5CONH_2$

(ii) CH_3CH_2CN, $CH_3CH_2NH_2$, CH_3CH_2OH

(iii) $C_6H_5NH_2$, $C_6H_5N_2Cl$, C_6H_5OH

(iv) CH_3CONH_2, CH_3NH_2, CH_3OH

(v) CH_3CH_2CN, $CH_3CH_2CONH_2$, $CH_3CH_2NH_2$

Q. 6. Accomplish the following conversions :

(i) $C_6H_5NO_2 \rightarrow C_6H_5 - COOH$

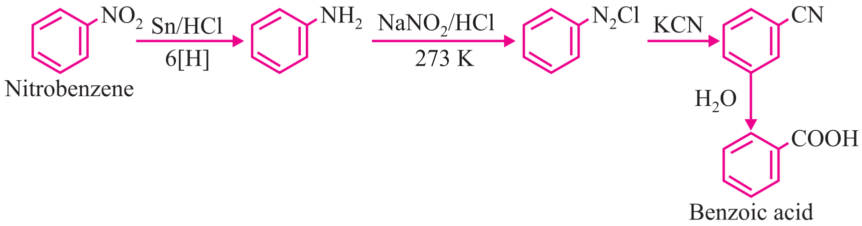
(ii) Benzene → m-bromophenol

(iii) $C_6H_5COOH \rightarrow C_6H_5NH_2$

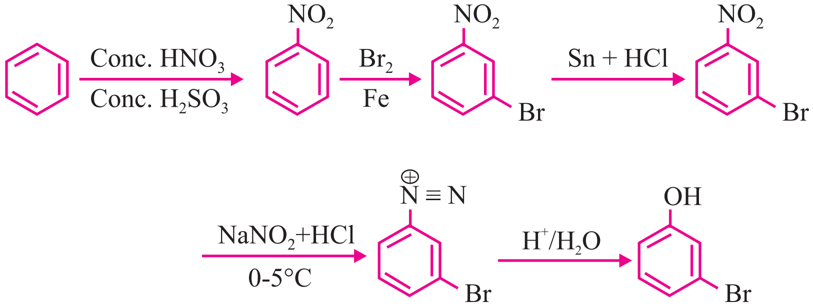
(iv) Aniline → 2, 4, 6 tribromoaniline

(v) Benzylchloride → 2-phenyl ethanamine

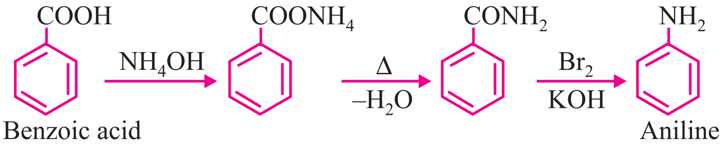
Ans. (i)



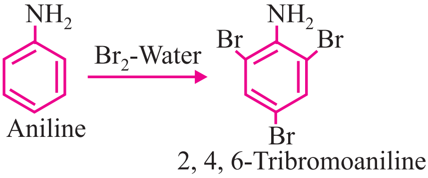
(ii)



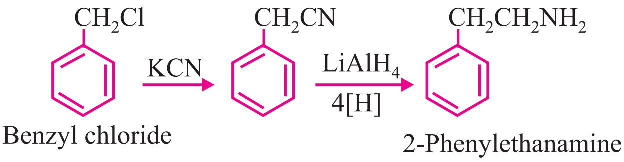
(iii)



(iv)



(v)



Q. 7. Given reasons : (i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$

(iii) Although –NH_2 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 13

BIOMOLECULES

1. **Carbohydrates :** These are optically active polyhydroxy aldehydes or ketones or the compounds which produce these on hydrolysis.

2. **Classification :**

   (i) Monosaccharides : Those carbohydrates which cannot be hydrolysed into further simpler carbohydrates. *E.g.,* glucose, fructose, galactose etc.

   (ii) Disaccharides : Those carbohydrates which produces two monosaccharides on hydrolysis. *E.g.,* sucrose, maltose and lactose.

   (iii) Oligosaccharides : Those carbohydrates which give two to ten monosaccharides on hydrolysis.

   (iv) Polysaccharides : Those carbohydrates which on hydrolysis give large number of monosaccharides hydrolysis. *E.g.,* starch, cellulose, glycogen.

3. **Sugar :** Carbohydrates which are sweet in taste.

   (i) Reducing sugars : Those which reduce Fehling's or Tollen's reagent due to availability of free aldehydic groups. *E.g.,* glucose, fructose, galactose.

   (ii) Non-reducing sugars : Those which do not reduce Fehling's or Tollen's reagent. They do not have free aldehydic group. *E.g.,* sucrose.

4. **Glucose :** It is a monosaccharide with molecular formula $C_6H_{12}O_6$.

5. **Preparation :**

   (i) From sucrose :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad \text{(only from sucrose)}$$

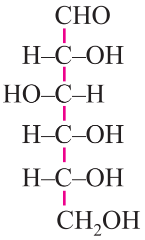
   (ii) From starch :

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

6. **Structure :**

Fischer structure :

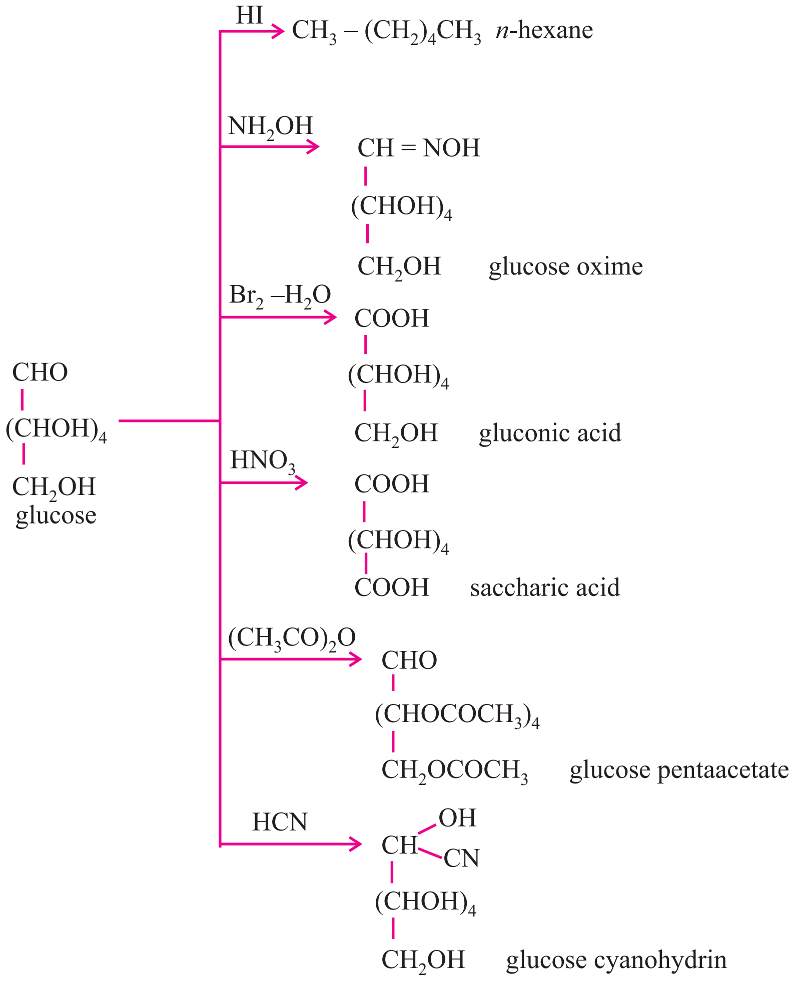
(+) glucose has 'D' configuration as shown :



D-(+)-glucose

‘D’- means – OH group on first chiral ‘C’ from the bottom is on right hand and (+) means it is dextrorotatory *i.e.,* it rotates plane polarized light towards right.

Reactions of glucose :



Objections against open chain structure of glucose

The open chain structure was unable to explain the following reactions :

(a) It does not give the 2, 4-DNP test, Schiff's test and does not form the hydrogensulphite product with $NaHSO_3$.

(b) The pentacetate of glucose does not react with NH_2OH, indicating the absence of free aldehydic group.

(c) Glucose exist in 2 different crystalline forms α and β forms. These are called anomers. They differ in optical rotation, they also differ in melting point.

After which a close chain (cyclic) structure of glucose was proposed by Haworth.

* Anomers are isomers which have a different configuration at C-1 functional group c-atom

7. **Glycosidic linkage :** The linkage between two monosaccharide units through oxygen is called the glycosidic linkage.

8. **Proteins :** These are macro molecules made up of amino acids joined by amide linkage [– (– CONH –) –] is here called as peptide linkage. These are required for growth and development of the body.

9. **Amino acids :** These contain an amino (- NH_2) and an acidic (- COOH) group and are therefore amphoteric in nature. In solution they exist in the form of zwitter ion (a dipolar ion).

10. **Classification**

Fibrous Protein	Glubular Protein
(i) Polypeptide chains run par`allel or anti-parallel and held together by hydrogen and disulphide bonds.	(i) Chains of polypeptide coil around to give a spherical shape.
(ii) Generally insoluble in water *e.g.*, keratin, collagen, myosin, fibroin.	(ii) Usually soluble in water, *e.g.*, insulin, thyroglobin, albumin, haemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.

11. **Structure and shape of protein (Ref. page no. 416 NCERT Book)**

Primary structure	Secondary structure	Tertiary structure	Quaternary structure
The specific sequence of amino acids in the polypepide chain. Change in amino acids sequence changes the protein completely. They have covalent bonds.	It is the shape in which the long polypeptide chain can exist. It is of two types : α-helix and β-pleated. These structures arise due to regular folding of the backbone of the polypeptide chain due to H-bonding between the $C = O$ and $– NH –$ groups of the peptide bond.	Represents overall folding of the polypeptide chain. It gives rise to the fibrous or globular molecular shapes. Forces stabilizing the 2° and 3° structures are hydrogen bonds, disulphide linkages, van der Waal's and electrostatic forces of attraction.	Protein can be composed of two or more polypeptide chains called sub-units. The spatial arrangement of these sub-units with respect to each other is quaternary structure of the protein.

12. **Native state of protein :** The parental state or the natural state in which the protein is found.

13. **Denaturation of protein :** Destruction of the native state of protein is denaturation. It can be brought by physical and chemical methods. The 2° and 3° structures are destroyed, only 1° structure is retained.

Enzymes : These are biocatalyst and generally globular proteins *e.g.,* invertase, zymase, phenylalanine hydroxylase, urease etc.

Main characteristics of enzymes :

(i) It speed up the biological reaction upto million times.

(ii) It is highly specific and work on lock and key theory.

(iii) It is highly sensitive to pH and temperature.

14. **Vitamins :** They are organic compounds required in the diet in small amounts to perform specific biological functions for maintenance of optimum growth and health of the organism. They are classified as follows :

(i) **Fat soluble vitamins :** Vitamin A, D, E and K. They are stored in liver and adipose tissues.

(ii) Water soluble vitamins : B group vitamins and vitamin C. They need to supplied regularly in diet as they are excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Their deficiency causes diseases. (Ref. table in page no. 418 of NCERT Book)

Biotin (Vit H) is however neither fat nor water soluble. Its deficiency leads to loss of hair.

15. **Nucleic acids :** These are biomolecules which are long chain polymers of nucleotides. They are of two types :

(i) Deoxyribonucleic acid (DNA)

(ii) Ribonucleic acid (RNA)

16.

Vitamin	**Deficiency disease**
A	Xerophthalmia, night blindness
B_1	Beri-beri
B_2	Ariboflavinosis, cheilosis, burning sensation of skin
B_{12}	Pernicious anaemia, inflammation of tongue and mouth
C	Scurvy
D	Rickets & osteomalacia
E	Increased fragility of RBC and muscular weakness
K	Increased blood clotting time
H	Loss of hair

17. Hormones are chemical substances which are produced in ductless glands in the body.

18. Nuceloside = Base + Sugar

Nucleotide = Base + Sugar + Phosphoric acid

19.

DNA	**RNA**
(i) Double helical.	(i) Single stranded.
(ii) Sugar is 2-deoxyribose.	(ii) Sugar is ribose.
(iii) Bases : A, T, G, C.	(iii) Bases : A, U, G, C.
(iv) Property of replication.	(iv) Do not replicate.
(v) It is responsible for transmission of heredity character.	(v) Helps in protein biosynthesis.

MULTIPLE CHOICE QUESTIONS

1. Which of the following statement is not true about glucose?

(a) it is an aldohexose

(b) on heating with HI it forms n-hexane

(c) it is present in furanose form

(d) it does not give 2, 4-DNP test

2. Which of the following acids is a vitamin?

(a) aspartic acid (b) ascorbic acid

(c) aoiphic acid (d) saccharic acid

3. Which of the following base is not present in RNA?

(a) adenine (b) uracil

(c) thymine (d) cytosine

4. Which of the following vitamins can be stored in our body?

(a) vitamin B_1 (b) vitamin B_2

(c) vitamin B_6 (d) vitamin B_{12}

5. Which one given below is non-reducing sugar?

(a) glucose (b) sucrose

(c) maltose (d) lactose

6. In a protein molecule amino acids are linked together by:

(a) peptide bond (b) dative bond

(c) glycosidic bond (d) phospodiestes bond

7. In DNA_1 the complementary bases are:

(a) adenine and thynine ; guanine and eytosine

(b) adenine and thymine; guanine and uracil

(c) adenine and guanine; thymine and cytosine

(d) uracil and adenine; cytosine and guanine

8. Deficiency of vitamin B_1, cause the disease:

(a) convulsions (b) beri-beri

(c) cheilosis (d) sterility

9. One strand of DNA has the sequence. ATGCTT, the sequence of complementary strand would be:

(a) TCCGAA (b) TACGTA

(c) TACGAA (d) TAGCTA

10. The correct statement regarding RNA and DNA is:

(a) The sugar component RNA is arabinose and sugar in DNA is ribose

(b) The sugar component in RNA is 2'deoxyribose and the sugar component in DNA is arabinose.

(c) The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose.

(d) The sugar component in RNA is ribose and sugar component in DNA is 2'-deoxyribose.

11. Which of the following vitamin given below is water soluble?

(a) vitamin C
(b) vitamin D
(c) vitamin K
(d) vitamin E

12. In both DNA and RNA, base and phosphate esterlinkage are at

(a) C_5' and C_2' respectively of sugar molecule

(b) C_2^1 and C_5^1 respectively of sugar molecule

(c) C_3' and C_5^1 respectively of sugar molecule

(d) C_5^1 and C_1^1 respectively of sugar molecule

13. The two functional groups present in a typical carbohydrates are:

(a) —OH and —COOH
(b) —CHO and —COOH
(c) > C═O and —OH
(d) —CHO and —COCl

14. The presence or absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA.

(a) 1st
(b) 2nd
(c) 3rd
(d) 4th

15. Which of the following is called invert sugar

(a) lactose
(b) sucrose
(c) maltose
(d) glucose

16. Carbohydrates which give two molecules of mono-saccharides are called disaccharides. These are:

(a) maltose
(b) cellulose
(c) maltase
(d) lactose

17. Starch is a mixture of:

(a) amylom
(b) amylopectin
(c) amylose
(d) β-D-glucose

18. Which of the following contain transition metal?

(a) Vitamin B-12
(b) Chlorophyl
(c) Haemoglobin
(d) RNA

19. Which of the following has glycosidic linkage?

(a) Maltose
(b) Anylose
(c) galactose
(d) sucrose

20. Fibrous proteins are present in:

(a) myosin
(b) albumin
(c) collagen
(d) fibroin

Assertion and Reasoning Type

The question given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(a) Assertion and reason both are CORRECT and reason is the CORRECT explanation of the assertion.
(b) Assertion and reason both are wrong statements.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
(e) Assertion and reason both are correct statements but reasson is not correct explanation of assertion.

21. Assertion : A solution of sucrose in water is dextro rotatory but on hydrolysis in presence of little HCl it becomes laevorotatory.

Reason : Sucrose on hydrolysis gives unequal amount of glucose and fructose as a result sign of rotation changes.

22. Assertion : Fructose does not contain aldehyde group but still reduce Tollen's reagent.

Reason : In the presence of base, fructose undergoes rearrangement to form glucose and mannose.

Matching Column Type

23. Match the carbohydrate in Column I with its characteristic given in Column II

Column-I	**Column-II**
(A) Lactose	(p) Ketohexose
(B) Starch	(q) Disaccharide
(C) Sucrose	(r) Polysaccharide
(D) Fructose	(s) on hydrolysis gives β-D-glucose and β-D-galactose

(a) A–s, B–r, C–p, D–q
(b) A–p, B–q, C–r, D–s
(c) A–r, B–s, C–p, D–q
(d) A–s, B–r, C–q, D–p

24. Match the carbohydrate in Column I with its characteristic given in Column II

Column-I	Column-II
(A) Keratin	(p) protein
(B) Haemoglobin	(q) β-pleated protein
(C) Riboflavin	(r) α-amino acid
(D) Glycine	(s) Water soluble vitamin

(a) A–p, B–q, C–s, D–r
(b) A–q, B–p, C–s, D–r
(c) A–q, B–p, C–r, D–s
(d) A–s, B–r, C–q, D–p

25. The no. of chiral carbon present in β-D-(+)-glucose is:

0	1	2	3	4	5	6	7	8	9

Answers

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

11. (a) **12.** (c) **13.** (c) **14.** (b) **15.** (b)

16. (a, d) **17.** (b, c) **18.** (a, c) **19.** (a, b, d) **20.** (a, c, d)

21. (c) **22.** (a)

23. (a)—(q, s), (b)—(r), (c)—(q), (d)—(p)

24. (a)—(p, q), (b)—(p), (c)—(s), (d)—(r)

25. 5

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Name polysaccharides which is stored in the liver of animals.

Ans. Glycogen.

Q. 2. What structural feature is required for a carbohydrate to behave as reducing sugar ?

Ans. The carbonyl group of any one monosaccharide present in carbohydrate should be free.

Q. 3. Give the significance of (+) sign in the name D-(+)-glucose.

Ans. (+) sign indicates dextro-rotatory nature of glucose.

Q. 4. Glucose is an aldose sugar but it does not react with sodium hydrogen sulphite. Give reason.

Ans. The – CHO group reacts with – OH group at C-5 to form a cyclic hemiacetal.

Q. 5. Why is sucrose called invert sugar ?

Ans. When sucrose is hydrolysed by water, the optical rotation of solution changes from positive to negative.

Q. 6. Name the amino acid which is not optically active.

Ans. Glycine.

Q. 7. Give reason :

Amylase present in the saliva becomes inactive in the stomach.

Ans. HCl present in stomach decreases the pH.

Q. 8. Which forces are responsible for the stability of α-helical structure of proteins ?

Ans. Hydrogen bonding.

Q. 9. Which nucleic acid is responsible for carrying out protein synthesis in the cell ?

Ans. RNA (Ribonucleic acid)

Q. 10. When RNA is hydrolysed, there is no relationship among quantities of different bases obtained. What does this fact suggest about structures of RNA ?

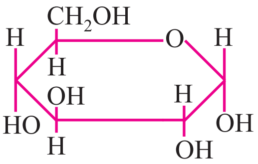
Ans. RNA is single stranded.

Q. 11. What type of linkage holds together the monomers of DNA and RNA ?

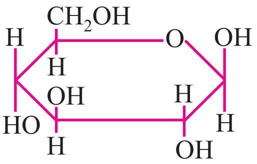
Ans. Phosphodiester linkage.

Q. 12. Give the Howarth projection of D-glucopyranose.

Ans.



α-D(+) Glucopyranose



β-D(+) Glucopyranose

Q. 13. Name the vitamin responsible for coagulation of blood.

Ans. Vitamin K.

Q. 14. Where does the water present in the egg go after boiling the egg ?

Ans. On boiling, during denaturation process water gets absorbed in denaturated proteins.

Q. 15. What is native state of protein ?

Ans. The energetically most stable shape of the protein at normal pH and temperature is called native state.

Q. 16. Why is cellulose not digested in human body ?

Ans. It is due to the fact that human beings do not have enzyme to digest cellulose.

Q. 17. Name the enzyme that is used to dissolve blood clots ?

Ans. Streptokinase.

Q. 18. Name two diseases caused due to deficiency of enzymes.

Ans. Albinism and phenyl keto urea.

Q. 19. Give one example of : (a) water soluble, (b) fat soluble vitamins.

Ans. (a) Vitamin C (b) Vitamin D

Q. 20. Name a protein which is insoluble in water.

Ans. Keratin.

Q. 21. Name the deficiency disease resulting from lack of Vitamin 'A' in the diet.

Ans. Night blindness, Xerophthalmia.

Q. 22. Mention two important functions of carbohydrates in plants.

Ans. Major energy source, storage molecules like starch in plants.

Q. 23. Name two of the different types of RNA molecules found in cells of organisms.

Ans. tRNA, mRNA, rRNA.

Q. 24. The deficiency of which vitamin causes the disease pernicious anaemia ?

Ans. Vitamin B_{12}.

Q. 25. Why are carbohydrates generally optically active ?

Ans. Because they contain one or more chiral atom.

Q. 26. During curdling of milk, what happens to sugar present in it ?

Ans. Lactose changes to lactic acid.

Q. 27. What are the products of hydrolysis of lactose ?

Ans. β-D-galactose and β-D-glucose.

Q. 28. The two strands in DNA are not identical but complementary. Explain.

Ans. Base pairing rule is followed; A = T and G ≡ C.

Q. 29. If one strand of DNA has the sequence 5'-G-G-A-C-T-A-C-T-3', what is the sequence of bases in the complementary strand ?

Ans. 3'-C-C-T-G-A-T-G-A-5'

Q. 30. What are monosaccharides ?

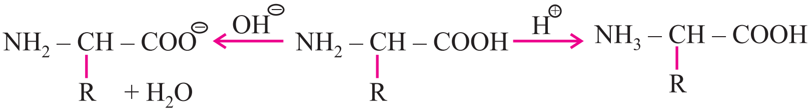
Ans. Sugars which cannot be hydrolysed to give simpler units or compounds.

