STUDENT SUPPORT MATERIAL

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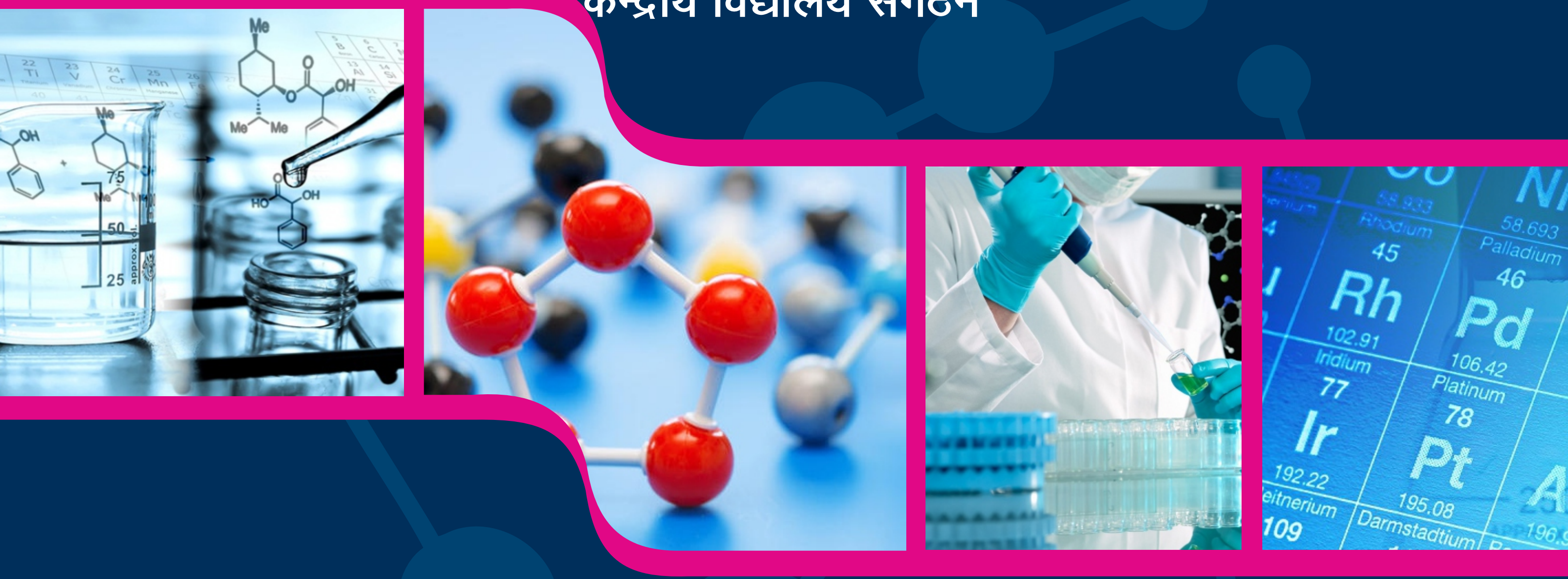
केन्द्रीय विद्यालय संगठन



Session : 2019-20

Class-XII
CHEMISTRY

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आयुक्त
Santosh Kumar Mall, I.A.S.
Commissioner

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A WORD TO MY DEAR STUDENTS

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

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

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

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

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

Happy learning!

28/10

Santosh Kumar Mall
Commissioner, KVS

FOREWORD

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

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

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

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

Best of Luck.

U.N. Khaware
Additional Commissioner (Acad.)

Chemistry

STUDENT SUPPORT MATERIAL

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CONTENTS

SOLUTIONS (UNIT-1)

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

EXPRESSING CONCENTRATIONS OF SOLUTIONS

- Mass percentage: Mass of solute per 100g of solution Mass % = (mass of solute / total mass of solution) X 100
- Volume percentage : volume of solute per 100ml of solution Volume % = (volume of solute/ total volume of solution) X 100
- Parts per million: parts of a component per million (10^6) parts of the solution.

ppm=no. of parts of the component / total no. of parts of all components of the sol. X10^6

- Mole fraction(x): It is the ratio of no. of moles of one component to the total no. of all the components present in the solution. For binary solution:-the no. of moles of A and B are n_A and n_B respectively

so, $x_A=n_A/n_A+n_B$; $x_B=n_B/n_A+n_B$

In binary solution $x_A+x_B=1$

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

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

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

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

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

HENRY'S LAW

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

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

$P=K_HX$

K_H is Henry's law constant .

APPLICATION OF HENRY'S LAW

- To increase the solubility of CO_2 in soda water and soft drinks the bottle is sealed under high pressure.
- To avoid bends, toxic effects of high concentration of nitrogen in the blood the tanks sd Used by scuba divers are filled with air diluted with He.

RAOULT'S LAW :- it states that :

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

$P_A=P^0{}_A X_A$ $P_B=P^0{}_B X_B$

The total pressure is equal to sum of partial pressure. $P_{total}=P_A+P_B$

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

$$P_A \alpha X_A \qquad P_A=P^0{}_A X_A$$

IDEALSOLUTION

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

CONDITIONS

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

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

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

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

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

CONDITIONS :

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

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

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

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

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

Ex: mixture of ethanol and acetone .

$P_A > P_A^0 X_A$; $P_B > P_B^0 X_B$

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

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

III. Ex: mixture of chloroform and acetone .

IV. $P_A < P_A^0 X_A$; $P_B < P^0_B X_B$

V. ΔH_{mix} = negative ΔV_{mix} = negative

AZEOTROPE

Mixture of liquid having the same composition in liquid and vapour phase and boil at constant temp.

Azeotropes are of two types :-

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

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

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

1. RELATIVE LOWERING OF VAPOUR PRESSURE

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

$X_B = n_B / n_A + n_B$

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

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

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

2. ELEVATION OF BOILING POINT

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

K_b = molal elevation constant / Ebullioscopic constant

m = molality

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

3. DEPRESSION IN FREEZING POINT

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

K_f = molal depression constant / Cryoscopic constant

m = molality

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

4. OSMOTIC PRESSURE

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

$\Pi = CRT$

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

$R = 0.0821$ L atm mol^{-1}; T= temperature in kelvin

ISOTONIC SOLUTION

Two solutions having same osmotic pressure and same concentration are called isotonic solutions.

Hypertonic solution have higher osmotic pressure and hypotonic solution have lower osmotic pressure than the other solution.

0.91% of sodium chloride is isotonic with fluid present inside blood cell.

VAN'T HOFF FACTOR (i)

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

i = normal molecular mass/ observed molecular mass

= observed colligative properties / calculated value of colligative properties

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

MODIFIED FORMS OF COLLIGATIVE PROPERTIES

1) $P^0_A - P_A / P^0_A = i \, n_B / n_A$
3) $\Delta T_b = iK_b \, m$
4) $\Delta T_f = iK_f \, m$
5) $\Pi = iCRT$

FREQUENTLY ASKED QUESTIONS (1 MARK QUESTIONS)

Q 1. Two liquids X and Y boil at 380 K and 400K respectively, which of them is more volatile?

Ans. X is more volatile since it has low boiling point.

Q2. How does the molarity of a solution change with temperature?

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

Q3. Under what condition do non ideal solutions show negative deviation ?

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

Q4. What are minimum boiling azeotropes? Give one example.

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

Q5. What do you understand by the term that K_f for water is 1.86 K kg/mol?

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

Q6. Why is osmotic pressure of 1M KCl higher than 1M urea solution ?

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

Q 7. What is the value of van't Hoff factor for a dilute solution of

(i) K_2SO_4 in water

(ii) acetic acid in benzene.

Ans .(i) 3 (ii) 1/2

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

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

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

(c) Assertion is true but reason is false.

(d) Both assertion and reason are false.

1. Assertion : In an ideal solution, $\Delta_{mix}H$ is zero.
   Reason : In an ideal solution, A - B interactions are lower than A-A and B-B interactions.
   (Ans -c)
2. Assertion : Osmosis does not take place in two isotonic solutions separated by semi-permeable membrane.
   Reason : Isotonic solutions have same osmotic pressure. (Ans - a)
3. Assertion : Lowering of vapour pressure is not dependent on the number of species present in the solution.
   Reason : Lowering of vapour pressure and relative lowering of vapour pressure are colligative properties. (Ans - d)
4. Assertion : 1 M solution of KCl has greater osmotic pressure than 1 M solution of glucose at same temperature.
   Reason : In solution KCl dissociates to produce more number of particles. (Ans - a)
5. Assertion : Two liquids nitric acid and water form a maximum boiling azeotrope when mixed in the ratio of 68% and 32% respectively.
   Reason : Interaction between nitric acid and water are stronger than nitric acid - nitric acid interactions and water - water interactions. (Ans - a)

One - word answers

1. Liquid 'Y' has higher vapour pressure than liquid ' X' . Which of them will have higher boiling point. (Ans - X)
2. Liquids A and B on mixing produce a warm solution. Which type of deviation from Raoult's law is shown? (Ans - Negative deviation)
3. Under what condition Van't Hoff factor is less than 1? (Ans - Association)

2 MARKS QUESTIONS

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

Ans. Henry's Law: It states that "the partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of the gas (x) in the solution", and is expressed as: $p = K_H \chi$ where, K_H is the Henry's Law constant

Significance of K_H: Higher the value of Henry's law constant K_H, the lower is the solubility of the gas in the liquid.

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

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

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

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

i) N-hexane and n-octane

ii) methanol and acetone

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

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

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

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

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

$= 6.5/456.5 \times 100 = 1.424\%$

3 MARK QUESTIONS

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

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

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

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

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

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

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

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

Ans. ΔT_b =100.42°C-100°C=0.42°C or 0.42K; W_A =500g; K_b =0.512Kkg/mol;

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

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

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

Q4. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27^{0}C.

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

Molar mass of CaCl ,M =40+2 X 35.5 = 111 g mol^{-1}

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

= 3.42g

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

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

$$0.112\ K = \frac{1000 \times 4.9 \times 3.26}{226 \times M_B}$$

M_B = 1000X4.90X3.26/226X0.1112=63g/mol

No. of Se atoms in a molecule=631g / mol/78.8 g/mol=8

Therefore, molecular formula of Selenium = Se_8

5 MARKS QUESTION

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

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

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

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

OR

$$p_A = p_A^o x_A$$

According to Henry's Law, the partial pressure of a gas in vapour phase (p) is Directly proportional to mole fraction (x) of the gas in the solution.

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

i.e; $p \propto x$

only the proportionality constant K differs from p^0. Thus, it becomes a special case of Henry's law in which $K_H = p_A^o$.

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

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

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

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

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

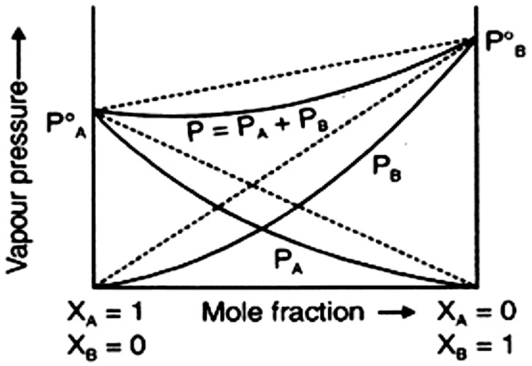
ii) Name the type of deviation shown by this system from Raoult's law.

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

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

v) Give an example of such a system.

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



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

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

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

Dividing (ii) by (i), we get

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

hence molality = 9.8 m

b) i) Stronger

ii) Negative deviation

iii) Negative

iv) Negative

v) 20% acetone and 80% chloroform by mass

vi) maximum boiling azeotrope

ASSIGNMENT

Q1. Define mole fraction

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

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

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

Q5. State any two characteristics of ideal solutions.

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

Q7. Define molal elevation constant or ebullioscopic constant.

Q8. What is “reverse osmosis “ ?

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

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

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

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

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

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

(MULTIPLE CHOICE QUESTION)MCQ

1. Which of the following units is useful in relating concentration of solution with its vapour pressure?
(i) mole fraction
(ii) parts per million
(iii) mass percentage
(iv) molality

2. On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?
(i) Sugar crystals in cold water.
(ii) Sugar crystals in hot water.
(iii) Powdered sugar in cold water.
(iv) Powdered sugar in hot water.

3. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is __________.
(i) less than the rate of crystallisation
(ii) greater than the rate of crystallisation

(iii) equal to the rate of crystallisation
(iv) zero

4. A beaker contains a solution of substance ‘A’. Precipitation of substance ‘A’ takes place when small amount of ‘A’ is added to the solution. The solution is _________.
(i) saturated
(ii) supersaturated
(iii) unsaturated
(iv) concentrated

5. Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon ____________.
(i) Temperature
(ii) Nature of solute
(iii) Pressure
(iv) Nature of solvent

6. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to ____________.
(i) low temperature
(ii) low atmospheric pressure
(iii) high atmospheric pressure
(iv) both low temperature and high atmospheric pressure

7. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult’s law?
(i) Methanol and acetone.
(ii) Chloroform and acetone.
(iii) Nitric acid and water.
(iv) Phenol and aniline.

8. Colligative properties depend on ____________.
(i) the nature of the solute particles dissolved in solution.
(ii) the number of solute particles in solution.
(iii) the physical properties of the solute particles dissolved in solution.
(iv) the nature of solvent particles.

9. Which of the following aqueous solutions should have the highest boiling point?
(i) 1.0 M NaOH
(ii) 1.0 M Na_2SO_4
(iii) 1.0 M NH_4NO_3
(iv) 1.0 M KNO_3

10. The unit of ebulioscopic constant is _______________.
(i) K kg /mol or K $(\text{molality})^{-1}$
(ii) mol kg/ K or $K^{-1}(\text{molality})$
(iii) kg mol^{-1} K^{-1} or $K^{-1}(\text{molality})^{-1}$
(iv) K mol kg^{-1} or K (molality)

11. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is _____________.

(i) the same
(ii) about twice
(iii) about three times
(iv) about six times

12. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because _____________.

(i) it gains water due to osmosis.
(ii) it loses water due to reverse osmosis.
(iii) it gains water due to reverse osmosis.
(iv) it loses water due to osmosis.

13. At a given temperature, osmotic pressure of a concentrated solution of a substance _____________.

(i) is higher than that at a dilute solution.
(ii) is lower than that of a dilute solution.
(iii) is same as that of a dilute solution.
(iv) cannot be compared with osmotic pressure of dilute solution.

14. Which of the following statements is false?

(i) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.

(ii) The osmotic pressure of a solution is given by the equation $\Pi = CRT$ (where C is the molarity of the solution).

(iii) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is $BaCl_2 > KCl > CH_3COOH >$ sucrose.

(iv) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.

15. The values of Van't Hoff factors for KCl, NaCl and K_2SO_4, respectively, are _____________.

(i) 2, 2 and 2
(ii) 2, 2 and 3
(iii) 1, 1 and 2
(iv) 1, 1 and 1

16. Which of the following statements is false?

(i) Units of atmospheric pressure and osmotic pressure are the same.

(ii) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.

(iii) The value of molal depression constant depends on nature of solvent.

(iv) Relative lowering of vapour pressure, is a dimensionless quantity.

17. Value of Henry's constant K_H ____________.

(i) increases with increase in temperature.

(ii) decreases with increase in temperature.
(iii) remains constant.
(iv) first increases then decreases.

18. The value of Henry's constant K_H is _____________.
(i) greater for gases with higher solubility.
(ii) greater for gases with lower solubility.
(iii) constant for all gases.
(iv) not related to the solubility of gases.

19. If two liquids A and B form minimum boiling azeotrope at some specific composition then _______________.
(i) A–B interactions are stronger than those between A–A or B–B.
(ii) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution.
(iii) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution.
(iv) A–B interactions are weaker than those between A–A or B–B.

20. We have three aqueous solutions of NaCl labeled as 'A', 'B' and 'C' with concentrations 0.1M, 0.01M and 0.001M, respectively. The value of van't Hoff factor for these solutions will be in the order______.
(i) $iA < iB < iC$
(ii) $iA > iB > iC$
(iii) $iA = iB = iC$
(iv) $iA < iB > Ic$

Answers:

(i) 2. (iv) 3. (iii) 4. (ii), [Hint : If added substance dissolves, the solution is unsaturated. If it does not dissolve solution is saturated. If precipitation occurs solution is supersaturated.] 5. (iii) 6. (ii), [Hint : Body temperature of human beings remains constant.] 7. (i) 8. (ii) 9. (ii) 10. (i) 11. (iii) 12. (iv) 13. (i) 14. (i) 15. (ii) 16. (ii) 17. (i) 18. (ii) 19. (i) 20. (iii)

FLOW CHART

Expressing Conc of Solution

- Mass Percentage: $w/w = \frac{W_B \times 100}{W_A+W_B}$
- Mass by Vol %: $(W/V) = \frac{W_B \times 100}{V(\text{in ml})}$
- Mole Fraction: $X_A = \frac{n_A}{n_A+n_B}$
- Molality: $m = \frac{n_B}{W_A\ (\text{in Kg})}$
- Volume % (v/ v): $= \frac{V_B \times 100}{V_A+V_B}$
- Parts per million: $(ppm) = \frac{W_B \times 10^6}{W_A+W_B}$
- Molarity: $M = \frac{n_B}{V\ (\text{in L})}$
- Mole Fraction: $X_B=n_B/\ n_A+n_B$

Colligative Properties

- Relative lowering of Vapour Pressure: $\frac{P^\circ_A - P_A}{P^\circ_A} = X_b$
- Elevation in B.P:
  - $\Delta T_b = K_b \times m$
  - $\Delta T_b = T_b - T^\circ_b$
- Depression in F. P:
  - $X_b \Delta T_f = K_f \times m$
  - $P^\circ A \Delta T_f = T_f^\circ - T_f$
- Osmotic Pressure:
  - $\pi = CRT$
  - $\pi = \frac{n_B}{V} RT$

SOLUTIONS

- Ideal Solution
  - i) $P_A = P^o_A X_A$
    - $P_B = P^o_B X_B$
  - ii) $\Delta H=0$
  - iii) $\Delta V=0$
- Non Ideal Solution
  - Positive Deviations
    - (i) $P_A > P^o_A X_A$
      - $P_B > P^o_B X_B$
    - (ii) $\Delta H > O$ (+ve)
    - (iii) $\Delta V > O$ (+ve)
  - Negative Deviations
    - i) $P_A < P^o_A X_A$
      - $P_B < P^o_B X_B$
    - ii) $\Delta H < O$ (-ve)
    - iii) $\Delta V < O$ (-ve)

ELECTROCHEMISTRY (UNIT-2)

KEY POINTS

Resistance – obstacle to the flow of electricity.

Resistivity – resistance offered by the conductor when it is of unit length and has unit area of cross section.

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

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

Second law–when same amount of electricity is passed through different electrolytic solution, amount of substance deposited is proportional to the chemical equivalent weights.

5. Fuel cell– it converts combustion energy of fuel into electricity. H_2 and CH_4 can be used as fuel in it.
6. Corrosion–corrosion of metal is an electrochemical phenomenon.
7. Anode :- $2\,Fe \rightarrow 2Fe^{2+} + 4\,e^-$ (oxidation)

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

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

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

Prevention of corrosion

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

IMPORTANT FORMULAE

S. No	Formula	What to calculate	Another form of the formula
1	$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$	Cell potential of a cell can be calculated by this equation	$E^\circ cell = E^\circ_R - E^\circ_L$
2	$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log 1/[M]$ +[	Cell potential of a half cell can be calculated by this expression	
3	$E_{cell} = E^0_{cell} - \frac{0 \cdot 0591}{n} \log [P]/[R]$	Cell potential of a cell can be calculated by this expression	
4	$E^\circ cell = \frac{0.0591}{n} \log K_c$	To calculate cell potential from Kc and vice versa	$\log K_c = \frac{n \times E^\circ cell}{0.0591}$
5	$\Delta G^\circ = -nF E^\circ_{cell}$	To calculate cell potential from free energy change and vice versa	$E^\circ_{cell} = -\Delta G^\circ / nF$
6	$R = \rho\, {}^{l}/_{A}$	To calculate resistance	$\rho = \frac{R A}{l}$
7	$G^* = R \acute{K}$	To calculate cell constant	$\acute{K} = G/R$
8	$\Lambda_m = \frac{K \times 1000}{M}$	To calculate the molar conductivity	
9	$W = Z \times I \times t$ $Z = E/96500$	Amount of a substance produced at any electrode	
10	$\underline{W1} = W2\ E1\ /E2$	Amount of a substance produced at an electrode of different cells connected in a series	

Frequently asked question

1 Mark

1).What is meant by limiting molar conductivity?

Ans Molar conductivity of an electrolyte at infinite dilution**.**

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

Ans. $\Lambda_m = k(1000\backslash M)$

3.) What is meant by limiting molar conductivity ?

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

4.) What is the unit of molar conductivity?

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

5.) What is the effect of dilution of concentration on specific conductance?

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

6.) What type of metals can be used in cathodic protection of iron against rusting?

Ans. A metal which is more electropositive than iron i.e. having lower reduction potential. Example- Zn, Mg etc.

7. Why mercury cell gives constant voltage throughout its life?

Ans. As the overall reaction does not involve any ion in solution whose conc. can change during its life.

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Current stops flowing when $E_{cell} = 0$.
Reason : Equilibrium of the cell reaction is attained. (Ans - a)

2. Assertion : A standard hydrogen electrode is also called reversible electrode.
Reason : It can act on both as anode as well as cathode in an electrochemical cell. (Ans - a)

3. Assertion : Kohlrausch law helps to find the molar conductivity of weak electrolyte at infinite dilution.
Reason : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally. (Ans - a)

4. Assertion : When a copper wire is dipped in silver nitrate solution, there is no change in the colour of the solution.
Reason : Copper cannot displace silver from its salt solution. (Ans - d)

5. Assertion : Fluorine is the best oxidising agent.
Reason : Fluorine has highest reduction potential. (Ans - a)

One - word answer

1. How much electricity in terms of Faraday is required to produce 100g of Ca from molten $CaCl_2$? (5F)

2. Name the solid substance produced, during the discharge of lead- storage battery. (Ans - Lead sulphate)

2 marks

1. What is fuelcell ? Write two chemicals which can be used as fuel.

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

Methane and hydrogen can be used as fuel $2H_2(g)+4OH^-(aq) \rightarrow 4H_2O(l)+4e^-$

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

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

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

Discharge reaction –

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

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

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

3.) How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of

2.00 A for three hours ?

Molar mass of $Hg(NO_3)_2$= 200.6 g/mol

Ans. Current = 2A

Time = 3h = 3(60)(60)s

w = Zlt

Z for Hg in compound =200.6/2F

w= 200.6x2x(3)(60)(60)/2(96500)

w= 22.45g

number of moles = 22.45\200.6 = 0.112 mol

4.) Represent the galvanic cell in which the following reactions take place

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

i.) Which one of the electrodes is negatively charged ?

ii.) Write the reaction taking place at each of the electrodes.

iii.) Name the carrier of current within the cell.

Ans .The cell is represented as

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

i) Zn electrode is negatively charged

ii) At anode

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

At cathode

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

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

5.) State Faraday's laws. How much charge is required for the reduction of 1 mole of Cu^{2+} to Cu?

Ans. Statements $Cu^{2+} + 2e \rightarrow Cu$

Charge required for the reduction of 1 mole $Cu^{2+} = 2F$

=2(96500 C)

= 193000C

3 marks

1.) Determine the value of equilibrium constant and ΔG^0 for the following reaction :

$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(S)$ ($E^0 = 1.05V$)

Ans. n=2 $\Delta G^0 = -nFE^0$

$\Delta G^0 = -2\ (96500)\ C\ (1.05)\ V$

$\Delta G^0 = -202650\ Jmol^{-1} = -202.65\ kJ\ mol^{-1}$

$-nFE^0 = -2.303 RT \log K_c$

$\log K_c = nE^0/0.0591$

=2(1.05/0.0591) = 35.532 g

K_c = antilog 35.532

$K_c = 3.411 \times 10^{35}$

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

Ans. $E_{cell} = 0.059V$

$E^0Cu = 0.34V$ $[Cu^{+2}] = 0.1M$

$E_{cell} = E^0_{cell} - 0.0591/n \log[Ni^{2+}(aq)]/[Cu^{2+}(aq)]$ $0.059 = E^0cell - 0.059/2 \log(0.01/0.1)$

$0.059 = E^0_{cell} - 0.0295 \log\frac{1}{10}$

$0.059 = E^0_{cell} - 0.0295\ (\log 1 - \log 10)$

$= E^0_{cell} - 0.0295(-1)$ $0.059 = E^0_{cell} + 0.0295$

$E^0_{cell} = 0.05g - 0.0295 = 0.0295V$

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

$0.0295 = 0.34 - E^0_{anode}$

$E^0_{anode} = 0.34 - 0.0295 = 0.3105V$

3) The resistance of conductivity cell filled with 0.1 M KCl solution is 100 Ohm. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02 M KCl solution . Conductivity of 0.1 M KCl solution is 1.29 m^{-1}

Ans. i) Cell constant G = conductivity (resistance)

= 1.29 S m^{-1} (100Ω) 129 m^{-1} or 1.29 cm^{-1}

ii) conductivity of 0.02 M KCl solution

(k) = cell constant /resistance = 1.29 cm^{-1}/520Ω

2.48 x 10^{-3} S cm^{-1}

iii) molar conductivity = k x 1000\M = 2.48 x 10^{-3} x 1000/0.02

= 124S cm^2 mol^{-1}

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

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

Cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ Anode reaction : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$ Overall reaction : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

5 marks questions

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

ii.) The resistance of a conductivity cell containing 0.001M KCl solution at 298K is 1500Ω. What is the cell constant, if the conductivity of 0.01M KCl solution at 298 K is

0.146X (10^{-3}) S cm^{-1} ?