Q. 31. What is the difference between native protein and denatured protein ?

Ans. Proteins found in a biological system with unique 3D-structure and biological activity is called native protein. When native protein is subjected to physical and chemical change, protein loses its biological activity and is called denatured protein.

Q. 32. Amino acids are amphoteric in nature. Explain.

Ans. It can react with acid and base both as per the following reaction :



$$NH_2-\underset{\underset{\textstyle R}{|}}{CH}-COO^{\ominus} + H_2O \xleftarrow{OH^{\ominus}} NH_2-\underset{\underset{\textstyle R}{|}}{CH}-COOH \xrightarrow{H^{\oplus}} NH_3-\underset{\underset{\textstyle R}{|}}{CH}-COOH$$

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Define the following terms in relation to proteins :

(i) Peptide linkage **(ii) Denaturation**

Ans. (i) Peptide linkage : A link between two amino acids with loss of water – CO – NH – peptide linkage.

(ii) A process that changes the three dimensional structure of native protein is called denaturation of protein. It results into breaking of hydrogen bonds and disulphide linkages. Thus, a completely denatured protein has a shape of random coil.

Q. 2. List the reactions of glucose which cannot be explained by its open chain structure.

Ans. (i) Despite having the aldehyde group, glucose does not give 2, 4 DNP test or Schiff's test.

(ii) It does not form hydrogensulphite addition product with $NaHSO_3$.

(iii) The penta acetate of glucose does not react with hydroxylamine indicating the absence of free – CHO group.

Q. 3. Explain what is meant by :

(i) Biocatalyst

Ans. (i) Biocatalysts are the catalysts which increases the rate of metabolism/ biochemical reactions.

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) Glycosidic linkage

Ans. (i) The linkage between the monosaccharide units through oxygen is called glycosidic linkage.

Q. 6. Name the product of hydrolysis of sucrose. Why is sucrose not a reducing sugar ?

Ans. On hydrolysis, sucrose gives equimolar mixture of D-(+)-glucose and D-(–)-fructose. Sucrose is not a reducing sugar as glucose and fructose are linked through their reducing centres in structure of sucrose.

Q. 7. State clearly what are known as nucleotides and nucleosides.

Ans. A nucleoside contain only two basic components of nucleic acids *i.e.,* pentose sugar and nitrogenous base.

A nucleotide contains all the three basic components of nucleic acids *i.e.,* a phosphoric acid group, pentose sugar and nitrogenous base.

Q. 8. Describe what do you understand by primary structure and secondary structure of proteins.

Ans. Primary structure of proteins : The protein in which amino acids linked with each other in a specific sequence is said to be the primary structure of that protein.

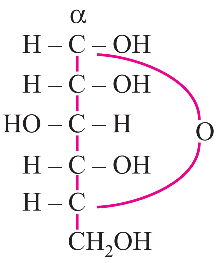
Secondary structure of proteins : It refers to the shape in which a long polypeptide chain can exist *i.e.,* α-helix and β-pleated structure.

Q. 9. What is essentially the difference between α-form of glucose and β-form of glucose ? Explain.

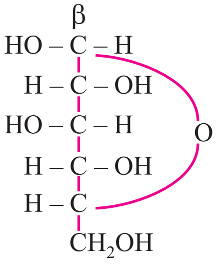
Ans. α-form of glucose and β-form of glucose differ only in the configuration of the hydroxyl group at C_1 in cyclic structure of glucose/hemiacetal form of glucose.

Q. 10. What are anomers ? Give the structures of two anomers of glucose.

Ans. Monosaccharides which differs in configuration at functional *gp-c*-atom (C_1 and C_2), *e.g.,* α-glucose and β-glucose.



α-Glucose



β-Glucose

Q. 11. Write the hydrolysed product of :

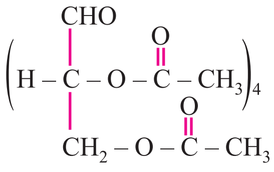
(i) Maltose **(ii) Cellulose**

Ans. (i) α-D-glucose (ii) β-D-glucose

Q. 12. (i) Acetylation of glucose with acetic anhydride gives glucose penta-acetate. Write the structure of penta acetate.

(ii) Explain why glucose penta acetate does not react with hydroxylamine ?

Ans. (i)



$$\begin{array}{l} \qquad\mathrm{CHO} \\ \left(\mathrm{H-\overset{|}{\underset{|}{C}}-O-\overset{\overset{O}{\|}}{C}-CH_3}\right)_4 \\ \qquad\mathrm{CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3} \end{array}$$

Glucose pentaacetate

(ii) The molecule of glucose penta acetate has a cyclic structure in which – CHO is involved in ring formation.

Q. 14. What are vitamins ? How are they classified ?

Ans. Vitamins are a group of biomolecules (other than carbohydrates, fats and proteins) most of which cannot be produced by body but must be supplied in small amount to perform specific biological functions of the body.

Types :

(i) Water soluble vitamins : Vitamin B and C.

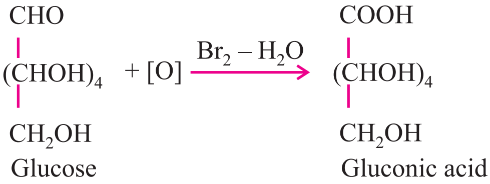
(ii) Fat soluble vitamins : Vitamin A, D, E and K.

Q. 14. Write the products of oxidation of glucose with :

(i) Bromine water

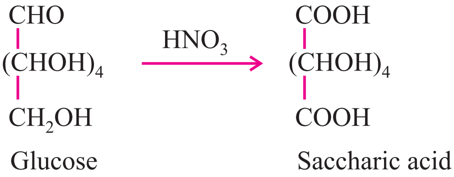
(ii) Nitric acid

Ans. (i)



$$\underset{\text{Glucose}}{\begin{array}{c}\text{CHO}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\end{array}} + [\text{O}] \xrightarrow{Br_2 - H_2O} \underset{\text{Gluconic acid}}{\begin{array}{c}\text{COOH}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\end{array}}$$

(ii)



$$\underset{\text{Glucose}}{\begin{array}{c}\text{CHO}\\ |\\ (\text{CHOH})_4\\ |\\ \text{CH}_2\text{OH}\end{array}} \xrightarrow{HNO_3} \underset{\text{Saccharic acid}}{\begin{array}{c}\text{COOH}\\ |\\ (\text{CHOH})_4\\ |\\ \text{COOH}\end{array}}$$

Q. 15. 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. 16. (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. 17. 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. 18. 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.

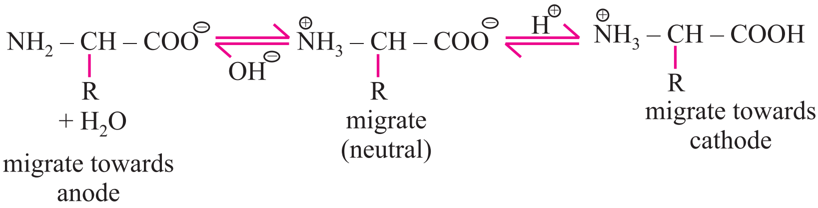
Non-essential amino acids are those which are produced by our body, *e.g.,* glycine, alanine.

Q. 19. 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 *p*K*a* values.

Ans. (i)



$$\underset{\substack{|\\ \text{R}\\ +\,\text{H}_2\text{O}}}{\text{NH}_2-\text{CH}-\text{COO}^{\ominus}} \underset{\text{OH}^{\ominus}}{\rightleftharpoons} \underset{\substack{|\\ \text{R}}}{\overset{\oplus}{\text{N}}\text{H}_3-\text{CH}-\text{COO}^{\ominus}} \overset{\text{H}^{\oplus}}{\rightleftharpoons} \underset{\substack{|\\ \text{R}}}{\overset{\oplus}{\text{N}}\text{H}_3-\text{CH}-\text{COOH}}$$

(ii) Due to zwitter ion formation.

Q. 20. Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.

Ans. Protein albumin present in egg white gets denatured *i.e.,* 2° & 3° structures are destroyed and 1° structure is retained.

Q. 21. 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.

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. 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. 3. (i) Name the four bases present in DNA.

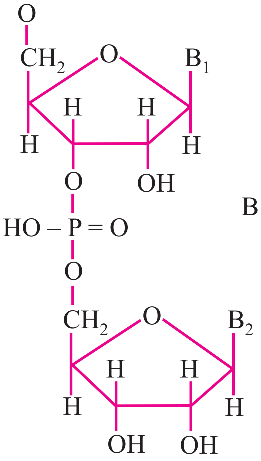
(ii) Which of them is not present in RNA ?

(iii) Give the structure of a nucleotide of DNA.

Ans. (i) Adenine, Guanine, Thymine, Cytosine.

(ii) Thymine.

(iii)



B_1 & B_2 = Nitrogeneous bone (Adenine, guanine, Cytosine or thymine)

Q. 4. 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. 5.(i) Fructose contains a keto group but still it reduces Tollen's reagent. Explain.

(ii) Give the chemical name and sources of :

(a) Vitamin C **(b) Vitamin B_1**

UNIT 14

Polymers

1. **Polymer :** It is a very large molecule having molecular mass 10^3-10^7 g mol^{-1}. They are formed by joining together repeating structural units, called monomers.

2. **Classification of Polymers :**

   (a) Based on Source :

   - (i) **Natural :** Found in plants and animals, e.g., Proteins, cellulose, natural rubber, silk, wool.
   - (ii) **Synthetic :** Man-made, e.g., Nylon, polyster, neoprene, bakelite, teflon, PVC, polystyrene.
   - (iii) **Semisynthetic :** Natural but modified by man e.g. cellulose nitrate.

   (b) Based on Structure :

   - (i) **Linear polymers :** This consist of long and straight chain repeating units, e.g., Polythene (HDPE), PVC, nylon, polyester.
   - (ii) **Branched polymers :** This contain linear chains having some branches, e.g., amylopectin, glycogen etc.
   - (iii) **Cross-linked polymers :** Strong covalent bonds are present between various linear polymer chains, e.g., Bakelite, urea-formaldehyde polymer, melamine, formaldehyde polymer etc.

   (c) Based on mode of polymerization :

   - (i) **Addition polymers :** These are formed by the repeated addition of monomer molecules possessing multiple bonds, e.g., polythene, polypropene, polystyrene, PMMA (polymethyl metha crylate).
   - (ii) **Condensation polymers :** These are formed by the repeated condensation reaction of different bifunctional or trifunctional monomers with the elimination of small molecules like water, HCl, NH_3, alcohol, etc., e.g., Bakelite, nylon, polyster, urea-formaldehyde resin.

   (d) Based on molecular forces :

   - (i) **Elastomers :** Forces of interaction between polymer chains is weakest, e.g., natural rubber, neoprene, vulcanized rubber.

(ii) **Fibers :** Strong hydrogen bonds are present between the polymer chains. They have high tensie strength, e.g., Nylon, polyster, silk, wool, orlon, rayon etc.

(iii) **Thermoplastics :** They are linear/slightly branched chains molecules capable of repeated softening on heating and hardening on cooling, e.g., Polythene, PVC, polystyrene, polypropene.

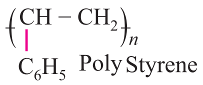
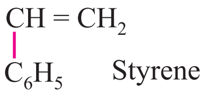
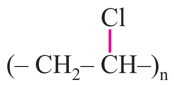
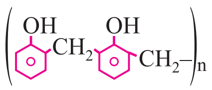
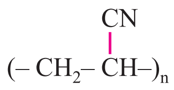
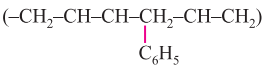
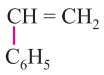
(iv) **Thermosetting plastics :** They are cross-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g., Bakelite, urea-formaldehyde resin.

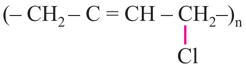
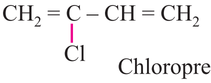
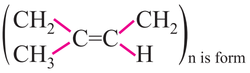
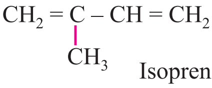
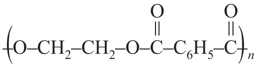
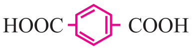
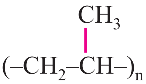
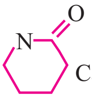
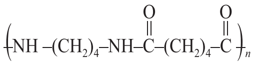
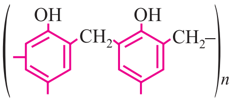
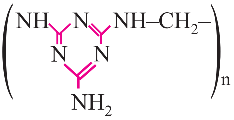
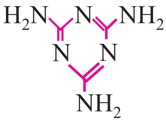
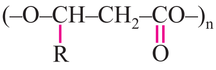
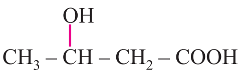
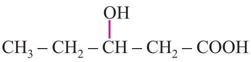
(e) **Based on growth of polymerization :** Depending upon the mechanism of polymerization, polymers are classified as :

(i) **Addition polymers or Chain growth polymers :** They follow mostly free radical mechanism.

(ii) **Condensation polymers or Step growth polymers :** Because they are formed in gradual steps.

Polymers and Their Monomers

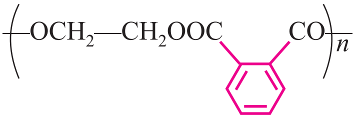
S. No.	Name of Polymer	Structure	Monomer	Uses
1.	Polythene	$(-CH_2-CH_2-)_n$	$CH_2=CH_2$	As insulator, anticorrosive, packing material, household and laboratory wares.
2.	Polystyrene	 $\left(\underset{C_6H_5}{CH}-CH_2\right)_n$ Poly Styrene	 $\underset{C_6H_5}{CH}=CH_2$ Styrene	As insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinylchloride (PVC)	 $(-CH_2-\overset{Cl}{CH}-)_n$	$CH_2=CHCl$ Vinyl chloride	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or Teflon	$(-CF_2-CF_2-)_n$	$CF_2=CF_2$ TFE	As lubricant, insulator and making cooking wares.
5.	NOVOLAC		(a) HCHO (b) C_6H_5OH	In making bonding give varnishes, lacquers etc.
6.	Polyacrylonitrile (Orion) (Acrilian)	 $(-CH_2-\overset{CN}{CH}-)_n$	$CH_2=CHCN$ Acrylonitrile	In making synthetic fibres and synthetic wool.
7.	Styrene butadiene rubber (SBR or Buna-S)	 $(-CH_2-CH-CH-CH_2-\underset{C_6H_5}{CH}-CH_2)$	(a) $CH_2=CH-CH=CH_2$ (b)  $\underset{C_6H_5}{CH}=CH_2$	In making automobile tyres and footwear.

8.	Nitrile rubber (Buna-N)	 $(-CH_2-CH-CH-\underset{\substack{|\\ CN}}{CH_2}-CH-CH_2)$	(a) $CH_2 = CH - CH = CH_2$ (b)  $\underset{\substack{|\\ CN}}{CH} = CH_2$	In making oil seals, manufacture of hoses and tank linings.
9.	Neoprene	 $(-CH_2-C=CH-\underset{\substack{|\\ Cl}}{CH_2}-)_n$	 $CH_2 = \underset{\substack{|\\ Cl}}{C} - CH = CH_2$ Chloroprene	As insulator, making conveyor belts and printing rollers.
10.	Natural rubber (NR)		 $CH_2 = \underset{\substack{|\\ CH_3}}{C} - CH = CH_2$ Isoprene	In making erasers, tyres, tubes, valcanised rubber etc.
11.	Terylene (Dacron)	 $\left(O-CH_2-CH_2-O-\overset{\substack{O\\ \|}}{C}-C_6H_5-\overset{\substack{O\\ \|}}{C}\right)_n$	(a)  (b) $HO - CH_2 - CH_2 - OH$	For making fibres, safety belts, tyre cords, tents etc.
12	Polypropene = P Propene	 $(-CH_2-\overset{\substack{CH_3\\ |}}{CH}-)_n$	Propen $CH_3 - CH = CH_2$	Ropes, toys, pipes, fibre etc. strings.
13.	Glyptal		 $HO - CH_2 = CH_2 - OH$	As binding material in preparation of mixed plastics and plants.
14.	Nylon 6	 $(NH - [CH_2]_5 - \overset{\substack{O\\ \|}}{C} -)_n$	 Capralactum	In making fibres, plastics, tyre cords and ropes.
15.	Nylon 66	 $\left(NH-(CH_2)_4-NH-\overset{\substack{O\\ \|}}{C}-(CH_2)_4-\overset{\substack{O\\ \|}}{C}\right)_n$	(a) $HOOC - (CH_2)_4 - COOH$ (b) $H_2N - (CH_2)_6 - NH_2$	In making brushes, synthetic fibres, parachutes, ropes and carpets.
16.	Bakellite		(a) HCHO (b) C_6H_5OH	For making gears, protective coating and electrical fittings.
17.	Urea formaldehyde resin	$(- NH - CO - NH - CH_2 -)_n$	(a) HCHO (b) NH_2CONH_2	For making unbreakable cups and laminated sheets.
18.	Melamine formaldehyde resin		(a)  (b) HCHO	In making plastic crockery, unbreakable cups and plates.
19.	Poly-β-hydroxy butyrate-co-β-hydroxy valerate [PHBV]	 $(-O-\underset{\substack{|\\ R}}{CH}-CH_2-\underset{\substack{\|\\ O}}{CO}-)_n$ $R = CH_3C_2H_5$	 $CH_3 - \overset{\substack{OH\\ |}}{CH} - CH_2 - COOH$  $CH_3 - CH_2 - \overset{\substack{OH\\ |}}{CH} - CH_2 - COOH$	As packaging, orthopaedic devices and in controlled drug release.

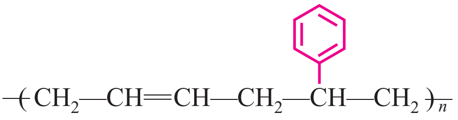
MULTIPLE CHOICE QUESTIONS

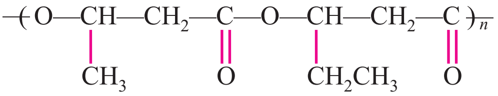
1. **An example of biopolymer is :**
   - (a) Tefflon
   - (b) Rubber
   - (c) Nylon-66
   - (d) DNA
2. **Which of the following polymer do not involve cross linkage?**
   - (a) Melamine
   - (b) Bakelite
   - (c) Polythene
   - (d) Vulcanised rubber
3. **Polymer obtained by condensation polymerisation is:**
   - (a) Polythene
   - (b) Tefflon
   - (c) Phenol-formaldehyde
   - (d) Nitrite rubber
4. **Which is an example of thermosetting plastic?**
   - (a) Polythene
   - (b) PVC
   - (c) Neophene
   - (d) Bakelite
5. **Natural rubber is a polymer of:**
   - (a) Butadine
   - (b) Ethyne
   - (c) Styrene
   - (d) Poly isophene
6. **Terylene is a condensation product of ethylene glycol and**
   - (a) Benzoic acid
   - (b) Pnthalic acid
   - (c) Salicyclic acid
   - (d) Terephthalic acid
7. **The process involving heating of natural rubber with sulphur is known as:**
   - (a) vulcanisation
   - (b) galvanisation
   - (c) sulphonation
   - (d) Bessemerisation
8. **The interparticle forces present in Nylon-66 are:**
   - (a) Vauder wall's forces
   - (b) Hydrogen bonding
   - (c) Dipole dipole interactions
   - (d) None of these
9. **Which of the following polymers of glucose is stored by animals?**
   - (a) Cellulose
   - (b) Anylose
   - (c) Amylopectin
   - (d) G-lycogen
10. **The commercial name of polyacrylonitrite is ....**
    - (a) Dacron
    - (b) Orlon (acrilaw)
    - (c) PVC
    - (d) Bakelite

11. In which of the following polymers ethylene glycol is one of the monomer units?

(a) 

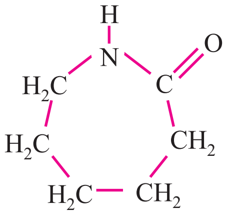
(b) $-\!(CH_2-CH_2)_n-$

(c) 

(d) 

$$-\!(O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}})_n-$$

12. Which of the following polymer can be formed by using the following monomer unit?



(a) Nylon 6, 6
(b) Nylon 2-nylon6
(c) Melamine polymer
(d) Nylon-6

13. Which of the following all characteristics of thermosetting polymers?

(a) Heavily branched cross linked polymers
(b) I inrar slightly branched long chain molecule
(c) Become infusible on moulding so cannot be reused.
(d) Soften on heating and harden on cooling, can be reused.

14. Which of the following monomers form biodegradable polymers?

(a) 3-hydroxybutanoic acid + 3 – hydroxypentanoic acid
(b) G-lycins + amino caproic acid
(c) Ethylene glycol + phthalic acid
(d) Capulactum

15. Which of the following polymers can have strog intermolecular forces.

(a) Nylon
(b) Polystyrene
(c) Rubber
(d) Polyesters

Matching Column Type

16. Match the polymers given in Column-I with their commercial names given in column-II.

(i) polyster of glycol and phthalic acid
(ii) Copolymer of 1, 3-butadine
(iii) Phenol and formaldehyde
(iv) Polyester of glycol and brepthalic acid
(v) Copolymer of 1, 3-butadiene and acrylonitrite

(a) Novolac
(b) G-lyptal
(c) Buna-S
(d) Bura-N
(e) Dacron

17. Match the polymers given in column-I with the type of linkage present in them given in column-II.

(i) Terylene
(ii) Nylon
(iii) Cellulose
(iv) Protein
(v) RNA

(a) Glycosidic linkage
(b) Ester linkage
(c) Phosphodiester linkage
(d) Amide linkage

Assertion and Reason Type

Note : *In the following questions a statement of assertion followed by a statement of reason in given. Choose the correct answer out of the following choices.*

(a) Assertion and reason both are correct statement but reason does not explain assertion.
(b) Assertion and reason both are correct statements and reason explains the assertion.
(c) Both assertion and reason are wrong statement.
(d) Assertion is correct statement and reason is wrong statement.
(e) Assertion is wrong statement and reason is correct statement.

18. Assertion : Polymerides are bust used as fiber because of high tensile strength.

Reason : Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close tracking of chains and increase the crystalline character, hence, provide high tensile strength to polymers.

19. Assertion : Network polymers are thermosetting.

Reason : Network polymer have high molecular mass.

Integer Type Question

20. The number of thermoplastic polymers among tefflon, polythene, PVC, polystyrene, bakelite, nylon 6, Melamine formaldehyde, PMMA, are:

0	1	2	3	4	5	6	7	8	9

ANSWERS

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

11. (a) **12.** (d) **13.** (a, c) **14.** (a, b) **15.** (a, d)

16. (i)—(b), (ii)—(c), (iii)—(a), (iv)—(d)

17. (i)—(b), (ii)—(d), (iii)—(a), (iv)—(d), iv)—(c)

18. (b) **19.** (a) **18.** 6

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.

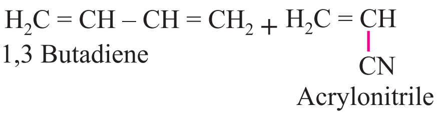
Ans. Natural rubber or Buna-S or Buna-N or Neoprene.

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.



$$\underset{\text{1,3 Butadiene}}{H_2C = CH - CH = CH_2} + \underset{\text{Acrylonitrile}}{H_2C = \underset{\displaystyle CN}{\underset{|}{CH}}}$$

Q. 5. Is $\left[H_2C\,CH(C_6H_5) \right]_n$ a homopolymer or copolymer ? Why ?

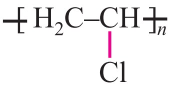
Ans. Homopolymer, because it is formed by polymerization of one kind of monomer species.

Q. 6. Write the structure and one use of urea formaldehyde resin.

Ans. $\left[HNCONHCH_2 \right]_n$

It is used in unbreakable crockery.

Q. 7. Is



$$\left[H_2C - \underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n$$

a homopolymer or a copolymer ?

Ans. Homopolymer.

Q. 8. Which of the following is natural polymer ?

Buna-S, Proteins, PVC

Ans. Proteins.

Q. 9. Based on molecular forces what type of polymer is neoprene ?

Ans. Elastomer.

Q. 10. Which of the following is a fibre ?

Nylon, Neoprene, PVC

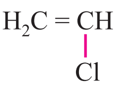
Ans. Nylon

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Draw the structure of monomers of each of the polymers :

(i) PVC **(ii) Nylon-6**

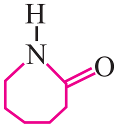
Ans. (i)



$H_2C=\underset{\underset{Cl}{|}}{CH}$

Vinyl chloride

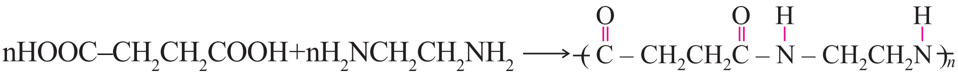
(ii)



Caprolactum

Q. 2. What is the repeating unit in the condensation polymer obtained by combining $HOOCCH_2CH_2COOH$ (succinic acid) and $H_2NCH_2CH_2NH_2$ (ethylene diamine) ?

Ans.



$$nHOOC\text{–}CH_2CH_2COOH+nH_2NCH_2CH_2NH_2 \longrightarrow \left(\overset{\overset{O}{\|}}{C} - CH_2CH_2\overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - CH_2CH_2\overset{\overset{H}{|}}{N} \right)_n$$

Q. 3. Draw the structure of monomers of the following polymers :

(i) Teflon **(ii) Polythene**

Ans. (i) $F_2C=CF_2$ Tetrafluoroethene

(ii) $H_2C=CH_2$ Ethene

Q. 4. Name the two groups into which polymers are classified on the basis of magnitude of intermolecular forces.

Ans. (i) Elastomers

(ii) Fibres

(iii) Thermoplastic polymers

(iv) Thermosetting polymers

Q. 5. Mention two important uses of each of the following :

(i) Bakelite **(ii) Nylon-6**

Ans. (i) Bakelite : For making combs, electrical switches, handles of utensils, computer disc etc.

(ii) Nylon-6 : For making tyre cords, fabrics, ropes etc.

Q. 6. Distinguish between homopolymers and copolymers with an example of each.

Ans. Homopolymers : Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers. For example, Polythene.

Copolymers : Polymers whose repeating structural units are derived from two or more types of monomer units are called copolymers. For example, Nylon-6, 6.

Q. 7. What is step growth polymerisation ? Explain with an example.

Ans. Step growth polymerisation involves condensation between monomers having multifunctional groups. It is also known as condensation polymerisation. E.g.,

$$nHOOC–(CH_2)_4–COOH + nH_2N–(CH_2)_6NH_2$$

$$\longrightarrow \left(\overset{O}{\overset{\|}{C}} - (CH_2)_4\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6\overset{H}{\overset{|}{N}}\right)_n + (2n–1)H_2O$$

Nylon 6, 6

Q. 8. What is the difference between elastomers and fibres ? Give one example of each.

Ans. Elastomers : Polymers in which the intermolecular forces of attraction between the polymer chains are weakest are called elastomers. E.g., Natural rubber.

Fibres : Polymers in which intermolecular forces of attraction are the strongest are called fibres. E.g., Nylon-6, 6.

Q. 9. Mention the important uses of each :

(i) Nylon-6, 6 **(ii) PVC**

Ans. (i) Uses of Nylon-6, 6 :

(a) It is used in making carpets, textile fibres etc.

(b) It is used for making elastic hosiery.

(ii) Uses of PVC :

(a) It is used for making raincoats, hand bags etc.

(b) It is used in making water pipes.

Q. 10. Arrange the following polymers in the order of increasing intermolecular forces :

(i) Nylon-6, Buna-S, Polythene

(ii) Nylon-6, Neoprene, Polyvinyl chloride

Ans. (i) Buna-S < Polythene < Nylon-6

(ii) Neoprene < Polyvinyl chloride < Nylon-6

Q. 11. Define thermoplastic and thermosetting polymers. Give one example of each.

Ans. Thermoplastics : Polymers in which the intermolecular forces of attraction are in between those of elastomers and fibres are called thermoplastics. E.g., Nylon-6, PVC, etc.

Thermosetting polymers : These are semi-fluid substances with low molecular masses which when heated in a mould undergo a permanent change in chemical composition to give hard, infusible and insoluble mass. E.g., Bakelite.

Q. 12. What is biodegradable polymer ? Give an example of a biodegradable polymer.

Ans. Biodegradable polymers are those which are decomposed by micro organisms. E.g., PHBV (Poly-B-hydroxybutyrate – Co – B – hydroxyl valerate).

Q. 13. How does vulcanization change the character of natural rubber ?

Ans. It introduce sulphur bridge or cross-link between polymer chain.

Q. 14. Name a polymer each for the following applications :

(i) Insulation of electrical switches

(ii) Making laminated sheets

Ans. (i) Bakelite (ii) Urea formaldehyde resin

Q. 15. How does the presence of double bonds in rubber influence their structure and reactivity ?

Ans. Natural rubber is a cis-polyisoprene. These cis- double bonds do not allow to polymer unit to come close for effective interaction. Hence rubber show elasticity.

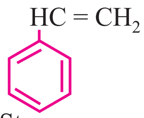
SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Write the names and structure of the monomers of the following polymers :

(i) Buna-S **(ii) Neoprene** **(iii) Nylon-6**

Ans. (i) Buna-S :

$H_2C = CH - CH - CH_2$ and



1, 3-Butadiene

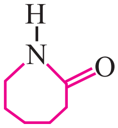
Styrene

(ii) Neoprene :

$$H_2C = \overset{\overset{\text{Cl}}{|}}{C} - CH = CH_2$$

Chloroprene

(iii) Nylon-6 :



Caprolactum

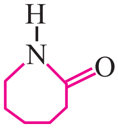
Q. 2. Write names and structure of monomers of following polymers :

(i) Bakelite **(ii) Nylon-6** **(iii) Polythene**

Ans. (i) Phenol and formaldehyde

$C_6H_5OH + HCHO$

(ii) Caprolactum



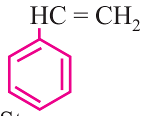
(iii) Ethene

$H_2C = CH_2$

Q. 3. Write names and structure of monomers of following polymers :

(i) Polystyrene **(ii) Dacron** **(iii) Teflon**

Ans. (i) Styrene



Styrene

(ii) Ethylene glycol + Terephthalic acid

(iii) Tetrafluoroethene

$F_2C = CF_2$

Q. 4. (i) What is the role of t-butyl peroxide in the polymerisation of ethane ?

(ii) Identify the monomers in the following polymer :

$$+ \mathbf{HN(CH_2)_6NHCO(CH_2)_4CO} +$$

(iii) Arrange the following polymers in the increasing order of their intermolecular forces :

Polystyrene, Terylene, Buna-S

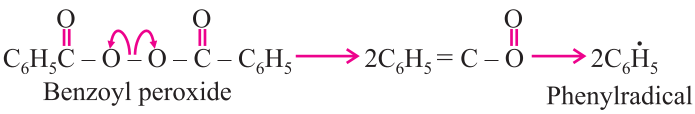
Ans. (i) Catalyst/initiator of free radical

(ii) Hexamethylenediamine and adipic acid

(iii) Buna-S < Polystyrene < Terylene

Q. 5. Write the mechanism of free radical polymerisation of ethane.

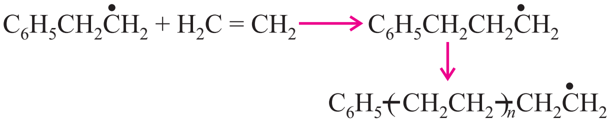
Ans. (i) Chain initiation step



$$C_6H_5\overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - C_6H_5 \longrightarrow 2C_6H_5 = C - \overset{O}{\overset{\|}{O}} \longrightarrow 2C_6\dot{H}_5$$

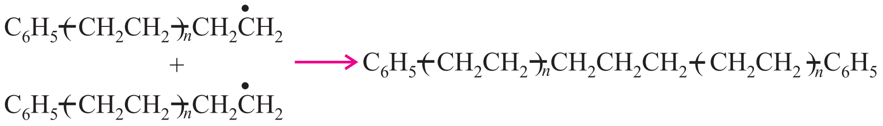
$C_6\dot{H}_5 + H_2C = C_2 \rightarrow C_6H_5CH_2\dot{C}H_2$

(ii) Chain propagating step



$$C_6H_5CH_2\dot{C}H_2 + H_2C = CH_2 \longrightarrow C_6H_5CH_2CH_2\dot{C}H_2 \downarrow C_6H_5 + CH_2CH_2 +_n CH_2\dot{C}H_2$$

(iii) Chain terminating step

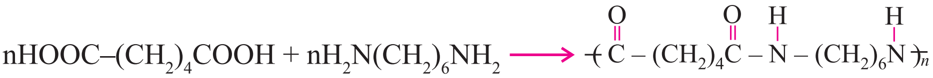


$$C_6H_5\left(CH_2CH_2\right)_nCH_2\dot{C}H_2 + C_6H_5\left(CH_2CH_2\right)_nCH_2\dot{C}H_2 \longrightarrow C_6H_5\left(CH_2CH_2\right)_nCH_2CH_2CH_2\left(CH_2CH_2\right)_nC_6H_5$$

Q. 6. Write chemical equation for the synthesis of :

(i) Nylon-6, 6 (ii) Neoprene (iii) Terylene

Ans. (i) Nylon-6, 6 :



$$nHOOC\text{–}(CH_2)_4COOH + nH_2N(CH_2)_6NH_2 \longrightarrow \left(\overset{O}{\overset{\|}{C}} - (CH_2)_4\overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6\overset{H}{\overset{|}{N}} \right)_n$$

Nylon 6, 6

Adipic acid Hexamethylene diamine

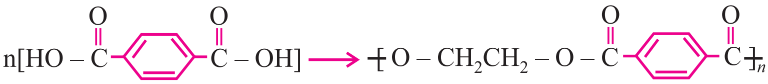
(ii) Neoprene :

$$H_2C = \overset{Cl}{\overset{|}{C}} - CH = CH_2 \longrightarrow \left(H_2C - \overset{Cl}{\overset{|}{C}} = CHCH_2 \right)_n$$

Chloroprene Neoprene

(iii) Terylene :

$nHO\text{–}CH_2CH_2OH$ +
Ethylene glycol



Terephthlic acid Tereylene

Q. 7. Write the monomers which are used for the synthesis of following polymers :

(i) Terylene (ii) Polythene (iii) Bakelite

Indicate the type of polymerisation for each which forms polymers.

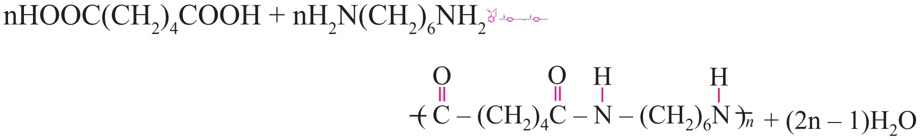
Ans.	Monomers	Type of polymerisation
(i)	Ethylene glycol + Terephthalic acid	Condensation
(ii)	Ethene	Addition
(iii)	Phenol + Formaldehyde	Condensation

Q. 8. How are polymers classified on the basis of mode of polymerisation ? Explain with examples.

Ans. Addition polymers : Are formed by repeated addition of a large number of same or different monomers possessing double or triple bonds. E.g., Polythene.

$$n\underset{\text{Ethene}}{H_2C=CH_2} \rightarrow \underset{\text{Polythene}}{(H_2C-CH_2)_n}$$

Condensation polymers : Are formed by repeated condensation reaction between two bifunctional or trifunctional monomer units usually with the elimination of small molecules like water, alcohol, ammonia, etc. E.g., Nylon-6, 6.

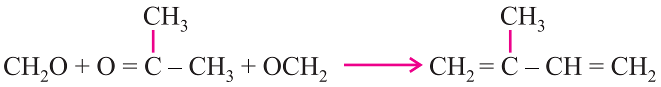


$$nHOOC(CH_2)_4COOH + nH_2N(CH_2)_6NH_2 \rightarrow \left(\overset{\overset{O}{\|}}{C}-(CH_2)_4\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6\overset{\overset{H}{|}}{N}\right)_n + (2n-1)H_2O$$

Nylon 6, 6

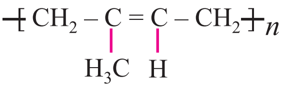
Q. 9.A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mol of $CH_3-\overset{\overset{O}{\|}}{C}-CHO$. Write the structure of monomer and polymer and each step of reaction.

Ans. Structure of monomer :



$$CH_2O + O=\overset{\overset{CH_3}{|}}{C}-CH_3 + OCH_2 \longrightarrow CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2$$

Structure of polymer :



$$\left(CH_2-\underset{\underset{H_3C}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_2\right)_n$$

Q. 10.Can a copolymer be formed in both addition and condensation polymerisation ? Explain with examples.

Ans. Yes. Buna-S, Buna-N : Addition polymer

Nylon-6, 6, terylene : Condensation

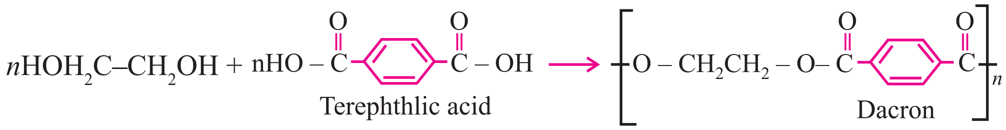
LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. How are following polymers obtained ? Write the names and structures of monomers and structure of respective polymers :

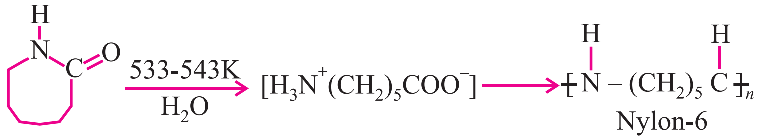
(i) Dacron **(ii) Nylon-6** **(iii) Buna-N**

(iv) Glyptal **(v) PHBV**

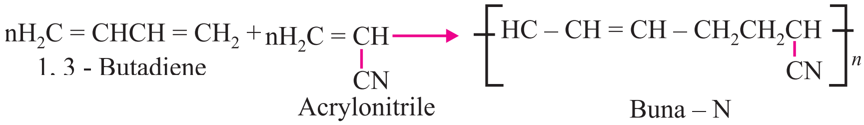
Ans. (i) Dacron : By condensation polymerisation.



(ii) Nylon-6 : By condensation polymerisation.

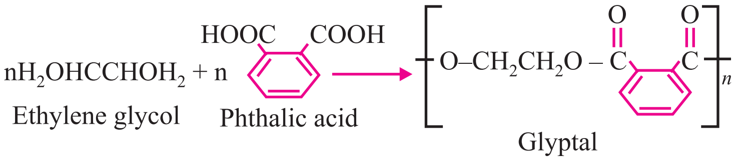


(iii) Buna-N : By addition polymerisation.

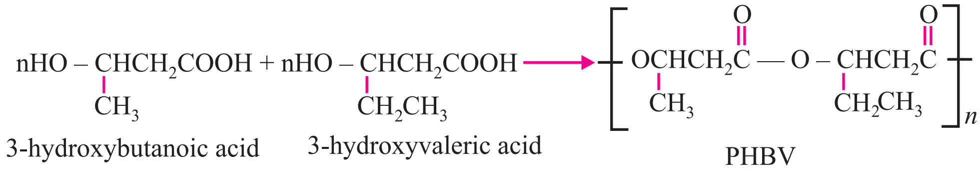


$$nH_2C = CHCH = CH_2 + nH_2C = \underset{CN}{\underset{|}{CH}} \longrightarrow \left[HC - CH = CH - CH_2CH_2\underset{CN}{\underset{|}{CH}} \right]_n$$

(iv) Glyptal : By condensation polymerisation.



(v) PHBV : By condensation polymerisation.



$$nHO - \underset{CH_3}{\underset{|}{CH}}CH_2COOH + nHO - \underset{CH_2CH_3}{\underset{|}{CH}}CH_2COOH \longrightarrow \left[O\underset{CH_3}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}} - O - \underset{CH_2CH_3}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}} \right]_n$$

UNIT 15

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, rantidine, cimetidine.

8. **Anti Histamines :** The drugs which interfere with the natural action of histamines and prevent the allergic reaction. *E.g.,* Rantidine, Bromphenisamine, seldone.

9. **Tranquilizers :** The class of chemical compounds used for the treatment of stress, mild or even severe mental diseases. *E.g.,* depression, Iproniazid, Phenelzine (antidepressant), chlordiazeopoxide, meprobamati (mild tranquilizes), veronal, amytal, seconal, equamil.

10. **Analgesics :** They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system. *E.g.,* Aspirin, seridon, phenacetin.

11. **Antimicrobials :** They tend to prevent/destroy or inhibit the pathogenic action of microbes as bacteria, virus, fungi etc. They are classified as :

    (i) **Antibiotics :** Those are the chemical substances which are produced by micro-organisms. *E.g.,* Penicillin, Ofloxacin.

    Narrow spectrum antibiotics : These are effective mainly against gram positive or gram negative bacteria. *E.g.,* Penicillin, streptomycin.

    Broad spectrum antibiotics : They kill or inhibit a wide range of micro-organisms. *E.g.,* Chloramphenicol, tetracycline, amoxycillin, ampicillin, oflexauin, vancomyain.

    (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 of phenol 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. **Antioxidants:** They help in food preservation by retarding the action of oxygen on food. e.g., Butylated hydroxy toluene (BHT) Butylated hydroxyanisole (BHA), SO_2, sulphite used as antioxidant for wine and beer.

16. **Cleansing Agents :**

    (i) **Soaps :** They are sodium or potassium salts of fatty acids. They are obtained by the saponification reaction, when fatty acids are heated with aqueous sodium hydroxide. They do not work well in hard water.

    (ii) **Toilet soaps :** That are prepared by using better grade of fatty acids and excess of alkali needs to be removed. Colour and perfumes are added to make them attractive.

    (iii) **Medicated soaps :** Substances or medicinal value are added. *E.g.,* Bithional, dettol.

17. **Synthetic Detergents :** They are cleaning agents having properties of soaps, but actually contain no soap. They can be used in both soft and hard water. They are :

    (i) **Anionic detergents :** They are sodium salts of sulphonated long chain alcohols or hydrocarbons. *E.g.,* Sodium lauryl sulphonate. They are effective in acidic solution.

    $$CH_3(CH_2)CH_2OH \rightarrow CH_3(CH_2)_{10}CH_2OSO_3H \rightarrow CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$$

    (lauryl alcohol) (sodium lauryl sulphonate)

    (ii) **Cationic detergents :** They are quarternary ammonium salts of amines with acetates, chlorides or bromides. They have germicidal properties and expensive used in hair conditioners $CH_3(CH_6)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$. *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.

MULTIPLE CHOICE QUESTIONS

1. **Which of the following is not a tranguilizer?**
   (a) Barbituric acid (b) Second
   (c) Luminal (d) Phenactin

2. **Which of the following is not an antibiotic?**
   (a) Chloramphenicol (b) Sulphadiazine
   (c) Pencillin (d) Bithional

3. **2-Acetoxy benzoic acid is:**
   (a) antiseptic (b) antipyretic
   (c) antibiotic (d) mordant dye

4. **Which of the following is used as an antioxidant in foods?**
   (a) saccharin (b) Methylated hydroxyanisole
   (c) Ormeloxifene (d) Cochinical

5. **Which is the correct statement about birth control pells?**
   (a) contain estrogen only (b) contain progesterone only
   (c) contain a mixture of iestrogen and progesterone derivative
   (d) Progesterone enhances ovulation.

6. **Which statement about aspirin is not true.**
   (a) Aspirin belongs to narcotic analgesies
   (b) It is effective in relieving pain
   (c) It has antiblood clotting action
   (d) It is a neurologically active drug.

7. **Salvassam is arsenic containing drug which was first used for the treatment of ....**
   (a) Syphilis (b) Typhoid
   (c) Meningites (d) Dysentry

8. **A narrow spectrum antibiotic is active against ....**
   (a) gram positive or gram negative bacteria
   (b) gram negative bacteria only
   (c) single organism or one desease
   (d) both gram positive and gram negative bacteria.