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

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

Cell constant G = k(R)

= 0.146 x 10^{-3} x 1500= 0.219 cm^{-1}

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

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

takes place , identify the cathode and the anode reaction in it.

ii) Write Nernst equation. Calculate the emf of the following cell:

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

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

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

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

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

Cu is acting as anode whereas Ag is acting as cathode

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

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

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

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

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

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

Assignment

1. Calculate the emf of the cell: $Mg|Mg^{2+}(0.001M)||Cu^{2+}(0.0001M)|Cu$

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

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

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

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

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

4. Calculate the potential of the following cell reaction at 298 K. $Sn^{4+}(1.50M) + Zn(s) \rightarrow Sn^{2+}(0.5M) + Zn^{2+}(2.0M)$

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

5. How many moles of electrons are required to

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

(ii) Produce 10.0g of Al from molten Al_2O_3. [**Hints:** (i) 5 mol of electron (ii) 1.11 mol Al]

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

[Hints; Acidic NH_4Cl corrodes the Zinc container]

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

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

[**Hints**: It can be increased by

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

b. by increasing the temperature].

9. Calculate emf of the following cell at 298K $Zn/Zn^{2+}(10^{-4}M)|| Cu^{2+}(10^{-2}M)/Cu$

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

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

11. Explain the meaning of the terms:

(a) Ionic mobility

(b) Over potential

12. What is electrochemical series? List its two characteristics.

13. Account for the following observations:

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

(b) Ordinary dry cells are not rechargeable.

14. Explain the following observations:

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

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

MULTIPLE CHOICE QUESTION (MCQ)

1. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called ___________.
(i) Cell potential
(ii) Cell emf
(iii) Potential difference
(iv) Cell voltage

2. Which of the following statement is not correct about an insert electrode in a cell?
(i) It does not participate in the cell reaction.
(ii) It provides surface either for oxidation or for reduction reaction.
(iii) It provides surface for conduction of electrons.
(iv) It provides surface for redox reaction.

3. An electrochemical cell can behave like an electrolytic cell when ____________.
(i) Ecell = 0
(ii) Ecell > Eext
(iii) Eext > Ecell
(iv) Ecell = Eext

4. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is ___________.
⒞ (i) 1F (ii) 6F (iii) 3F (iv) 2F

5. The cell constant of a conductivity cell _____________.
(i) changes with change of electrolyte.
(ii) changes with change of concentration of electrolyte.
(iii) changes with temperature of electrolyte.
(iv) remains constant for a cell.

6. While charging the lead storage battery ______________.
(i) $PbSO_4$ anode is reduced to Pb.
(ii) $PbSO_4$ cathode is reduced to Pb.
(iii) $PbSO_4$ cathode is oxidised to Pb.
(iv) $PbSO_4$ anode is oxidised to PbO_2.

7. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that ____________. (i) this redox couple is a stronger reducing agent than the H^+/H_2 couple.
(ii) this redox couple is a stronger oxidising agent than H^+/H_2.
(iii) Cu can displace H_2 from acid.
(iv) Cu cannot displace H_2 from acid.

8. Conductivity of an electrolytic solution depends on ____________.
(i) nature of electrolyte.
(ii) concentration of electrolyte.

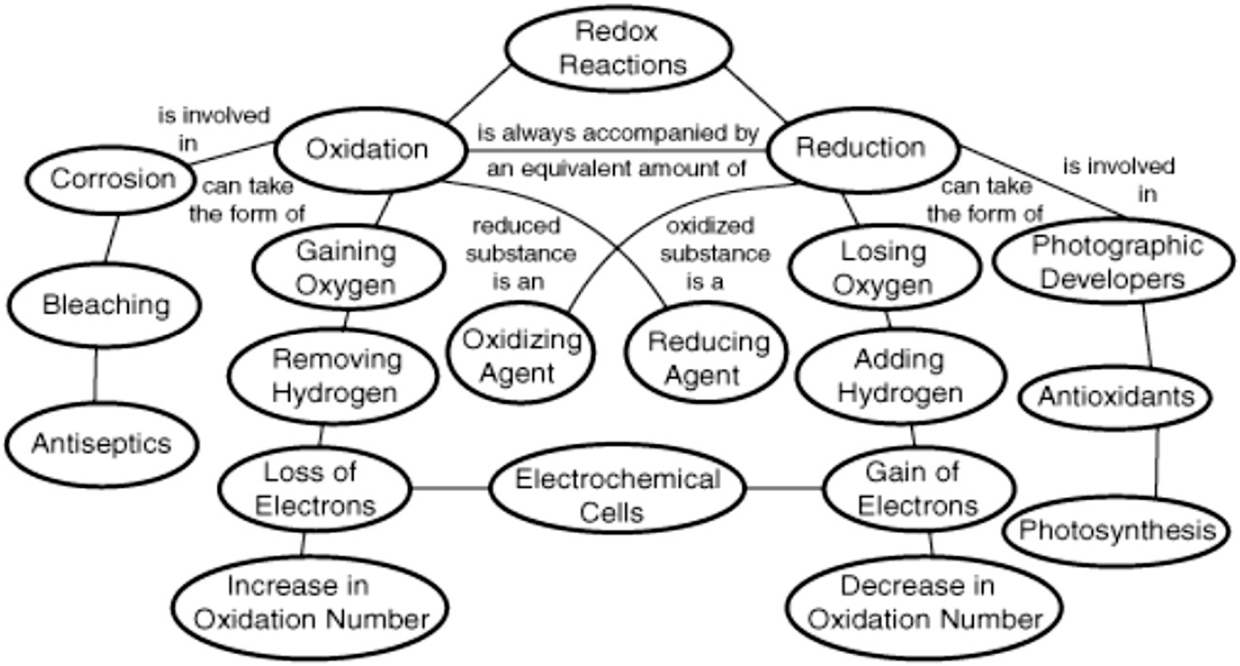
(iii) power of AC source.
(iv) distance between the electrodes.

9. What will happen during the electrolysis of aqueous solution of $CuSO_4$ by using platinum electrodes?
(i) Copper will deposit at cathode.
(ii) Copper will deposit at anode.
(iii) Oxygen will be released at anode.
(iv) Copper will dissolve at anode.

10. What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?
(i) Copper will deposit at cathode.
(ii) Copper will dissolve at anode.
(iii) Oxygen will be released at anode.
(iv) Copper will deposit at anode.
11. Molar conductivity of ionic solution depends on ___________.
(i) temperature.
(ii) distance between electrodes.
(iii) concentration of electrolytes in solution.
(iv) surface area of electrodes.
12. For the given cell, $Mg|Mg^{2+}||Cu^{2+}|Cu$
(i) Mg is cathode
(ii) Cu is cathode
(iii) The cell reaction is $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$
(iv) Cu is the oxidising agent
13. Under what condition is $E_{Cell} = 0$ or $\Delta_rG = 0$?
14. What is electrode potential?
15. Give an example of antirust solution.
Answers:
1. (iii)
2. (iv)
3 (iii)
4. (iii)
5. (iv)
6. (i)
7. (ii), (iv)
8 (i), (ii)
9. (i), (iii)
10. (i), (ii)
11. (i),(iii)

12. (ii,iii)
13.When the cell reaction reaches equilibrium.
14. Tendency to lose and gain electron.
15. Alkaline chromate solution

ELECTROCHEMISTRY MIND MAP



CHEMICAL KINETICS (UNIT- 3)

KEY CONCEPTS

1. Rate of reaction:- For a reaction R → P,

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

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

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

2. Unifying rate of reaction

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

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

Similarly, for the reaction

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

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

3. Differential rate law (Rate law)

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

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

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

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

This is differential rate equation.

Order of reaction:- For the reaction $a\,A + b\,B \rightarrow c\,C + d\,D$ Rate = $K[A]^x[B]^y$

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

Note:-

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

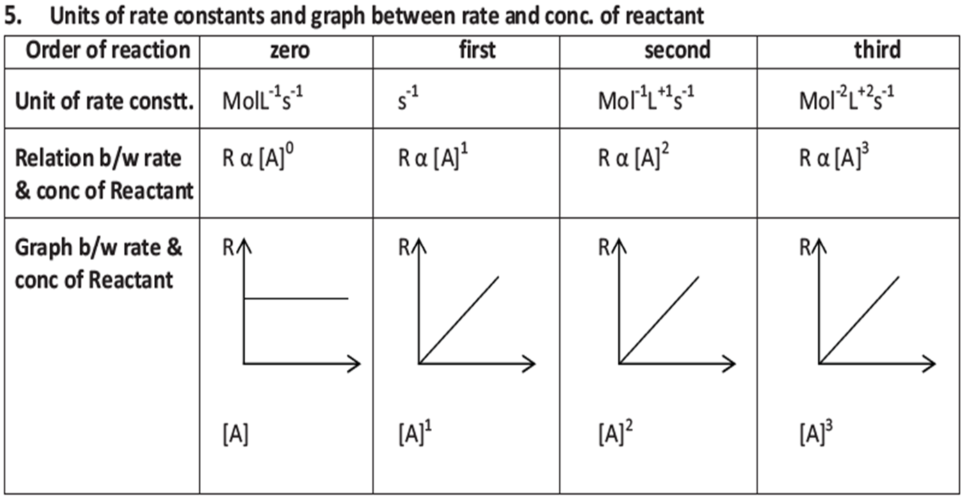
ii. if x + y = 2, reaction is called **II order reaction**.

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

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

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

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



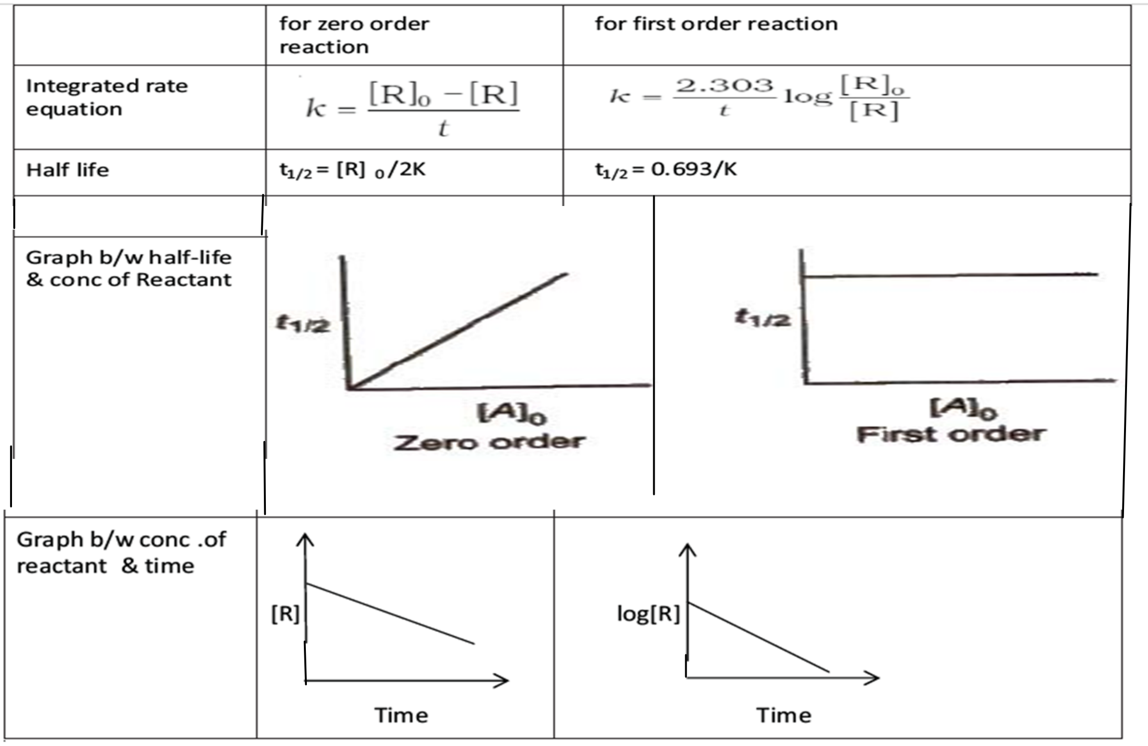
5. Units of rate constants and graph between rate and conc. of reactant

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

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

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

2. For I order reaction $t_{1/2}$ is independent of conc of reactant.
3. t α [conc]$^{1-n}$ $_{1/2}$whe n = order of reaction.



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

7. Arrhenius equation

log K = log A – E_a/2.303RT

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

IMPORTANT DEFINITIONS

1 Pseudo first order reaction:- A bimolecular reaction, in which one reactant is present in large excess and rate of reaction is independent of its concentration. Such a reaction is called pseudo first molecular reaction.

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

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

Types of reaction based on molecularity

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

NOTE:-

i. It is theoretical value.

ii. It cannot be zero or a non integer.

iii. molecularity greater than three is not observed.

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

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

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

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

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

NOTE:-

i. Order of a reaction is an experimental quantity

ii. It can be zero and even a fraction

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

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

Eg. The reaction $2O_3$ ✸ $3O_2$ complete $2O_3 \rightarrow 3O_2$

$O_3 \longrightarrow O_2 + O$ step1 fast reaction

$O + O_3 \longrightarrow 2O_2$ step2 slow reaction

Thus the reaction has two elementary steps.

NOTE:-

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

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

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

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

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

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

8. Examples- Zero order reaction: $H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$

I order reaction : All natural and artificial radioactive reactions.

II order reaction : $H_2 + I_2 \longrightarrow 2HI$.

IMPORTANT QUESTIONS

1 MARK QUESTIONS

Q1. How does catalyst alter rate of a reaction?

Ans. It increases rate of reaction by providing a new path having low activation energy.

Q 2. A reaction is 50% complete in 2 hours and 75% completes in 4 hours. What is the order of the reaction?

Ans . Since half life remains constant so it is a first order reaction.

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

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

Q 4. Define the term : activation energy

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

Q5. What is the unit of rate constant for a Pseudo first order reaction?

Ans s^{-1}

Q6. Give an example of pseudo first order reaction.

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

Q7. The rate constant of a reaction is 0.005 $mol L^{-1} s^{-1}$. What is the order of this reaction?

Ans Zero order reaction

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. **Assertion :** Complex reaction takes place in different steps and the slowest step determines the rate of reaction.
   Reason : Order and molecularity of a reaction are always equal. (Ans - c)
2. Assertion : Rate of reaction increases with increase in temperature.
   Reason : Number of effective collisions increases with increase in temperature. (Ans - a)
3. Assertion : Order of a reaction with respect to any reactant or product can be zero, positive, negative and fractional.
   Reason : Rate of a reaction cannot decrease with increase in concentration of a reactant or product. (Ans - c)
4. Assertion : The rate of a reaction sometimes does not depend on concentration.
   Reason : Lower the activation energy faster is the reaction. (Ans - b)
5. Assertion : For a certain reaction, a large fraction of molecules has energy more than the threshold energy, still the rate of reaction is very slow.
   Reason : The colliding molecules must not be properly oriented for effective collisions. (Ans - a)

One - word answer

1. The magnitude of which parameter changes by the use of a catalyst?
   (Ans - Activation energy)
2. What is the molecularity of pseudo first order reaction ? (Ans - 2)

2 MARKS QUESTIONS

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

Ans Rate = – change in conc. of A/2 x time interval
= – [0.4-0.5]/2X10 = 0.005 mol $litre^{-1} min^{-1}$

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

Ans Given = 60 s^{-1}, $[R]_0$ =1, [R]=1/16, t = ?
t = 2.303/k $\log[R]_0/[R]$
= 2.303/60 log 16 = 3.84X10^{-2} s

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

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

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

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

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

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

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

3 MARKS QUESTIONS

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

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

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

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

$= 2.303/t \log 10^3$

$t = 6.909/k$

For half-life of the reaction $t_{1/2} = 0.693/k$

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

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

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

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

$E_a = 18230.8J$

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

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

$A = 1.61$

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

Ans Given t =40min, $[R]_0 = 100$, $[R]=100-30=70$

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

$= 2.303/40 \log 100/70$

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

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

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

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

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

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

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

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

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

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

Therefore,

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

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

iii) rate constant for the reaction K = Rate/$[A]^1 [B]^2$

$= 6.0 \times 10^{-3} / /[0.1]^1 [0.1]^2 = 6.0\ mol^{-2}L^2s^{-1}$.

5 MARKS QUESTIONS

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

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

(i) Write the differential rate equation.

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

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

Ans (a) Given $t_{1/2}$ = 5730 years, $[R]_o$=100, [R]=80

$K = 0.693/t_{1/2} = 0.693/5730 = 1.21X10^{-4}\ year^{-1}$

$t = 2.303/K \log [R]_o/[R] = 2.303/1.21X10\ \ \log 100/80 = 1.9033X10^{-4} (\log 100 - \log 80)$

$= 1.9033X\ 10^{-4}$ (2-1.9031) = $1.9033X\ 10^{-4}$ (0.0969) = 1845 year

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

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

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

ASSIGNMENTS

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

Q2. Define collision frequency. 1

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

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

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

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

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

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

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

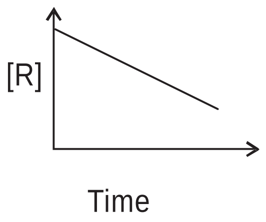
Q10. For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data are obtained. 5

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

Calculate the rate constant.

HOTS QUESTION

1 Consider the reaction R → P. the change in concentration of R with time is shown in the following plot :



I. Predict the order of reaction

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

iii. What does the slope of the above line indicate?

MCQ

1. The role of a catalyst is to change ______________.
(i) Gibbs energy of reaction. (ii) enthalpy of reaction. (iii) activation energy of reaction. (iv) equilibrium constant.

2. In the presence of a catalyst, the heat evolved or absorbed during the reaction ___________.
(i) increases. (ii) decreases. (iii) remains unchanged. (iv) may increase or decrease

3.Which of the following statements is not correct about order of a reaction.

(i) The order of a reaction can be a fractional number.
(ii) Order of a reaction is experimentally determined quantity.
(iii) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
(iv) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

4. Which of the following statements is correct?
(i) The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
(ii) The rate of a reaction is same at any time during the reaction.
(iii) The rate of a reaction is independent of temperature change.
(iv) The rate of a reaction decreases with increase in concentration of reactant(s).

5.A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?
(i) 1.26×10^{15} s (ii) 2.52×10^{14} s (iii) 2.52×10^{28} s (iv) infinite

6. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be Rate = k [A][B]. Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be______.
(i) the same (ii) doubled (iii) quadrupled (iv) halved

7. Which of the following statements is incorrect about the collision theory of chemical reaction?
(i) It considers reacting molecules or atoms to be hard spheres and ignores their structural features.
(ii) Number of effective collision determines the rate of reaction.
(iii) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.
(iv) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

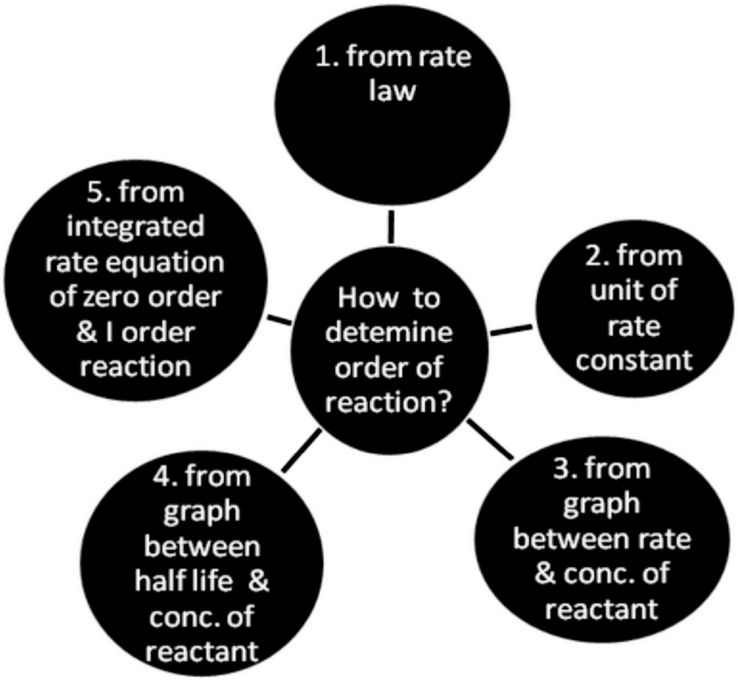
8. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?
(i) Order is same as molecularity.
(ii) Order is less than the molecularity.
(iii) Order is greater than the molecularity.
(iv) Molecularity can never be zero.

9. In any unimolecular reaction ______________.
(i) only one reacting species is involved in the rate determining step.
(ii) the order and the molecularity of slowest step are equal to one.
(iii) the molecularity of the reaction is one and order is zero.
(iv) both molecularity and order of the reaction are one.

10. For a complex reaction ______________.
(i) order of overall reaction is same as molecularity of the slowest step.
(ii) order of overall reaction is less than the molecularity of the slowest step.
(iii) order of overall reaction is greater than molecularity of the slowest step.
(iv) molecularity of the slowest step is never zero or non interger.

ANSWER KEY:1.(iii) 2.(iii) 3.(iii) 4.(i) 5.(ii) 6.(iii) 7.(iii) 8.(i),(iv) 9.(i),(ii) 10.(i),(iv)

MIND MAP



SURFACE CHEMISTRY (UNIT 4)

KEY POINTS

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

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

Also movement of the particles are restricted in this process. Therefore $\Delta S = -ve$ According to Gibbs Helmholtz equation : $\Delta G = \Delta H - T\Delta S$, or $\Delta G = (-\Delta H) - T(-\Delta S)$

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

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

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

Characteristics of physical adsorption: Lack of specificity, low enthalpy of adsorption, reversible in nature, no activation energy required, decrease with increase in temperature .

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

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

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

(Its a plot/curve between extent of adsorption(x/m) and pressure P at constant T).

Freundlich adsorption Isotherm

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

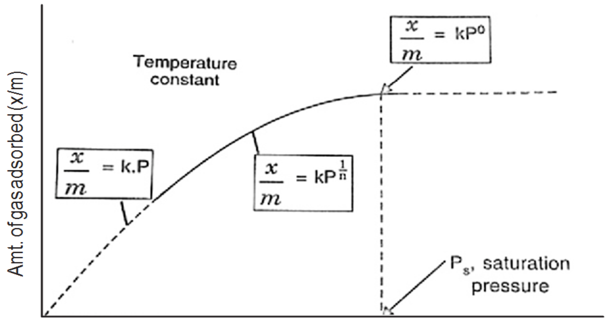
$\log x/m = \log k + 1/n \log P$

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

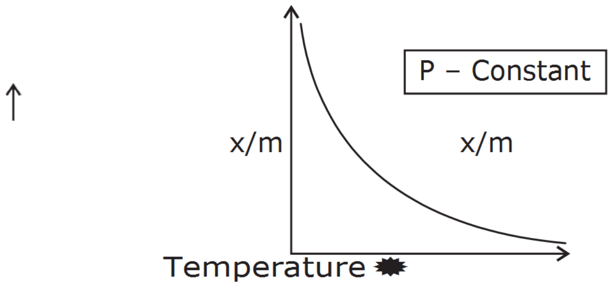
When $1/n=0$, x/m = constant which shows that adsorption is independent of pressure.

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

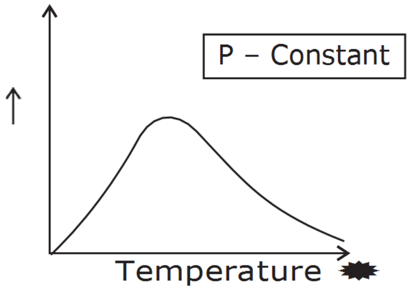
- The variation in the amount of gas adsorbed by the adsorbent with temperature at constant pressure can be expressed by means of a curve termed as adsorption isobar.



Adsorption isotherm in term of Freundlich.



Physical adsorption



Chemical adsorption

Factors Affecting adsorption

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

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

Extent of adsorption (x/m) α 1/T.

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

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

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

APPLICATIONS OF ADSORPTION:

(a) Gas masks
(b) Production of high vacuum
(c) Humidity control
(d) Removal of colouring matter from solutions
(e) Heterogeneous catalysis
(f) Separation of inert gases
(g) Softening of hard water
(h) De-ionization of water

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

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

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

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

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

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

FEATURES OF SOLID CATALYSTS-

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

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

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

$$CO(g) + 3H_2\,(g) \xrightarrow{\boxed{Ni}} CH_4 + H_2O$$

$$CO(g) + 2H_2(g) \xrightarrow{\boxed{Cu/ZnO\text{-}Cr_2O_3}} CH_3OH(g)$$

$$CO(g) + H_2(g) \xrightarrow{\boxed{Cu}} HCHO$$

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

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

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

COLLOIDAL STATE

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

Classification is based on following criteria

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

Dispersion phase {DP} and Dispersion medium {DM}

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

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

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

Classification based on type of particles of the dispersed phase

- **Multimolecular colloids:** Consists of aggregates of a large number of atoms or whose diameter is less than 1 nm. Ex Au sol
- **Macromolecular colloids:** In these colloids the molecules have sizes and dimensions to colloidal particles. Ex: proteins, starch, cellulose.
- **Associated colloids:** At low concentrations, behave as normal, strong electrolytes and at higher concentrations exhibit colloidal state properties due to the formation of aggregated particles (micelles). eg Soaps and detergents
- The temperature only above which the formation of micelles takes place is called **Kraft temperature (T_K) .**
- **Critical Micelle Concentration:** The concentration above which micelle formation takes place is

Preparation of Lyophobic sols

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

$SO_2 + 2H_2S \rightarrow 3S\ (sol) + 2H_2O$

- **Reduction :** Silver colloids are prepared by passing H_2 through a saturated aqueous solution of silver oxide at

65° C.

- **Hydrolysis :** Dark brown $Fe(OH)_3$ colloidal solution is prepared by adding $FeCl_3$ into boiling water**.** $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$
- **Double decomposition :** Arsenious sulphide colloidal solution is prepared by passing of H_2S gas into a solution of As_2O_3.
- **Exchange of solvent :** Colloidal solution of phosphorus is prepared by addition of alcohol into **a** solution phosphorous in excess water.
- **Dispersion methods & Mechanical disintegration**
- **Peptisation :** Process of converting of a fresh precipitate into colloidal particles by adding suitable electrolyte is known as peptisation.

e.g. $Fe(OH)_3$ solution is formed from $FeCl_3$.

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

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

Properties of colloids:

- **Optical properties: Tyndall effect :** Due to scattering of light by colloidal particles by which the beam of light becomes visible.
- **Brownian movement:** Zig- zag movement of colloidal particles due to collision between particles of DP & DM, responsible for stability of colloids.
- **Electrophoresis:** Movement of colloidal particles under influence of electric field**.**
- **Electro-osmosis:** molecules of dispersion medium allowed to move under influence of electic fileld
- **Coagulation or flocculation:** Process of settling of colloidal particles into precipitate or float on surface by addition of electrolytes.

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

For negatively charged sol, the coagulating power of electrolytes are:

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

For positively charged, then the coagulating power of electrolytes follow the following order:

$K_4[Fe(CN)_6] > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

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

. **Types of emulsions:**

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

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

(a) Rubber plating (b) Sewage disposal (c) Smoke screen

(d) Purification of water (e) Cleaning action of soap (f) In medicine

(h) Photography (i) Artificial rain (g) Formation of delta

FREQUENTLY ASKED QUESTIONS

Very short answer type questions (1 mark each)

Q1.What is the sign of ΔH and ΔS for adsorption of bromine on charcoal?

Ans. Both ΔH and ΔS are negative.

Q2. Why are substances like platinum and palladium often used for carrying out electrolysis of aqueous solutions?

A2. Platinum and palladium are inert materials & are not attacked by the ions of the electrolyte or the products of electrolysis therefore used as electrodes for carrying out the electrolysis.

Q3. Why does physisorption decreases with the increase of temperature?

A3. Physisorption is an exothermic process i.e, heat is produced in the process.

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

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

Q4). Why is it necessary to remove CO when ammonia is obtained by Haber's process?

A4). CO acts as a poison for the catalyst in the manufacture of ammonia by Haber's process**.**

Q5) What is the physical states of dispersed phase and dispersion medium of froth?

A5. Dispersed phase is gas, dispersion medium is liquid.

Q 6. What is shape selective catalysis?

A 6. It is the catalytic reaction that depends upon the pore structure of the catalyst and size of the reactant and product molecules.

Q7. Why lyophilic colloids are more stable than lyophobic colloids?

A 7. Due to (i) solvation (ii) charge on the colloidal particles .

Q8) What is the cause of Brownian movement among colloidal particles?

A8 Due to unequal collision between particles of dispersed phase and dispersion medium.

Q9) Write the main reason for the stability of colloidal sols.

A9. Brownian movement / charge on colloidal particles.

Q10) Give an example of micelle system?

A10. Sodium stearate ($C_{17}H_{35}COO^-Na^+$).

Q11) Write down the example of positively charged sol?

A11. Ferric hydroxide sol**.**

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

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

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

(c) Assertion is true but reason is false.

(d) Both assertion and reason are false.

1. Assertion : A colloidal sol scatters light but a true solution does not.

Reason : The particles in a colloidal sol move slowly than in a true solution. (Ans - b)

2. Assertion : Activation energy for both the forward and backward reactions is lowered to the same extent by a catalyst.

Reason : A reaction cannot become fast by itself unless a catalyst is added. (Ans - c)

3. Assertion : Hydrolysis of ester is an example of auto - catalytic reaction.

Reason : A catalyst speeds up the process without participating in the mechanism. (Ans - c)

4. Assertion : Hydrated ferric oxide can be easily coagulated by sodium phosphate in comparison to KCl.

Reason : Phosphate ions has higher negative charge than chloride ions. Hence, they are more effective for coagulation. (Ans - a)

5. Assertion : During preparation of ice - cream, gelatin is added in it.

Reason : Ice -creams are emulsions which get stabilised by gelatin as it acts as an emulsifying agent. (Ans - a)

One - word Answer

1. Which phenomenon is responsible for formation of delta? (Ans - Coagulation)
2. Name a cheap material useful for causing artificial rain ? (Ans - Electrified sand)

SHORT ANSWER QUESTIONS (2 marks each)

Q9). Explain what is observed

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

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

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

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

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

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

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

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

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

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

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

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

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

Q13) Differentiate between lyophilic colloids and lyophobic colloids?

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

SHORT ANSWER QUESTIONS

(3 MARKS EACH)

Q14) Account for the following:

(i) What is colloidion?

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

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

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

(ii) Alum coagulates colloidal impurities present in water.

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

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

(ii) What is electrophoresis due to ?

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

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

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

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

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

(i) An aerosol **(ii) A hydrosol** **(iii) An emulsion A16.** (i) An aerosol is a colloidal dispersion of liquid in a gas, eg, fog

(ii) A hydrosol is a colloidal sol. of a solid in water as the dispersion medium, eg, starch sol.
(iii) An emulsion is a colloidal system with dispersed phase as well as dispersion medium as liquids, eg, oil in water.

Q17) Account for the following:

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

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

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

A17. (i) Minimum quantity of an electrolyte required to cause precipitation of a sol is called its coagulating value. Greater the charge and smaller the amount of electrolyte required for precipitation higher is the coagulating power of electrolyte.
(ii) River water is a colloidal sol. of clay and sea water contains a lot of electrolytes . Coagulation takes place at the meeting place of sea and river water the coagulated clay forms delta.
(iii) Chemisorption involves formation of bonds for which activation energy is required**.**

LONG ANSWER QUESTIONS

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

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

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

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

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

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

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

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

A19. (i) Kraft temperature- a particular temperature only above which formation of micelles takes place.
(ii) Zeta potential- it is the potential difference between the fixed and diffused layer of opposite charges around the colloidal particles.

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

b. $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

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

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ASSIGNMENT

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

(i) micelles (ii) peptization (iii) desorption (b) Explain what is observed when,

(i) an electric current is passed through As_2S_3 sol

(ii) a beam of light is passed through a sol.

7. “Chemisorption is highly specific.” Illustrate with an example.
8. “Adsorbents in finely divided form are more effective.” Why?
9. Name two compounds used as adsorbent for controlling humidity.
10. Name the catalyst used in the following process :

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

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

11. What happens:

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

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

12. Suggest a mechanism of enzyme catalysed reaction along with the diagram.
13. Diffrentiate between(a) catalysts and enzymes

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

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

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

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

MCQ ON SURFACE CHEMISTRY

1. In Freundlich Adsorption isotherm, the value of 1/n is

a)1 in case of physical adsorption

b)1 in case of chemisorption

C)Between 0 and 1 in all cases

d)Between 2 and 4 in all cases

2. Which one of the following statement is incorrect about enzyme catalysis?
a) Enzymes are denaturated by ultraviolet rays and at high temperature
b) Enzymes are least reactive at optimum temperature
c) Enzymes are mostly proteinous in nature
d) Enzyme action is specific
3. The protecting power of lyophilic colloidal sol is expressed in terms of
a) Critical miscelle concentration
b) Oxidation number
c) Coagulation value
d) Gold number
4. Which one of the following is an example for homogenous catalysis?
a) Hydrogenation of oil
b) Manufacture of ammonia by Haber's process
c) Manufacture of sulphuric acid by Contact process
d) Hydrolysis of sucrose in presence of dilute hydrochloric acid
5.Which one of the following does not involve coagulation?
a) Peptization
b) Formation of delta regions
c) Treatment of drinking water by potash alum
d) Clotting of blood by the use of ferric chloride
6. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is
(a) Na_2SO_4
(b) $CaCl_2$
(c) $Al_2(SO_4)_3$
(d) NH_4Cl
7. Which of the following statements is incorrect regarding physisorption?
(a) It occurs because of van der Waals forces
(b) More easily liquefiable gases are adsorbed readily
© Under high pressure it results into multimolecular layer on adsorbent surface
(d) Enthalpy of adsorption (ΔH adsorption) is low and positive
8.Rate of physical adsorption increase with
(a) increase in temperature
(b) decrease in pressure
© decrease in temperature
(d) decrease in surface area
9.Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005 respectively. The correct order of their protective powers is
(a)B < D < A < C
(b)D < A < C < B
© C < B < D < A

(d)A < C < B < D

10.The Langmuir adsorption isotherm is deduced using the assumption

(a) The adsorbed molecules interact with each other.

(b) The adsorption takes place in multilayers.

© The adsorption sites are equivalent in their ability to adsorb the particles.

(d) The heat of adsorption varies with coverage.

11.A plot of log x/m versus log p for the adsorption of a gas on a solid gives a straight line with slope equal to

(a) N

(b) 1/n

© log K

(d) - log K

12. In Langmuir's model of adsorption of a gas on a solid surface

(a) the adsorption at a single site on the surface may involve multiple molecules at the same time.

(b) the mass of gas striking a given area of surface is proportional to the pressure of the gas.

© the mass of gas striking a given area of surface is independent of the pressure of the gas.

(d) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered.

13.Which of the following electrolyte will have maximum flocculation value for $Fe(OH)_3$ sol?

(a) Na_2S

(b) $(NH_4)_3PO_4$

© K_2SO_4

(d) NaCl

14. Which one of the followings forms micelles in aqueous solution above certain concentration?

(a) Dodecyl trimethyl ammonium chloride

(b) Glucose

© Urea

(d) Pyridinium chloride

15.During the adsorption of Krypton on activated charcoal at low temperature

A $\Delta H < 0$ and $\Delta S < 0$

B $\Delta H > 0$ and $\Delta S < 0$

C $\Delta H > 0$ and $\Delta S > 0$

D $\Delta H < 0$ and $\Delta S > 0$

16.The basic principle of Cottrell's precipitator is

A Le-Chatelier's principle

B Peptisation

C neutralisation of charge on colloidal particles

D scattering of light

17.The colour of sky is due to

A absorption of light by atmospheric gases

B wavelength of scattered light

C transmission of light

D All of these

18. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is

A $CH_3(CH_2)_{15}N+(CH_3)_3Br-$

B $CH_3(CH_2)_{11}OSO_3-Na+$

C $CH_3(CH_2)_{16}COO-Na+$

D $CH_3(CH_2)_{11}N+(CH_3)_3Br-$

19. $2SO_2(g) \overset{V_2O_5}{\rightleftharpoons}$ is an example for

A irreversible reaction

B heterogenous catalysis

C homogenous catalyst

D neutralization reaction

20. When a sulphur sol is evaporated sulphur is obtained. On mixing with water sulphur sol is not formed. The sol is

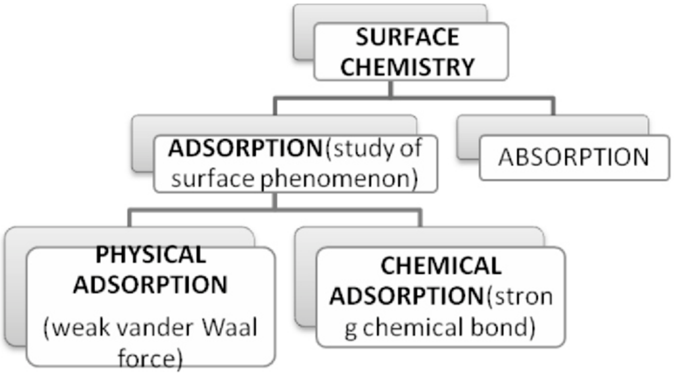
A Reversible

B Hydrophobic

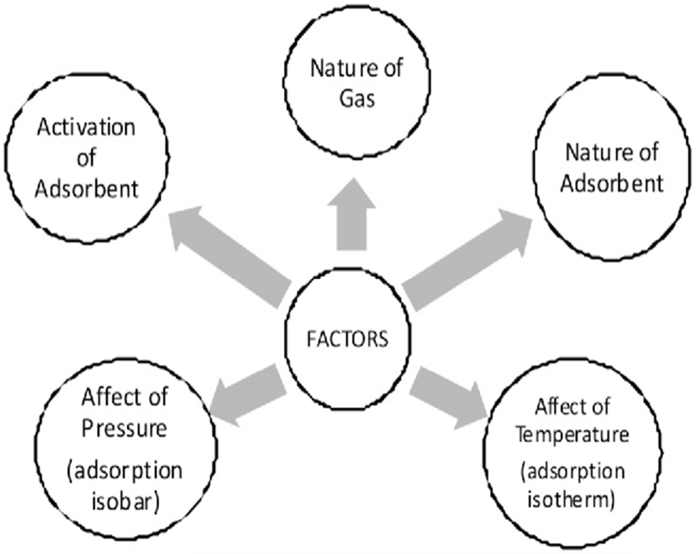
C Hydrophilic

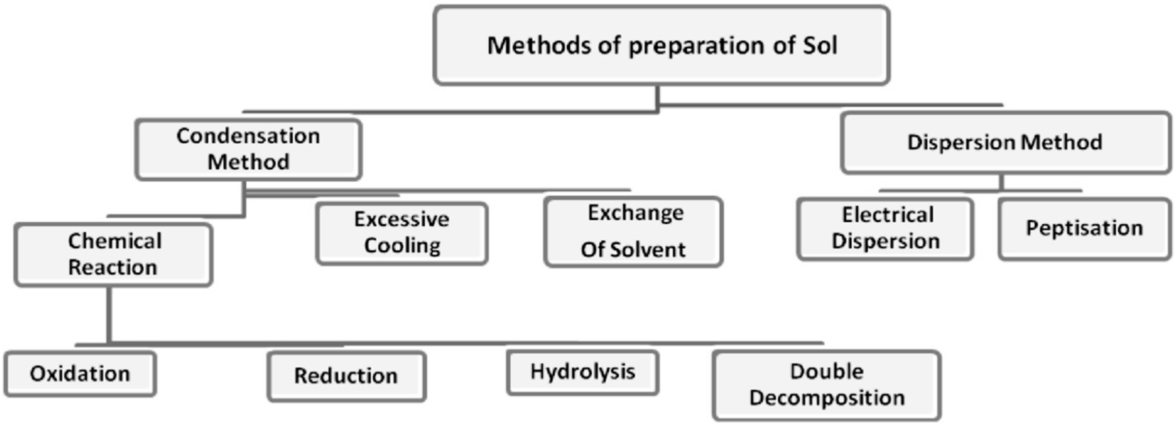
D Lyophilic

ANSWERS
1.C 2.B 3.D 4.D 5.A 6.C 7.D 8.C 9.D 10.C 11.B 12.B 13.D 14.A 15.A 16.C 17.B 18.(C) 19.B 20.B



FACTORS AFFECTING ADSORPTION OF GASES ON SOLIDS





Classification of Colloids

- a) Based on Physical State
  - Solid + Solid = Solid Sol
  - Solid + Liquid = Sol
  - Solid + Gas = Aerosol
  - Liquid + Solid = Gel
  - Liquid + Liquid = Emulsion
- B) Based on Interaction of Dispersed Phase & Dispersion Medium
  - Lyophilic Colloid
  - Lyophilic Colloid
- C) Based on Types of Particles of Dispersed Phase
  - Macromolecular
  - Multimolecular
  - Associated

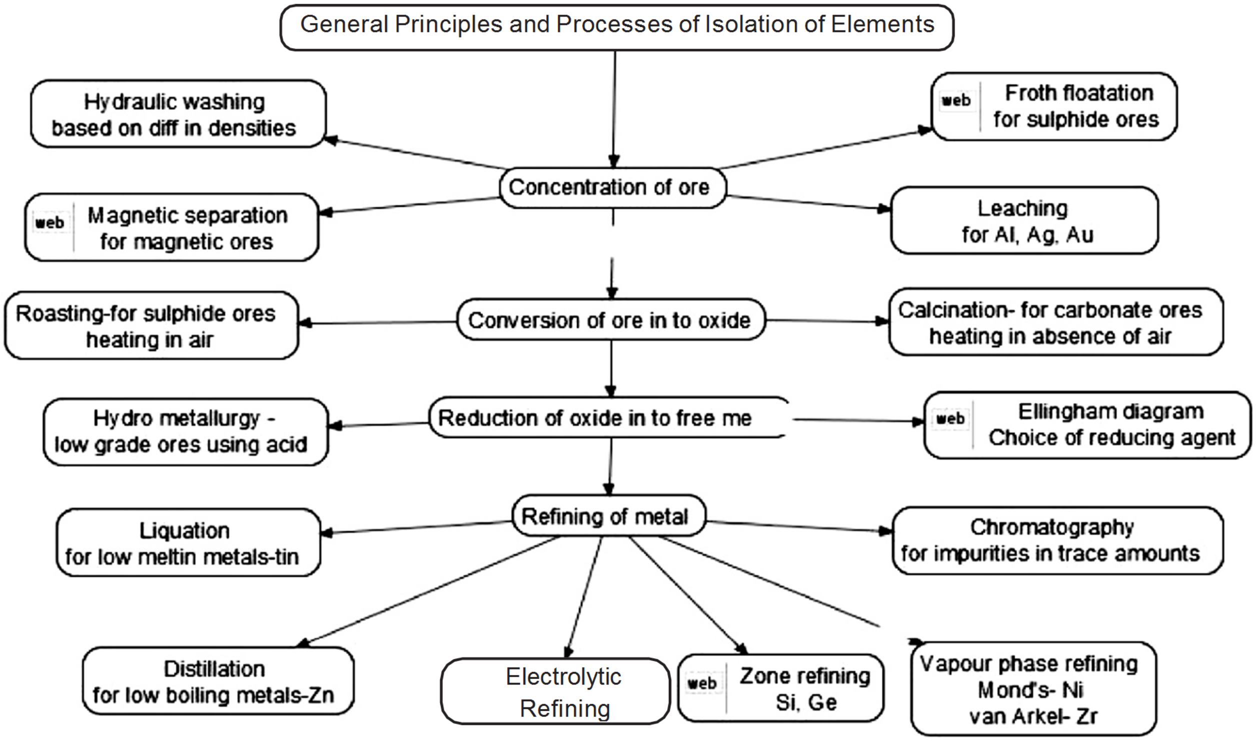
Properties of Colloids

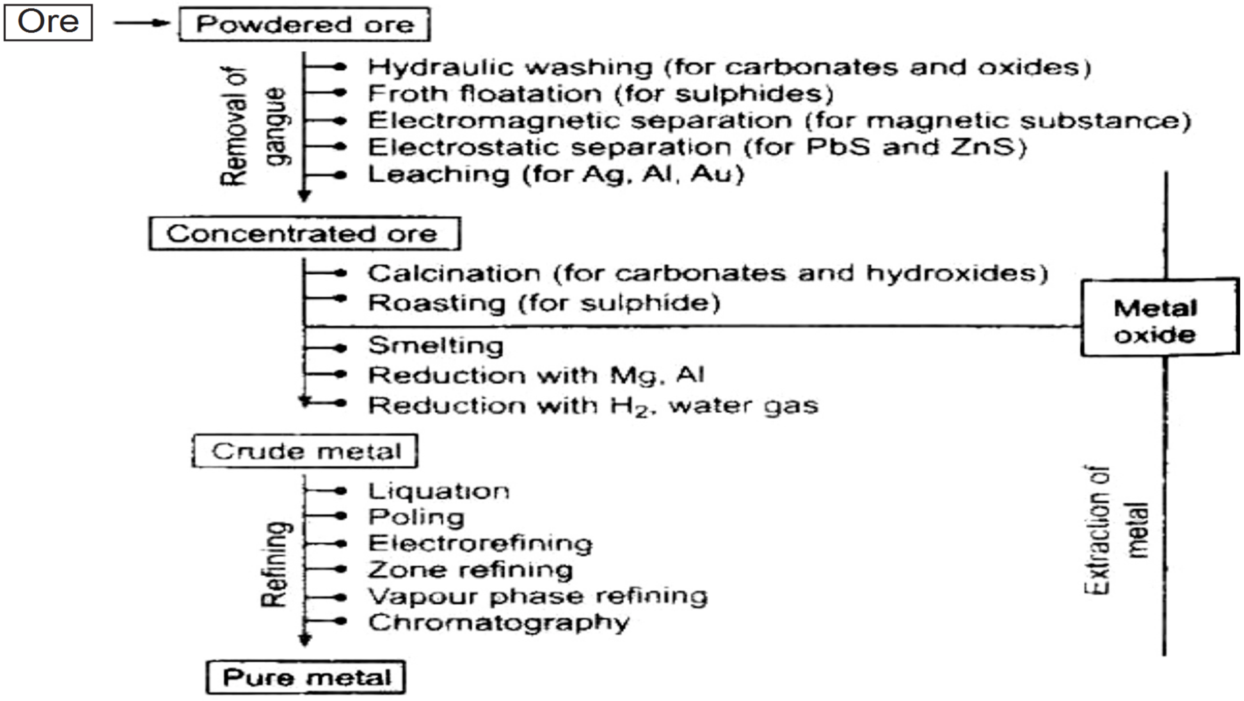
- Tyndall effect : scattering of light, path of light visible.
- Show Colligative properties:
- Brownian movement : Zig Zag movement of particles
- Charge on the colloidal particles due to prefrential adsorption of ions, nature of charge is same on all particles
- Electrophoresis: movement of colloidal particles towards oppositely charged electrode in presence of external field.
- Electro-osmosis: movement of particles of dispersion medium in applied electric field.
- Coagulation : Process of setting of colloidal particles

Purification of colloidal solution

- DIALYSIS : Process of removing impurities by using semi permeable membrane.
- ULTRA FILTRATION : using special filters which are permeable to all ionic substances except colloidal particles
- ELECTRODIALYSIS: when dialysis is carried out with an electric field applied.

GENERAL PRINCIPLES AND PROCESS OF ISOLATION OF ELEMENTS (UNIT- 5)





FLOW SHEET FOR EXTRACTION OF IRON:-

Iron ore(Magnetite Fe_3O_4)(Haematite Fe_2O_3)

Concentration is done by Gravity separation followed by magnetic separation

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

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

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

FLOW SHEET FOR EXTRACTION OF ALUMINIUM:-

Bauxite, $Al_2O_3.2H_2O$

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

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

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

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

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

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

By this process 98.8% pure Aluminum is obtained.

VERY SHORT ANSWER TYPE QUESTION

Q.1. What is slag? **(1 mark)**

A.1. It is easily fusible material, which is formed when gangue still present in roasted ore combines with the flux. e.g. CaO (flux) + SiO_2 (gangue) → $CaSiO_3$ (slag)

Q.2.Name the metals which can be refined by zone refining.

A3.Silicon, Germanium, Gallium.

Q.3.What is the principle of chromatography?

A3. It is based on adsorption

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

A.4. Graphite rods act as anode, are attacked by oxygen to form CO_2 and sois replaced from time to time.

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

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

Q.6. What are depressants?

A.6. It is possible to separate two sulphide ore by adjusting proportion of oil to water in froth flotation process by using a substance known as depressant.e.g. NaCN is used to separate ZnS and PbS.

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

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

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

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

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

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

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

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

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below.

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Copper is obtained during extraction from cuprous oxide, is called blister copper.
Reason : It has shining surface like blister. (Ans - c)

2. Assertion : Carbon and hydrogen are good reducing agents but they are not used to reduce metal oxides at high temperature.
Reason : They react with metals to form carbides and hydrides at high temperature.
(Ans - a)

3. Assertion : Sulphide ores are converted to oxides before reduction.
Reason : Sulphides can not be reduced easily while oxides can be easily reduced.
(Ans - a)

One - word answer

1. Name a method used for refining Indium. (Ans - Zone refining)
2. Name the method of extraction of low - grade copper . (Ans - Hydrometallurgy)

SHORT ANSWER TYPE QUESTION

Q.1 Describe the method of refining of nickel.

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

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

At 450–470K : $Ni(CO)_4 \longrightarrow Ni + 4CO$

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

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

In this method, a rod of impure metal is moved slowly over circular heater. The portion of the metal being heated melts & forms the molten zone. As this portion of the rod moves out of heater, it solidifies while the impurities pass into molten zone. The process is repeated to obtain ultrapure metal and end of rod containing impure metal is cut off.

Q .3 Write the principle of electro-refining.

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

At Cathode :- $Cu^{2+} + 2e^- \longrightarrow Cu$

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

Q. 4 Write difference between calcination and roasting.

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

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

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

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

Q.6 Explain the role of –(i) CO in the purification of Nickel (ii) SiO_2 in the extraction of copper from copper matte.

A6.(i) It forms a volatile complex with Ni while impurities do not.

(ii)It remove the impurities FeO to form $FeSiO_3$ which is removed as slag .

SHORT ANSWER TYPE QUESTION

(3 marks)

Q.1 Explain the following:-

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

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

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

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

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

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

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

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

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

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

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

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

$Fe_2O_3\ x\ H_2O \rightarrow Fe_2O_3 + xH_2O$.

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

iv) Smelting of roasted ore: A mixture of ore, coke & $CaCO_3$ is smelted in long BLAST FURNACE.

Following reaction takes place at different temperature zones :-

i) Zone of reduction:- Temperature range 250°C–700°C $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$

$FeO + CO \longrightarrow Fe + CO_2$

ii) Zone of slag formation:- Temperature range 800°C – 1000°C $CaCO_3 \longrightarrow CaO + CO_2$

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

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

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

$$CO_2 + C \longrightarrow 2CO$$

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

$$C + O_2 \longrightarrow CO_2$$

Thus, Pig iron is obtained from blast furnace.