9. **The compound that causes general antideprssant action on the central nervous system belongs to the class of ....**
   (a) analyceies (b) tranquilizers
   (c) narcotic analyseies (d) antihistamines

10. Equanil is ....

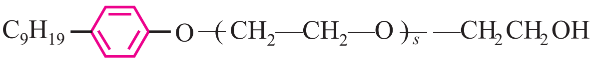
(a) artificial sweetener (b) tranquilizer

(c) anthistamine (d) antifertility drug

11. Which of the following is an example of liquid dishevashing detergent?

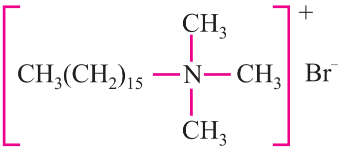
(a) $CH_3(CH_2)_{10}—CH_2OSO_3^-Na^+$

(b)



(c)

(d)



$\left[CH_3(CH_2)_{15}-\overset{CH_3}{\underset{CH_3}{N}}-CH_3 \right]^+ Br^-$

12. Which of the following is not a target molecule for drug function in body?

(a) Carbohydrates (b) Lipids

(c) Vitamins (d) Proteins

13. Which of the following are net used as food preservatives?

(a) Table salt (b) Sodium hydrogencarbonate

(c) Cane sugar (d) Benzoic acid

14. Which of the following statements are correct about barbiturates?

(a) Hypnoties or sleep producing agents

(b) These are tranquilizers

(c) Non-narcotic analgesics

(d) Pain reducing without disturbing the nervous system.

15. Which of the following are antidepressants?

(a) 1 proniazed (b) phenelzine

(c) equanil (d) salvarsan

Matching Column Type

16. Match the medicines given in column I with their use given in column II.

Column I	Column II
(i) Rantidine	(a) Tranquilizer
(ii) Furacine	(b) Antibiotic
(iii) Phenelzine	(c) Antihistaminl
(iv) Chloramphenicol	(d) Antiseptic
(e) Antifertility drug	

17. Match the class of compounds given in column with their functions given in column II.

Column I	Column II
(i) Antagonists	(a) Communicate message between two nuerons and that between neurons to muscles
(ii) Agonists	(b) Bind to the receptor site and inhibit its natural function
(iii) Chemical messenger	(c) Crucial to body's communication process
(iv) Inhibitors	(d) Nimic the natural messenger
(v) Receptor	(e) Inhibit activities of enzymes

Assertion and Reason Type Questions

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

(a) Assertion and reason both are correct statement but reason does not explain assertion.
(b) Assertion and reason both are correct and reason explains the assertion.
(c) Both assertion and reason are wrong statement
(d) Assertion is correct statement reason in wrong statement.
(e) Assertion is wrong statement reason is correct statement.

18. Assertion : Enzymes have active sites that hold substrate molecule for a chemical reaction.

Reason : Drugs complete with natural substrate by attaching covalently to the active site of enzyme.

19. Assertion : Competitive inhibitors complete with natural substrate for this attachment on the active sites of enzymes.

Reason : In competitive inhibition, inhibitor binds to the alhesteric site of the enzyme.

Integer Type Questions

20. The number of antibiotics among the following is ampicillin, sulphanilamide, veronal, equanil, serotonin, luminal, seconal.

0	1	2	3	4	5	6	7	8	9

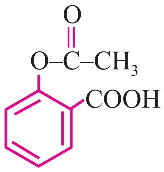
ANSWERS

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

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

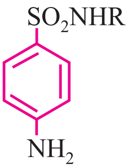
Q. 1. Write the formula and IUPAC name of aspirin.

[*Hint :*



[IUPAC name : 2-Acetoxybenzoic acid]

Q. 2. Name the type of drugs having following structural formula :



[*Hint :* Sulpha drugs]

Q. 3. Name two types of the drugs classified on the basis of pharmacological effect.

[*Hint :* Analgesics, Antiseptics.]

Q. 4. What is the role of Bithional in toilet soaps ?

[*Hint :* To impart antiseptic properties to soaps.]

Q. 5. Why is sodium benzoate added to packed containers of jams and pickles ?

[*Hint :* It prevents spoilage of jams and pickles due to microbial growth. It is a food preservative.]

Q. 6. Why the receptors embedded in cell membranes show selectivity for one chemical messenger over the other ?

[*Hint :* The active site of receptor has specific shape and specific functional groups which can bind only specific messenger which fits in.]

Q.7. With reference to which classification has the statement 'Ranitidine is an antacid' been given ?

[*Hint :* Classification based on pharmacological effect.]

Q.8. Give the name of medicine used for the treatment of syphilis.

[*Hint :* Salvarsan.]

Q.9. Give the composition of tincture of iodine.

[*Hint :* 2-3% solution of iodine in alcohol-water mixture.]

Q.10.How does aspirin act as analgesic ?

[*Hint :* Aspirin inhibits the synthesis of prostaglandins which cause pain.]

Q.11.Name the antiseptic agents present in dettol.

[*Hint :* Chloroxylenol and Terpinol.]

Q.12.What precaution should be taken before administrating penicillin to a patient ?

[*Hint :* To confirm beforehand that the patient is not allergic to penicillin.]

Q.13.Explain why aspirin finds use in prevention of heart attacks ?

[*Hint :* Due to anti blood clotting activity.]

Q.14.Mention one use of drug meprobamate.

[*Hint :* Antidepressant drug.]

Q.15.Name the derivative of sucrose which tastes like sugar and can be safely used by weight conscious people.

[*Hint :* Sucrolose.]

Q.16.Why synthetic detergents are preferred over soaps for use in washing machines ?

[*Hint :* They work well even with hard water and not form any scum.]

Q.17.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 :* Sulphite.]

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.,* Bromopheniramine, seldane.]

Q. 2. What are narcotic and non-narcotic analgesics ? Give one example of each.

[*Hint :* Non-narcotics are the drugs which relieve or decrease pain without causing unconsciousness. Example, Aspirin.

Nartotics analgesics are those drugs which relieve pain, but produce sleep and unconsciousness. Example, Morphine.]

Q. 3. Explain the following terms as used in medicinal chemistry :

(i) Target molecules **(ii) Enzyme inhibitors**

[*Hint :* (i) Drugs that interact with biomolecules such as lipids, carbohydrates, proteins and nucleic acids, are called target molecules.

(ii) They inhibit the catalytic activity of the enzyme.]

Q. 4. Give one important use of each of the following :

(i) Equanil **(ii) Morphine**

[*Hint :* (i) Tranquilizer (antidepressant).

(ii) Narcotic analgesics]

Q. 5. What are neurologically active drugs ? Give two examples.

[*Hint :* Tranquilizers and analgesics are neurologically active drugs. Example : Equanil, morphine.]

Q. 6. (i) What are antibiotics ?

(ii) What is meant by the term broad spectrum antibiotic ?

[*Hint :* (i) A substance produced wholly or partly by chemical synthesis which in low concentration inhibits the growth or destroys microorganism by interfering with their metabolic processes.

(ii) Antibiotics which kills or inhibits wide range of bacteria.]

Q. 7. From the given examples – ciprofloxacin, phenelzine, morphine, ranitidine – choose the drug used for :

(i) treating allergic conditions **(ii) to get relief from pain**

[*Hint :* (i) Ranitidine (ii) Morphine]

Q. 8. Why a drug should not be taken without consulting a doctor ? Give two reasons.

[*Hint :* (i) To avoid side effects caused by drug.

(ii) To have the advice for proper dose of drug.]

Q. 9. State the main difference between bacteriostatic and bactericidal antibiotics. Give one example of each.

[*Hint :* Bacteriostatic antibiotics have inhibitory effect while bactericidal antibiotics have killing effect on microbes.

Example : Bacteriostatic antibiotic : Tetracycline

Bactericidal antibiotic : Ofloxacin]

Q.10.What are antifertility drugs ? Name the constituents of an oral contraceptive.

[*Hint :* Drugs used to check pregnancy in women to control birth rate. Oral contraceptives contains a mixture of synthetic estrogen and progesterone derivatives.]

Q.11.What do you mean by non-biodegradable detergents ? How can we make biodegradable detergents ?

[*Hint :* Detergents which cannot be degraded by nature. Biodegradable detergents can be prepared by minimising the branching of the hydrocarbon chain, as unbranched chains can be biodegraded.]

Q.12.If water contains dissolved calcium hydrogencarbonate, which out of soap and detergent, will you prefer to use ? Why ?

[*Hint :* We will use detergent because it will not form insoluble precipitate with Ca^{2+}.]

Q.13.What are barbiturates ? What is the action of barbiturates on human body ?

[*Hint :* Barbaturic acid derivatives are called barbiturates. They are hypnotic (sleep inducing agents and tranquilizers e.g., valium, serotonin).]

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, chloamphenicol, bithional.

(iii) Sucralose, aspartame, alitame, sodium benzoate.

[*Hint :* (i) Terfenadine is antihistamine other three are used as tranquilizers.

(ii) Chloramphenicol is a broad spectrum antibiotic. Other three have antiseptic properties.

(iii) Sodium benzoate is a food preservative. Other three are artificial sweetners.]

Q. 3. Give the main function of following in the body of human beings :

(i) Enzymes

(ii) Receptor proteins

(iii) Neurotransmitter

[*Hint :* (i) Catalyse biochemical reactions.

(ii) Important for the communication system of the body.

(iii) They control mood changes in organisms.]

Q. 4. Identify the class of drug :

(i) Phenelzine (Nardin)

(ii) Aspirin

(iii) Cimetidine

[*Hint :* (i) Antidepressant drug (ii) Analgesics and antipyretic

(iii) Antihistamine]

Q. 5. Give the pharmacological function of the following type of drugs :

(i) Analgesics (ii) Tranquilizers (iii) Antifertility drugs

[*Hint :* (i) Which reduce or abolish pain.

(ii) They are neurologically active drugs used to treat mental diseases.

(iii) Drugs used to check pregnancy in women to control birth rate.]

Q. 6. Give the name of medicine used in the treatment of following diseases :

(i) Typhoid **(ii) Join pain (in Arthritis)**

(iii) Hypertension

[*Hint :* (i) Antibiotics (ii) Non-narcotic analgesics (iii) Tranquilizers]

Q. 7. Give the class of drugs to which these substances belong :

(i) Bithional **(ii) Amoxycillin** **(iii) Salvarsan**

[*Hint :* (i) Antiseptic (ii) Broad spectrum antibiotic

(iii) Antimicrobial (antibacterial)]

Q. 8. How are antiseptics different from disinfectants ? How does an antibiotic different from these two ? Give one example of each of them.

[*Hint :* Antiseptics may kill or stop the growth of microbes and safe for living tissues, where an disinfectants kill microbes but not safe for living tissues. While antibiotic are produced by micro-organism, can inhibit the growth of other micro-organism.

Example : Antiseptic : 0.2% phenol, Disinfectant : 1% phenol, Antibiotic : Penicillin]

Q. 9. Explain the following terms with suitable examples :

(i) Cationic detergents

(ii) Anionic detergents

(iii) Non-ionic detergents

[*Hint :* (i) Those in which cationic part of the molecule is involved in cleansing action. E.g., cetyltrimethyl ammonium bromide.

(ii) Those in which anionic part of the molecule is involved in cleansing action. *E.g.,* sodium laurylsulphate.

(iii) Which do not contain any ion in their constitution. *E.g.,* Lauryl alcohol ethoxylate.]

Q.10. Classify the following as cationic detergents, anionic detergents or non-ionic detergents :

(i) $CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$

(ii) $[CH_3-(CH_2)_{15}N(CH_3)_3]^+Br^-$

(iii) 

Where ($n = 5 - 10$)

[*Hint :* (i) Anionic detergent (ii) Cationic detergent

(iii) Non-ionic detergent]

Q. 11. How do enzyme inhibitors work ? Distinguish between competitive and non-competitive enzyme inhibitors.

[*Hint :* An enzyme inhibitor either blocks the active site of enzyme or changes the shape of the active site by binding at an allosteric site. They are of two types :

(i) Competitive enzyme inhibitor competes with natural substance for their attachment on the active sites of enzymes.

(ii) Non-competitive enzyme inhibitor binds at allosteric site and changes the shape of the active site in such a way that the substrate cannot recognize it.]

Q. 12.(i) What class of drug is Ranitidine ?

(ii) If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergents, which will you use for cleaning clothes ?

(iii) Which of the following is an antiseptic :

0.2% phenol or 1% phenol

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. (i) Discuss two ways in which drugs prevent the attachment of native substrate on active site of an enzyme.

(ii) What are antibiotics ? Distinguish between narrow spectrum and broad spectrum antibiotics. Classify the following into bactericidal bacteriostatic antibiotics :

Tetracycline, Penicillin, Ofloxacin and Chloramphenicol.

Q. 2. What are detergents ? How are they classified ? Why are detergents usually preferred to soaps for washing clothes ? Give an example of detergents.

SOLVED SAMPLE PAPER
CBSE DELHI-2017

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 : 1

   $(CH_3CH_2)_2\ NCH_3$

   For a reaction $R \longrightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction ?

3. Write the structure of l-Bromo-4-chlorobut-2-ene. 1

4. Write one similarity between Physisorption and Chemisorption. 1

6. Complete the following reactions : 2

   (i) $NH_3 + 3C/_2\text{(excess)} \longrightarrow$

   (ii) $XeF_6 + 2H_2O \longrightarrow$

OR

What happens when

(i) $(NH_4)_2Cr_2O_7$ is heated ?

(ii) H_3PO_3 is heated ?

Write the equations. 2

7. Define the following terms :

   (i) Colligative properties

   (ii) Molality (m)

8. Draw the structures of the following : 2

   (i) $H_2S_2O_7$

   (ii) XeF_6

9. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (^m) is 39.05 S $cm^2 mol^{-1}$. 2

   Given $\lambda°(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda°(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

10. Write the equations involved in the following reactions : 2

    (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. 3

    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 $[Co(NH_3)_6][Cr(CN)_6]$?

    (ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless ? (At. no. of Ni = 28)

    (iii) Write the IUPAC name of the following complex :

    $[Co(NH_3)_5(CO_3)]Cl$. 3

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 3

15. Following data are obtained for the reaction: 3

    $N_2O_5 \rightarrow 2NO_2 + O_2$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(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: 3

2-Bromopentane, 2-Bromo-2 methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-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 concentraed by froth floatation process preferably?

(c) What is the significance of leaching in the extraction of aluminium? 3

18. Write structures of compounds A, B and C in each of the following reactions : 3

(i) $C_6H_5Br \xrightarrow{\text{Mg / dry ether}} A \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } CO_2(g)} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } SNCl_2 / HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$

OR

Do the following conversions in not more than two steps :

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Prapanone to Propene

19. Write the structures of the monomers used for getting the following polymers : 3

(i) Dacron

(ii) Melamine - formaldehyde polymer

(iii) Buna-N

20. Define the following : 3

(i) Anionic detergents

(ii) Broad spectrum antibiotics

(iii) Antiseptic

21. Give reasons: 3

(i) Thermal stability decreases from H_2O to H_2Te.

(ii) Fluoride ion has higher hydration enthalpy than chloride ion.

(iii) Nitrogen does not form pentahalide.

22. Give reasons : 3

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although $-NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

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. 4

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 : 5

(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 $Cr_2O_7^{2-}$ 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. 5

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})

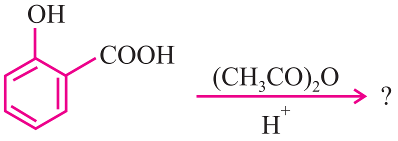
(b) Give reasons :

(i) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.

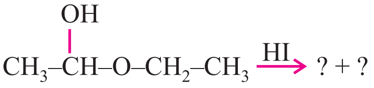
(ii) Silicon on doping with Phosphorus forms n-type semiconductor.

(iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

26. (a) (i) 2



(ii)



$CH_3-\overset{\overset{OH}{|}}{C}H-O-CH_2-CH_3 \xrightarrow{HI} ? + ?$

(iii) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} ?$

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol

OR

(a) Write the formula of reagents used in the following reactions:

(i) Bromination of phenol 2, 4, 6-tribromophenol

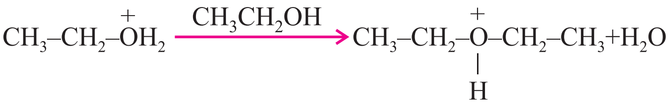
(ii) Hydroboration of propene and then oxidation to propanol.

(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 cuuved arrow notation) of the following reaction:

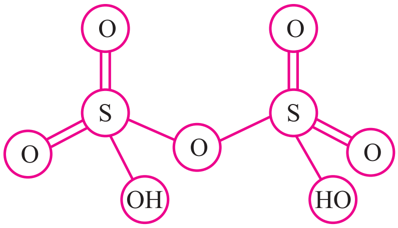
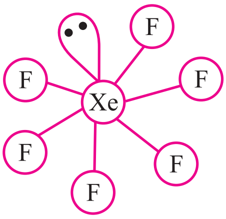


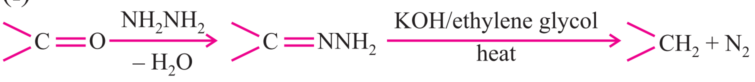
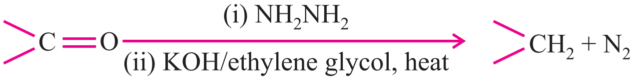
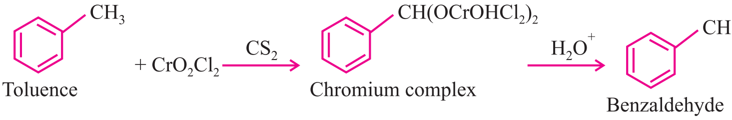
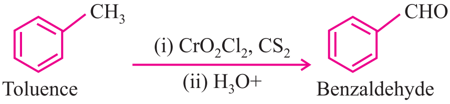
$$CH_3{-}CH_2{-}\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} CH_3{-}CH_2{-}\underset{\displaystyle H}{\underset{|}{\overset{+}{O}}}{-}CH_2{-}CH_3 + H_2O$$

❑❑❑

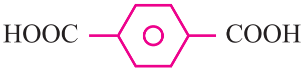
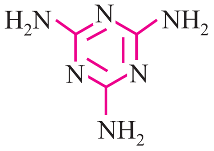
MARKING SCHEME

CBSE DELHI-2017

Q.No.	Value Points	Marks
1.	MnO_4^- / $KMnO_4$	1
2.	N-Ethyl-N-methylethanamine	1
3.	First order	1
4.	$BrCH_2CH = CHCH_2Cl$	1
5.	Both are surface phenomenon / both increase with increase in surface area (or a other correct similarity)	1
6.	(i) $NH_3 + 3\ Cl_2\ (excess) \rightarrow NCl_3 + 3HCl$ (ii) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$	1 1
	OR	
	(i)$(NH_4)_2Cr_2\ O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$ (ii)$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$	1 1
7.	(i)Properties that are independent of nature of solute and depend on number of moles of solute only. (ii)Number of moles of solute dissolved per kg of the solvent.	1 1
8.	(i)  (ii) 	1, 1
9.	$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COO^-} + \Lambda^\circ_{H^+}$ $40.9 + 349.6 = 390.5$ S cm²/mol Now, $\alpha = \Lambda_m / \Lambda^\circ_m$. $= 39.05 / 39.5 = 0.1$	½ ½ ½ ½

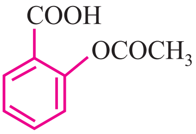
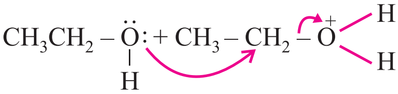
10.	(i)  $>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$ or (ii)  $>C=O \xrightarrow[\text{(ii) KOH/ethylene glycol, heat}]{\text{(i) }NH_2NH_2} >CH_2 + N_2$  Or 	1 1
11.	$\Delta T_f = K_f m$ Here, $m = w_2 \times 1000/ M_2 x W_2$ $273.15 - 269.15 = K_f \times 10 \times 1000/ 342 \times 90$ $K_f = 12.3$ K kg/mol $\Delta T_f = K_f\, m$ $= 12.3 \times 10 \times 1000/ 180 \times 90$ $= 7.6$ K $T_f = 273.15 - 7.6 = 265.55$ K (or any other correct method)	½ 1 ½ 1
12.	(i) m = Zlt $= \frac{108 \times 2 \times 15 \times 60}{1 \times 96500}$ = 2.01 g (or any other correct method) (ii) Cells that converts the energy of combustion of fuels directly into electrical energy.	½ 1 ½ 1
13.	(i) Coordination isomerism (ii) Unpaired electrons in $[Ni(H_2O)_6]^{2+}$ / d-d transition (iii) Pentaamminecarbonatocobalt(lll) Chloride	1 1 1

14.	(i) Lyophobic are liquidf (dispersion medium)-hating and lyophillic are liquid(dispersion medium)-loving colloids.	1
	(ii) Solution is a Homogenous mixture while colloid is heterogenous mixture / does not show Tyndall effect -shows Tyndall effect.	1
	(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)	1
15.	(a) $k = \frac{2.303}{t} \log \frac{[A]^{\circ}}{[A]}$	½
	$= \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}}$	½
	$= \frac{2.303}{300} \log 2 = 2.31 \times 10^{-3} s^{-1}$	
	At 600s, $k = \frac{2.303}{t} \log \frac{[A]^{\circ}}{[A]}$	½
	$= \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}}$ $= 2.31 \times 10^{-3} s^{-1}$	½
	k is constant when using first order equation therefore it follows first order kinetics.	1
	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) $t_{1/2} = 0.693/k$ $= 0.693/2.31 \times 10^{-3}$ = 300 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	1 1 1
17.	(i) The impurities are more soluble in the melt than in the solid state of the metal. (ii) PbS (iii) Impurities like SiO_2 etc are removed by using NaOH solution and pure alumina is obtained .	1 1 1
18.	(i) A : C_6H_5MgBr B : C_6H_5COOH C : C_6H_5COCl (ii) A : CH_3CHO B : $CH_3CH(OH)CH_2CHO$ C : $CH_3CH = CHCHO$	1 1 1
	OR	
18.	(i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{H_2,Pd-BaSO_4} C_6H_5CHO$ (ii) $C_6H_5C_2H_5 \xrightarrow{K_2Cr_2Or/H^+} C_6H_5COOH$ (iii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3$ $\xrightarrow{conc.\ H_2SO_4} CH_3CH=CH_2$ (or any other correct method)	1 1 1
19.	(i) $HOCH_2CH_2OH$ +  (ii)  + HCHO (iii) $CH_2 = CH - CH = CH_2 + CH_2 = CHCN$	½+½ ½+½ ½+½
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.	1 1 1