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

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

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

Extraction from Bauxite ore involves the following two stages :-

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

ii) Electrolysis of pure alumina in molten cryolite

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

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$ and impurities of Fe_2O_3. TiO_2 & SiO_2 are removed Na $[Al(OH)_4]$, then reacts with CO_2 then pure Alumina is obtained.

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

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

At cathode: $Al^{3+} + 3e^- \longrightarrow Al$,

At anode : $2O^{2-} \longrightarrow O_2 + \boxed{2e^-}$

By this process 98.8% pure Aluminum is obtained.

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

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

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

ASSIGNMENT

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

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

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

Q4 Why copper *matte* is put in silica lined converter?

Q5 What is the role of cryolite in the metallurgy of aluminium?

Q6 Out of C and CO, which is a better reducing agent for ZnO ?

Q .The iron pillar near Qutab Minar in Delhi is made up of wrought iron. This iron pillar was made around 400 BC by the Indian iron workers. Though wrought iron rust slowely with time but the Indian iron workers have developed a process which prevented the wrought iron pillar from rusting even after thousands of years. The rusting has been prevented because of the formation of a thin film of magnetic oxide of iron on the surface as a result of finishing treatment given to the pillar, painting it with a mixture of different salts, then heating and quenching(rapid cooling). The iron pillar is 8m high and 600kg in weight. This iron pillar stands in good condition more than 200 years after it was made. The iron pillar at Delhi is a wonder of ancient Indian metallurgy. It tells us that ancient Indians had good knowledge of metals and their alloys

(i) What is an alloy?

(ii) Name two alloys of iron.

(iii) How is an alloy made?

(iv) What are the constituents of stainless steel?

(v) Name any 2 properties of alloys which are different from the properties of the constituent metals.

Answer)

(i) An alloy is a homogeneous mixture of two or more metals (or a metal and small amount of non metals)

(ii) Steel and stainless steel.

(iii) An alloy is prepared by mixing the various metals in molten state in required proportions, and then cooling their mixture to the room temperature.

(iv) Stainless steel is an alloy of iron, chromium and nickel.

(V) a. Alloys are harder and stronger than the metals from which they are made.

b. Alloys are more resistant to corrosion.

MULTIPLE CHOICE QUESTIONS (MCQ) (1 Mark)

1-What is the role of Zinc metal in the extraction of Silver.

(i) As Oxidising agent (ii) As Reducing agent (iii) Both of them (iv) None of them

1-Ans.(ii)

2-Name the method that is used for the refining of Nickel

(i)Mond's Process (ii) Electrolytic Refining (iii) Zone Refining (iv) All of them

2-Ans.(i)

3- Which reducing agent is employed to get copper from leached low grade copper ore.

(i)N_2 (ii) H_2 (iii) Coke (iv) CO

3-Ans.(ii)

4-Name the depressant which is used to separate ZnS and PbS ores in froth flotation process.

(i) NaCN (ii) NaOH (iii) NaCl (iv) KCl

4-Ans.(i)

5-Silica is used as a flux in the extraction of Metals which is an example of

(i)Basic (ii) Neutral (iii) Acidic (iv) Amphoteric

5-Ans.(iii)

6- What name is given to Carbon Reduction process for extracting the metal.

(i)Roasting (ii) Calcination (iii) Electrolytic (iv) Smelting

6-Ans.(iv)

7-Which process is generally used for the concentration of sulphide ores

(i)Hydraulic Washing (ii) Magnetic Separation (iii) Froth Flotation (iv) Distillation

7-Ans.(iii)

8-Which metal is obtained by reacting the ore with dilute sodium cyanide solution.

(i)Gold (ii) Silver (iii) Iron (iv) Gold

8-Ans.(ii)

9-Which one of the purest form of commercial iron

(i)Pig Iron (ii) Steel (iii) Wrought Iron (iv) None of them

9-Ans.(iii)

10-Name the process by which an ore of tin containing $FeCr_2O_4$ is concentrated.

(i)Magnetic Separation (ii) Liquation (iii) Froth Floatation (iv) Leaching

10-Ans.(i)

P-Block Elements (UNIT- 6)

The general valence shell electronic configuration of p-block elements-$ns^2\ np^{1-6}$

Group-16thELEMENTS

KEY POINTS :-

1. O,S,Se,Te and Po are present in G-16th Their general electronic conf. of last shell is ns^2, np^4.
2. Atomic and ionic radii increases down the group while ionization enthalpy and electro-negativity decreases with increase in atomic number.
3. Because of compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative up to polonium..
4. Members of group 16 show oxidation number -2, +2, +4 and +6. But oxygen shows +1 state in O_2F_2.
5. They make MO_2 and MO_3 type oxides. SO_2 is reducing agent whereas TeO_2 is oxidizing agent.
6. O_2 is gas and other elements are solid.
7. O_2 and S_2 in vapour state are paramagnetic.
8. **CONTACT PROCESS OF MANUFACTURE OF SULPHURIC ACID:-**

$S + O_2 \longrightarrow SO_2\ (g)$

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (Catalyst-V_2O_5) $\Delta H = -196.6$ kJ/mol

$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

1 MARK QUESTIONS

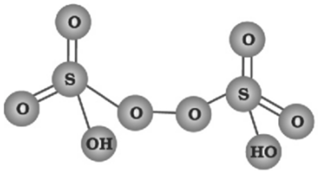
1) Sulphur has more tendency to show catenation than oxygen

Ans.) Due to stronger S-S bond and due to small size and greater interelectronic repulsion O-O bond is weakened so it can't show catenation.

2) Oxygen is a gas but sulphur is a solid.

Ans.) Due to small size oxygen makes $p\Pi$-$p\Pi$ bond and exists as O=O. That is why oxygen is gas but sulphur is bigger in size and can't make $P\pi$-$P\pi$ bond so exists as polymeric fluid form.

3) Draw structure of $H_2S_2O_8$



Peroxodisulphuric acid
($H_2S_2O_8$)

4.) H_2S is more acidic than H_2O

Ans.) Bond dissociation enthalpy of S-H bond is lesser than O-H bond due to bigger size of sulphur.

5.) OF_6 compound is not known, why?

Ans.) Due to the absence of d-orbital in oxygen, it can't make OF_6.

2 MARKS QUESTIONS

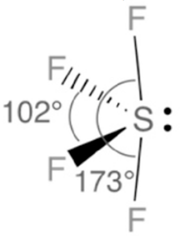
1 a) SF_6 is kinetically an inert substance or SF_6 does not hydrolyse easily. Why?

Ans.) SF_6 is less reactive because S atom is stearically protected by 6 fluorine atoms.

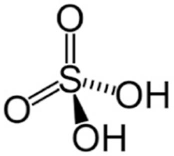
b) H_2O is liquid while H_2S is a gas.

Ans.) H_2O is liquid due to intermolecular H- bonding.

2. Draw the structure of SF4 Ans.) SF_4 has See-Saw



3. Draw structure of H_2SO_4



4. (a) In which form sulphur shows paramagnetism?

Ans.) In vapour state.

(b) Sulphur in vapour state exhibits paramagnetic behavior. Why?
Ans) S_2 contains unpaired electrons in antibonding M.O.

3 MARKS QUESTIONS

Q.1 Complete the following chemical equation

i.) $SO_3 + H_2SO_4 \rightarrow$

ii.) $Fe^{3+} + SO_2 + H_2O \rightarrow$

iii) $SO_2 + MnO_4^- + H_2O \rightarrow$

Ans.) i.) $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

ii.) $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

iii). $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

Q 2. (a) H_2S is less acidic than H_2Te. Why?

Ans. Bond dissociation enthalpy of H-S bond is less

(b) Boiling point of H_2O is more than H_2S. Why?

Ans. Water has intermolecular H-bonding due to more electronegativity and small size of oxygen atom. Hydrogen sulphide is unable to form hydrogen bond.

Group 17th elements

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17th.

A) Important reactions

1. $2F_2 + 2H_2O \rightarrow 4HF + O_2$
2. $Cl_2 + H_2O \rightarrow HCl + HOCl$
3. $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$
4. $H_2S + Cl_2 \longrightarrow 2HCl + S$

5. In excess of NH_3:- $8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$

6. In excess of Cl_2 :- $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

7. In cold and dilute NaOH :- $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

8. In hot and conc. NaOH:□ $6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

9. $SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$

10. $I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$

11. $Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured substance + O → Colourless substance(permanent bleach)

B) Reasoning questions

1. Halogens have maximum negative electron gain enthalpy($\Delta_{eg}H$)

Ans Because they have smallest size in their respective periods

2. F has less electron gain enthalpy than that of Cl but fluorine is stronger oxidizing agent than chlorine.

Ans F is stronger oxidizing agent due to its low bond dissociation enthalpy and high hydration enthalpy.

3 . F exhibits only -1 oxidation state, other halogen shows +1,+3,+5,+7 oxidation states or F does not exhibit any positive oxidation state. Explain.

Ans F is most electronegative element and due to absence of d□orbitals it can not expand its octet so it does not exhibit positive oxidation state.

4. Iron reacts with HCl gives Fe(II)chloride and not Fe(III)chloride. Why?

Ans $Fe + 2HCl \rightarrow FeCl_2 + H_2$ H_2 liberated prevents the oxidation of $FeCl_2$ to $FeCl_3$

5. Why bond dissociation enthalpy of F_2 is less than Cl_2 ?

Ans Due to very small size of F there is lone pair repulsion in F_2 so it has low bond dissociation enthalpy.

6. Fluorine does not undergo disproportionation. Explain.

Ans Disproportionation means simultaneous oxidation-reduction. F being the most electronegative element undergoes only reduction but not oxidation.

7. Bleaching by Cl_2 is permanent but by SO_2 is temporary. Why ?

Ans Cl_2 bleaches by oxidation while SO_2 does it by reduction. The reduced product gets oxidized again in air and the colour returns.

8. HF has lower acid strength than HI. Ex[plain.

Ans Due to larger size of I, the H-I bond is weaker than H□F bond so HI is stronger acid.

9. I_2 is more soluble in KI than in water. Why?

Ans I_2 forms complex with KI

i.e $KI + I_2 \rightarrow 2KI_3$

10. Why HClO is stronger acid than HIO?

Ans ClO^- is more stable than IO^- because Cl is more electronegative, so HClO is stronger acid than HIO.

11. Why $HClO_4$ is stronger acid than $HClO_3$?

Ans ClO_4^- is more stable than ClO_3^- due to more no. of resonating structures.

12 OF_2 should be called fluoride of oxygen and not oxide of F, explain.

Ans Because F is more electronegative than O

13. Interhalogens are more reactive than halogens or ICl is more reactive than I_2?

Ans They are polar and have weaker X-X' bond.

14. HF is stored in wax coated glass bottle

Ans Because HF reacts with alkali present in glass.

15 MF is more ionic than MCl (M is alkali metal)

Ans Because F^- is smaller than Cl^- and hence it is less polarisable.

16. $Cl_2+KI \rightarrow$ brown colour, but excess Cl_2 turns it colourless

Ans Cl_2 is stronger oxidizing agent than I_2. It first oxidizes KI into I_2 which imparts brown colour.
$Cl_2+KI \rightarrow I_2+2KCl$ In excess of Cl_2, I_2 is further oxidized to HIO_3 which is colourless.

$I_2+6H_2O+5Cl_2 \longrightarrow 2HIO_3+10HCl$

17. Why $HClO_4$ is stronger acid than H_2SO_4?

Ans Oxidation state of Cl in $HClO_4$ is +7. Oxidation state of S in H_2SO_4 is +6. Greater is the oxidation state of central atom, more is the acidic strength.

18. Give the reason for bleaching action of Cl_2.

Ans Bleaching action is due to oxidation. $Cl_2+H_2O \rightarrow 2HCl+O$

Coloured substance + O $\rightarrow$ Colourless substance

19 Name two poisonous gases which can be prepared from chlorine gas.

Ans phosgene ($COCl_2$), tear gas (CCl_3NO_2)

20. Write two uses of ClO_2.

Ans ClO_2 is used

i) as a bleaching agent for paper pulp and textiles

ii) in water treatment.

21. Why are halogens coloured?

Ans due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours.

22 .How can you prepare (i) Cl_2 from HCl and (ii) HCl from Cl_2? Write reactions only

Ans (i) $MnO_2+4HCl \rightarrow MnCl_2+Cl_2+2H_2O$ (ii) $H_2+Cl_2 \rightarrow 2HCl$

23. With what neutral molecule is ClO^- isoelectronic?

Ans OF_2 (other example is ClF. It is a Lewis base)

24. Write balanced equations for the following:

(i) NaCl is heated with sulphuric acid in the presence of MnO_2.

(ii) Chlorine gas is passed into a solution of NaI in water.

Ans (i) $4NaCl+MnO_2+4H_2SO_4 \rightarrow MnCl_2+4NaHSO_4+2H_2O+Cl_2$

(ii) $I_2+6H_2O+5Cl_2 \longrightarrow 2HIO_3+10HCl$

25. Write the reactions of F_2 and Cl_2 with water.

Ans 1. $2F_2+2H_2O \longrightarrow 4HF+O_2$

2. $Cl_2+H_2O \longrightarrow HCl+HOCl$

26. Why are halogens strong oxidising agents?

Ans i) ready acceptance of an electron

ii) Small atomic sizes

iii) highly electronegative nature

iv) Highly negative value of E^0_{red} are the reasons for the strong oxidising nature of halogens.

27. Explain why fluorine forms only one oxoacid, HOF.

Ans Due to high electro negativity and small size, fluorine forms only one oxoacid, HOF.

28 Explain why in spite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Ans Because electron density on oxygen atom is much higher than that of Cl atom.

29. ClF_3 exists but FCl_3 does not. Or F never acts as central atom in the inter halogen compounds.

Ans Because F is more electronegative than Cl

30. F_2 is the most reactive of all the four common halogens, explain .

Ans Because of low F-F bond dissociation enthalpy

31. HOI is a weaker acid than HOCl

Ans Because Cl is more electronegative than I.

C. Arrange the following as the property indicated against them.

1 F_2, Cl_2, Br_2, I_2 (increasing order of Boiling Point)

Ans $F_2 < Cl_2 < Br_2 < I_2$

2 F_2, Cl_2, Br_2, I_2 (increasing order of bond dissociation enthalpy.)

Ans $I_2 < F_2 < Br_2 < Cl_2$

3 F, Cl, Br, I (increasing order of electron gain enthalpy)

Ans I < Br < F < Cl

4 HF , HCl, HBr, HI (increasing order of acidic strength)

Ans HF < HCl < HBr < HI

5 MF, MCl, MBr, MI (decreasing order of ionic character)

Ans MF > MCl > MBr > MI

6 HClO, $HClO_2$, $HClO_3$, $HClO_4$ (increasing order of acidic strength) Ans $HClO < HClO_2 < HClO_3 < HClO_4$

7 HF, HCl, HBr, HI (decreasing order of B.P.)

8 Ans HF > HBr > HI > HCl

GROUP 18th ELEMENTS

KEY POINTS

GROUP 18 ELEMENTS **: He, Ne, Ar, Kr, Xe & Rn**

General electronic configuration: ns^2np^6

- **Atomic radii**- large as compared to other elements in the period since it corresponds to Van der waal radii.
- **Inert-** due to complete octet of outermost shell, very high ionization enthalpy and more positive electron gain enthalpies.

The first noble compound prepared by Neil Barlett was $Xe^+PtF_6^-$

$O_2^+PtF_6^-$ led to the discovery of $XePtF_6$ since first ionization enthalpy of molecular oxygen ($1175 kJmol^{-1}$) was almost identical with that of xenon ($1170 kJmol^{-1}$).

PROPERTIES

1) $Xe(g)+F_2(g) \xrightarrow{673K bar} XeF_2(g)$
2) $Xe(g)+2F_2(g) \xrightarrow{873K, 7bar} XeF_2(s)$
3) $Xe(g)+3F_2(g) \xrightarrow{573K, 60\text{-}70bar} XeF_6(s)$
4) $XeF_4+O_2F_2 \rightarrow XeF_6+O_2$
5) $2XeF_2+2H_2O \rightarrow 2Xe+4HF+O_2$
6) $XeF_6+MF \rightarrow M^+[XeF_7]^-$
7) $XeF_2+PF_5 \rightarrow [XeF]^+[PF_6]^-$
8) $6XeF_4+12H_2O \rightarrow 4Xe+2XeO_3+24HF+3O_2$
9) $XeF_6+3H_2O \rightarrow XeO_3+6HF$
10) $XeF_6+2H_2O \rightarrow XeO_2F_2+4HF$(partial hydrolysis)

1 mark questions:

Q1 Why among the noble gases only Xenon is well known to form chemical compounds?

Ans. Xenon has the largest atomic size and the smallest I.E. of all the noble gases

Q2 Name the geometries of $XeOF_4$ and XeO_3.

Ans. $XeOF_4$ is square pyramidal while XeO_3 is pyramidal.

1 marks questions:

Q1 Account for the following

(i) Noble gases are mostly chemically inert.

(ii) Deep sea divers use a mixture of He (80%) and O_2 (20%) instead of air for breathing.

Ans. (i) It is due to stable electronic configuration and high ionization enthalpies of noble gases.

Ans. (ii) Unlike N_2 of air, He is least soluble in blood even under high pressure. Therefore it does not create any problem.

Q2 (a) What prompted Bartlett to the discovery of noble gas compound?

(b) State two importance of noble gases.

Ans. (a) The ionization enthalpy of Xe is similar to that of O_2 . He first prepared compond $O_2^+PtF_6^-$. It prompted bartlett to prepare compond in which O_2 of $O_2^+PtF_6^-$ could be replaced by Xe. This is how $Xe^+PtF_6^-$ was prepared .

Ans. (b) (i) Ar is used in electric bulbs. (ii) Xe is used in head lights of cars these days.

Q3 Apply VESPR theory to deduce the structure of XeF_4 and XeF_6 .

Ans. XeF_4 has square planar structure due to presence of 4 bonded pairs of electrons and 2 lone pairs of electrons. XeF_6 has distorted octahedral structure due to presence of one lone pair of electrons and six bonded pairs of electrons.

2 marks Question

Q1 Write down the equations for the hydrolysis of XeF_4 and XeF_6. Which of these two reactions is a redox reaction?

Ans (i) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(ii) $XeF_6 + 3H_2O \rightarrow XeO_3 +$ 6HF

Reaction:

(i) is redox reaction. Reaction

(iii) Is not a redox reaction because the oxidation states of all the elements before and after remain the same.

Q2 (i) Why do noble gases have comparatively large atomic size?

(ii) Noble gases are mostly chemically inert.

(iii) XeF_2 has a straight linear structure and not a bent angular structure.

Ans (i) Due to completely filled valence shell electronic configuration ,repulsive interaction

Start taking place in the atom, due to which, the atomic size increases in noble gases.

(ii) It is due to stable electronic configuration and high ionization enthalpy of noble gases.

(iii) Due to sp^3d hybridisation of Xe, it has trigonal bipyramid geometry. Three equatorial positions are occupied by lone pairs of electrons to minimize repulsion, giving a linear shape to the molecule.

ASSIGNMENT

Q1 Noble gases have comparatively large atomic size. Why?

Q2 Helium is used in diving apparatus. Why?

Q3 Draw the structure of i) XeF_4 ii) XeO_3

Q4 Give 2 uses of Argon.

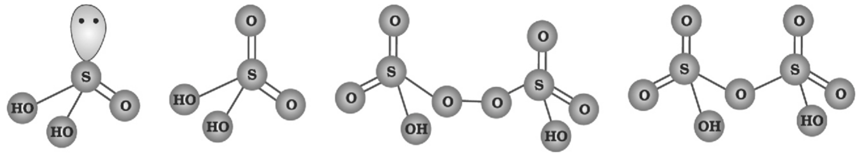
Q5 Complete the following reactions

  i. $6XeF_4 + 12H_2O \rightarrow$

  ii. $XeF_6 + 3H_2O \rightarrow$

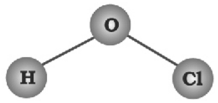
  iii. $XeF_6 + 2H_2O \rightarrow$ (partial hydrolysis)

Oxoacids of Sulphur

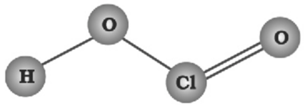


Sulphurous acid (H_2SO_3) Sulphuric acid (H_2SO_4) Peroxodisulphuric acid ($H_2S_2O_8$) Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

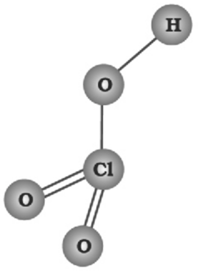
Oxoacids of chlorine



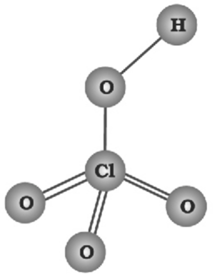
Hypochlorous acid



Chlorous acid



Chloric acid

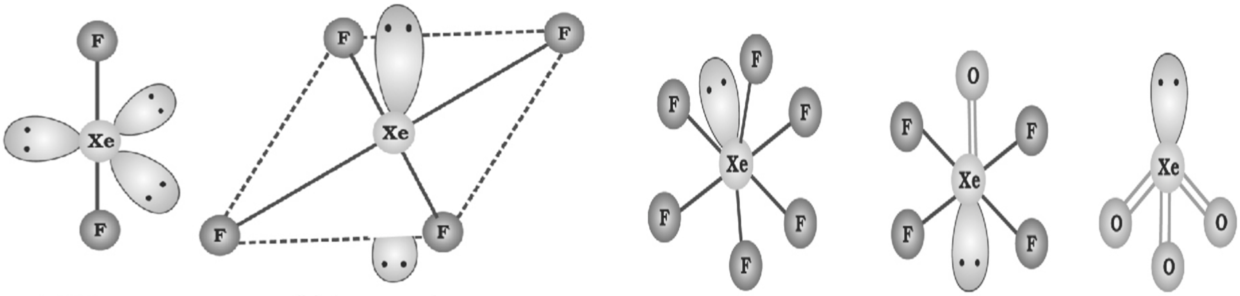


Perchloric acid

Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid
Halic (III) acid (Halous acid)	-	HOClO (chlorous acid)	-	-
Halic (V) acid (Halic acid)	-	HOClO2 (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII)acid (Perhalicacid)	-	$HOClO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)

The structures of (a) XeF_2 (b) XeF_4 (C) XeF_6 (d) $XeOF_4$ and (e) XeO_3



(a) Linear (b) Square planar (c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Covalency of oxygen cannot exceed 2 unlike sulphur which can show +4 or +6.
Reason : Oxygen atom does not have d - orbitals. (Ans - a)

2. Assertion : Sulphur trioxide is not directly dissolved in water to form sulphuric acid.
Reason : It results in the formation of dense fog of sulphuric acid which is difficult to condense. (Ans - a)

3. Assertion : Ozone layer in the upper region of atmosphere protects earth from UV radiations of sun.
Reason : Ozone is a powerful oxidising agent as compared to oxygen. (Ans - b)

4. Assertion : SF_6 cannot be hydrolysed but SF_4 can be.
Reason : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6. (Ans - a)

One - word answer

1. Identify the compound of sulphur, used as anti-chlor. (Ans - Sulphur dioxide)
2. What type of bleaching action is shown by chlorine? (Ans - Permanent)

OBJECTIVE TYPE QUESTIONS

1. Molecular shapes of SF_4, CF_4 and XeF_4 are –
(a) The same with 2, 0 and 1 lone pairs of electrons respectively
(b) The same with 1, 1 and 1 lone pairs of electrons respectively
(c) Different with 0, 1 and 2 lone pairs of electrons respectively
(d) Different with 1, 0 and 2 lone pairs of electrons respectively

2. Which of the following is planar?
(a) XeO_4 (b) XeO_3 (c) XeO_2F_2 (d) XeF_4

3. Total number of lone pairs of electrons in $XeOF_4$ is –
(a) 0 (b) 1 (c) 2 (d) 3

4. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimise –
(a) lone pair-bond pair repulsion only
(b) bond pair- bond pair repulsions only
(c) lone pair-lone pair and lone pair-bond pair repulsions
(d) lone pair-lone pair repulsions only

5. Which among the following factors is most important in making fluorine the strongest oxidizing agent?
(a) electron affinity (b) ionization energy

(c) hydration energy (d) bond dissociation energy

6. Which one of the following oxides is expected to exhibit paramagnetic behaviour?

(a) CO_2 (b) ClO_2 (c) SO_2 (d) SiO_2

7. Which one of the following arrangements represent the correct order of electron gain enthalpy (with negative sign) of the given atomic species?

(a) F < Cl < O < S (b) S < O < Cl < F

(c) O < S < F < Cl (d) Cl < F < S < O

8. Which of the following contains maximum number of lone pairs of electrons on the central atom?

(a) ClO_3^- (B) XeF_4 (c) SF_4 (d) I_3^-

9. 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)

10. Which products are expected from the disproportionation reaction of hypochlorous acid?

(a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$

(c) HCl and Cl_2O (d) HCl and $HClO_3$

11. Which is the strongest acid?

(a) H_2SO_4 (b) HCl (c) $HClO_4$ (d) HNO_3

12. The bleaching action of $CaOCl_2$ is due to –

(a) nascent oxygen (b) chlorine (c) HClO (d) HCl

13. Which of the following orders is not in accordance with the property stated against it?

(a) $F_2 > Cl_2 > Br_2 > I_2$; bond dissociation energy

(b) $F_2 > Cl_2 > Br_2 > I_2$; oxidizing power

(c) HI > HBr > HCl > HF; acidic property power

(d) $F_2 > Cl_2 > Br_2 > I_2$; electronegativity

14. Identify the incorrect statement among the following:

(a) Br_2 reacts with hot and strong NaOH solution to give NaBr, $NaBrO_3$ and water.