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.	1 1 1 .
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	1 1 1
23.	(i) concerned , caring, socially alert, leadership (or any other 2 values) (ii) starch (iii) a -Helix and B-pleated sheets (iv) Vitamin B / B_1 / B_2/ B_6 / C (any two)	1 1 1 1
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 Mn^{2+} has d^5 as a stable configuration whereas Cr^{3+} is more stable due to stable t^3_{2g} (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)	1 1 1 1 1
	OR	
	(a) i) In p block elements the difference in oxidation state is 2 and in transition metals the difference is 1	1

<table>
<tr><td></td><td>(ii) Cu^+, due to disproportionation reaction / low hydration enthalpy</td><td>1</td></tr>
<tr><td></td><td>(iii) Due to formation of chromate ion / CrO_4^{2-} ion, which is yellow in colour</td><td>1</td></tr>
<tr><td></td><td>(b) Actinoids are radioactive , actinoids show wide range of oxidation states</td><td>1 + 1</td></tr>
<tr><td>25.</td><td>(a) $\rho = (zxM) / a^3 \times Na$</td><td>½</td></tr>
<tr><td></td><td>$11.5 = z \times 93 / [(300 \times 10^{-10})^3 \times 6.02 \times 10^{23}]$</td><td>1</td></tr>
<tr><td></td><td>Z = 2.0</td><td>½</td></tr>
<tr><td></td><td>Body centred cubic(bcc)</td><td>1</td></tr>
<tr><td></td><td>(b)</td><td></td></tr>
<tr><td></td><td><table>
<tr><td>Amorphous solids</td><td>Crystalline solids</td></tr>
<tr><td>Short range order</td><td>Long range order</td></tr>
<tr><td>Isotropic</td><td>Anisotropic</td></tr>
</table></td><td>1+1</td></tr>
<tr><td></td><td>(or any other correct difference)</td><td></td></tr>
<tr><td></td><td>OR</td><td></td></tr>
<tr><td>25.</td><td>(a) n = given mass / molar mass</td><td>½</td></tr>
<tr><td></td><td>= 8.1 127 mol</td><td></td></tr>
<tr><td></td><td>Number of atoms = $\frac{8.1}{27} \times 6.022 \times 10^{23}$</td><td>½</td></tr>
<tr><td></td><td>Number of atoms in one unit cell= 4 (fee)</td><td>½</td></tr>
<tr><td></td><td>Number of unit cells = $[\frac{8.1}{27} \times 6.022 \times 10^{23}] / 4$</td><td>½</td></tr>
<tr><td></td><td>$= 4.5 \times 10^{22}$</td><td></td></tr>
<tr><td></td><td>Or</td><td></td></tr>
<tr><td></td><td>27g of Al contains = 6.022×10^{23} atoms</td><td>½</td></tr>
<tr><td></td><td>8.1g of Al contains =(6.022×10^{23} / 27) × 8.1</td><td>½</td></tr>
<tr><td></td><td>No of unit cells = total no of atoms / 4</td><td>1</td></tr>
<tr><td></td><td>$= [\frac{8.1}{27} \times 6.022 \times 10^{23}] / 4$</td><td></td></tr>
<tr><td></td><td>$= 4.5 \times 10^{22}$</td><td>1</td></tr>
<tr><td></td><td>(b) (i) Due to comparable size of cation and anion / large size of sodium ion</td><td></td></tr>
<tr><td></td><td>(ii) P has 5 valence e^-, an extra electron results in the formation of n-type semiconductor.</td><td></td></tr>
</table>

	(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.	
	OR	
26.	(a) (i) 	1
	(ii) $(CH_3)_2CHOH$ and CH_3CH_2I	1
	(iii) $CH_3CH = CHCHO$	1
	(i) Add neutral $FeCl_3$ to both the compounds, phenol gives violet complex,	1
	(ii) Add anhy $ZnCl_2$ and cone. HCl to both the compounds, (or any other correct test) 2-methyl propan-2-ol gives turbidity immediately.	1
	OR	
	(a) (i) Aq. Br_2	1
	(ii) B_2H_6 , H_2O_2 andOH^-	1
	(b) (i) ethanol < phenol < Nitrophenol	1
	(ii) propane < propanal < propanol	1
	(c)  $CH_3CH_2-\underset{\substack{\mid\\H}}{\ddot{O}}: + CH_3-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix}$	1

SOLVED SAMPLE PAPER
CBSE DELHI-2018

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.*

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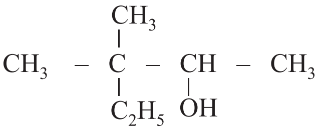
1. Write the IUPAC name of the following: 1



$$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}} - \underset{\displaystyle OH}{CH} - CH_3$$

2. Out of chlorbenzene and benzyl chiroide 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 $[Pt(en)_2Cl_2]$. 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 chemtcel 2

   (a) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow$

   (b) $MnO_4^- + H_2O + I^- \longrightarrow$

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

$$2N_2O_2(g) \longrightarrow 4NO_2\,(g) + O_2\,(g),$$

the rate of fromation of NO_2 (g) is 2.8×10^{-3} M S^{-1}, Calculate the rate of disappearance of N_2O_5 (g).

9. Among the hydrides of Group-15 elements, which have the 2

(a) lowest boiling point?

(b) maximum basic charncter?

(c) higest bond character?

(d) maximum reducing character?

10. Calculate the freezing point of a containing 60 g of ghucose 2

(Molar mass = 180 g mol^{-1}) in 250 g of water.

(K_f of water = 1.86 K kg mol^{-1})

11. An element 'X' (At mass = 40 g mol^{-1}) having f.c.c. structore, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4 g of 'X' ($N_A = 6.022 \times 10^{23}$ mol^{-1}) 3

12. Given resaons for the following: 3

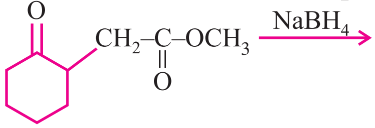
(a) Mesasurenent of osinotic pressure method is preferred for the determination of molar masses of macmolecules such as proteins and polymers.

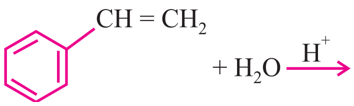
(b) Aquatic snimals are comfortable in colt water than in wam water.

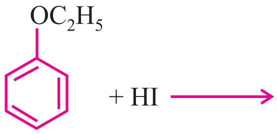
(c) Elovation of boting point 1 M KCl solution is nearly doubte than that of 1 M sugar solution.

13. Write the structures of the main products in the following reactions. 3

(i)



(ii) 

(iii) 

14. (a) Write the formuta of the following coordination compound.

Iron (III) hexacyanoferrate (II)

(b) What type of isomerism is exhibited by the compiex $[Co(NH_3)_5Cl]SO_4$?

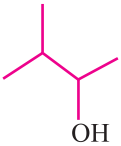
(c) Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$ (Atomic No. oF Co = 27) 3

15. (A), (B) and (C) are thrce non-cyclic fuactional isomsers of a carbonyl compound with molecular formula C_4H_8O 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).

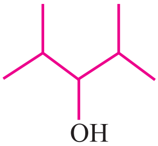
(a) Write the structuress of (A), (B), (C) and (D).

(b) Out of (A), (B) and (C) isomers, which one least redctive towards addition of HCN? 3

16. (a) Identify the chiral molcule 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 alcoholie KOH. 3

17. Give reasons:

(a) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(b) Iron has higher enthalpy of atomisation than of copper.

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. 3

18. Write the ehemical reactions lnvolved in the proecess of extraction of Gold. Explain the role of dilute NaCN and Zn in this proeess. 3

19. Define the following with, an example each. 3

    (a) Polysaccharides

    (b) Denatured protion

    (c) Essential amino acids

OR

    (a) Writh the product when D glucose reacts with conc. HNO_3.

    (b) Amino acide 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 lodine? Write its one use.

    (c) Among the following, which one acts as a food Preservative?

    Aspartame, Aspirin, Sodium Benzoate, Parcetamol. 3

22. What happeas when

    (a) a freshly propared perciptiate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution?

    (b) persistent dialysis of a colloidal solution is carried out?

    (c) an emulation is centrifuged? 3

23. Shyam went to a grocery shop to purchase some food items. The shopkeeper packed all the ftems in polythene bags and gave them to Shyam. But Shyam refused to accpt 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

    Anwer 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 caleulate the e.m.f of the following cell at 298 K:

$Sn\ (s)\ /\ [Sn^{2+}\ (0.004\ M)\ ||\ H^{+}\ (0.020)\ M]\ /\ H_2\ (g)\ (I\ bar)\ |\ Pt\ (s)$

(b) Give reasons:

(i) On the basis of E° values. O_2 gas should be libersted at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH_3COOH dereases on dilution. 5

OR

(a) For the reaction

$$2AgCl\,(s) + H_2\,(g)\,(1\text{ atm}) \longrightarrow 2Ag\,(s) + 2H^{+}\,(0.1\text{ M}) + 2Cl^{-}\,(0.1\text{ M}).$$

$\Delta G° = -43600$ 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:

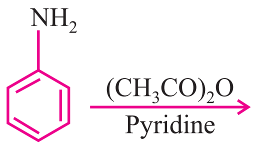
(i) $(CH_3)_2$ NH is more hasic than $(CH_3)_3N$ in an aqueous solution.

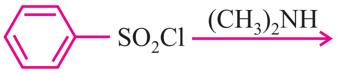
(ii) Aromatic diazonium salts are more stable than sliphatic diazonium salts. 5

OR

(a) Write the stcuctores of the main products of the following reaction:

(i)



(ii) 

(iii) 

(b) Give a simple chemical test to distinguish between Aniline and N,N-dimethylamline.

(c) Arrange the following in the increasing order pK$_b$ values:

$C_6H_5NH_2$, $C_2H_3NH_2$, $C_5H_6NHCH_3$

26. (a) Give reasons: 5

(i) H_3PO_3 undergoes disproportionstion reaction but H_3PO_4 does not.

(ii) When Cl_2 reacts with excess of F_2, CIF_3 is formed and not FCl_3.

(iii) Dioxygen is a gas while Sulphur is a solid at room temperature.

(b) Fraw the structures of the following:

(i) XeF_4

(ii) $HClO_3$

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) Wirte 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:

HF, HCl, HBr, HI

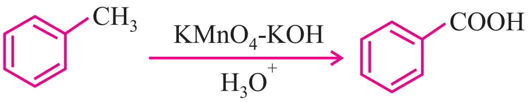
(c) Complete the following reaction:

$$XeF_4 + SbF_5 \longrightarrow$$

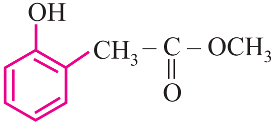
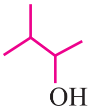
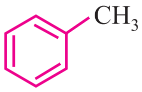
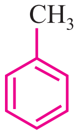
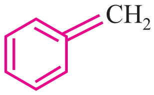
❑❑❑

MARKING SCHEME

CBSE DELHI-2018

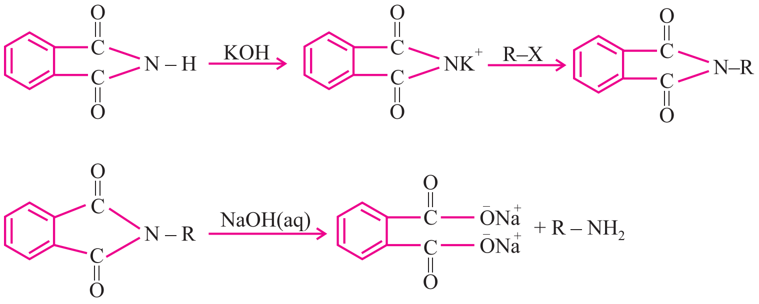
Q.No.	Value Points	Marks
1	3,3 - Dimethylpentan-2-ol	1
2	Benzyl chloride; Due to resonance, stable benzyl carbocation is formed.	½ ½
3	Selectivity of a catalyst	1
4	Coordination Number = 6 , Oxidation State = +2	½, ½
5	Shows metal deficiency defect / It is a mixture of Fe^{2+} and Fe^{3+}/Some Fe^{2+} ions are replaced by Fe^{3+} / Some of the ferrous ions get oxidised to ferric ions.	1
6	(a)$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ (b)$2MnO_4^- + H_2O + I^- \longrightarrow 2\ MnO_2 + 2OH^- + IO_3^-$ (Half mark to be deducted in each equation for not balancing)	1 1
7.	(a) $CH_3CHO \xrightarrow{\text{(i) } CH_3MgBr\text{, Dry ether (ii) } H_2O/H^+} CH_3CH(OH)CH_3 \xrightarrow{CrO_3} CH_3COCH_3$ (b)  (or any other correct method)	1 1
7	(a) because the carboxyl group is deactivating and the catalyst aluminiumchloride (Lewis acid) gets bonded to the carboxyl group (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).	1 1

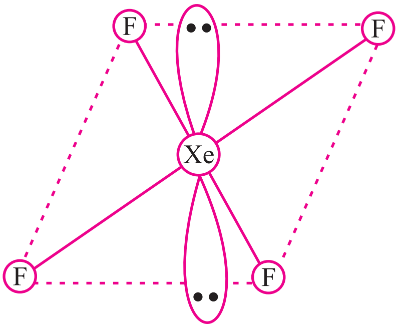
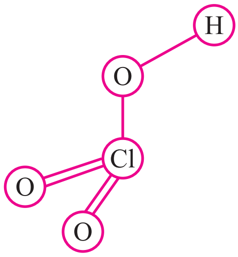
8	$\text{Rate} = \frac{1}{4}\frac{\Delta(NO_2)}{\Delta(t)} = -\frac{1}{2}\frac{\Delta(N_2O_5)}{\Delta(t)}$ $\frac{1}{4}(2.8\times10^{-3}) = -\frac{1}{2}\frac{\Delta(N_2O_5)}{\Delta(t)}$ Rate of disappearance of N_2O_5 $\left(-\frac{\Delta(N_2O_5)}{\Delta(t)}\right) = 1.4\times10^{-3}\,M/S$ (Deduct half markif unit is wrong or not written)	½ ½ 1
9	(a) PH_3 (b) NH_3 (c) NH_3 (d) BiH_3	½ ½ ½ ½
10.	$\Delta T_f = K_f m$ $= K_f \frac{w_2 \times 1000}{M_2 \times w_1}$ $= \frac{1.86 \times 60 \times 1000}{180 \times 250}$ $= 2.48\ K$ $\Delta T_f = T_f{}^\circ - T_f$ $2.48 = 273.15 - T_f$ $T_f = 270.67\ K/270.52\ K/-2.48\ ^\circ C$	½ ½ ½ ½
11.	$d = \frac{zM}{a^3 N_A}$ $= \frac{4 \times 40}{(4\times10^{-8}) \times 6.022 \times 10^{-23}}$ $= 4.15\ g/cm^3$ 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)	½ ½ ½ ½ ½ ½

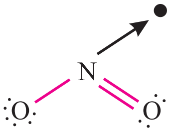
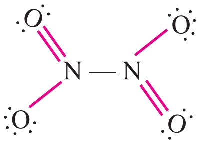
12.	(a) As compared to other colligative properties, its magnitude is large even for very dilute solutions/ macromolecules are generally not stable at higher temperatures and polymers have poor solubility / pressure measurement isaround the room temperature and the molarity of the solution is usedinstead of molality.	1
	(b) Because oxygen is more soluble in cold water or at low temperature.	1
	(c) Due to dissociation of KCI / KCI (aq) → $K^+ + CI^-$, i is nearly equal to 2	1
13.	(ii) $C_6H_5CH(OH)CH_3$	1
		1
	(iii) $C_2H_5I + C_6H_5OH$ (No splitting of marks)	1
14.	(a) $Fe[Fe(CN)_6]_3$	1
	(b) Ionisation isometism	1
	(c) sp^3d^2, 4	1
15.	(a) A = $CH_3CH_2CH_2CHO$	½
	B = CH_3COCH_2CH	½
	C = $(CH_3)_2CHCHO$	½
	D = $CH_3CH_2CH_2CH_3$	½
	(b) B	1
16.	(a) 	1
	(b) 	1
	(c)  or 	1

17.	(a) The comparatively high value for Mn Shows that Mn^{2+} $(d)^5$ is paricularly stable / Much larger third ionisation energy of Mn (where the required change is from ds to (f)	1
	(b) Due to higher number of unpaired electrons.	1
	(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.	1
18.	$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$	1
	$2[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$	1
	(No marks will be deducted for not balancing)	
	NaCN leaches gold/NaCN acts as a leacing agent / complexing agent Zn acts as reducing agent / Zn displaces gold.	1
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)	1
	(b) Proteins that lose their biological activity / proteins in which secondary and tertiary structures are destroyed Curdling of milk (or any other)	1
	(c) Amino acids which cannot be synthesised, in the body. Valine / Leucine (or any other)	1
	OR	
19.	(a) Saccharic acid / $COOH\text{-}(CHOH)_4\text{-}COOH$	1
	(b) Due to the presence of carboxyl and amino group in the same molecule / due to formation of zwitter ion or dipolar ion.	1
	(c) a-helix has intramolecular hydrogen bonding while β pleated has intermolecular hydrogen bonding/α-helix results due to regular coiling of polypeptide chains while in β pleated all polypeptide chains are stretched and arranged side by side.	1

20.	$k_2 = 0.693/20$, $k_1 = 0.693/40$	1
	$\log \frac{k_2}{k_1} = \frac{E_2}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ $k_2/k_1 = 2$	1
	$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{320-300}{320 \times 300}\right]$, $Ea = 27.66\ KJ\ Mol^{-1}$	1
21.	(a) To impart antiseptic properties	1
	(b) 2-3% solution of iodine in alcohol- water mixture/ iodine dissolved in alcohol , used as an antiseptic/ applied on wounds.	½,½
	(c) Sodium benzoate / Aspartame	1
22.	(a) Peptisation occurs / Colloidal solution of $Fe(OH)_3$ is formed	1
	(b) Coagulation occurs	1
	(c) Demulsification or breaks into constituent liquids	1
23.	(a) Concerned about environment, caring, socially alert, law abiding citizen (or any other 2 values)	½,½
	(b) Low density polythene is highly branched while high density polythene is linear.	1
	(c) As it is non-biodegradable .	1
	(d) Which can be degraded by microorganisms, eg PHBV (or any other correct example)	½,½
24.	(a) (i) $Sn + 2\ H+ \rightarrow Sn^{2+} + H_2$ (Equation must be balanced)	1
	$E = E° \ \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[H^+]^2}$	½
	$= [0\ (-\ 0.14)] - 0.0295 \log \frac{(0.004)}{(0.02)^2}$	½
	$= 0.14 - 0.0295 \log 10 = 0.11\ V / 0.1105V$	1
	(b) (i) Due to overpotential/ Overvoltage of O_2	1
	(ii) The number of ions per unit volume decreases.	1

	OR	
24.	(a) $\Delta G^\circ = - nFE^\circ$	½
	$-43600 = - 2 \times 96500 \times E^\circ$	
	$E^\circ = 0.226$ V	
	$E = E^\circ - 0.059/2 \log ([H^+]^2 [Cl^-]^2 /[H_2])$	½
	$= 0.226 - 0.059/2 \log[(0.1)^2 \times (0.1)^2] / 1$	½
	$= 0.226 - 0.059 /2 \log 10^{-4}$	½
	$= 0.226 + 0.118 = 0.344$ V	
	(Deduct half mark if unit is wrong or not written)	1
	(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)	1
25	(a) (i) Ar/ R-CONH$_2$ + Br$_2$ + 4 NaOH $\longrightarrow$ Ar/ R-NH$_2$ + 2NaBr + Na$_2$CO$_3$ + 2 H$_2$O	1
	(ii) $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2Cl + NaCl + 2H_2O$	1
	(or any other correct equation)	
	(iii) 	1
	(b) (i) Because of the combined factors of inductive effect and solvation or hydration effect	1
	(ii) Due to resonance stabilisation or structural representation / resonating structures.	1
	OR	

25.	(a) (i) $C_6H_5NHCOCH_3$	1
	(ii) $C_6H_5SO_2N(CH_3)_2$	1
	(iii) C_6H_6	1
	(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)	1
	(c) $C_2H_5NH_2 \longrightarrow C_6H_5NHCH_3 \longrightarrow C_6H_5NH_2$	
26.	(a)(i) In +3 oxidation state of phosphorus tends to disproportionate to higher and lower oxidation states / Oxidation state of P in H_3PO_3 is +3 so it undergoes disproportionation but in H_3PO_4 it is +5 which is the highest oxidation state, so it cannot.	1
	(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 C*l* atoms around it.	1
	(iii) Oxygen has multiple bonding whereas sulphur shows catenation / Due to pπ-pπ 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.	1
	(b) (i)  (ii) 	1, 1

26.	(a) (i) A = NO_2, B = N_2O_4	½, ½
	 	½,½
	(iii) Because NO_2 dimerises to N_2O_4/NO_2 is an odd electron species.	1
	(b) HI > HBr > HCl > HF	1
	(c) $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$	1

* Note : VAlue Based Question is not included in new blue print.

❑❑❑

PRACTICE-PAPER (Solved)

CHEMISTRY (Theory)

Time : 3 Hrs. ***M.M.: 70***

Instructions:

- *(i) All questions are compulsory.*
- *(ii) Section A : Q. no. 1 to 5 are very short-answer questions and carry 1 mark each.*
- *(iii) Section B : Q. no. 6 to 12 are short-answer questions and carry 2 marks each.*
- *(iv) Section C : Q. no. 13 to 24 are also short-answer questions and carry 3 mark each.*
- *(v) Section D : Q. no. 25 to 27 are long-answer questions and carry 5 mark each.*
- *(vi) There is no overall choice. However, an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choice in such questions.*
- *(vii) Use log tables if necessary. Use of calculators is not allowed.*

Section : A

1. Why are medicines more effective in colloidal state?

Or

What is difference between an emulsion and a gel?