(b) Ozone reacts with SO_2 to form SO_3

(c) Silicon reacts with NaOH (aq) in the presence of air to give Na_2SiO_3 and H_2O

(d) Cl_2 reacts with excess of NH_3 to give N_2 and HCl

15. The correct order of acid strength is –

(a) $HClO_4 < HClO_3 < HClO_2 < HClO$

(b) $HClO_2 < HClO_3 < HClO_4 < HClO$

(c) $HClO_4 < HClO < HClO_3 < HClO_2$

(d) $HClO < HClO_2 < HCLO_3 < HClO_4$

16. The isoelectronic pair is –

(a) Cl_2O, ICl_2^- (b) ICl_2^-, ClO_2 (c) IF_2^+, I_3^- (d) ClO_2^-, ClF_2^+

17. When XeF_4 is treated with water, it forms –

(a) Only Xe (b) both Xe and XeO_3

(c) only XeO_3 (d) Both XeO_3 and $XeOF_4$

ANSWER KEY

1	D	11	C
2	D	12	A
3	B	13	A
4	C	14	D
5	C	15	D
6	B	16	D
7	D	17	B
8	D		
9	D		
10	D		

d & f BLOCK ELEMENTS (UNIT- 7)

- d-block consists of elements belonging to group 3-12.
- The general electronic configuration of these elements in (n-1) d^{1-10} ns^{1-2}. They contain unpaired d-electron either in elementary or most commonly occurring oxidation state.
- Transition elements exhibits metallic character, high densities, high melting and boiling point due to strong interatomic interaction between partially filled d-orbits.'
- Transition elements show variable oxidation state due to small energy difference between (n-1)d & ns orbitals.
- Transition metals show colour due to presence of unpaired electron in (n-1)d orbital of penultimate shell which undergoes d-d transition generally
- Transition metal elements are paramagnetic due to presence of unpaired e^{-}.
- Most of transition form complex compounds due to (I) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.
- Transition elements have lower value of reduction potential due to high ionization potential, high heat of sublimation and low enthalpy of hydration.
- Transition elements form interstitial compounds because as small atoms like C, N, O, H. occupy the voids and get bonded to the atom of transition metals.
- Transition elements form alloys due to similar ionic radii as they can mutually substitute their position in the crystal lattice.
- The oxides of transition metals in lower oxidation states are basic, intermediate oxidation states are amphoteric, highest oxidation state are acidic.
- The highest oxidation state of an element is equal to no. of unpaired electrons present in (n-1)d & ns orbitals.

LANTHANOIDS

- In lanthanoids filling of electrons take place in 4f orbital which is 3rd antipenultimate shell. last shell or
- General electronic configuration is $[Xe]4f^{1-14}5d^{0-1}6s^{2}$.
- Elements after lanthanum having atomic number 58 to 71 are called lanthanoids.
- Principal oxidation state is +3 although Ce shows +4 and Eu +2 due to stable configuration. So Ce (IV) is good oxidizing and Sm (II) is good reducing agent.
- Due to poor shielding effect of electrons. There is a steady decrease in lanthanoids and its trivalent ions known as lanthanoid contraction.

ACTINOIDS

- The 14 elements after actinium having atomic number 90 to 113 are collectively known as Actinoids
- The general electronic configuration of these elements is $[Rn]5f^{1-14}, 6d^{0-1}, 7s^2$.
- The size of actinoids and its trivalent ion decreases from Ac to Lw due to poor shielding of 5f electrons. It is known as actinoid contraction.
- Chemical of actinoids is very complex due to their ability that exist is different oxidation state. More so they are radioactive.

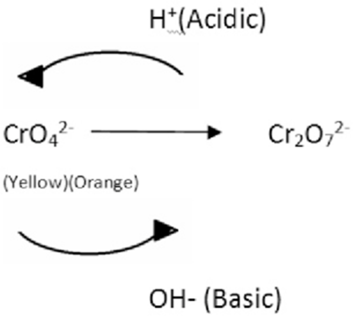
POTASSIUM DICHROMATE

Preparation: - from chromite ore $FeCr_2O_4$

I. Conversion of chromite ore to sodium chromate.
II. Conversion of sodium chromate to sodium dichromate.
III. Conversion of sodium dichromate to potassium dichromate.

IV. Following reaction takes place:-

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
$$2Na_2Cr_2O_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$



EFFECT OF pH

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Chemical properties

Sodium and potassium dichromates acts as strong oxidising agents in acidic medium.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Oxidation Reaction

$$6I^- \longrightarrow 3I_2 + 6e^-,\ 3H_2S \longrightarrow 6H^+ + 3S + 6e^-,\ 6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-,\ 3Sn^{2+} \longrightarrow 3Sn^{4+} + 6e^-$$

POTASSIUM PERMANGANATE

Preparation: - From pyrolusite ore

I. Conversion of pyrolusite ore into potassium manganate
II. Conversion of potassium manganate to potassium permanganate Following reactions take place:-

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Chemical Properties

Potassium permanganate is a powerful oxidising agent. <u>Neutral solution</u>

$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]$

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4\ OH^-$

<u>Alkaline solution</u>

$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + 5\ [O]$

$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

<u>Acidic solutions</u>

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

FREQUENTLY ASKED QUESTIONS

(1 mark)

Q.1. Cu^+ is not stable in aqueous solution. Why?

Ans. In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

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

The higher stability of Cu^{2+} in aqueous solution may be attributed to its greater negative $\Delta_{hyd}H$ than that of Cu^+. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

Q.2. Which is a stronger reducing agents – Cr^{2+} or Fe^{2+} and why?

Ans. Cr^{2+} is a stronger reducing agent than Fe^{2+} because after the loss of one electron Cr^{2+} becomes Cr^{3+} which has more stable t_{2g}^3 (half filled) configuration in medium like water.

Q.3. Arrange the following increasing order of acidic character: CrO_3, CrO , Cr_2O_3

Ans. $CrO < Cr_2O_3 < CrO_3$. Higher the oxidation state, more will be acidic character.

Q.4. Calculate the 'spin only' magnetic moment of M^{2+}(aq) ion.(Z=27)

Ans. Electronic configuration of the M^{2+} ion (Z=27) would be M^{2+}(aq): (Ar) $3d^7$

It would contain three unpaired electrons. The 'spin only' magnetic moment is given by the relation :

$\mu = \sqrt{n\ (n+2)}$ BM = $\sqrt{3\ (3+2)}$ BM = 3.87 BM

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Cu^{2+} iodide is not known.
   Reason : Cu^{2+} oxidises I^- to iodine. (Ans - a)
2. Assertion : $KMnO_4$ acts as an oxidising agent in acidic, basic or neutral medium.
   Reason : It oxidises ferrous sulphate to ferric sulphate. (Ans - b)
3. Assertion : Reactivity of transition elements decreases almost regularly from Sc to Cu.
   Reason : There is regular increase in I. E. across the series. (Ans - a)
4. Assertion : Cu^+ ion is not stable in aqueous solution.
   Reason : Large value of I.E. of Cu is compensated by much more negative hydration energy of Cu^{2+} (aq). (Ans - a)
5. Assertion : Zr and Hf have almost equal atomic and ionic radii.
   Reason : They show lanthanoid contraction. (Ans - a)

One - word answer

1. Which magnesium based alloy is used to produce bullets ? (Ans - Misch metall)

2. Name the green coloured compound which is used to prepare $KMnO_4$ in neutral /acidic solution. (Ans K_2MnO_4)

2 marks questions

Q1. Why do Zr and Hf exhibit almost similar properties?

Ans. Zr and Hf have similar ionic size due to its lanthanoid contraction. So they exhibit similar properties.

Q2. Why are Zn, Cd and Hg not regarded as transition elements?

Ans. Zn, Cd, Hg neither in their ground state nor in oxidized state have partially filled d-orbital. Thus they are not regarded as transition elements.

Q3. What are alloys? Name one important alloy which contains some of the lanthanoid metals. Mention its use.

Ans. Alloys are homogeneous mixtures of metals with metals or non-metals.

Misch metall (pyrophoric alloy) consists of lanthanoid metal Ce= 40.5%, neodymium 44%, iron 4-5% and traces of S, C, Ca and Al. Misch metall is used to make bullets, shells and light flints.

Q4. $La(OH)_3$ is a stronger base than $Lu(OH)_{3.}$ Why?

Ans. Lu^{3+} is smaller in size than La^{3+} due to lanthanoid contraction. Due to smaller size of Lu^{3+}, Lu- O bond is stronger than La-O bond in the respective hydroxides. Due to weaker La-O bond, $La(OH)_3$ behaves as a stronger base.

Q5. Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.

Ans. Lanthanoids exhibit oxidation states of +2, +3 and +4. This is because of large energy gap between 4f, 5d and 6s subshells. Actinoids show +3, +4, +5, +6 and +7 oxidation states because 5f, 6d and 7s energy levels are nearly same.

3 marks questions

Q 1. What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

Ans. Lanthanoid contraction: Steady decrease in the size of the lanthanoids with increase in the atomic number across the period. The electrons of 4f orbitals offer imperfect / poor shielding effect in the same subshell.

Consequence:

i) Due to this 5d series elements have nearly same radii as that of 4d series.

ii) Decrease in the basic strength from $La(OH)_3$ to $Lu(OH)_{3.}$

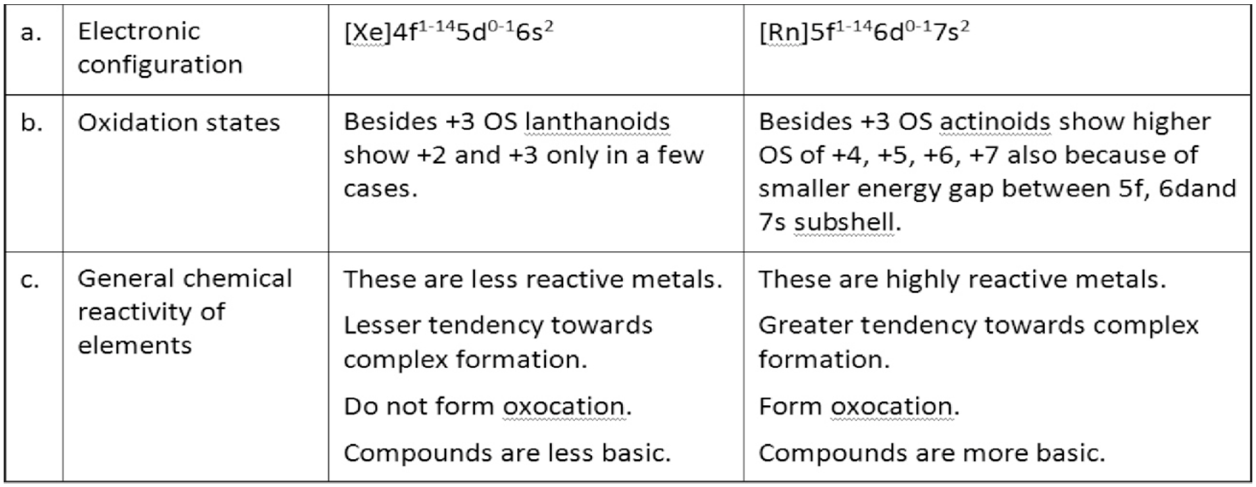
iii) Due to similar atomic size there is difficulty in separation of lanthanides.

Q 2. Compare lanthanoids and actinoids with reference to their:

a. Electronic configuration of atoms

b. Oxidation states of elements

c. General chemical reactivity of elements.



a.	Electronic configuration	$[Xe]4f^{1-14}5d^{0-1}6s^2$	$[Rn]5f^{1-14}6d^{0-1}7s^2$
b.	Oxidation states	Besides +3 OS lanthanoids show +2 and +3 only in a few cases.	Besides +3 OS actinoids show higher OS of +4, +5, +6, +7 also because of smaller energy gap between 5f, 6dand 7s subshell.
c.	General chemical reactivity of elements	These are less reactive metals. Lesser tendency towards complex formation. Do not form oxocation. Compounds are less basic.	These are highly reactive metals. Greater tendency towards complex formation. Form oxocation. Compounds are more basic.

Q3. How would you account for the following:

a. Mn(III) undergoes disproportionation reaction easily.

b. Co(II) is easily oxidized in the presence of strong ligands.

Ans. a. Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled d- orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

b. Co(II) has electronic configuration $3d^7 4s^0$, i.e., it has three unpaired electrons. In the presence of strong ligands, two unpaired electrons in 3d-subshell pair-up and third unpaired electron shifts to higher energy subshell from where it can be easily lost and hence oxidized to Co(III).

Q.4 Give reasons for the following:

i) First ionisation energies of 5d elements are higher than those of 3d and 4d elements. Actinoid conctraction is greater from element to element than lanthanoid contraction.

Ans. i) Because of weak shielding (or screening) effect of 4f electrons, the effective nuclear charge acting on the valence electrons in 5d elements is quite high. Hence, the first ionisation energies of 5d elements are higher than those of 3d and 4d elements.

ii) This is because the 5f electrons themselves provide poor shielding from element to element in the series.

Q.5. Explain the following observations about the transition / inner transition elements:

i) There is, in genera,l an increase in density of element from titanium (Z=22) to copper (Z=29).

ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements(3rd series).

iii) The greatest number of oxidation states are exhibited by the members in the middle of a transition series.

Ans i) Because of decrease in atomic size from titanium to copper.

ii) Because of high enthalpies of atomization of heavy transition elements.

iii) Because of the involvement of both (n-1)d and ns electrons in bonding.

5 marks question

Q. 1- Assign reasons for the following:

a) The enthalpies of atomization of transition elements are high.

b) The transition metals and many of their compounds act as good catalysts.

c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic number.

d) The transition elements have great tendency for complex formation.

e) Transition metals generally form coloured compounds.

Ans- a) This is because transition elements have strong metallic bonds as they have large number of unpaired electrons, therefore they have greater interatomic overlap.

b) The catalytic activity of transition metals is attributed to the following reasons-

i) Because of their variable oxidation state, transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.

ii) In some cases, the transitions metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers due to poor shielding effects of the d-electrons, the net electrostatic attraction between the nucleus and the outermost electrons increases.orbital's of suitable energy, small size of cations and higher nuclear charge.

d) Due to presence of unpaired electrons in d-orbitals which undergoes d-d transition.

Q.2 a) Complete and balanced the following reactions:

i) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow$

ii) $MnO_4^- + SO_3^{2-} + H^+ \longrightarrow$

b) With reference to structural variability and chemical reactivity, write the difference between lanthanoids and actinoids.

c) Name a member of lantanoids series which is well known to exhibit +4 oxidation state.

Ans. a) i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

ii) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

b) Lanthanoids-

i) Atomic or ionic radii does not show much variation.

ii) Besides +3 oxidation state, they show +2 and +4 oxidation states in few cases.

Actinoids-

i) Atomic or ionic radii show many variations.

ii) Besides +3 oxidation states, they show higher oxidation states of +4, +5, +6, +7, also.

c) Cerium.

ASSIGNMENT

Q.1 Which of the 5d series of the transition metals exhibit the largest number of oxidation state and why?

Q.2 Why is the highest oxidation state of a metal exhibited in its oxide and fluoride only?

Q.3 Explain why Cu^+ ion is not stable in aqueous solution?

Q.4 What are interstitial compounds? Why are such compounds well known among transition metals?

Q.5 Describe the preparation of potassium dichromate from chromite ore. What is the effect of increasing pH on the solution of potassium dichromate?

Q.6 Draw the structure of following: a) CrO_4^{2-} b) MnO_4^- c) $Cr_2O_7^{2-}$

Q.7 What are the characteristics of the transition elements and why are they called transition elements? Which of the d-block elements may not be regarded as the transition metals?

Q.8 What is meant by disproportionation? Give 2 examples of disproportionation.

Q.9 The halides of transition metals become more covalent with increasing oxidation state of the metal. Why?
[Hint: Fajan's rule]

PROPERTIES OF d-BLOCK ELEMENTS	COMPOUND OF d-BLOCK ELEMENTS	f-BLOCK ELEMENTS
Physical Properties 1. They have high mp, bp, conductivity, ductility etc. 2. They are hard and volatile except Zn, Cd and Hg[due to absence of (n-1)d electrons.] **Enthalpy of Atomisation** 1. It is the energy required to convert the metallic crystal into atom. 2. It first increases upto middle and then decreases.	**Potassium Dichromate** 1.Prepared as Chromite $\xrightarrow{Na_2CO_3}$ Chromate $\downarrow H^+$ $K_2Cr_2O_7 \xleftarrow{KCl}$ Dichromate of Na 2. $Cr_2O_7^{2-} \xrightarrow{OH- \ \& \ H+} CrO_4^{2-}$ 3. It oxides I^- to I_2, H_2S to S, Fe^{2+} to Fe^{3+} and itself reduced to Cr^{3+}	**Lanthanoids** 1. EC = $5d^{0-1}$, $6s^2$, $4f^{1-14}$ 2. Atomic and Ionic radii decrease from La to Lu and this decrease is called **lanthanoid contraction.** It is due to poor shielding of f-orbitals. 3. Common OS = +3 4. They are paramagnetic, coloured, have IE comparable to Ca.
Atomic and Ionic Radii 1. It usually decreases with increase in atomic number across a series due to increase in effective nuclear charge. 2. At the end of the series, it increases due to increased repulsive forces.	**Potassium Permanganate** 1. Prepared as Pyrolusite(MnO_2) $\xrightarrow{KOH \ \& \ O2}$ MnO_4^{2-} $\downarrow$ H^+ Mno_4^- 2. In acidic medium it oxides I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, H_2S to S and itself reduced to MnO_4^-	**Consequences of lanthanoid contraction** 1. Decrease in basic character of oxide and hydroxides from La to Lu. 2. Same size of Zr and Hf, Nb and Ta, etc. **Actinoids** 1. EC = $6d^{0-1}$, $7s^2$, $5f^{1-14}$ 2. Show actinoid contraction. 3. Show large number of OS due to less difference in energy of 6d, 7s and 5f orbitals. 4. Mostly Radioactive. 5. They are also coloured and paramagnetic.
Ionisation Enthalpy It increases with decrease in size. **Oxidation State(OS)** Show oxidation state from +2 to +7 but +3 is most common. Maximum OS = (n-1)d unpaired e^- + ns e^-.	**Catalytic Property** They act as good catalyst due to their variable valency and vacant d-orbitals. **Alloy Formation** They form alloy with other metals. Alloy of Hg is called Amalgam.	
Standard Reduction Potential Its negative value decreases from left to right with exception of Mn, Zn and Ni.	**Complex Formation** They all form complex due to their small size, high charge density and vacant d orbitals.	
Magnetic Property and Colour These are generally paramagnetic and coloured due to the presence of unpaired d-electrons.	**Interstitial Compounds** They trap small atoms like C, H, N etc., in their crystals to modify properties.	

OBJECTIVE TYPE QUESTIONS

Q1. Which of the following arrangements does not represent the correct order of the property stated against it?

A $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
B $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
C $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
D Sc < Ti < Cr < Mn : number of oxidation states

Q. 2 Which of the following lanthanoid ions is diamagnetic?

(At. nos. Ce = 58, Sm = 62, Eu = 63, Yb = 70)

A Ce^{2+}
B Sm^{2+}
C Eu^{2+}
D Yb^{2+}

Q. 3 $KMnO_4$ can be prepared from K_2MnO_4 as per the reaction:

$$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^{-} + MnO_2 + 4OH^{-}$$

The reaction can go to completion by removing OH^{-} ions by adding

A KOH
B CO_2
C SO_2
D HCl

Q. 4 Which of the following statements about the interstitial compounds is incorrect?

A They retain metallic conductivity
B They are chemically reactive
C They are much harder than the pure metal
D They have higher melting points than the pure metal

Q. 5 All the metals form oxides of the type MO except

A copper
B barium
C silver
D lead

Q.6 Among the following, the coloured compound is

A CuCl
B $K_3[Cu(CN)_4]$
C CuF_2
D $[Cu(CH_3CN)_4]BF_4$

Q.7 How many ‘d’ electrons are in present Cr^{2+} ion

A 4

B 5

C 6

D 3

Q.8 Cyanide process is used for extraction of

A Ag

B Ni

C Pt

D Zn

Q.9 Extraction for zinc blende is achieved by

A electrolytic reduction

B roasting followed by reduction with carbon

C roasting followed by reduction with another metal

D roasting followed by self reduction

Q.10 Formation of coloured solution is possible when metal ion in the compound contains

A paired electrons

B unpaired electrons

C lone pair of electrons

D none of these

Q.11 Identify the incorrect statement among the following

A d-Block elements show irregular and erratic chemical properties among themselves

B La and Lu have partially filled d orbitals and no other partially filled orbitals

C The chemistry of various lanthanoids is very similar

D 4f and 5f orbitals are equally shielded

Q.12 Which one of the following ions exhibit colour in aqueous solution

A Sc^{3+}

B Ni^{2+}

C Ti^{4+}

D Zn^{2+}

Q.13 Which one of the following is a diamagnetic ion?

A Co^{2+}

B Cu^{2+}

C Mn^{2+}

D Sc^{3+}

Q.14 Which ore contains both iron and copper?

A Cuprite

B Chalcocite

C Chalcopyrite

D Malachite

Q.15 Which pair of compounds is expected to show similar colour in aqueous medium?

A $FeCl_2$ and $CuCl_2$

B $VOCl_2$ and $CuCl_2$

C $VOCl_2$ and $FeCl_2$

D $FeCl_2$ and $MnCl_2$

Q.16 Zn does not show variable valency because of

A complete d sub-shell

B inert pair effect

C $4s^2$ sub-shell

D None of these

Q.17 When copper pyrites is roasted in excess of air, a mixture of CuO + FeO is formed as impurities. This can be removed as slag during reduction of CuO. The flux added to form slag is:

A SiO_2, which is an acid flux

B Lime stone, which is a basic flux

C SiO_2, which is basic flux

D CaO; which is basic flux

Q.18 'Hydride Gap' is referred to which region of the periodic table?

A Groups 3, 4 and 5

B Groups 5, 6 and 7

C Groups 4, 5 and 6

D Groups 7, 8 and 9

Q.19 Which of the statements is not true?

A $K_2Cr_2O_7$ solution in acidic medium is orange

B $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7

C On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed

D $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

Q.20 Which one of the following sets correctly represents the increase in the paramagnetic property of the ion?

A $Cu^{2+} < V^{2+} < Cr^{2+} < Mn^{2+}$

B $Cu^{2+} < Cr^{2+} < V^{2+} < Mn^{2+}$

C $Mn^{2+} < V^{2+} < Cr^{2+} < Cu^{2+}$

$Mn^{2+} < Cu^{2+} < Cr^{2+} < V^{2}$

Answers:

1. A 2. D 3. C 4. C 5. B 6 . B 7. A 8. A 9. B 10. B 11. D
12. B 13. D 14. C 15. B 16. A 17. A 18. D 19. D 20. A

COORDINATION COMPOUNDS (UNIT- 8)

Difference between coordination compound and double salt:

Coordination compound	Double salt
A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules are bonded to the metal atom or ion by a coordinate bond.	When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called double salts
Example: $K_4[Fe(CN)_6]$	Example: $FeSO_4$. $(NH4)_2SO_4.6H_2O$ (Mohr's salt)
They do not dissociate into simple ions when dissolved in water.	They dissociate into simple ions when dissolved in water.

Werner's coordination theory: Werner was able to explain the nature of bonding in complexes. The postulates of Werner's theory are:

a. Metal shows two different kinds of valencies: primary valency and secondary valency

Primary valence	Secondary valence
This valence **Is normally** ionisable.	This valence is non-ionisable.
It is equal to positive charge on central metal atom	The secondary valency equals the number of ligand atoms coordinated to the metal. It is also called coordination number of the metal.
These valencies are satisfied by negatively charged ions.	It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.
Example: in $CrCl_3$, the primary valency is three. It is equal to oxidation state of central metal ion.	

b. The ions/groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

c. The most common geometrical shapes in coordination compounds are octahedral, square planar and tetrahedral.

Isomers : Two or more compounds which have same chemical formula but different arrangement of atoms are called isomers, Types of isomerism:

a. Structural isomerism

i. Linkage isomerism
ii. Solvate isomerism or hydrate isomerism
iii. Ionisation isomerism
iv. Coordination isomerism

b. Stereoisomerism

I. Geometrical isomerism
ii. Optical isomerism

Structural isomerism: This type of isomerism arises due to the difference in structures of coordination compounds. Structural isomerism, or constitutional isomerism, is a form of isomerism in which molecules with the same molecular formula have atorns bonded together in different orders.

a. **Ionisation isomerism:** This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

Example: $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

b. **Solvate isomerism:** It is isomerism in which solvent is involved as ligand. If solvent is water it is called hydrate isomerism.

e.g. $[Cr(H_2O)_3Cl_3]$ and $[CrCl_2(H_2O)_4Cl_2.2H_2O$

c. **Linkage isomerism:** Linkage isomerism arises in a coordination compound containing ambidentate ligand. In this isomerism, a ligand can form linkage with metal through different atoms.

Example: $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$

d. **Coordination isomerism:** This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Example: $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$

Stereoisomerism: This type of isomerism arises because of different spatial arrangement.

a. Geometrical isomerism: It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.

b. Optical isomerism: .Optical isomers are *non* superimposable mirror images of each other.