2. Arrange the following in increasing order of base strength in gas phase:

$(C_2H_5)_3$ N, $C_2H_5NH_2$, $(C_2H_5)_2$ NH

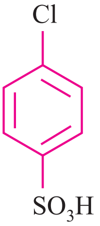
3. Why conductivity of silicon increases on doping with phosphorus?

4. What is the basic structural difference between glucose and fructose?

Or

Write the products obtained after hydrolysis of lactose.

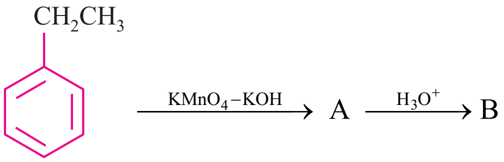
5. Write IUPAC name of the given compound :



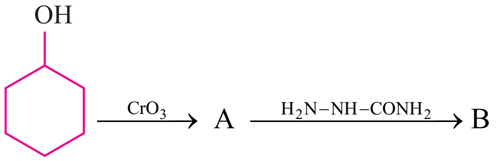
SECTION : B

6. Write structures of compounds A and B in each of the following reactions :

(i)



(ii)



7. For a reaction

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

(i) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

(ii) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(a) Write rate law for the reaction.

(b) Write the overall order of reaction.

(c) Out of steps (1) and (2), which one is rate determining step?

8. Write two differences between an ideal solution and a non-ideal solution.

9. When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (A). Compound (A) disproportionates in acidic solution to give purple compound (B). An alkaline solution of compound (B) oxidises KI to compound (C) whereas an acidified solution of compound (B) oxidises KI to (D). Identify (A), (B), (C) and (D).

10. Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex.

Or

Using IUPAC norms write the formulae for the following :

(i) Pentaamminenitrito-O-cobalt (III) chloride

(ii) Potassium tetracyanidonickelate (II)

11. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is:

(i) diamagnetic

(ii) more stable

(iii) outer orbital complex and

(iv) low spin complex? (Atomic no. of CO = 27)

12. Write balanced chemical equations for the following processes :

(i) XeF_2 undergoes hydrolysis.

(ii) MnO_2 is heated with conc. HCl.

Or

Arrange the following in order of property indicated for each set:

(i) H_2O, H_2S, H_2Se, H_2Te – increasing acidic character

(ii) HF, HCl, HBr, HI – decreasing bond enthalpy

SECTION : C

13. An element crystallizes in fcc lattice with a cell edge of 300 pm. The density of the element is 10.8 cm^{-3}. Calculate the number of atoms in 108 g of the element.

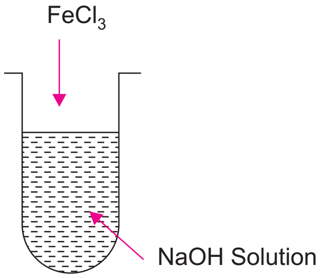
14. A 4% solution (w/w) of sucrose ($M = 342\ g\ mol^{-1}$) in water has a freezing point of 271.15 K. Calculate the freezing point of 5% glucose ($M = 180\ g\ mol^{-1}$) in water.

(Given : Freezing point of pure water = 273.15 K)

15. The decomposition of NH_3 on platinum surface is zero order reaction. If rate constant (k) is $4 \times 10^{-3}\ Ms^{-1}$, how long will it take to reduce the initial concentration of NH_3 from 0.1 M to 0.064 M.

16. (i) What is the role of activated charcoal in gas mask?

(ii) A colloidal sol is prepared by the given method in figure. What is the charge on hydrated ferric oxdide colloidal particles formed in the test tube? How is the sol represented?



(iii) How does chemisorption vary with temperature.

17. (i) Write the role of 'CO' in the purification of nickel.

(ii) What is the role of silica in the extraction of copper?

(iii) What type of metals are generally extracted by electrolytic method?

18. Give reasons for the following:

(i) Transition metals form alloys.

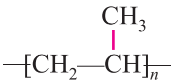
(ii) Mn_2O_3 is basic whereas Mn_2O_7 is acidic.

(iii) Eu^{2+} is a strong reducing agent.

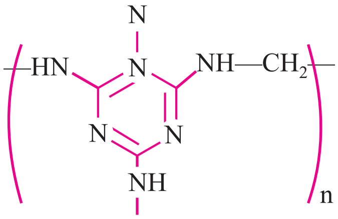
19. Write the structure of monomers used for getting the following polymers:

(i) Nylon 6, 6 (ii) Glyptal (iii) Buna-S

Or

(i) Is  $-[CH_2-\overset{\overset{CH_3}{|}}{C}H]_n-$ a homopolymer or copolymer? Give reason.

(ii) Write the monomers of the following polymer:



(iii) What is the role of sulphur in vulcanization of rubber?

20. (i) Why bithional is added in soap?

(ii) Why magnesium hydroxide is a better antacid than sodium bicarbonate?

(iii) Why soaps are biodegradable whereas detergents are non-biodegradable?

Or

Define the following terms with a suitable example in each:

(i) Antibiotics

(ii) Artificial sweeteners

(iii) Analgesics

21. Write the structures of main products when benzene diazonium chloride reacts with the following reagents:

(i) CuCN (ii) CH_3CH_2OH (iii) KI

22. (i) Out of $(CH_3)_3C—Br$ and $(CH_3)_3$ C—I, which one is more reactive towards S_N1 and why?

(ii) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(iii) Why dextro and laevo rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation?

23. Differentiate between the following :

(i) Amylose and Amylopectin

(ii) Peptide linkage and Glycosidic linkage

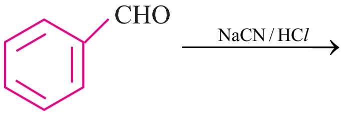
(iii) Fibrous proteins and Globular proteins

Or

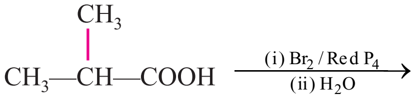
Write chemical reactions to show that open structure of D-glucose contains the following:

- (i) Straight chain
- (ii) Five alcohol groups
- (iii) Aldehyde as carbonyl group

24. Complete the following reactions:

(i) 

(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \rightarrow$

(iii) 

$CH_3—\overset{CH_3}{\overset{|}{C}H}—COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2 / \text{Red } P_4}$

Or

Write chemical equations, for the following reactions:

- (i) Propanone is treated with dilute $Ba(OH)_2$
- (ii) Acetophenone is treated with Zn(Hg)/Conc. HCl
- (iii) Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$.

SECTION : D

25. (a) Give reasons for the following:

- (i) Sulphur in vapour state shows paramagnetic behaviour.
- (ii) N-N bond is weaker than P-P bond.
- (iii) Ozone is thermodynamically less stable than oxygen.

(b) Write the name of gas released when Cu is added to

- (i) dilute HNO_3 and
- (ii) Conc. HNO_3

Or

(a) (i) Write the disproportionation reaction of H_3PO_3.

(ii) Draw the structure of XeF_4.

(b) Account for the following:

(i) Although Fluorine has less negative electron gain enthalpy yet F_2 is strong oxidizing agent.

(ii) Acidic character decreases from N_2O_3 to Bi_2O_3 in group 15.

(c) Write a chemical reaction to test sulphur dioxide gas. Write chemical equation involved.

26. E°_{Cell} for the given redox reaction is 2.71 V

$Mg_{(s)} + Cu^{2+}_{(0.01\ M)} \longrightarrow Mg^{2+}_{(0.001M)} + Cu_{(s)}$

Calculate E_{cell} for the reaction. Write the direction of flow of current when an external opposite potential applied is:

(i) less than 2.71 V and

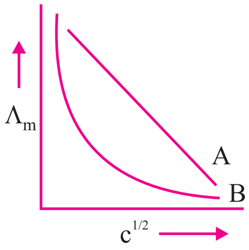
(ii) greater than 2.71 V

Or

(a) A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell Y.

(Molar mass : Fe = 56 g mol^{-1} Zn = 65.3 g mol^{-1}, 1 F = 96500 C mol^{-1})

(b) In the plot of molar conductivity (^ m) vs square root of concentration ($c^{1/2}$) following curves are obtained for two electrolytes A and B :



Answer the following:

(i) Predict the nature of electrolytes A and B.

(ii) What happens on extrapolation of ^ m to concentration approaching zero for electrolytes A and B?

27. (a) How do you convert the following :

(i) Phenol to Anisole

(ii) Ethanol to Propan-2-ol

(b) Write mechanism of the following reaction :

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

(c) Why phenol undergoes electrophilic substitution more easily than benzene?

Or

(a) Account for the following:

(i) o-nitrophenol is more steam volatile than p-nitrophenol.

(ii) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butylmethylether.

(b) Write the reaction involved in the following :

(i) Reimer-Tiemann reaction

(ii) Friedal-Crafts Alkylation of Phenol

(c) Give simple chemical test to distinuish between Ethanol and Phenol.

❑❑❑

MARKING SCHEME (PRACTICE PAPER)

CHEMISTRY (Theory)

Section : A

1. Due to large surface area these are easily assimilated or adsorbed.

Or

Emulsion–both dispersed phase and dispersion medium are liquid.

Gel–Dispersed phase is liquid while dispersion medium is solid.

2. $C_2H_5\,NH_2 < (C_2H_5)_2N < (C_2H_5)_3N$.

3. Due to formation of n-type semiconductor providing free electrons.

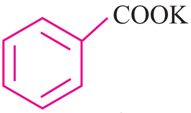
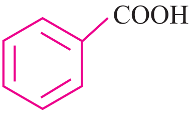
4. Glucose has aldehydic group while fructose has ketonic group/Glucose is aldose while fructose is ketose.

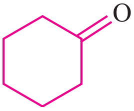
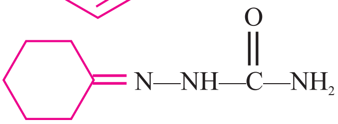
Or

Glucose and Galactose.

5. 4-Chlorobenzenesulphonic acid

Section : B

6. (i) A =  B = 

(ii) A =  B = 

7. (i) Rate = $k\,[H_2O_2][1]$

(ii) order = 2

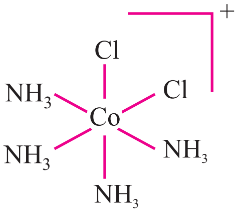
(iii) Step 1

8.

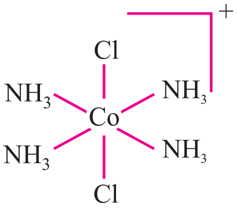
Ideal	**Non-ideal**
Obeys Roult's law at all range of concentration	Does not obey
$\Delta_{mix}H = 0, \Delta_{mix}V = 0$	$\Delta_{mix}H \neq 0, \Delta_{mix}V \neq 0$ (or any other difference)

9. A = K_2MnO_4/MnO_2^{2-}, B = $KMnO_4/MnO_4^{-}$, C = IO_3 or KIO_3, D = l_2

10. Tetraamminedichloridochromium (III) ion



cis



trans

Or

(i) $[Co(NH_3)_5ONO]Cl_2$

(ii) $K_2[Ni(CN)_4]$

11. (i) $[Co(C_2O_4)_3]^{3-}$ (ii) $[Co(C_2O_4)_3]^{3-}$

(iii) $[CoF_6]^{3-}$ (iv) $[Co(C_2O_4)_3]^{3-}$

12. (i) $2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

(ii) $HF > HCl > HBr > HI$

SECTION : C

13. $d = \frac{zm}{a^3 N}$; m = Mass of element, N = number of atoms

$$N = \frac{108 \times 4}{10.8 \times 27 \times 10^{-24}} = 1.48 \times 10^{24} \text{ atoms}$$

Or

$$M = \frac{a^3 \times N_a \times d}{Z}$$

$$= \frac{27 \times 10^{-24} \times 6.022 \times 10^{23} \times 10.8}{4} = 43.88 \text{ g mol}^{-1}$$

43.88 g mol^{-1} contains 6.02×10^{23} atoms

So, 108 g contains $= \frac{6.02 \times 10^{23} \times 108}{43.88} = 1.48 \times 10^{24}$ atoms

14. $\Delta T_f = K_f m$

$$K_f = \Delta T_f \times \frac{M_2 \times w_1}{w_2 \times 1000}$$

$$= \frac{2 \times 342 \times 96}{4 \times 1000} = 16.4 \text{ K}$$

$$\Delta T_f = K_f m$$

$$= \frac{K_f w_2 \times 1000}{M_2 \times w_1} = \frac{16.4 \times 5 \times 1000}{95 \times 180} = 4.8 \text{ K}$$

$$\Delta T_f = T_f^\circ - T_f$$

$$4.8 = 273.15 - T_f$$

$$T_f = 268.35 \text{ K}$$

15. $t = \frac{[R]0 - [R]t}{k} = \frac{[0.1 - 0.064]}{4 \times 10^{-3}} = 9$ sec

16. (i) Adsorption of toxic gases

(ii) Negative charge; Fe_2O_3, XH_2O/OH^-

(iii) Increases with increase in temperature/First increases then decreases

17. (i) To produce a volatile complex, which decomposes on further heating to give pure nickel.

(ii) To remove impurities (FeO) by forming a slag./Acts as a flux.

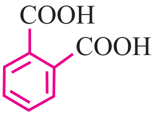
(iii) More reactive metals having large negative electrode potential.

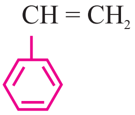
18. (i) Due to comparable radiki / comparable size.

(ii) In Mn_2O_3, Mn is in + 3 (lower) oxidation state while in Mn_2O, Mn is in higher oxidation state (+ 7)

(iii) Because its stable oxidation state is + 3.

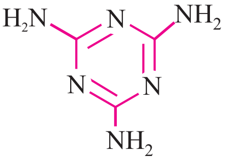
19. (i) $HOOC(CH_2)_4$ COOH, H_2N $(CH_2)_6$ NH_2

(ii) HO-CH_2-CH_2-OH, 

(iii) $CH_2 = CH - CH = CH_2$, 

Or

(i) Homopolymers, single repeating unit



(ii) HCHO (or names of monomers)

(iii) Sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.

20. (i) To impart antiseptic properties.

(ii) Magnesium hydroxide is better alternatives because of being insoluble, it does not increase the pH above neutrality.

(iii) Because in soaps hydrocarbon chains are not branched.

Or

(i) An antibiotic refers to a substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes. Penicillin

(ii) Chemicals which are sweet in taste and with low calories, eg-Saccharin

(iii) Analgesics reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system. Aspirin (or any other correct example)

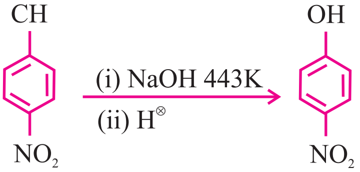
21. (i)

(i)

(ii)

(iii)

22. (i) $(CH_3)_3$ Cl, Due to large size of iodine / better leaving group / Due to lower electronegativity.



(ii)

(iii) Because enantiomers have same boiling points / same physical properties.

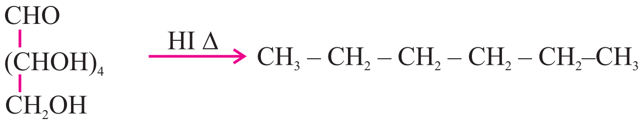
23. (i) Amylose is water soluble component while amylopectin is water insoluble.

(ii) Peptide linkage is —CONH— formed between two amino acids while glycosidic linkage is an oxide linkage between two monosaccharides.

(iii) In fibrous protein, the polypeptide chains run parallel while in globular, the chains of polypeptides coil around to give a spherical shape (or any other correct difference).

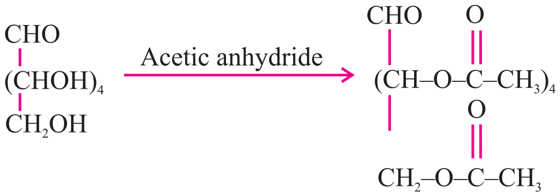
Or

(i)



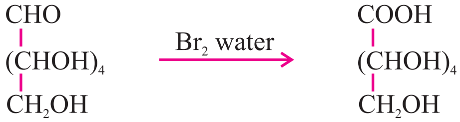
$$\begin{array}{l}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}\xrightarrow{HI\ \Delta}CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

(ii)



$$\begin{array}{l}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}\xrightarrow{\text{Acetic anhydride}}\begin{array}{l}CHO\quad\ \ O\\|\qquad\quad\ \ \|\\(CH-O-C-CH_3)_4\\|\qquad\quad\ \ O\\ \qquad\quad\ \ \ \|\\CH_2-O-C-CH_3\end{array}$$

(iii)



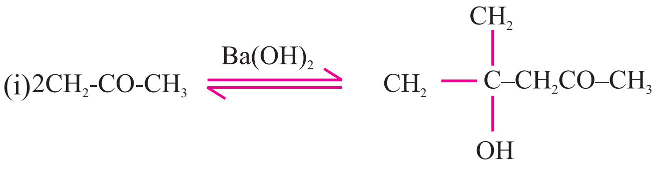
$$\begin{array}{l}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}\xrightarrow{Br_2\ water}\begin{array}{l}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}$$

24. (i) C_6H_5—CH(OH)—CN

(ii) $2CH_3COCH_2C_6H_5 + CdCl_2$

(iii) $(CH_3)_2$—C(Br)COOH

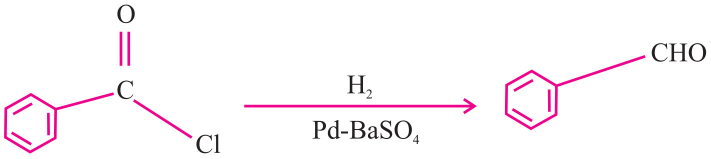
Or



$$(i)2CH_2\text{-}CO\text{-}CH_3\ \xrightleftharpoons{Ba(OH)_2}\ CH_2-\begin{array}{c}CH_2\\|\\C\\|\\OH\end{array}-CH_2CO-CH_3$$

(ii)

(iii)



SECTION : D

25. (a)(i)In vapour state sulphur partly exists as S_2molecule which has two unpaired electrons like O_2.

(ii) Due to greater interelectronic repulsion.

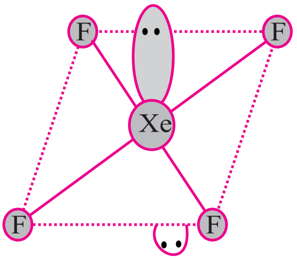
(iii) Because decomposition of ozone into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive), resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

(b) (i) NO gas/Nitric oxide

(ii) NO_2 gas/Nitrogen dioxide

Or

(a) (i) $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$



(b) (i) Due to small size and low bond dissociation enthalpy

(ii) As the size increases, electronegativity decreases/non-metallic character decreases

(c) $5SO_2 + 2MnO_4 + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

26.
$$E_{cell} = E°_{Cell} - \frac{0.059}{n}\log K_c$$
$$= E°_{Cell} - \frac{0.059}{2}\log\frac{10^{-3}}{10^{-2}}$$
$$= 2.71 + 0.0295$$
$$E_{cell} = 2.7395\ V$$

(i) Cu to Mg / Cathode to anode / Same direction

(ii) Mg to Cu / Anode to cathode / Opposite direction

Or

(a) $m = z I t$

$$2.8 \text{ g} = \frac{56 \times 2 \times t}{2 \times 96500}$$

$$t = 4825 \text{ s}$$

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

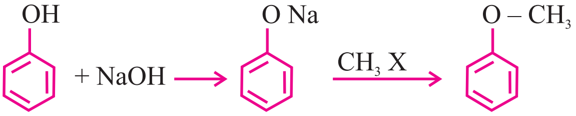
$$\frac{2.8}{mZn} = \frac{56}{2} \times \frac{2}{65.3}$$

$$mZn = 3.265 \text{ g}$$

(b) (i) A strong electrolyte, B-Weak electrolyte

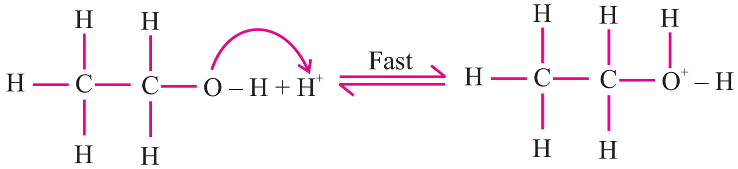
(ii) ^° m for weak electrolytes cannot be obtained by extrapolation while ^° m for strong electrolytes can be obtained as intercept.

27. (a) (i)

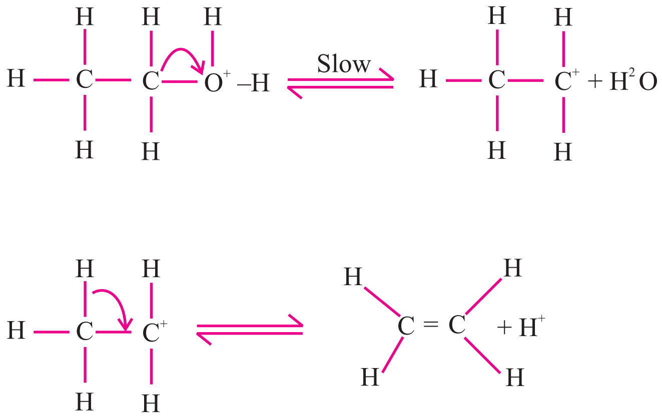


$CH_3CH_2OH \xrightarrow{\text{PCC, Heat}} CH_3-CHO \xrightarrow{\text{(i) CH3MgBr (ii) H+}} CH_3CH(OH)-CH_3$

(ii)



(b)

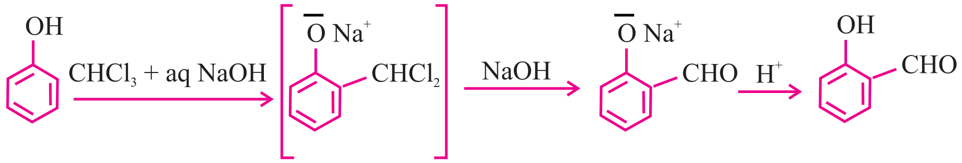


(c) Due to resonance stabilisation.

Or

(a) (i) o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding.