VALENCE BOND THEORY

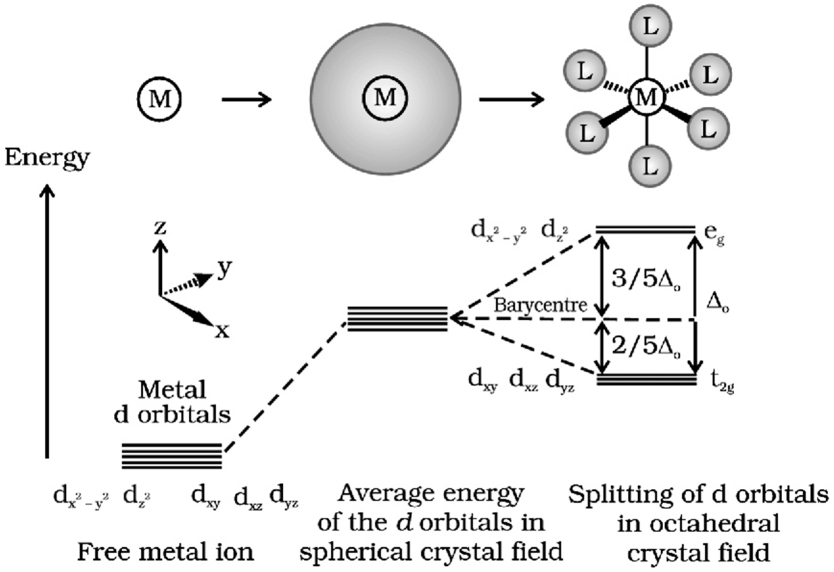
Coordination number	Type of hybridisation	tribution of hybrid orbitals in space
4	sp^3	tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2 (nd orbitals are involved - outer orbital complex or high spin or spin free complex)	Octahedral
6	d^2sp^3 (n–1) d orbitals are involved - inner orbital or low spin or spin paired complex)	Octahedral

Magnetic properties of coordination compounds: A coordination compound is paramagnetic in nature, if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

Magnetic moment = $[n (n + 2)]^{1/2}$ where n is number of unpaired electrons.

Crystal Field Theory: It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. It is theoretical assumption.

Crystal field splitting in octahedral coordination complexes:



NEGATIVE LIGANDS		CHARGE	NEUTRAL LIGANDS		CHARGE
CN^-	Cyano	-1	NH_3	Ammine	0
Cl^-	Chlorido	-1	H_2O	Aqua/aquo	0
Br^-	Bromido	-1	NO	Nitrosyl	0
F^-	Fluoride	-1	CO	Carbonyl	0
SO_4^{2-}	Sulphato	-2	PH_3	Phosphine	0
$C_2O_4^{2-}$	Oxalato	-2	$CH_2–NH_2$	(1,2–Ethanediamine)	0
$\bar{N}H_2$	Amido	-1	POSITIVE LIGANDS		
NH^{2-}	Imido	-2	$\overset{+}{N}H_2–NH_3$	Hydrazinium	+1
ONO^-	Nitrito–O	-1	NO^+	Nitrosonium	+1
NO_2^-	Nitro	-1	$\overset{+}{N}O_2$	Nitronium	+1
NO_3^-	Nitrato	-1			
SCN^-	Thiocyanato	-1			
NCS^-	Isothiocyanato	-1			
$CH_2(NH_2)COO^-$	Glycinato	-1			

1 Mark- Questions

Q.1 The spin only magnetic moment of $[MnBr]^{2-}$ is 5.9 BM. Predict the geometry of the complexion.

Ans. Mn^{2+} in the complex has Co-ordination No. 4, so it has a tetrahedral geometry.

Q.2 $CusO_4 5H_2O$ is blue in color white $CuSO_4$ is colorless Why?

Ans. d-d Transition is possible in $CuSO_4 5H_2O$, so it shows Color. $CuSO_4$ due to the absence of water (ligand) CFT is not – possible, it is so colored.

3. Write the state of hybridisation of the Compound $[Cr(NH_3)_6]^{3+}$

Ans. d^2sp^3 geometry octahedral

Q.4 Give the formula of the given Co-ordination compound Ni ion is bound to two water molecules and two oxalate ions.

Ans. $[Ni(H_2O)_2(OX)_2]^{2-}$

Diaquadioxalato nickelate (II)

ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below.

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

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

(c) Assertion is true but reason is false.

(d) Both assertion and reason are false.

1. Assertion : $[Co(NH_3)Br]SO_4$ gives white precipitate with barium chloride.
   Reason : The complex dissociates in the solution to give Br^- and SO_4^{2-} . (Ans - c)
2. Assertion : According to crystal field theory during complex formation, the d - orbitals split and form two sets of orbitals t_{2g} and e_g.
   Reason : Splitting of d - orbitals occurs only in case of strong field ligands. (Ans - c)
3. Assertion : $[Fe(H_2O)_6]^{2+}$ is sp^3d^2 hybridised and paramagnetic complex ion.
   Reason : It has four unpaired electrons. (Ans - a)
4. Assertion : Low spin tetrahedral complexes are not formed.
   Reason : For tetrahedral complexes, CFSE is lower than pairing energy. (Ans - a)
5. Assertion : $[FeF_6]^{3-}$ is paramagnetic.
   Reason : F^- is a weak field ligand, hence does not cause pairing of electrons. (Ans - a)

One - word answer

1. Name a ligand involved in synergic bonding. (Ans - CO)
2. Why gemstones produce colours? (Ans - d- d transition)

Two marks Question

Q.1 Arrange the following complexes the order of increasing electrical conductivity.

$[Co(NH_3)_3Cl_3]$, $Co(NH_3)_5Cl]Cl_2$,

$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$ Ans. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl$

$<[Co(NH_3)_5 Cl]Cl_2 <[Co(NH_3)_6]Cl_3$

Q.2 How many geometrical isomers are possible in the following co□ordination entities: $[Cr(C_2O_4)_3]^{3-}$ $[CoCl_3(NH_3)_3]$.

Ans. (i) Nil

(ii) 2 (fac-and mer-isomer).

Three marksquestion

Q.1 Discuss nature of bonding in the following co□ordination entities on the basis of valence bond theory.

i) $[Fe(CN)□]^{4-}$

(ii) $[FeF□]^{3-}$

(iii) $[CoF□]^{3-}$.

Co-ordination	Electronic	Charge on Configuration of Central Metal ion	ridisation the Ion	Geometry	Magnetic Behaxion
$[Fe(CN)_6]^{4-}$, CN^- Strong Ligand So low spin Complex & Inner Complex	$3d^6 4s^2$	Fe^{2+}	d^2sp^3 XX | XX | XX | XX | XX | XX $d^2 sp^3$	Octahedral	Diamagnetic
$[FeF_6]^{3-}$ weak Ligand & High- spin complex And outer orbital complex	$3d^6 4s^2$	Fe^{3+}	$sp^3 d^2$ XX | XX | XX | XX | XX | XX	octahedral	diamagnetic
$[COF_6]^{3-}$ F□ is weak Ligand high spin Complex outer Orbital complex	$3d^7 4s^2$	Co^{3+}	sp^3d^2 XX | XX | XX | XX | XX | XX	octahedral	diamagnetic

Q.3 Write the formulae for the following co-ordination compounds:

(a) Tetra ammineaquochlorido cobalt (III) chloride

(b) Potassium tetrahydroxozincate (II)

(c) Potassium trioxalatoaluminate (III)

Ans. (a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$

(b) $K_2[Zn(OH)_4]$

(c) $K_3[Al(C_2O_4)_3]$

Q.4 Write the IUPAC names of the following co-ordination compounds:

(a) $[Pt(NH_3)_2Cl(NO_2)]$

(b) $K_3[Cr(C_2O_4)_3]$

(c) $[CoCl_2(en)_2]Cl$

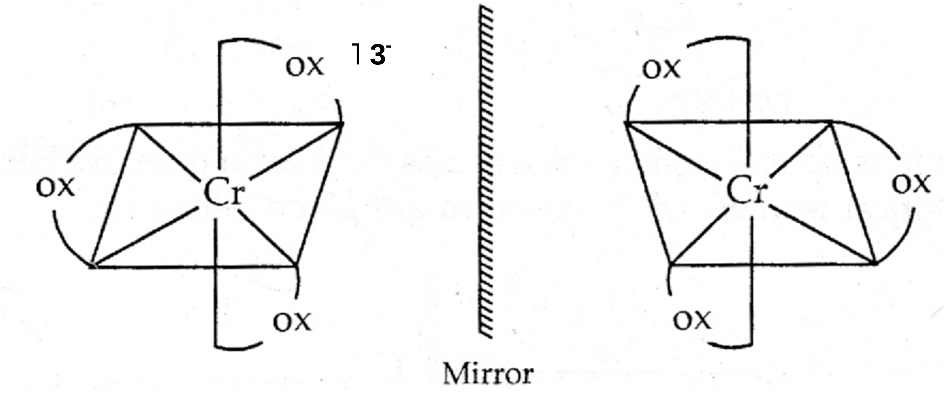
Ans. (a) Diamminechloridonitrito – N- platinum(II)

(b) Potassium trioxalatochromate (III)

(c) Dichloridobis(ethane-1, 2-diammine cobalt(III) chloride

Q-5 Draw the structures of optical isomers of: $[Cr(C_2O_4)_3]^{3-}$

$]^{3-}$



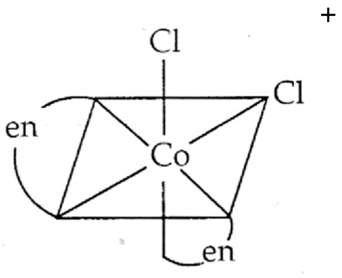
Q.6 A solution of $[Ni(H_2O)_6]^{2+}$ is green, but a solution of $[Ni(CN)_4]^{2-}$ is colourless.Explain.

ANS. In $[Ni(H_2O)_6]^{2+}$, H_2O is a weak field ligand. Therefore, there are unpaired electrons in Ni^{2+}. In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e. the possibility of d-d transition is present. Hence,$[Ni(H_2O)_6]^{2+}$ is coloured.

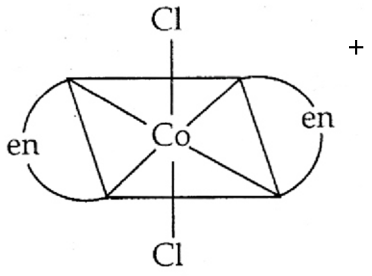
In $[Ni(CN)_4]^{2-}$, the electrons are all paired as CN^- is a strong field ligand. Therefore, d□d transition is not possible in $[Ni(CN)_4]^{2-}$. Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

Q.7 **Draw all the isomers (geometrical and optical) of: $[CoCl_2(en)_2]^+$**

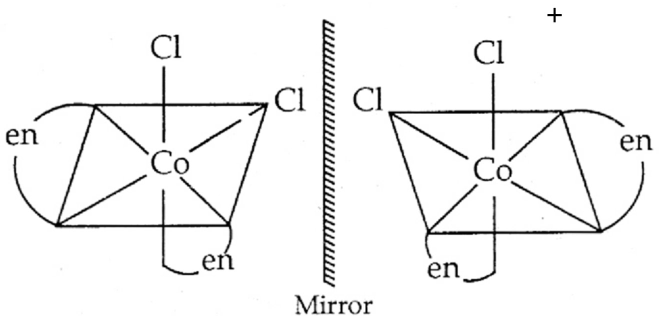
ANS. (i) $[CoCl_2(en)_2]^+$



cis-form



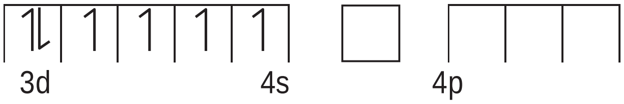
trans-form



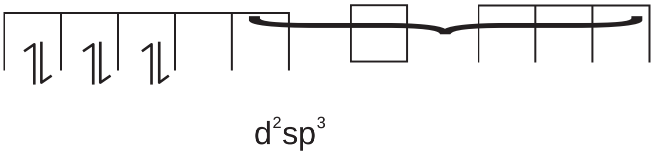
d- and *l*-forms of *cis*-$[CoCl_2(en)_2]$

Q8. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

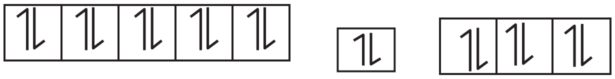
(i) $[Fe(CN)_6]^{4-}$In the above coordination complex, iron exists in the +2 oxidation state.Fe^{2+}: Electronic configuration is $3d^6$ orbitals of Fe^{2+} io6n:



As CN^- is a strong field ligand, it causes the pairing of the unpaired 3d electrons.Since there are six ligands around the central metal ion, the most feasible hybridization is d^2sp^3.
7



6 electron pairs from CN^- ions occupy the six hybrid d^2sp^3orbitals.Then, hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons)



6 pairs of electrons from 6 CN^- ions

ASSIGNMENT

Q.1 Why [Fe(CN)]$^{3-}$ is weakly paramagnetic while [Fe(CN)]$^{4-}$ is diamagnetic ?
Q.2 Why $[Ni(CO)_4]$ 6possesses tetrahedral geometry,while $[Pt(^6NH_3)_2Cl_2]$ is a square-planar?
Q.3 What are the factors on which the stability of a complex depends ?
Q.4 What is spectrochemical series?
Q.5 Explain the dissociation constant.
Q.6 Explain stepwise stability constant or overall stabilityconstant with example.
Q.7 How many geometrical isomers of $[Cr(en)_2Cl_2]^+$ exist? Which of these shows optical activity?
Q.8 Comment on the statement that all compounds containing carbon and metal are not organometallic.
Q.9 Outline the basic assumption of Werner's co-ordination theory.
Q.10 Write the application of co-ordination compounds and organometallic compounds.

OBJECTIVE TYPE QUESTIONS

1. Which of the following is a complex of metal other than transition metal?
(a) Haemoglobin (b) Chlorophyll (c) Ferrocene (d) Vitamin B_{12}

2. Which of the following is not a double salt but a coordinate compound?
(a) $KCl.MgCl_2.6H_2O$ (b) $FeSO_4.(NH_4)_2SO_4.6H_2O$ (c) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(d) $4KCN.Fe(CN)_2$

3. The donor atoms in ethylenediaminetetraacetate ion is
(a) two N and two O (b) two N and four O (c) four N and two O (d) three N and three O

4. The correct I.U.P.A.C. name of the complex, $Fe(C_5H_5)_2$ is
(a) cyclopentadienyliron(II) (b) bis(cyclopentadienyl)iron(II)
(c) dicyclopentadienyliron(II) (d) ferrocene(0)

5. The geometrical isomerism in coordination compounds is exhibited by
(a) square planar and tetrahedral complexes
(b) square planar and octahedral complexes
(c) tetrahedral and octahedral complexes
(d) square planar, tetrahedral, octahedral comp.

6. Which of the following is not optically active?
(a) $[Co(en)_3]^{3+}$ (b) $[Cr(ox)_3]^{3-}$ (c) cis-$[CoCl_2(en)_2]^+$ (d) trans-$[CoCl_2(en)_2]^+$

7. The complex ion $[Cu(NH_3)_4]^{+2}$ is
(a) tetrahedral and paramagnetic (b) tetrahedral and diamagnetic
(c) square planar and paramagnetic (d) square planar and diamagnetic

8. The hybrid state of Co in high spin complex, $K_3[CoF_6]$ is
(a) sp^3d^2 (b) sp^3 (c) d^2sp^3 (d) sp^3d

9. In an octahedral crystal field, the t_{2g} orbital are
(a) raised in energy by 0.4 Δ_o (b) lowered in energy by 0.4 Δ_o
(c) raised in energy by 0.6 Δ_o (d) lowered in energy by 0.6 Δ_o

10. If $\Delta_o < P$, then the correct electronic configuration for d^4 system will be
(a) $t_{2g}^4\ e_g^0$ (b) $t_{2g}^3\ e_g^1$ (c) $t_{2g}^0\ e_g^4$ (d) $t_{2g}^2\ e_g^2$

11. The tetrahedral complexes are generally high spin. This is because
(a) $\Delta_t < P$ (b) $\Delta_t > P$ (c) $\Delta_t = P$ (d) none of these

12. Which of the following is correct related with Irving William's order?
(a) $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$ (b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$
(c) $Fe^{2+} < Mn^{2+} < Ni^{2+} < Co^{2+}$ (d) $Co^{2+} < Mn^{2+} < Fe^{2+} < Ni^{2+}$

13. Class "a" acceptors are the metal ions belonging to
(a) group 11 and 12 elements (b) inner transition elements
(c) transition elements of group 3 - 6 (d) transition elements of group 7 – 9

14. Wilkinson's catalyst, $[Rh(Ph_3P)_3Cl]$ is used for
(a) hydrogenation of carboxylic acids (b) hydrogenation of alkynes
(c) hydrogenation of alkenes (d) polymerization of alkenes

15. Zeigler Natta catalyst is used for
(a) synthesis of methanol (b) polymerization of olefins
(c) cracking of hydrocarbons (d) hydrogenation of alkenes

16. Among the compounds 1,2, and 3, $[Ni(CO)_4]$ -1, $[Ni(CN)_4]^{2-}$ - 2 and $[NiCl_4]^{2-}$ - 3, the correct statement is

(a) 1, 3 are diamagnetic while 2 is paramagnetic

(b) 2, 3 are diamagnetic while 1 is paramagnetic

(c) 1, 2 are diamagnetic while 3 is paramagnetic

(d) 1 is diamagnetic while 2, 3 are paramagnetic

17. Which of the following is a complex salt?

(a) Fischer's salt (b) Mohr's salt (c) Glauber's salt (d) Microcosmic salt

18. In which of the following compounds, the central atom obey E.A.N. rule?

(a) $K_3[Fe(CN)_6]$ (b) $[Cu(NH_3)_4]SO_4$ (c) $K_4[Fe(CN)_6]$ (d) $[NiCl_4]^{2-}$

19. The total number of isomers of the complex $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ is

(a) 3 (b) 6 (c) 5 (d) 4

Passage – 1: When crystals of $CuSO_4.4NH_3$ are dissolved in water, then there is hardly any evidence for the presence of Cu^{2+} ions or NH_3 molecules. A new ion $[Cu(NH_3)_4]^{2+}$ is furnished in which ammonia molecules are directly linked with the metal ion, Cu^{2+}. Similarly, the aqueous solution of $Fe(CN)_2.4KCN$ does not give the test for Fe^{2+} and CN^- ions but gives test for new ion, $[Fe(CN)_6]^{4-}$. These ions are known as complex ions.

1.The primary and secondary valency of copper in the complex $[Cu(NH_3)_4]SO_4$ are

(a) 2, 4 (b) 4, 2 (c) 0, 4 (d) 1, 4

2.The E.A.N. of the central metal ion in the complex $[Fe(CN)_6]^{4-}$ is

(a) 26 (b) 37 (c) 36 (d) 35

3.The hybridization state of the Cu in the compound $[Cu(NH_3)_4]SO_4$ is

(a) sp^3 (b) sp^2d (c) sp^3d^2 (d) dsp^2

4. Which of the following statement is correct?

(a) $[Cu(NH_3)_4]^{2+}$ is diamagnetic while $[Fe(CN)_6]^{4-}$ is paramagnetic

(b) $[Cu(NH_3)_4]^{2+}$ is paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic

(c) both are paramagnetic

(d) both are diamagnetic

5. For the complex ion, $[Cu(NH_3)_4]^{2+}$, the stability constant is

(a) $[Cu(NH_3)_4]^{2+} / [Cu^{2+}][NH_3]^4$ (b) $[Cu^{2+}][NH_3]^4 / [Cu(NH_3)_4]^{2+}$

(c) more if instability constant is more (d) is less if instability constant is less

Passage – 2: The coordination number of Ni^{2+} is 4 in both the complexes.

$NiCl_2 + KCN \rightarrow$ "A" (cyano complex) and $NiCl_2 + HCl$ (excess) $\rightarrow$ "B" (chloro complex).

6. The I.U.P.A.C. name of "A" and "B" are respectively

(a) potassium tetracyanidonickelate (II) and potassium tetrachloridonickelate (II)

(b) tetracyanidopotassiumnickelate (II) and tetrachloridopotassiumnickelate (II)

(c) tetracyanidonickel (II) and tetrachloridonickel (II)

(d) none of above is correct

7. Predict the magnetic nature of "A" and "B".

(a) Both are diamagnetic

(b) both are paramagnetic

(c) "A" is diamagnetic & "B" is paramagnetic

(d) "A" is paramagnetic & "B" is diamagnetic

8. The hybridization state of “A” and “B” is respectively

(a) dsp^2 & sp^3 (b) sp^3 & sp^3 (c) dsp^2 & dsp^2 (d) sp^3 & dsp^2

Answer key:

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

Passage – 1:

1	**2**	**3**	**4**	**5**
a	**c**	**d**	**b**	**a**

Passage – 2:

6	**7**	**8**
a	**c**	**a**

HALOALKANES AND HALOARENES (UNIT - 9)

The placement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkylhalide (haloalkane) and arylhalide (haloarene), respectively

$$Ar - H + X_2 \xrightarrow[\Delta]{Fe} Ar\text{-}X + H\text{-}X$$

$$R\text{-}H + X_2 \xrightarrow{h\nu} R\text{-}X + H\text{-}X$$

(A) IMPORTANT NAME REACTIONS

i) Finkelstein Reaction

$$R\text{-} X + Na\ I \xrightarrow{\text{Dry Acetone}} R\text{-} I + Na\ X$$

II) Swarts Reaction

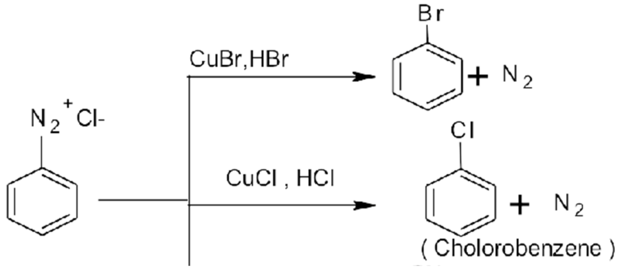
$$R\text{-} X \xrightarrow{\text{Ag F, } Hg_2F_2\text{, Co } F_2 \text{ OR Sb } F_3} R\text{-}F$$

1. Carbylamines reaction

$$R-NH_2 + CHCl_3 + 3\,KOH \longrightarrow R.NC + 3KCl + 3H_2O$$

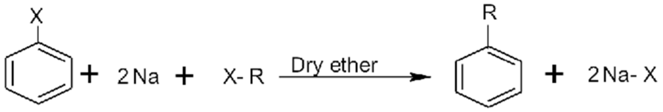
$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

2. Sandmeyer's reaction

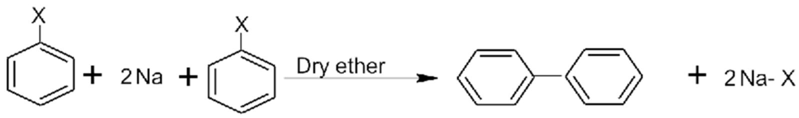


3. **Wurtz Reaction** $R-X + 2Na + RX \longrightarrow R - R + 2\ NaX$ (in dry ether)

4. **Wurtz Fittig reaction:-**



5. Fittig reaction



6. **Grignard reagent:** $RMgX + H_2O \rightarrow RH + Mg(OH)X$

(B) IMPORTANT MECHANISM

i) Nucleophilic Substitution ii) Elimination reaction iii) Electrophilic substitution

i) Nucleophilic Substitution :- it involves the replacement of an atom or group of atoms by a nucleophile (electron rich species)

A-B + Nu →A- Nu +B

It is of two types:-

a) Unimolecular nucleophi lic substitution reaction (S_N1)

b) Bimolecular nucleophilic substitution reaction (S_N2^2)

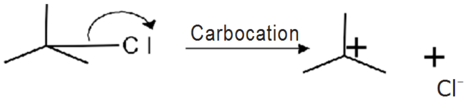
a) Unimolecular substitution reaction (S_N1)

(i) it involves two steps

(ii) in this retention/Racemization of configuration take place.

(iii) unimolecular and all are first order.

Mechanism (**step 1**) formation of carbocation.

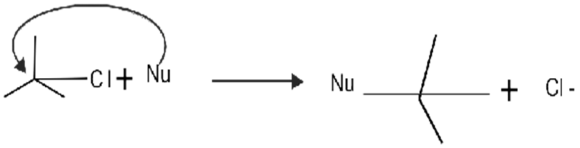


Step 2 Attack of nucleophile on carbocation

(front/rear end)

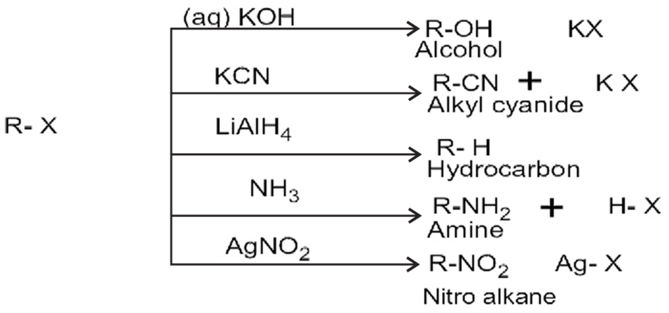
Order of reactivity: 3^{0}> 2^{0}>1^{0} (Because 3^{0} carbocation is more stable)

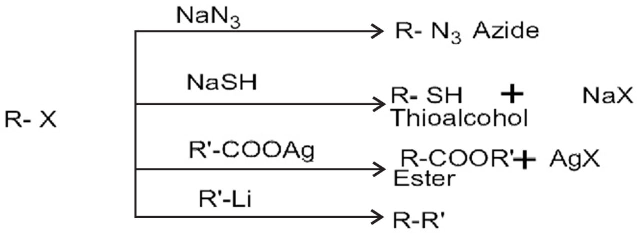
(b) **Bimolecular Nucleophilic Substitution S_N2**(i) it involves one step. (ii) in this inversion of configuration takes place. (iii) bimolecular mechanism: .in this nucleophile attacks from the backside Where halogen atom is attached. It facilitates the departure of leaving halide group.



Order of reactivity:-1^{0}>2^{0}>3^{0}(Because of less steric hindrancein 1^{0} alkylhlide)

Nucleophilic substitution reaction of alkyl halides





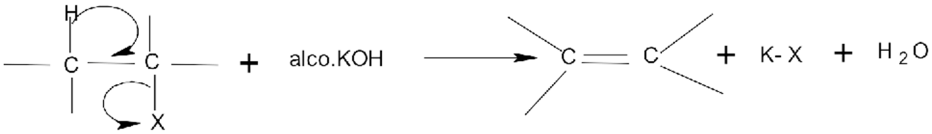
R-X + AgCN → RNC + AgX

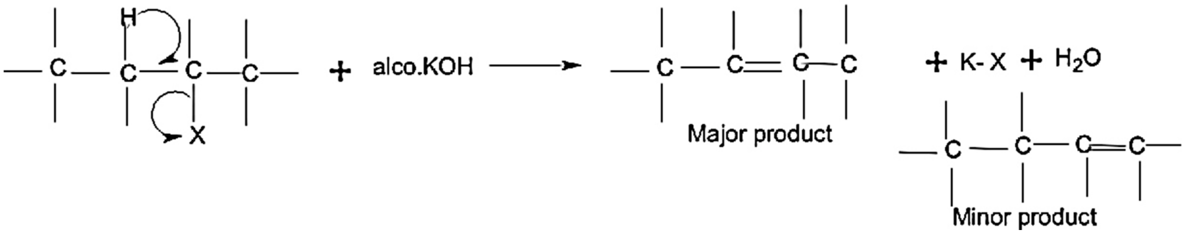
R-X + Na-C ≡C-R → R-C≡ C-R + Na-X

R-X + KNO_2 → R-O-N=O + KX

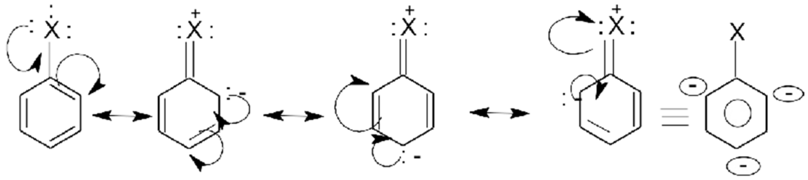
ii) Elimination reaction : Haloalkanes having hydrogen atom, when heated with alcoholic KOH, there is elimination of hydrogen atom from β-carbon and a halogen atom from the α- carbon atom & alkene is formed.

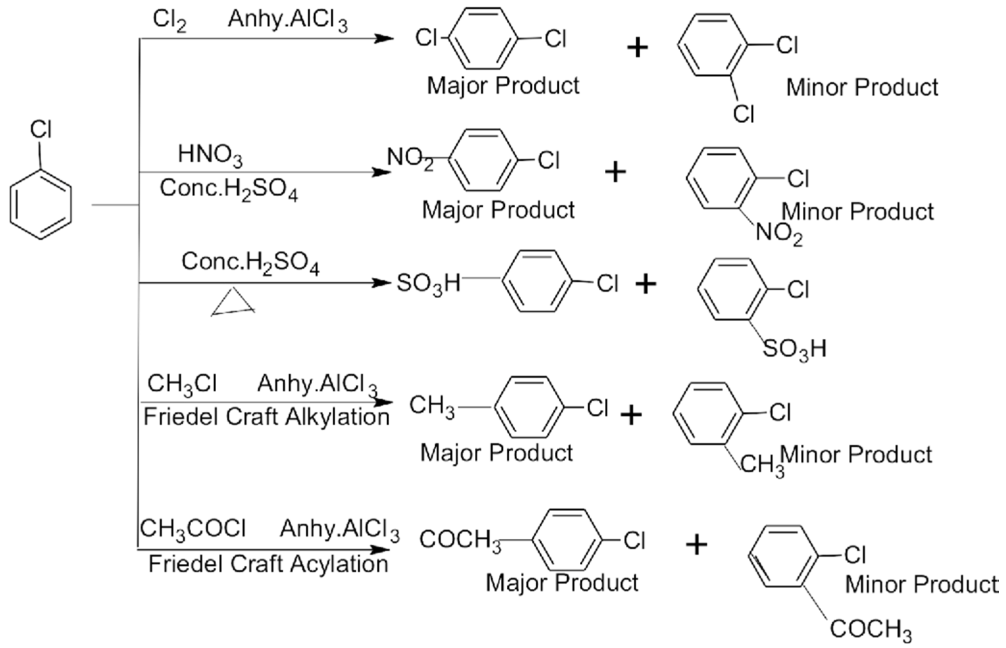
Saytzeff rule“*in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms*.”





iii) Electrophilic substitution:- substitution occurs at *ortho*- and *para*- positions with respect to the halogen atom.





Q.1 What are ambident nucleophiles? (1 Mark)

Ans. Nucleophiles which can attack through two different sites are called ambident nucleophiles. Example:-Cyanide ion: CN^- : & $C{=}N:^-$

Q.2 Which is a better nucleophile, a bromide ion or iodide ion? (1 Mark) Ans.

Iodide ion because it has lower electronegativity and larger size.

Q.3 Arrange the compounds of each set in order of reactivity towards S_{N2} displacement:

2- Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane. **(1Mark)**

Ans. The reactivity in S_{N2} reactions depend upon steric hindrance; more the steric hindrance slower the reaction. The order of reactivity in S_N2 reactions follows the order : $1^0 > 2^0 > 3^0$. 1- Bromopentane **>** 2-Bromopentane **>** 2-Bromo-2-methylbutane**.**

Q.4 Arrange the following in increasing order of boiling point.

$CH_3CH_2CH_2CH_2Br$, $(CH_3)_3CBr$, $(CH_3)_2CHCH_2Br$. **(1Mark)**

Ans. The boiling point increases as the branching decreases, so the increasing order of boiling point is:-$(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$

Q.5 Define optical activity? (1Mark)

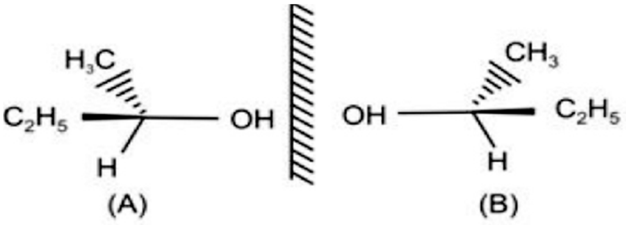
Ans. The compounds which rotate the plane of polarized light when it is passed through their solutions are called optically active compounds and this property is known as optical activity.

Q.6 What is racemic mixture or racemic modification? (1 Mark) Ans.

A mixture containing two enantiomers in equal proportions will have zero optical rotation, As the rotation due to one isomer will be cancelled by the rotation due to other isomer. Such a mixture is known as racemic mixture or racemic modification.

Q. 7 What are enantiomers? (1 Mark)

Ans. The stereo isomers related to each other as non-superimposable mirror images are called enantiomers.



ASSERTION -REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : S_N2 reactions do not proceed with retention of configuration.
   Reason : S_N2 reactions proceed in a single step. (Ans - b)
2. Assertion : Chloroform is generally stored in dark coloured bottles filled to the brim.
   Reason : Chloroform reacts with glass in the presence of sun light. (Ans - c)
3. Assertion : $CH_3\text{-}CH=CH_2 \xrightarrow[\boxed{Cl2\text{ , }773\text{ K}}]{} Cl\text{-}CH_2\text{-}CH=CH_2 + HCl$
   Reason : At high temperature, Cl_2 dissociates into chlorine free radicals which bring about allylic substitution. (Ans - a)
4. Assertion : Nucleophilic substitution reaction in an optically active alkyl halide gives a mixture of enantiomers.
   Reason : Reaction occurs by S_N1 mechanism. (Ans - a)
5. Assertion : Primary allylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides.
   Reason : Intermediate carbocation is stabilised by resonance. (Ans - a)

One - word answer

1. Name the poisonous compound obtained when chloroform is exposed to air, in presence of sunlight. (Ans - Phosgene)
2. Name the compound formed when Grignard' s reagent is exposed to moisture. (Ans - Alkane)

Q.8 Haloalkanes react with aq. KOH to form alcohols but react with alc. KOH to form alkenes. Why? (2 Marks)

Ans. KOH is a strong base, so it completely ionizes in aqueous solution. OH^- ions are strong nucleophile, so it replaces the halogen atoms and form alcohols. In contrast, an alcoholic solution of KOH contains alkoxide ($R\text{-}O^-$) ions which being a much stronger base than (OH^-) ions preferentially eliminates a molecule of HCl from an alkyl chloride to form an alkene.

Ans. Haloalkanes are more polar than haloarenes. As a result the carbon atom carrying the halogen in haloalkanes is more electron-deficient than that in haloarenes. So, haloalkanes undergo nucleophilic substitution more readily than haloarenes.

In contrast, haloarenes contain a benzene ring. Since the typical reactions of benzene are electrophilic substitutions, therefore, haloarenes undergo electrophilic substitution while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitution.

Q. 10 Explain why?

(a) Alkyl halides, though polar, are immiscible in water.

(b) Grignard reagents should be prepared under anhydrous conditions?(3 Marks)

Ans. (a) Alkyl halides are polar in nature but it is insoluble in water because alkyl halide molecules are held together by dipole-dipole attraction and water molecules are held together by H-bonds. More energy is required to overcome these attractive forces between the haloalkanes. But less energy is released when haloalkanes and water molecules come together, so haloalkanes are not soluble in water.

(b) Grignard reagents are very reactive, so they react with moisture and form alkane.

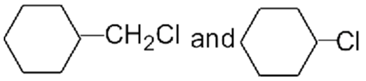
$$\text{R-Mg-X} + \text{H-OH} \rightarrow \text{R-H} + \text{Mg(OH)X}$$

Therefore, it must be prepared and stored under anhydrous conditions..

Q.9 Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Why? (3 Marks)

Assignment

Q1 In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?



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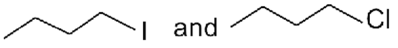
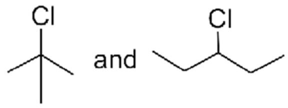


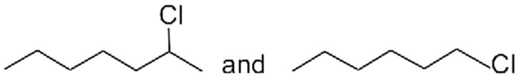
Q2 Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. Why?

Q3 In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)



(ii)



Q4 Why is sulphuric acid not used during the reaction of alcohols with KI?

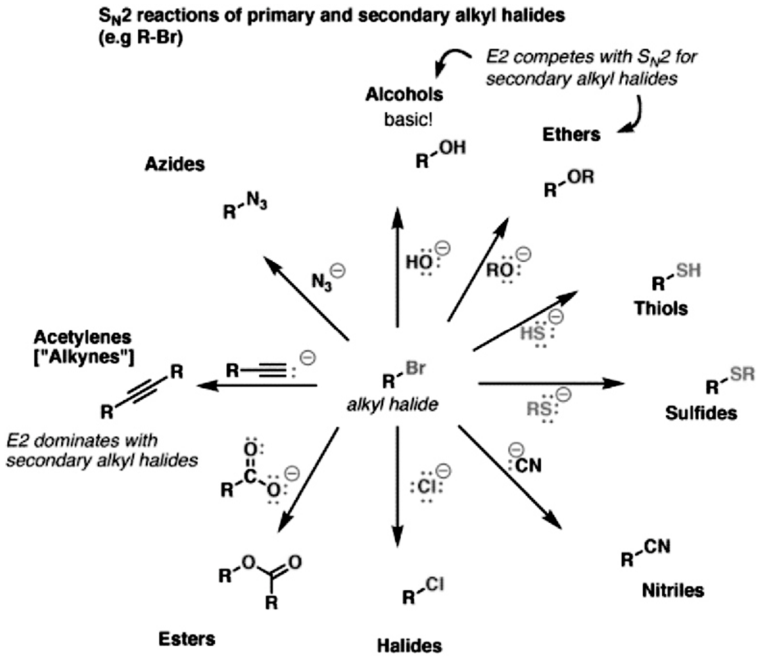
Q5 *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers. Discuss.

Q6 Hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Q7. Chloroform is stored in dark coloured & sealed bottle. Why?

Q8 Aryl halides cannot be prepared by the action of sodium halide in the presence of H_2SO_4. Why?

MIND MAP FOR CONVERSION



/thioethers

MUILTIPLE CHOICE QUESTION (MCQs)

1). Identiy the following compounds as primary halide:

- (i) 1-Bromobut-2-ene
- (ii) 4-Bromopent-2-ene
- (iii) 2-Bromo-2-methylpropane

Ans :(i) 1-Bromobut-2-ene (1^o alkyl halide)

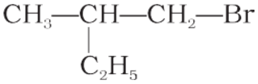
2). Which of the following compounds are gem-dihalides ?

(a) Ethylidene chloride (b) Ethylene dichloride

(c) Methyl chloride (d) Benzyl chloride

Ans : Option (a) is correct . In gem-dihalides both the halogens are attached to the same carbon atom.

3). Which is the correct IUPAC name for



$$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-Br$$

i)1-Bromo-2-ethylpropane ii)1-Bromo-2-ethyl-2-methylethane

iii)1-Bromo-2-methylbutane iv) 2-Methyl-1-bromobutane

Ans. iii)1-Bromo-2-methylbutane

4). What should be the correct IUPAC name for diethylbromomethane?

i)1-Bromo-1,1-diethylmethane ii)3-Bromopentane

iii)1-Bromo-1-ethylpropane iv)1-Bromopentane

Ans.ii). 3-Bromopentane

5). Which of the following is /are secondary bromide?

(i) CH_3CH_2Br

(ii) $(CH_3)_3C\ CH_2Br$

(iii) $CH_3CH(Br)CH_2CH_3$

(iv) $(CH_3)_2CBrCH_2CH_3$

Ans.(iii) $CH_3CH(Br)CH_2CH_3$

6.) Pure chloroform is obtained by treating

(i) Ethanol with bleaching powder (ii) Acetone with bleaching powder

(iii) Chloral with Sodium hydroxide (iv) CCl_4 with moist Iron

Ans : (iii) Chloral with Sodium hydroxide

7.) 1,1-Dichloropropane on hydrolysis gives

a) Propanone

b) Propanal

c) Ethanal

d) 1,1-Propandiol

Ans : b) Propanal

8.). Among the following , the molecule with the highest dipole moment is :

a) CH_3Cl

b) CH_2Cl_2

c) $CHCl_3$
d) CCl_4
Ans : a) CH_3Cl

9.) Which of the following represents Freon?
a) Ethylene dichloride
b) Ethylidene dichloride
c) Tetrafluoro ethylene
d) Dichlorodifluoromethane
Ans: d). Dichlorodifluoromethane

SHORT ANSWERED QUESTIONS (1-MARK)

1.Write the IUPAC name of $(CH_3)_3 CCH_2 Cl$
2.Which of the following under goes S_N1 faster: 2-chlorobutane or 1-chlorobutane
3. Arrange each set of compounds in order of increasing boiling points.
(i) Bromomethane, (ii) Bromoform, (iii) Chloromethane, (iv) Dibromomethane.
4.Write the product formed when toluene is chlorinated in presence of sunlight.
5.Write the product formed when n-butyl chloride is treated with alcoholic KOH ?
6. Which is a better nucleophile, a bromide ion or an iodide ion ?
7. Which has higher dipole moment, Chlorobenzene or Cyclohexyl chloride?
8. Draw the structure of DDT.
9. Expand BHC
10.How many centres of chirality are present in 3-Bromopent-1-ene.

ANSWERS

1. 1- chloro-2,2-dimethylpropane
2. 2-chlorobutane.
3. (iii) < (i)< (iv)< (ii)
4. Chloromethylbenzene
5. But-2-ene
6. Iodide ion
7. Cyclohexyl chloride
8. Correct structure(Dichloro diphenyl trichloroethane)
9. Benzenehexachloride
10. one

ALCOHOLS, PHENOLS AND ETHERS (Unit-10)

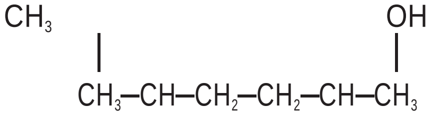
Definition:

An alcohol is any organic compound in which a hydroxyl functional group (−**OH**) is bound to a carbon atom, usually connected to other carbon or hydrogen atoms.

- $CH_3–CH_2–CH_2–OH$ 1-propanol OH

|

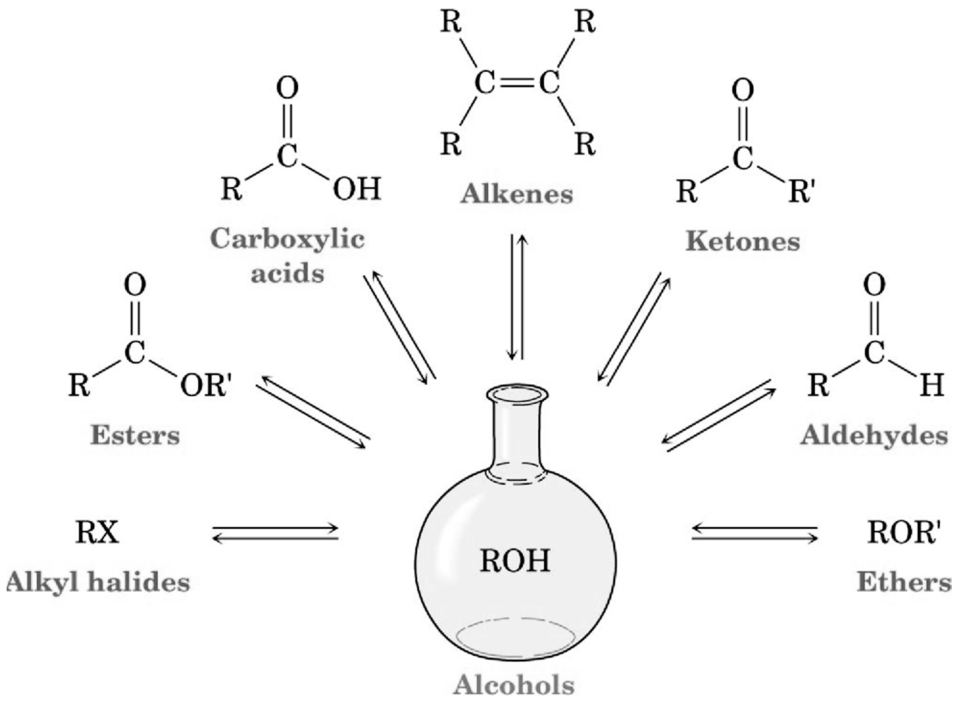
$CH_3–CH–CH_3$ 2-propanol



$$\begin{array}{l} CH_3 \qquad\qquad\qquad\qquad\qquad\quad OH \\ \ \ | \qquad\qquad\qquad\qquad\qquad\qquad\ \ | \\ CH_3–CH–CH_2–CH_2–CH–CH_3 \end{array}$$

5-methyl-2-hexanol

MIND MAP OF PROPERTIES OF ALCOHOL

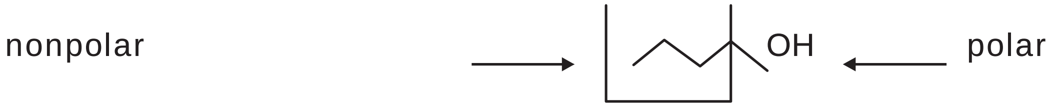


Physical Properties

1. **Alcohols are polar molecules (because of O-H and C-O).**
2. **Hydrogen bonding occurs between alcohol molecules relatively weak bond (represented by dots) O has a partially negative charge δ- & H has a partially positive charge.**
3. **They are weak acids (alkyl alcohols weaker than Phenol):**

Although alkyl alcohols have an -OH group, they do not ionize in water, whereas phenols ionize like acids (donating a proton to water).

4. Solubility in water(Molecular weight↑: solubility↓)



As the chain of the R group increases the hydrocarbon (**non- polar)** character of the compound also increases. Consequently, the **solubility** and **boiling point** of an alcohol are affected by the

1) Length of the carbon chain and

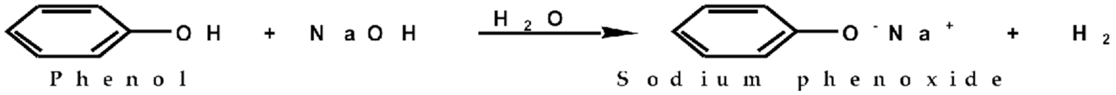
2) The shape of the molecule.

The **short** chain alcohols are **soluble** in water, whereas the **longer** chain alcohols are **insoluble** in water.

In general a molecule which is **more compact** (i.e., more branched) will be **more soluble** in water and will have **a lower boiling point** than the straight chain isomer. (for isomeric alcohol)

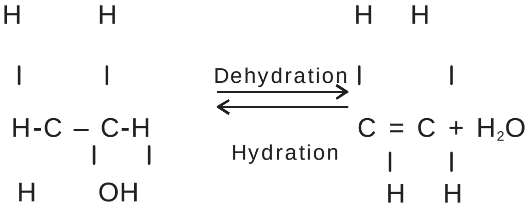
Chemical Properties of Alcohols

1. Acidity of Alcohols / Phenols



2. Acid-Catalysed Dehydration:

$CH_3CH_2OH \xrightarrow[180°C]{H_2SO_4} CH_2 + H_2O$



$$\begin{array}{c} H \quad H \\ | \quad\; | \\ H-C-C-H \\ | \quad\; | \\ H \quad OH \end{array} \underset{\text{Hydration}}{\overset{\text{Dehydration}}{\rightleftarrows}} \begin{array}{c} H \quad H \\ | \quad\; | \\ C=C \\ | \quad\; | \\ H \quad H \end{array} + H_2O$$

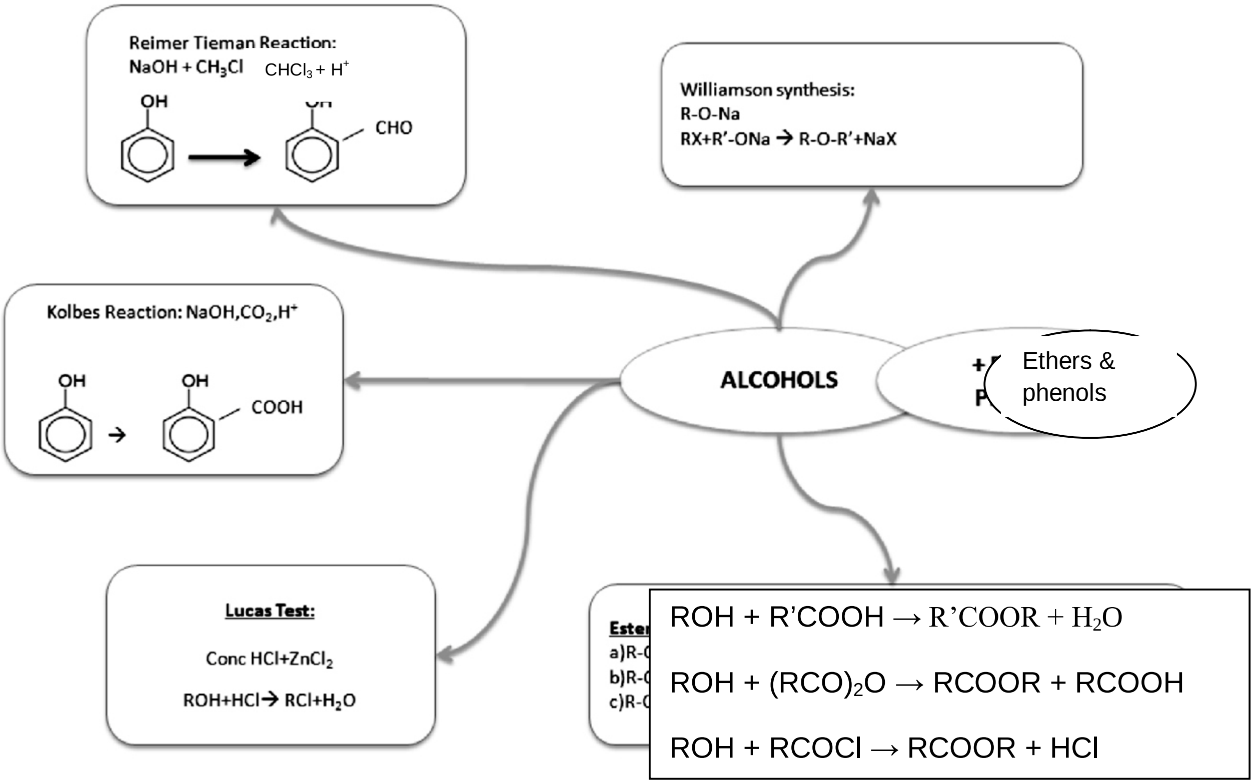
3. **Oxidation of Alcohols: (1°), (2°) & (3°)** Using potassium dichromate & sulphuric Acid as catalysts In the oxidation [O] of a primary alcohol(1°) , aldehyde is produced

Primary alcohol ⟶ aldehyde ⟶carboxylicacid

On oxidation of 2^0 alcohols a ketone is formed. Secondary alcohol ⟶ ketone

Tertiary alcohols do not oxidize.