(ii) Due to the formation of stable intermediate tertiary carbocation.



(ii) Award one mark if attempted in any way.

(c) Add neutral $FeCl_3$ to both the compounds, phenol will give violet colouration while ethanol does not.

❑❑❑

PRACTICE-PAPER (Unsolved)

CHEMISTRY (Theory)

Time : 3 Hrs. *M.M.: 70*

General Instructions:

(i) All the questions are compulsory and there are four sections A, B, C and D.

(ii) 1 to 10 are of multiple choice type questions and carry one mark each.

(iii) Question number 11 to 20 are very short answer type questions and carry one mark each.

(iv) Question number 21 to 27 are short answer type questions and carry two marks each.

(v) Question numbers 28 to 34 are long answer type-I and carry three marks each.

(vi) Question number 35 to 37 are long answer type-II questions and carry 5 marks each.

(vii) Use log tables if necessary. Use of calculators and any other electronic device is not allowed.

Section : A

1. Which is the addition polymer.

(a) Nylon-66 (b) Teflon (c) Polyester (d) PHBV

Or

Polymer used for the insulation of electrical cables is:

(a) PVC (b) Glyptal (c) Neoprene (d) All of these

2. Distillation is used for the refining of:

(a) Fe (b) Zn (c) Sn (d) Cu

3. Which of the following aqueous solutions should have the highest boiling point?

(a) 1 M NaOH (b) 1 M Na_2SO_4 (c) 1 M NH_4NO_3 (d) 1 M KNO_3

Or

10% solution of urea is isotonic with 6% solution of a non-volatile solute X. What is the molecular mass of solute X?

(a) $6\ g\ mol^{-}$ (b) $60\ g\ mol^{-1}$ (c) $36\ g\ mol^{-1}$ (d) $32\ g\ mol^{-1}$

4. The charge required for reducing 1 mole of MnO_4^- to Mn^{2+} is:

(a) 1.93×10^5 C (b) 2.8×10^5 C

(c) 4.3×10^5 C (d) 4.82×10^5 C

5. The unit of rate and rate constant are same for a:

(a) Zero order reaction (b) First order reaction

(c) Second order reaction (d) Third order reaction

6. Match the column I and column II and mark the appropriate choice.

(A) Diastase	(i) Proteins → peptones
(B) Pepsin	(ii) Glucose → ethyl alcohol
(C) Ptyalin	(iii) Starch → Maltose
(D) Zymase	(iv) Starch → Sugar

(a) A—(iv), B—(ii), C—(i), D—(iii) (b) A—(ii), B—(i), C—(iv), D—(iii)

(c) A—(i), B—(ii), C—(iii), D—(iv) (d) A—(iii), B—(i), C—(iv), D—(ii)

7. In XeF_2, XeF_4 and XeF_6 the number of lone pairs on Xe is respectively.

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

8. The number of moles of $KMnO_4$ in acidic medium that will be needed to react with one mole of sulphide ion is:

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) $\frac{1}{5}$

9. Propanone on reaction with alkyl magnesium bromide followed by hydrolysis will not produce.

(a) Primary alcohol (b) Secondary alcohol

(c) Tertiary alcohol (d) Carboxylic acid

10. In the following questions, a statement of assertion is followed by a statement of reason. Mark the Correct choice as:

(a) If both assertion and reason are true and reason in the correct explanation of assertion

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

Assertion: The order of basicity of amnines in the gaseous phase follows the order : 3° amines > 2° amines > 1° amines.

Reason: Amines have an unshared pair of electrons on nitrogen atom due to which they behave as lewis abse.

11. Why NaCl is used to clear snow from roads?

Or

Liquid A and B on mixing produce a warm solution.

Which type of deviation does this solution show?

12. Give one example of pseudo first order reaction.

13. Thermal stability of hydrides of group-16 elements decreases down the group. Why?

Or

Why ICl is more reactive than I_2?

14. Why do Zr and Hf exhibits similar properties?

Or

Why do transition metal show variable oxidation states.

15. $CuSO_4$ is colourless while $CuSO_4\ 5H_2O$ is coloured. Why?

Or

$[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless, why?

16. Out of  and Cl, which undergo SN^1 reaction faster and why?

Or

Why grignard reagent should be prepared under anhydrous conditions?

17. Why phenol is acidic in nature?

18. Arrange the following in order of their increasing reactivity toward HCN

CH_3CHO, CH_3COCH_3., HCHO, $C_2H_5\ COCH_3$.

19. What happens when aniline is treated with bromine?

20. Explain why aspirin finds use in prevention of heart attacks?

Section : A

21. Show that time required for 99% completionis twice the time required for the completion of 90% of reactions for a first order reaction.

Or

The decomposition of hydrocarbon follow the equation

$K = (4.5 \times 10^{11}\ 5^{-1})\ e^{-28000\ K/T}$ Calculate Ea.

22. Explain :

(i) Actinoid contraction is greater from element to element than canthanoid contraction. Why?

(ii) The enthalpies of atomisation of the transsition metals are high. Why?

Or

Complete the reactions :

(i) $Fe^{2+} + MnO_4^{-} + 8H^{+} \longrightarrow$

(ii) $CrO_4^{2-} + H^{+} \longrightarrow$

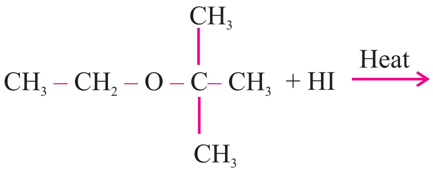
23. When an oxide of Mn (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark solution of compound (B). Compound (B) disproportionate in neutral or acidic solution to give purple compound (C). Identify A, B, C.

24. State the role of silica in the metallurgy of copper and crydit in the metallurgy of aluminium.

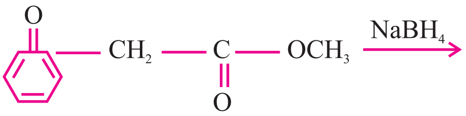
Or

Differentiate between roasting and calcination.

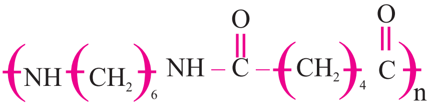
25. Complete the following reactions:

(i) 

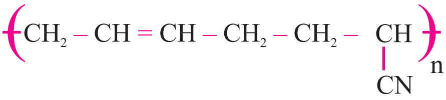
$$CH_3-CH_2-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + HI \xrightarrow{\text{Heat}}$$

(ii) 

26. Write the names of monomers of the following polymers:

(i) 

$$\left(NH\left(CH_2\right)_6 NH-\overset{O}{\overset{\|}{C}}-\left(CH_2\right)_4\overset{O}{\overset{\|}{C}}\right)_n$$

(ii) 

$$\left(CH_2-CH=CH-CH_2-CH_2-\underset{CN}{\underset{|}{CH}}\right)_n$$

27. How do antiseptics differ from disinfectants? Give one example of each.

Section : C

28. 2 g of benzoic acid (C_6H_5 COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dinner in solution?

Or

How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of both?

29. The following data were obtained during the first order thermal decomposition of N_2O_5(g) at constant volume

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

S.No.	Time/s	Total pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

30. Explain what is observed?

(i) When a beam of light is passed through a colloidel sol.

(ii) An electrolyte, NaCl is added to the hydrated ferric oxide sol.

(iii) Electric current is passed through a colloidal sol.

Or

(a) Describe Freundlich adsorption isotherm.

(b) What do you mean by activity and selectivity of catalysts?

31. Draw the figure to show the splitting of d-orbitals in an octahedral crystal field. How does the magnitude of Δ_0 decide the actual configuration of d-orbitals in a coordination entity?

Or

(i) Write IUPAC Name of the complen $[Co(en)_3]^{3+}$

(ii) Draw all the isomers (geometrical and optical) of

(a) $[Pt\ Cl_2\ (en)_2]^{2+}$

(b) $[Cr\ Cl_2(ox)_2]^{3-}$

32. Carry out the following conversions:

(i) Aniline to chlorobenzene

(ii) 2-Bromopropane to 1-Bromopropane

(iii) Benzene to diphenyl

33. Write short on the following :

(i) Carbylamine reaction

(ii) Hofmann's bromamide reaction

(iii) Gabriel phthalimide synthesis.

34. (i) Write the important structural and functional differences between DNA and RNA.

(ii) Write the hydrolysis products of sucrose.

SECTION : D

35. (i) Calculate ΔG^0 and log K_c for the following reaction at 298 K :

$$2Al(s) + 3Cu^{2+}\ (aq) \longrightarrow 2Al^{3+}\ (aq) + 3Cu(s)$$

Given : $E^0_{cell} = 2.02$ V

(ii) Using the E^0 values of A and B, predict which is better for coating the surface of iron $[E^0(Fe^{2+}/Fe) = -0.44\ V]$ to prevent corrosion and why?

Given : $E^0(A^{2+}/A) = -2.37$ V : $E^0(B^{2+}/B) = -0.14$ V

Or

(i) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

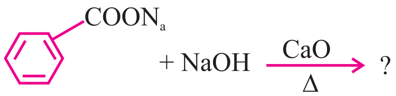
Given $\lambda^0(H^+) = 349.6$ S cm^2 mol^{-1} and

$\lambda^0(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

(ii) What type of battery is dry cell? Write the overall reaction occurring in dry cell.

36. (a) Write the product(s) in the following reactions :

(i) 

(ii) 

(iii) $CH_3 - CH = CH - CN \xrightarrow[\text{(b) } H_2O]{\text{(a) DIBAL-H}} ?$

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Butanal and Butan-2-one

(ii) Benzoic acid and Phenol

Or

(a) Write the reactions involved in the following :

(i) Etard reaction

(ii) Stephen reduction

(b) How will you convert the following in not more than two steps:

(i) Benzoic acid to Benzaldehyde

(ii) Acetophenone to Benzoic acid

(iii) Ethanoic acid to 2-Hydroxyethanoic acid

37. (a) Account for the following:

(i) Ozone is thermodynamically unstable.

(ii) Solid PCl_5 is ionic in nature.

(iii) Fluorine forms only one oxoacid HOF.

(b) DRaw the structure of

(i) BrF_5 (ii) XeF_4

Or

(i) Compare the oxidizing action of F_2 and Cl_2 by considering parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy.

(ii) Write the conditions to maximize the yield of H_2SO_4 by contact process.

(iii) Arrange the following in the increasing order of property mentioned :

(a) H_3PO_3, H_3PO_4, H_3PO_2 (Reducing character)

(b) NH_3, PH_3m AsH_3, SbH_3, BiH_3 (Base strength)

ANSWER

1. b or a **2.** b **3.** b or c **4.** d **5.** a **6.** d **7.** c **8.** a

9. a, b, d **10.** 6

11. It lowers freezing point of water.

Or

Negative deviation

12. Hydrolysis of an ester or any other correct example.

13. Because down the group E—H bond dissociation enthalpy decreases.

Or

Because I—Cl bond is weaker than I—I bond.

14. Due to lanthanide contraction.

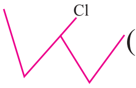
Or

Due to presence of vacant d-orbitals.

15. $CuSO_4$ does not have any ligand, so splitting of d-orbitals take place while $CuSO_4$, $5H_2O$ has water as ligand.

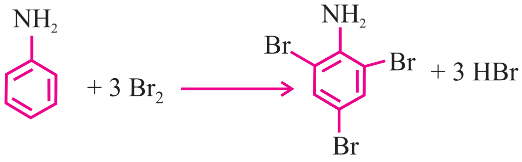
Or

Ti^{3+} has one unpaired electron while Sc^{3+} does not have any unpaired e^-, hence no d—d transition in SC^{3+}.

16.  (2° carbocation). or $RMgX + H_2O \rightarrow R-H + Mg\genfrac{}{}{0pt}{}{X}{OH}$

17. Due to stability of phenoxide ion by resonance.

18. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO$ M H—CHO

19. 

20. Due to antiblood clotting activity.

21. For first order reaction, $t = \frac{2.303}{} \log \frac{a_0}{}$

$$\therefore \qquad \frac{t_{99\%}}{t_{90\%}} = \frac{\log(a_0/0.01a_0)}{\log(a_0/0.1a_0)} = \frac{\log 0.01}{\log 0.1} = \frac{2}{1}$$

$$\Rightarrow \qquad t_{99\%} = 2 \times t_{90\%}$$

Or

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

$$\frac{Ea}{RT} = \frac{28000}{T}$$

$$\begin{aligned} E_a &= 28000 \times R \\ &= 28000 \times 8.314 \\ E_a &= 232.79 \text{ KJ mol}^{-1} \end{aligned}$$

22. (i) Due to poor shielding effect of 5f electrons.

(ii) Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction resulting in higher enthalpies of atomisation.

Or

(i) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

23. $A = MnO_2$

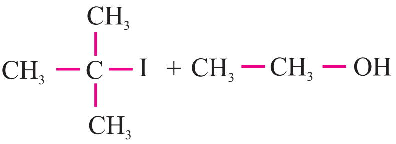
$B = K_2MnO_4$

$C = KMnO_4$

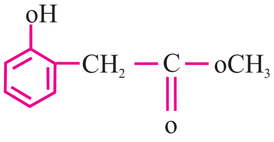
24. Silica act as flux in the metallurgy of Cu $SiO_2 + FeO \longrightarrow FeSiO_3$ and Gyolite is going to decrease the melting point of melt or mixture.

Or

Calcination is heating are in limited supply of oxygen/air, while roasting is heating are in a regular supply of air in a furnace at a temperature below the melting point of the metal.

25.


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I + CH_3-CH_3-OH$



26. (i) Hexamethylenediammine, Adipic acid (or their IUPAC names)

(ii) Buta-1, 3-diene, Acrylonitide

27. Antiseptics and disinfectants are the chemicals which either kill or prevent the growth of microorganisms, antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased spin surfaces, while disinfectants are applied on floors, drainage systems.

Example of antiseptics – Bithionol 0.1% phenol example of disinfectant : 1% phenol

28. NCERT Part-1 Solved Example 2.12 Page 57

Let mass of $Na_2CO_3 = xg$

$\therefore$ mass of $NaHCO_3 = (1 - x)$ g

$\therefore$ moles of Na_2CO_3 = moles of $NaHCO_3$

$$\frac{x}{106} = \frac{1-x}{84}$$

$x = 0.558$ g

Number of moles of $Na_2CO_3 = \frac{0.558}{106} = 0.00526$ mol

Number of moles of $NaHCO_3 = 0.00526$ mol

$Na_2CO_3 + 2HCl \longrightarrow 2\ NaCl + H_2O + CO_2$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

Total number of moles of HCl required

$$= (2 \times 0.00526) + 0.00526$$

$$= 0.01578 \text{ mol}$$

$\therefore$ Volume of 0.1 M HCl $= \frac{\text{Number of moles}}{\text{molarity}}$

$$= \frac{0.01578}{0.1} = 0.1578 \text{ L}$$

$$= 157.8 \text{ mL}$$

29. NCERT Part-1 solved example 4.6 page 107

30. (i) Scattering of light took place/Tyndal effect.

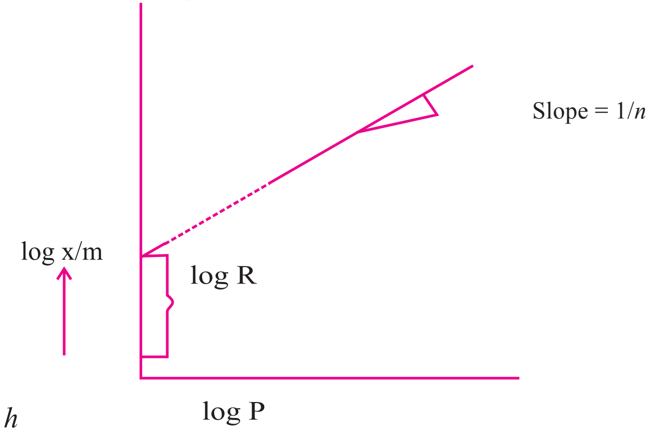
(ii) Coagulation took place

(iii) Electrophoresis/Coagulation took place.

Or

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

$$\log \frac{x}{m} = K + \frac{1}{n} \log p$$



(b) Activity means how many times catalyst is going to increase the rate of reaction and selectivity is its ability to direct a reaction to yield a particular product.

31. NCERT Page 251, Fig. 9.8.

If $\Delta_0 < P$, the fourth electron enters one of the *eg* orbitals giving the configuration t_{2g}^{2} eg^1. (High spin complex) If $\Delta_0 > P$, the fourth electron enters t_{2g} orbital with configuration t_{2g}^{4} eg^0. (Low spin complex)

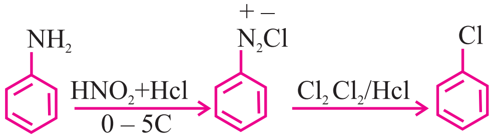
Or

(i) trisethylenediamminecobalt (III) ion.

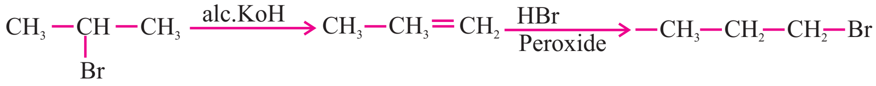
(ii) Fig 9.7 NCERT Page-245

(b) Example 9.6 NCERT 246

(i)

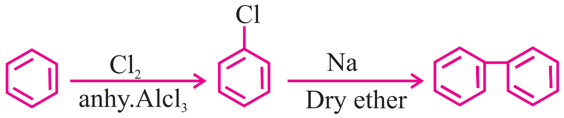


(ii)



$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{alc.KoH} CH_3-CH_3=CH_2 \xrightarrow[Peroxide]{HBr} -CH_3-CH_2-CH_2-Br$

(iii)

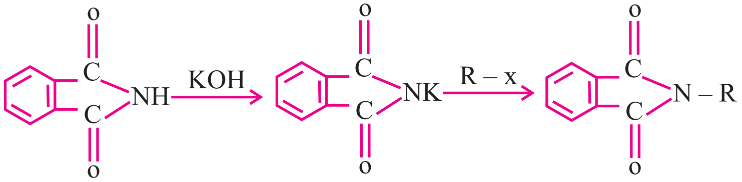


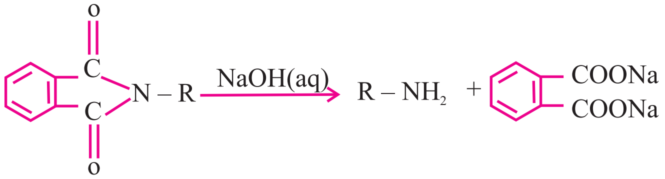
33. (i) $R—NH_2 + CHCl_3 + alc.\ 3KOH \xrightarrow{Heat} CH_3—CH{=\!=}CH_2$

$CH_3—CH_2—CH_2—Br$

(ii) $R—CONH_2 + Br_2 + 4NaOH \longrightarrow R—NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

(iii)





34. (i) DNARNA

Double helical	Single helical
2-Deoxyribose sugar	Ribose sugar
uracil absent	Thymine absent
property of replication	Do not replicant
Controls protein synthesis	Helps in protein synthesis

(ii) $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

35. (a) $DF^0 = -nF\,E^0_{cell}$

$DG^0 = -6 \times 96500 \times 2.02$

$$E^0_{cell} = \frac{0.059V}{n} \log Kc$$

$$\log Kc = \frac{2.02V \times 6}{0.059V} = 205.42$$

(b) A because is E^0 value is more negative.

Or

(a) $\wedge^\circ_m = \kappa \times 1000/C$

$= 3.905 \times 10^{-5} \times 1000/0.001$

$= 39.05$ S cm^2/mole

$$CH_3\,COOH \longrightarrow CH_3COO^- + H^+$$

$\wedge^0\ CH_3COOH = \lambda^0\ CH_3COO^- + \lambda^0H^+$

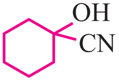
$= 349.6 + 40.9$

$\wedge^0\ CH_3COOH = 390.5$ S cm^2/mol

$= 0.1$

(b) Primary cell

$$Zn + 2NH^+_4 + 2MnO_2 \longrightarrow Zn^{++} + 2NH_3 + 2MnO(OH)$$

36. (a) (i) 

(ii) 

(iii) $CH_3—CH{=}CH—CHO$

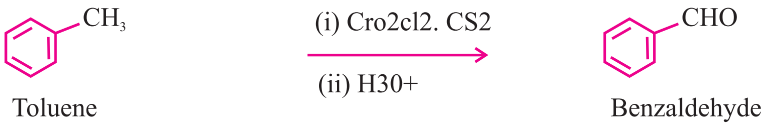
(b) (i) Tollen's reagent test : Add ammoniacal solution of silver nitrate (Tollen's Reagent) in both the solutions. Butanal gives silver mirror whereas Butan-2-one does not.

(ii) Add neutral $FeCl_3$ in both the solutions, phenol forms violet colour but benzoic acid does not.

Or

(a) (i) Etard reaction

or



(ii) Stephen reaction

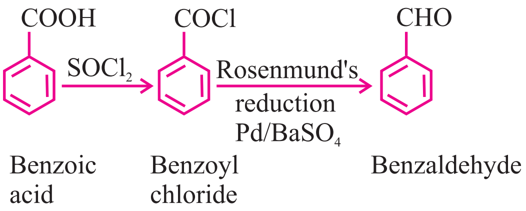
$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

or

$$RCN \xrightarrow[\text{(ii) } H_3O+]{\text{(i) SnCl2 + HCl}} RCHO$$

(b) (i) $RCN \xrightarrow[\text{(ii) } H_3O+]{\text{(i) SnCl2 + HCl}} RCHO$

(ii)

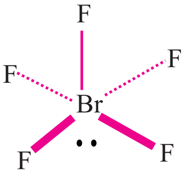


37. (a) (i) Endothermic compound/decomposition of ozone is exothermic is nature and ΔG is negative / decomposition of ozone is spontaneous.

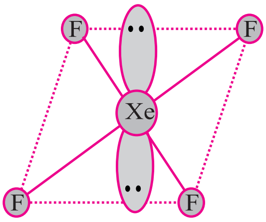
(ii) Exists as $[PCl_4]^+ [PCl_6]^+$

(iii) Shows only-1 oxidation state/most electronegative element/ absence of d-orbitals

(b) (i)



(ii)



Or

(i) 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 enthalpyof F^+ ion

(ii) Low temperature, high pressure and presence of catalyst

(iii) (a) $H_3PO_4 < H_3PO_3 < H_3PO_2$

(b) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

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PRACTICE-PAPER (Unsolved)

CHEMISTRY (Theory)

Time : 3 Hrs. *M.M.: 70*

General Instructions:

(i) *All the questions are compulsory and there are four sections A, B, C and D.*

(ii) *1 to 10 are of multiple choice type questions and carry one mark each.*

(iii) *Question number 11 to 20 are very short answer type questions and carry one mark each.*

(iv) *Question number 21 to 27 are short answer type questions and carry two marks each.*

(v) *Question numbers 28 to 34 are long answer type-I and carry three marks each.*

(vi) *Question number 35 to 37 are long answer type-II questions and carry 5 marks each.*

(vii) *Use log tables if necessary. Use of calculators and any other electronic device is not allowed.*

Section : A

1. Which of the following is an example of autoreduction?

(a) $Fe_3O_4 + 4\,CO \longrightarrow 3Fe + 4CO_2$ (b) $Cu_2O + C \longrightarrow 2Cu + CO$

(c) $Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$ (d) $2Cu_2O + Cu_2S \longrightarrow 6\,Cu + SO_2$

2. α-Helix structure of protein in stabilised by:

(a) peptide bonds (b) vanderwall force

(c) hydrogen bonds (d) dipole-dipole attraction

3. When alkaline $KMnO_4$ is treated with KI, the iodide ion is oxidised to

(a) I_2 (b) IO^- (c) IO_3^- (d) IO_4^-

Which of the following is correct

(a) aq Cu (II) is more stable

(b) aq.Cu(II) is less stable

(c) aq Cu(I) and aq Cu(II) are equally stable

(d) Stability of Cu(I) and aq Cu (II) depends on nature of salt

4. Freshly prepared precipitate sometimes gets converted to colloidal solution by–

(a) Co-agulation (b) electrolysis (c) diffusion (d) peptisation

Or

On the basis of data given below predict which of the following gases shows least adsorption on charcoal?

Gas :	CO_2	SO_2	CH_4	H_2
Critical templk :	304	630	190	33

(a) CO_2 (b) SO_2 (c) CH_4 (d) H_2

5. Arrange the following compounds in increasing order of boiling point

(i) propan-l-ol (ii) butan-2-ol (iii) butan-l-ol (iv) pentan-l-ol

(a) i < ii < iii < iv (b) i < iii < ii < iv (c) iv < iii < ii < i (d) ii < iii < i < iv

6. In comparison of 0.01 M solution of glucose the depression in freezing point of a 0.01 M $MgCl_2$ solution is :

(a) the same (b) about twice

(c) about three times (d) about six times

7. The most reactive amine towards dilute hydrochloric acid is :

(a) $CH_3—NH_2$ (b) $(CH_3)_2NH$ (c) $(CH_3)_3N$ (d) $C_6H_5—NH_2$

8. Λ°_{in} H_2O is equal to :

(a) $\Lambda^\circ_{in}(HCl) + \Lambda^\circ_{in}(NaOH) - \Lambda^\circ_{in}(NaCl)$

(b) $\Lambda^\circ_{in}(HNO_3) + \Lambda^\circ_{in}(NaNO_3) - \Lambda^\circ_{in}(NaOH)$

(c) $\Lambda^\circ_{in}(HNO_3) + \Lambda^\circ_{in}(NaOH) - \Lambda^\circ_{in}(NaNO_3)$

(d) $\Lambda^\circ_{in}(NH_4OH) + \Lambda^\circ_{in}(HCl) - \Lambda^\circ_{in}(NH_4Cl)$

9. Match the items given in Column I with items given in column II.

(i) Ranitidine	(i) Tranquilizer
(ii) Furnace	(ii) Antibiotic
(iii) Phenelzine	(iii) Antihistanine
(iv) Chloramphenicol	(iv) Antiseptic

Assertion and Reason Type

Note: In the following question a statement of assertion followed by a statement of reason is given. Choose correct answer out of the following choices.

(a) Assertion and reason both are correct statement but reason does not explain assertion.

(b) Assertion and reason both are correct and reason explains the assertion.

(c) Assertion is correct but reason is incorrect.

(d) Both assertion and reason are incorrect.

(e) Assertion is incorrect but reason is correct.

10. **Assertion :** Order of the reaction can be zero or fractional.

Reason : We cannot determine order from balanced chemical equaltion.

Very Short Answer Type Question

11. On mixing equal volume of water and ethanol, what type of deviation would you expect from Raoult's law?

Or

What happens when blood cells are placed in pure water?

12. Arrange the following in order of reactivity forwards SN^2 displacement:

1-Bromobutane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane

13. Write IUPAC name of $[Pt(en)_2Cl_2]$.

Or

Using IUPAC norms write formula of the following: Potassium trioxalatochromate(III).

14. Explain what is observed when an electrolyte, NaCl is added to Sol?

15. Sulphur has greater tendency for catenation than oxygen. Explain.

Or

Explain why ClF_3 exists but FCl_3 does not?

16. Define ideal solution

Or

Define Raoult's law for a solution containing volatile liquids.

17. Give IUPAC name of $CH_3—CH═CH—CH_2—COOH$

18. Which one of the two component of starch is water soluble?

19. Prepare aspirin from phenol.

20. Complete the reaction $NH_3 + Cl_2$ (excess) $\longrightarrow$

Or

Complete the reaction $MnO_2 + HCl \xrightarrow{\Delta}$

21. (a) What is tincture of iodine? Write its one use.

(b) Among the following, which one act as food preservative:

Aspartane, Aspirin, Sodium benzoate, Paracetamol

22. (a) Write the principle of method used for refining of germanium.

(b) Out of PbS and $PbCO_3$, which one is concentrated by froth floatation process preferably?

23. Account for the following:

(a) The lowest oxide of transition metal is basic whhereas the highest oxide is amphoteric or acidic.

(b) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali why?

Or

(a) Chemistry of actionoids is complicated as compared to lathanoids. Give reason

(b) How is variability in oxidation states of transition metal different from that of p-block elements?

24. A 10% solutions (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. Write the mechanism of following reaction :

$$2CH_3CH_2 – OH \xrightarrow[413\text{ K}]{\text{Conc } H_2SO4} CH_3CH_2 – O – CH_2 – CH_3$$

Or

How do you convert the following

(a) Phenol to anisole

(b) Propan-2-ol to 2-methyl propan-2-ol

26. (a) What is biodegradable polymer? Give one example.

(b) Write one structural difference between low density polythene and high density polythene.

(c) Write IUPAC names of the monomers of Terylene.

27. (a) When MnO_2 is fused with KOH and KNO_3 (oxidising agent) it gives a dark green compound (A). Compound (A) disproportionates in acidic solution to give purple coloured compound (B). An alkaline solution of compound (B) oxidises KI to compound (C), whereas an acidified solution of compound (B) oxidises KI to (D). Identify A, B, C, and D.

(b) Complete the reaction.

$$MnO_4^- + S_2O_3^{2-} + H_2O \longrightarrow$$

Or

(a) When chromite are $FeCr_2O_4$ is fused with NaOH in the 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 reaction with KCl form orange coloured crystalline compound (C) write formulae of compound A, B and C. Write one use of C.

(b) Complete the reaction.

$$Cr_2O_7^{2-} + Sn^{2+} + 4^{+} \longrightarrow$$

SECTION : C

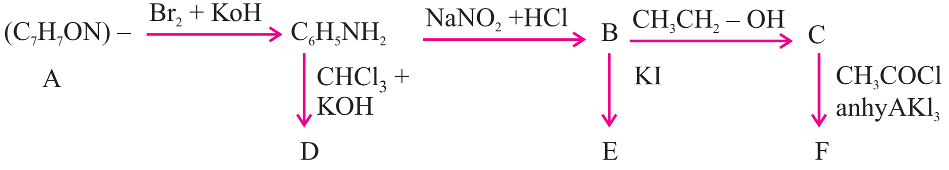
28. (a) What is the difference between nucleoside and nucleotide?

(b) Why vitamin C can not be stored in our body?

(c) Which one of the following is a non reducing sugar :

Glucose, maltose, sucrose

29. Write structures of A, B, C, D, E, F inthe following reactions :



(a) Write the structure of main product when aniline reacts with $(CH_3CO)_2O$/ pyridine

(b) Distinguish with the help of chemical test :

$(CH_3)_2NH$ and $(CH_3)_3N$

(c) Arrange the following in increasing order of their solubility in water

CH_3 CH_2—OH, $CH_3CH_2NH_2$, CH_3—NH—CH_3

30. (a) Give one example each of associated colloid and multimolecular colloid.

(b) Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason.

(c) What is role of charcoal in gas mask.

31. The following data were obtained during first order thermal decomposition of SO_2Cl_2 at a constant volume

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/S	Total pressure /atm
1	0	0.4
2	100	0.7

Calculate the rate constant

(Given log 4 = 0.6021, log 2 = 0.3010

32. Following compounds are given to you.

2-Bromopentane, 2-Bromo-2-methylbutanes, 1-Bromopentane

(a) Write the compound which is mos reactive towards SN^1 reaction.

(b) Write the compound which is optically active.

(c) Write the compound which is most reactive towards β-elimination.

Or

Give reason

(a) SN^1 reaction is accompanied by racemisation in optically active alkyl halides.

(b) The dipole moment of chlorobonzene is lower than that of cyclohexyl chloride.

(c) When NO_2 gp is present at ortho position of chlorobenzene it increases the reactivity of chloro benzene towards nuctophiolic substitution reaction.

33. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression 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 kkg mol^{-1}]

34. (a) Draw geometrical isomer of $[Pt(NH_3)_2Cl_2]$.

(b) On the basis of crystal field theory, write the electronic configuration of d^4 ion if $\Delta_0 < P$.

(c) Write hybridisation and magnetic behaviour of the complex $[Ni(CO)_4]$

Or

(a) Which of the following is more stable complex and why?

$[CO(NH_3)_6]^{3+}$ and $[CO(en)_3]^{3+}$

(b) When a Co-ordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of compound. Write the structural formula of complex.

(c) Why a solution of $[Ni(CN)_4]^{2-}$ is colourless?

SECTION : D

35. (a) Identify A, B, C, D in the following reactions :

$$(C_6H_5CH_2)_2\,Cd + 2CH_3COCl \longrightarrow A$$

(b) A, B and C are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomer A and C give positive Tollen's test whereas isomer B does not give Tollen's test but give positive iodoform test. Isomer A and B on reduction with Zn/Hg cone HCl give the same product D.

(i) Write structure of A, B, C and D

(ii) Out of A, B and C isomers, which one is least towards addition of HCN?

Or

(a) Identify A, B, C and D in the following reactions :

(b) Prepare benzoic acid from Ethylbenzene.

(c) Why pk_a of f-a_1COOH is lower than Cl—CH_2—COOH

(d) Distinguish propanal and propan one with the help of chemical test.

36. (a) Calculate emf of the following cell at 298 K

$$2\underset{(s)}{Cr} + 3Fe^{2+}(0.1M) \longrightarrow 2Cr^{3+}(0.01M) + 3\underset{(s)}{Fe}$$

[Given $\varepsilon(Cr^{3+}/Cr) = -0.74$ V, $\varepsilon°(fe^{2+}/fe) = -0.44$V]

(b) Why conductivity of electrolyte decreases with decreases in concentration?

(c) State Faraday's first law of electrolysis.

Or

(a) Resistance of a conductivity cell filled with 0.1 mol^{-1} KCl solution is 10Ω. If resistance of sane cell when filled with 0.02 mol^{-1} KCl solution is 520 Ω. Calculate the conductivity and molar conductivity of 0.02 mol^{-1} KCl solution. The conductivity of 0.1 mol^{-1} KCl solution is 1.29 S cm^2 mol^{-1}

(b) Define limiting molar conductivity.

(c) E_{cell} for the given redox reaction is 2.71 V Mg(s) + Cu^{2+}(0,01M) $\longrightarrow$ Mg^{2+} (0,001 M) + Cu(s)

Write the direction of flow of current when external potential applied is greater than 2.71 V.

37. (a) Draw structure of (i) $XeOF_4$ (ii) $HClO_3$

(b) Account for the following (i) Fluorine forms only one oxoacid HOF

(ii) Sulphur is paramagnetic is vapour state.

(c) Arrange in increasing order of boiling point H_2O, H_2S, H_2Se, H_2Te

Or

(a) What are the conditions to maximise yield of H_2SO_4 in contact process

(b) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(c) Complete the equation $XeF_2 + PF_5 \longrightarrow$

(d) There is large difference in boiling point of oxygen and sulphur. Give reason.

(e) Ozone is thermo dynamically unstable. Explain

PRACTICE-PAPER (Unsolved)

CHEMISTRY (Theory)

Time : 3 Hrs. *M.M.: 70*

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SECTION : A

1. At 25°C, E° for reaction, $Cu^{2+} + Sn(s) \rightarrow Cu(s) + Sn^{2+}$ is 0.118 V, the equilibrium constant for the reaction is:

(a) 10^8 (b) 10^4 (c) 10^{12} (d) 10^{16}

2. Hydrogen bonding is maximum in

(a) Ethanol (b) Diethyl ether (c) Ethyl chloride (d) Ethylamine

3. Artificial sweetner which is stable under cold conditions only is

(a) Alitame (b) Saccharine (c) Sucralose (d) Aspartame

4. The mass of glucose that should be dissolved in 50 g of water in order to produce the same lowering of vapour pressure as is produced by dissolving 1 g or urea in the same quantity of water is:

(a) 1g (b) 3 g (c) 6 g (d) 18 g

5. The formation of $O_2^+[Pt F_6]^-$ is the basis for the formation of Xenon fluorides. This is because:

(a) O_2 and Xe have comparable sizes (b) both O_2 and Xe are gases

(c) O_2 and Xe have comparable ionisation energies

(d) O_2 and Xe have comparable electronegativities.

Or

The number of hydrogen atom (s) attached to phosphorus atom in hypophosphorous acid is

(a) zero (b) two (c) one (d) three

6. If α is the degree of dissociation of $Na2SO_4$, the vant Hoff's factor (i) used for calculating the molecular mass is:

(a) 1 + α (b) 1 – α (c) 1 + 2α (d) 1 – 2α

Or

Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is:

(a) 1.14 mol kg^{-1}
(b) 3.28 mol kg^{-1}
(c) 2.28 mol kg^{-1}
(d) 0.44 mol kg^{-1}

7. Larger number of oxidation states are exhibited by the actionoids than those by the lanthanoids, the main reason being

(a) 4f orbitals more diffused than the 5f orbitals
(b) lesser energy difference between 5f and 6d than between 4f and 5d orbitals
(c) more energy difference between 5f and 6d than between 4f and 5d orbitals
(d) more reactive nature of the actionoids than the lanthanoids

8. Which of the following statements is true?

(a) H_3PO_3 is a stronger acid than H_3PO_4
(b) In aqueous medium HF is a stronger acid than HCl
(c) $HClO_4$ is a stronger acid than $HClO_3$
(d) NHO_3 is a stronger acid than HNO_2

9. The best reagent to convert pent-3-en-2-ol into pent -3-en-2-one is:

(a) Acidic permanganate
(b) Acidic dichromate
(c) Chromic anhydride in anhydrous medium
(d) Pyridinium chloro-chromate

10. The properties which depend on the number of moles is called ....

Assertion and Reason type Question

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

(b) Both assertion and reason are true and reason is the not correct explanation of assertion.

(c) Assertion is true and reason is false.

(d) Assertion is false and reason true.

11. Assertion-Deep sea divers use Helium and oxygen mixture for breathing. Reason-helium is not solube in blood like nitrogen.

12. Match the column and choose correct answer:

Column I (Acids)	**Column II** (Basicity)
(a) Sulphuric Acid	(p) 1
(b) Orthophosphoric acid	(q) 4
(c) Perchlorous acid	(r) 2
(d) Pyrophophoric acid	(s) 3

(a) A–p, B–q, C–r, D–s
(b) A–p, B–q, C–s, D–r
(c) A–r, B–q, C–p, D–s
(d) A–q, B–r, C–p, D–s

13. Why is adsorption always exothermic?

Or

How is Brownian movement responsible for the stability of sols?

14. For the reaction A → B, the rate of reaction becomes three times when the concenration, of A is increased by nine times. What is the order of reaction?

15. Write the Principle of Zone Refining?

16. Write the components of Lactose?

17. Amongst the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields a single monochloride.

18. Write the name of the biodegradable polymer used in orthopaedic devices.

Or

Write the monomer of polymer which is used in autotyres.

19. Give the IUPAC name and structure o the amine obtained when 3-chlorobutanamide undergoes Hoffmann bromamide reaction.

20. How many ions are produced from the complex, $[CO\ (NH_3)_6]\ Cl_2$ in solution? Low spin configuration are rarely observed in tetrahedral coordination entity formation. Explain.

SECTION : B

21. Explain the following :

(a)Out of Sc^{3+}, Co^{2+} and Cr^{3+} ions, only Sc^{3+} is colourless in aqueous solutions. (Atomic no. : Co = 27 Sc = 21 and Cr = 24)

(b) $La(OH)_3$ is more basic than $Lu(OH)_3$

22. (a) Pick out the odd one from among the following on the basis of their medicinal properties mentioning the reason : Luminal, Seconal, Phenacetin, Equanil.

(b) Give an example of a substance that can act as a disinfectant as well as antiseptic depending upon its concentration. (Specify concentration)

Or

(a) Name any two macromolecules chosen as drug targets.

(b) Which artificial sweetening agent is stable at cooking temperature.

23. Write the role of:

(a) NaCN in the extraction of gold from its ore.

(b) (II)Cryolite in the extraction of aluminium from pure alumina.

Or

(a) CO in the purification of Nickel.

(b) Pine oil in the Forth floatation process.

24. Identify the following:

(a) Transition metal of 3d series that exhibits the maximum number of oxidation states.

(b) An alloy consisting of approximately 95% lanthanoid metal used to produce bullet, shell and lighter flint.

25. Give the formula of monomers involved in the formation of the following polymers:

(a) Buna-N (b) Nylon-6

26. How will you convert?

(a) Propane 2 ol to 1-Bromo propane

(b) Phenol to Chlorobenzene

27. A first order reaction takes 40 minutes for 30% decomposition. Calculate t.

Or

Write the unit of rate constant for–

(i) First order reaction

(ii) Zero order reaction

SECTION : C

28. Give reason:

(*a*) Aniline gets coloured on standing in air for a long time.

(*b*) Secondary amine is more basic than primary and teritiary amines in an aqueous solution.

(*c*) Aniline is a weaker base than cyclohexylamine.

29. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is then added to this solution, the new vapour pressure becomes 2.9 kPa at 298 K. Calculate

(*i*) The molar mass of solute

(*ii*) Vapour pressure of water at 298 K.

Or

When 1.5 g of non-volatile solute was dissolved in 90 g of benzene, the boiling point of benzene is raised from 353.23 K to 353.93 K. Calculate the molar mass of the solute [Kb for benzene = 2.52 kg mol^{-1}]

30. Give reason for the following observations:

(*i*) When silver nitrate solution is added to potassium iodide solution, snegatively charged colloidal solution is formed.

(*ii*) Finely divided substance is more effiective as an adsorbent.

(*iii*) Lyophilic collooids are also are called reversible sol.

31. Write the product (s) formed when

(*i*) 2-Bromopropane undergoes dehydrohalogenation reaction.

(*ii*) Chlorobenzene undergoes nitration reaction.

(*iii*) Methylbromide is treated with KCN

32. A reaction is first order in A and second order in B

(*i*) Write the differential rate equation.

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

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

33. Explain the following:

(*i*) Amino acids behave like salts rather than simple amines or carboxylic acids.

(*ii*) The two strands of DNA are complementary to each other.

(*iii*) Reaction of glucose that indicates that the carbonyl group is present as an aldehydic group in the open structure of glucose.

OR

(*a*) Name the branched chain component of starch.

(*b*) Ribose in RNA and deoxyribose in DNA differ in the structure around which carbonatom?

(*c*) How many peptide linkages are present in a tripeptide?

34. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms A and B. the form Areacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia whereas B gives a pale yellow precipitate soluble in concentrated ammonia.

(*i*) Write the formulae of isomers A and B.

(*ii*) State the hybridisation of chromium in each of them.

(*iii*) Calculate the magnetic moment (spin only value) of the isomer A

SECTION D

35. (I) What happens when

(*a*) chlorine gas reacts with cold and dilute solution of NaOH?

(*b*) XeF_2 undergoes hydrolysis?

(*ii*) Assign suitable reason for the following:

(*a*) SF_6 in inert towards hydrolysis.

(*b*) H_3PO_3 is diprotic

(*c*) Out of noble gases only Xenon is known to form established chemical compounds.

OR

(a) Write balanced equations for the following reactions

(*i*) Chlorine reacts with dry slaked lime.

(*ii*) Carbon reacts with concentrated H_2SO_4.

(*iii*) Xenon hexafiuroide react with water (*b*) Describe the contact process for the manufacture of sulphuric acid with special reference to the reaction conditions, catalysts used and the yield in the process.

36. (*a*) Define the following terms:

(*i*) Molar conductivity (^m)

(*ii*) Secondary batteries

(*iii*) Fuel cell

(*b*) State the following laws:

(*i*) Faraday first law of elctrolysis

(*ii*) Kohlrausch's law of independent migration of ions

37. (a) Describe the following giving chemical equations:

(*i*) De-carboxylation reaction

(*ii*) Friedel-Crafts reaction

(*b*) How will you bring about the following conversions?

(*i*) Benzoic acid to Benzaldehyde

(*ii*) Benene to m-Nitroacetophenone

(*iii*) Benene to m-Nitroacetophenone

OR

(a) Write the chemical equations to illustrate the following name reactions:

(*i*) Etard reaction.

(*ii*) Rosenumnd's reaction.

(*c*) Give the mechanism of cyanohydrin formation when carbonyl compounds reaction with HCN in presence of alkali.

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