Tertiary alcohol → No reaction



$ROH + R'COOH \rightarrow R'COOR + H_2O$

$ROH + (RCO)_2O \rightarrow RCOOR + RCOOH$

$ROH + RCOCl \rightarrow RCOOR + HCl$

CONCEPTUAL QUESTIONS

Q1) Preparation of ethers by acid dehydration of secondary or 3^0 alcohols is not a suitable method?

Ans. The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) group is hindered. As a result elimination dominates substitution as 3^0 carbocation is more stable. Hence in place of ethers, alkenes are formed.

Q2) Phenols do not give protonation reactions readily. Why?

Ans. The lone pair on oxygen of O-H in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

REASONING QUESTIONS

Q1. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Ans. The molecules of butane are held together by weak van der Waal's forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

Q2. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

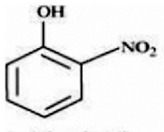
Ans. Alcohols can form hydrogen bonds with water and break the hydrogen bonds already existing between water molecules Therefore they are soluble in water, whereas hydrocarbons cannot form hydrogen bonds with water and hence are insoluble in water.

Q3 While separating a mixture of ortho and para nitro phenols by steam distillation, name the isomer which will be steam volatile. Give reason.

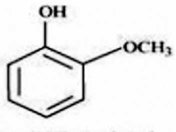
Ans. O-nitrophenol is steam volatile due to intramolecular hydrogen bonding and hence can be separated by steam distillation from p-nitrophenol which is not steam volatile because of inter-molecular hydrogen bonding.

Q4. Explain why is ortho-nitrophenol more acidic than ortho- methoxyphenol?

Ans. The nitro-group is an electron-withdrawing group. Therefore decreases the electron density of the ring as well as oxygen.. As a result, it is easier to lose a proton. Also, the o-nitrophenoxide ion formed after the loss of proton is stabilized by resonance. Hence, o- nitro phenol is stronger acid. On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density of the oxygen atom and hence, the proton cannot be given out easily. Therefore, o-nitrophenol is more acidic than o-methoxyphenol.



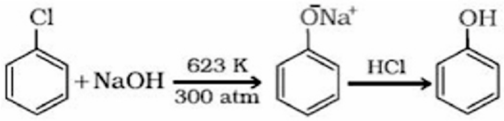
o – Nitrophenol



o – Methoxyphenol

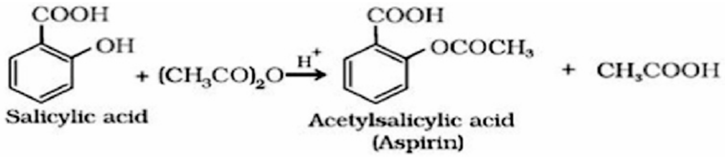
Q5. Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans. Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced.



Q6. How is aspirin (Acetylsalicylicacid) prepared from salicylic acid?

Ans. Acetylation of salicylic acid produces aspirin.



Q7. Which out of propan-1-ol and propan-2-ol is stronger acid?

Ans. Propan-1-ol is stronger acid than propan-2-ol. The acidic strength of alcohols is in the order $1^0>2^0>3^0$.

Q8. What is denaturation of an alcohol?

Ans. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Q9. Give IUPAC name of $CH_3OCH_2OCH_3$

Ans. Dimethoxymethane

Q10. Diethylether does not react with sodium. Explain.

Ans. Diethyl ether does not contain any active hydrogen.

ASSERTION - REASONING QUESTIONS

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below :

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Methyl alcohol is a weaker acid than water.
Reason : Among the aliphatic monohydric alcohols, methyl alcohol is the strongest acid. (Ans - b)

2. Assertion : o - Nitrophenol and p - Nitrophenol are separated by steam distillation.
Reason : o-Nitrophenol has intramolecular H - bonding while molecules of p-nitrophenol are linked by intermolecular H - bonding. (Ans - a)

3. Assertion : Phenols do not react with phosphorus halides while alcohols do not react.
Reason : In phenols C-O bond has partial double bond character due to resonance while it is not so in alcohols. (Ans - a)

4. Assertion : Phenol is acidic in nature.
Reason : Phenate ion is less resonance stabilised than phenol. (Ans - a)

One - word answer

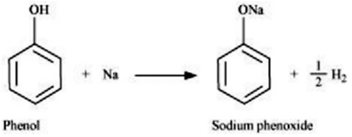
1. Name a compound which can be used as an anesthetic in surgery ? (Ans - Ethrane)
2. In Williamson synthesis , which type of halide should not be used ? (Ans - Tertiary alkylhalide)

2 MARKS QUESTIONS

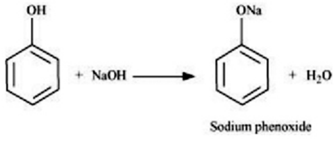
Q1. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Ans. The acidic nature of phenol can be represented by the following two reactions:

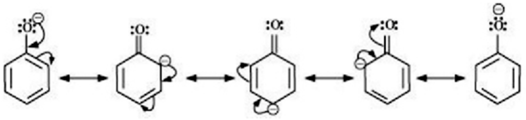
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water.

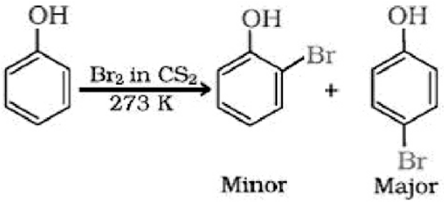


The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.

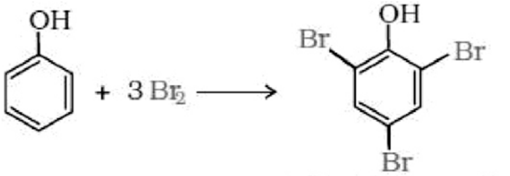


Q2. How does phenol react with Br_2 in CS_2 and bromine water?

Ans. (i) When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.



ii. When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



2,4,6-Tribromophenol

Q4. How do you account for the fact that unlike phenol, 2, 4-dinitrophenol and 2, 4, 6- trinitrophenol are soluble in aqueous solution of sodium carbonate?

Ans. 2, 4-Dinitrophenol and 2, 4, 6-trinitrophenol are stronger acids then carbonic acid (H_2CO_3) due to the presence of electron withdrawing $-NO_2$ group. Hence, they react with Na_2CO_3 to form their corresponding salts and dissolve in aq. Na_2CO_3 solution.

Q5. Account for the following

a. Boiling point of the C_2H_5OH is more than that of C_2H_5Cl

b. The solubility of alcohols in water decreases with increase in molecular mass.

Ans. a. Because of hydrogen bonding.

b. With increase in molecular mass the non-polar alkyl group becomes more predominant.

Q6. Answer the following

a. What is the order of reactivity of 1^0, 2^0 and 3^0 alcohols with sodium metal?

b. How will you account for the solubility of lower alcohols in water?

Ans, a. $1^0 > 2^0 > 3^0$

b. Here-OH group is predominant and the alcohol molecules can form hydrogen bonds with water molecules.

Q7. Give reasons:

i) Nitration of phenol gives ortho-and para-products only.

ii) Why do alcohols have higher boiling points than the haloalkanes of the same molecular mass?

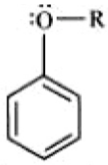
Ans. (1) -OH group increases the electron density more at ortho and para positions through its electron releasing resonance effect.

(2) Alcohols are capable of forming intermolecular H-bonds.while alkyl halide do not.

Q8. Explain the fact that in aryl alkyl ethers

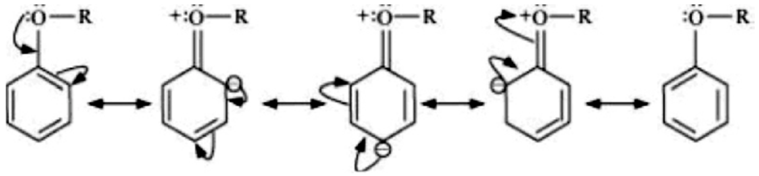
(i) The alkoxy group activates the benzene ring towards electrophilic substitution and

(ii) It directs the incoming substituents to ortho and parapositions in benzene ring.



Aryl alkyl ether

(Ans. (i) In arylalkylethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.



Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene.

Q9. How is 1-propoxypropane synthesized from propan-1-ol? Write mechanism of this reaction.

Ans. 1-propoxypropane can be synthesized from propan-1-ol by dehydration. Propan-1-ol undergoes dehydration in the presence of protic acids (such as H_2SO_4, H_3PO_4) to give 1-propoxypropane.

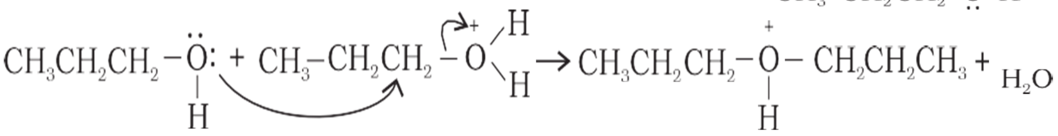
$$2CH_3CH_2CH_2 - OH \xrightarrow[413K]{H^+} CH_3CH_2CH_2 - O - CH_2CH_2CH_3$$

Propane-1-ol 1- Propoxypropane

The mechanism of this reaction involves the following three steps: Step 1: Protonation

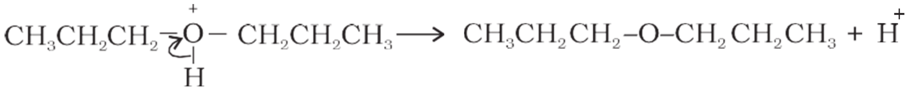
Step 2: Nucleophilic attack

$$CH_3-CH_2CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow CH_3-CH_2CH_2-\overset{+}{\ddot{\underset{\cdot\cdot}{O}}}-H$$



$$CH_3CH_2CH_2-\underset{H}{\underset{|}{\ddot{O}:}} + CH_3-CH_2CH_2-\overset{+}{O}\begin{matrix}H\\H\end{matrix} \rightarrow CH_3CH_2CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_2CH_3 + H_2O$$

Step 3: Deprotonation



$$CH_3CH_2CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2-O-CH_2CH_2CH_3 + H^+$$

ASSIGNMENT

Q1. How are primary, secondary and tertiary alcohols prepared from Grignard Reagents?

Q2. Give the equations of oxidation of primary, secondary and tertiary alcohols by Cu at 573K.

Q3. Show how will you synthesize:

(i) 1-phenylethanol from a suitable alkene.
(ii) Cyclohexylmethanol using an alkyl halide by an S_N2 reaction.
(iii) pentan-1-ol using a suitable alkyl halide?

Q4. How are the following conversions carried out?

(i) Propene → Propan-2-ol
(ii) Benzyl chloride → Benzyl alcohol
(iii) Ethyl magnesium chloride → Propan-1-ol.

Q5. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.
(ii) Oxidation of a primary alcohol to aldehyde.
(iii) Bromination of phenol to 2, 4, 6-tribromophenol.

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 What is the IUPAC name of Vinyl alcohol ?

(a) Ethanol
(b) Methanol
(c) Ethenol
(d) Methenol

ANS: (c)

Q.2. Which of the following is more acidic than alcohol ?

(a) Phenol
(b) Cyclohexanol
(c) Benzyl alcohol
(d) Ethenol

ANS: (a)

Q.3. Which one of the following compound is obtained by dehydrogenation of secondary alcohols?

a) Ketone
b) Aldehyde
c) Carboxylic acid
d) Amine

ANS: (a)

Q.4. The reaction of carboxylic acid and alcohol catalysed by conc.H_2SO_4 is called ?

a) Dehydration
b) Saponification
c) Esterification
d) Neutralisation

ANS: (c)

Q.5. Which of the following alcohol is most soluble in water

a) Propanol
b) Hexanol
c) Pentanol
d) Butanol

ANS:(a)

Q.6. On heating aqueous solution of benzene diazonium chloride , which of the following is formed

(a) benzene
(b) chloro benzene
(c) phenol
(d) aniline

ANS:(c)

Q.7. Catalytic dehydrogenation of a primary alcohol gives a

(a) Ketone

(b) Aldehyde

(c) Sec . alcohol

(d) Ester

ANS:(b)

Q.8 Ethyl alcohol obtained by fermentation of starch is called wash and what is its purity?

(a) 15%

(b) 99%

(c) 99.9%

(d) 95%

ANS:(a)

Q.9 Which chemical is used to distinguish between phenol and benzyl alcohol.

a). $NaHCO_3$

b). $FeCl_3$

c). Iodoform test

d). none of the above

ANS:(b)

Q.10 Which is most acidic

a). Phenol

b). 4-nitrophenol

c). Cresol

d). 2-nitrophenol

ANS:(d)

SHORT ANSWERED QUESTIONS [1-MARK]

1.Write the IUPAC names of $CH_2 = (CH)CH_2OH$

2.Which of the following has higher pKa value : Nitrophenol OR phenol

3. Arrange the following compounds in order of increasing boiling points.

(i) Bromoethane, (ii) Ethanol (iii) Methoxymethane

4. Write the structure of 2-Ethoxy-3-methyl pentane

5. Write the product formed when Ethoxy benzene reacts with HI

6. Which is more acidic : ortho-nitrophenol or ortho-methoxyphenol?

7. Name the chemical test used to distinguish between Phenol and Ethanoic acid?

8. Write the name of the product of reaction of Bromine in CS_2 with phenol

9. What is the condition of the compound to undergo Iodoform test?

10. Write the structure of cumene.

ANSWERS

1. Prop-2-en-1-ol

2. Phenol

3. (i)<(iii)<(ii)

4. CH_3-CH-CH[CH_3]-CH[OC_2H_5]-CH_3

5 Phenol + Iodoethane

6. ortho-nitrophenol (Due to electron withdrawing group)

7. $FeCl_3$ test or sodium bicarbonate test

8. o-bromophenol and p-bromophenol

9.precence of terminal methyl group with alcoholic / carbonyl group

10. CH_3-CH[C_6H_5]-CH_3 [Isopropylbenzene]

Aldehydes ,Ketones and Carboxylic Acids(UNIT-11)

- **Form aldehyde cannot be prepared by Rosenmund's reaction since formyl chloride is unstable at room temperature.**
- Benzaldehyde is less reactive than aliphatic aldehydes towards nucleophilic addition reaction.
- In reaction of toluene with CrO_3, acetic anhydride is used to protect benzaldehyde as benzylidenediacetate to avoid further oxidation to benzoic acid.
- Aromatic ketones are less reactive, they do not react with $NaHSO_3$.
- In reaction of aldehydes and ketones with ammonia derivatives, the medium should be slightly acidic (pH=4.5). In too highly acidic medium, ammonia derivatives being acidic form salts and not act as nucleophile
- Benzaldehyde although reduces Tollens' reagent, it does not reduce Fehling's and Benedictt's soluution.
- Ketones do not give Tollens reagent and Fehling's solution test.
- Only CH_3CHO and all methyl ketones give Iodoform test.
- A stronger acid has higher pK_b but lower pK_a.
- Benzoic acid is a stronger acid than acetic acid.
- -CHO and –COOH group, attached to benzene ring, are deactivating and m-directing.
- Methanoic acid decolouries the pink colour of acidified $KMnO_4$ solution but acetic acid does not.
- A 40% aqueous solution of fomaldehyde is known as formalin and is used to preserve biological specimens, and to prepare bakelite.
- Benzaldehyde is used in perfumery and in dye industries.

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

Q1. Arrange the following compounds in an increasing order of their reactivity towards nucleophilic addition reaction.

CH_3CHO, CH_3CH_2CHO ,CH_3COCH_3, $CH_3COCH_2CH_3$.

Ans. $CH_3COCH_2CH_3 < CH_3COCH_3 < CH_3CH_2CHO < CH_3CHO$

Q2. Name the reagent which is used to convert allylalcohol to propanol. Ans. PCC (Pyridinium Chlorochromate)

Q3. Name the aldehyde which does not give Fehling solution test.

Ans. Benzaldehyde.

Q4. Write IUPAC name of the compound $CH_2=CHCOCH_2COOH$

Ans. 3-Oxopent-4-enoic acid

Q5. Complete the reaction:

$$CH_3\text{-}C\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4}$$

Ans. $$CH_3\text{-}C\equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3COCH_3$$

ASSERTION - REASON TYPE QUESTIONS

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below.

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Carbonyl compounds take part in nucleophilic addition reactions.
Reason : These reactions are initiated by nucleophilic attack at the electron deficient carbon atom. (Ans - a)

2. Assertion : All aldehydes do not take part in aldol condensation.
Reason : In the aldol condensation, cabanion is generated by the abstraction of α - H atom by base. (Ans - b)

3. Assertion : Acetone is less reactive towards nucleophilic addition than acetaldehyde.
Reason : The alkyl groups hinder the nucleophilic attack on carbonyl carbon atom. (Ans - a)

4. Assertion : The α - H atom in carbonyl compounds is less acidic.
Reason : The anion formed after the loss of α - H atom is not resonance stabilized. (Ans - d)

5. Assertion : Aldehydes and ketones both react with Tollen’s reagent to form silver mirror.
Reason : Both aldehydes and ketones contain a carboxylic group. (Ans - d)

One - word answer

1. Name the reagent used to distinguish between methanoic acid and ethanoic acid.
(Ans - Tollen’ s reagent)

2. Name the product obtained by reaction of hydroxylamine with carbonyl compound?
(Ans - Oxime)

SHORT ANSWER TYPE QUESTIONS (2- MARKS)

Q1. Write chemical equation to illustrate following name reactions:-

(a) Cannizzaro's reaction
(b) Hell-Volhard- Zelinsky reaction

Ans. (a) Cannizzaro's reaction

$$HCHO \xrightarrow[NaOH]{} CH_3OH + HCOONa$$

(OR)

$$C_6H_5CHO \quad C_6H_5CH_2OH + C_6H_5COONa$$

(b) Hell - Volhard Zelinsky

$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/P(red)} R\text{-}CH(X)\text{-}COOH \qquad (X = Cl, Br)$$

Q2. Give a chemical test to distinguish between the following pairs:-

(i) Phenol and benzoic acid
(ii) Benzaldehyde and Acetophenone

Ans. (i) Benzoic acid reacts with $NaHCO_3$ giving CO_2 gas with effervescence where as phenol does not.

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2$$

(ii) Acetophenone on reacting with hot NaOH / I_2 gives yellow ppt of CHI_3 while

Benzophenone doesnot. $CH_3COC_6H_5 \xrightarrow{NaOH/I_2} CHI_3 + C_6H_5COONa$

Q3. Account for the following:-

(i) Chloroacetic acid $Cl\text{-}CH_2COOH$ is a stronger acid than acetic acid CH_3COOH.

(ii) Carboxylic acids do not give the reaction of carbonyl group.

Ans. (i) The–I effect of Cl atom in $ClCH_2COOH$ stabiles the $ClCH_2COO^-$ ion while +I effect of CH_3- group in CH_3COOH destabilizes the CH_3COO^-.

(ii) In the resonating structures of carboxylic acid and carbonyls, the carbonyl carbon of carboxylic acid is less electro-positive (less electrophile) than carbonyl carbon in aldehydes and ketones. Therefore carboxylic acids do not give the reaction of carbonyl group

Q4. Arrange the following.

(i) $C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH$ (decreasing order of their acidic character)

(ii) Ethanal, Propanal, Propanone, Butanone reaction (increasing order of their nucleophilic addition reaction)

Ans. (i) $NO_2\text{-}CH_2\text{-}COOH > F\text{-}CH_2\text{-}COOH > C_6H_5\text{-}COOH$

(ii) Butanone < Propanone < Propanal < Ethanal

Q5. An organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iododorm test. It does not reduce Tollens' or Fehling's reagent and does not decolourise bromine water also . On oxidation with chromic acid, it gives a carboxylic acid 'B' with molecular formula $C_7H_6O_2$. Deduce the structures A and B.

Ans. Since A does not give Fehling's or Tollen's test but gives iodoform test and 2,4-DNP test so it has CH_3CO- group. Hence:

$$\underset{(A)}{C_6H_5COCH_3} \xrightarrow[H_2CrO_4]{} \underset{(B)}{C_6H_5COOH}$$

OR

Write chemical equation for the following conversion (not more than two steps)

(i) Acetaldehyde to butane-1,3–diol

(ii) Acetone to propene

Ans. (i) $CH_3\text{-}CHO \longrightarrow CH_3\text{-}CHOH\text{-}CH_2\text{-}CHO \longrightarrow CH_3\text{-}CHOH\text{-}CH_2\text{-}CH2OH$

(ii) $CH_3COCH_3 \xrightarrow[NaOH]{} CH_3CH(OH)CH_3 \longrightarrow CH_3CH = CH_2$

$NaBH_4$

SHORT ANSWER TYPE QUESTIONS (3- MARKS)

Q1. Explain the following name reaction by giving one suitable example of each:-
(i) Wolff-kishner reduction (ii) Aldol condensation (iii) Clemensen's reduction

Ans. (i) Wolff-kishner reduction

$R_2CO \quad NH_2NH_2 \longrightarrow R_2C{=}NNH_2 \xrightarrow[\boxed{\text{Glycol/ HCl}}]{} RCH_2R$

(ii) Aldol condensation

Carbonyl compounds with α- hydrogen in basic medium undergo condensation to give Hydroxy aldehydes and ketones.

$CH_3CHO{+}NaOH \rightarrow CH_3{-}CHOH{-}CH_2{-}CHO \qquad CH_3{-}CH{=}CH{-}CHO + H_2O$

(iii) Clemensen's reduction

$R_2CO \xrightarrow[\boxed{\text{Zn-Hg/Conc. HCl}}]{} RCH_2R \xrightarrow[\boxed{\text{heat}}]{}$

Q2.

Write the products in the following reactions:

(a) $CH_3COCH_3 \xrightarrow[\boxed{\text{Zn-Hg/Conc.}}]{}$

(b) $H_3\text{-}CO\text{-}Cl + H_2 \xrightarrow{Pd - BaSO_4\ /S} ? \qquad \longrightarrow$

(c) $C_6H_5CHO + NaOH \rightarrow ?$

Ans. (a) $CH_3COCH_3 \xrightarrow{\boxed{\text{Zn-Hg/Conc. HCl}}} CH_3CH_2CH_3 + H_2O$

(b) $CH_3\text{-}CO\text{-}Cl + H_2 \xrightarrow[\boxed{Pd - BaSO_4\ /S}]{} CH_3CHO + HCl$

© $C_6H_5CHO + NaOH \rightarrow C_6H_5COONa + C_6H_5CH_2OH$

3 . Explain : (i) Ethanal is more reactive than acetophenone towards nucleophilic addition reaction.

(ii)$(CH_3)_3C-CHO$ does not undergo aldol condensation.

(iii)Carboxylic acids are higher boiling liquids than alcohols.

Ans. (i) The presence of two alkyl groups in ketones hinder the approach of nucleophile to carbonyl carbon, and reduce the positive charge on carbonyl carbon more effectively in ketones than in aldehydes.

(i) Due to unavailability of α-hydrogen in the given compound it does not undergo aldol condensation.

(ii) Due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding,(exist as dimer)

LONG ANSWER TYPE QUESTIONS (5-MARKS)

Q1. (a) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.

(b) How will you bring about the following conversions?

(i) Acetic acid to Acetaldehyde

(ii) Propylene to Acetone

(iii) Ethanal to but-2-enal

Ans. (a) (i) resonating structures of carboxylate ion are more stable than phenoxide ion.

(ii) Negative charge is dispersing on two electronegative oxygen in carboxylate ion whereas in phenoxide ion it is on one oxygen.

(b) Conversions:

(i) $CH_3COOH \xrightarrow{PCl5} CH_3COCl \xrightarrow{H2\ /Pd - BaSO4} CH_3CHO$

(ii) CH_3□$CH=CH_2 \xrightarrow{\boxed{H_2O/H^+}}$ CHOH□$CH_3 \xrightarrow[Cu/573K]{} CH_3COCH_3$

(iii) $CH_3CHO + NaOH \xrightarrow{} CH_3-CHOH-CH_2-CHO$ HEAT $\xrightarrow{} CH_3-CH=CH-CHO$

Q2. (a)

Write the structures of A,B, C and D in the following reactions:

$A \xrightarrow[Pd-BaSO_4]{+ H_2} \xrightarrow{\boxed{NaOH}} B$ C+D

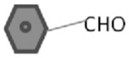
Ans : A- Benzoyl chloride B- Benzaldehyde

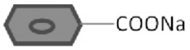
C - Benzylalcohol

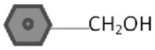
D - Sodium benzoate

(b) Distinguish between: (i) Acetone and Acetaldehyde (ii) Benzaldehyde and Benzophenone

Ans. (i)







prous

$CH_3CHO + 2Cu(OH)_2 + NaOH \rightarrow CH_3COONa + Cu_2O + 3H_2O$ (on heating)
(Red ppt)

(iii) Bezaldehyde gives Tollens' test, while benzophenonedoes not.

$C_6H_5CHO + 2[Ag(NH_3)_2] \rightarrow C_6H_5COONH_4 + 2Ag + 3NH_3 + H_2O$

ASSIGNMENT

1. Arrange the following:

(i) (a) Benzoic acid

(b) 4-Nitrobenzoic acid

(c) 3,4-Dintrobenzoic acid

(d) 4-Methoxybenzoic acid (increasing acidic character)

(ii) CH_3CHO, C_6H_5CHO, $HCHO$ (reactivity towards nucleophilic addition reaction)

2. Write the reaction mechanism for the reaction. R-CHO + HCN → R-CHCN-OH

3. Draw the molecular structure of the compounds:-

(i) 4- methylpent-3-en-2-one.

(ii) 3-Methylbutanal

(iii) Hexane-1,6-dioic acid

4. How will you prepare benzyl alcohol from benzaldehyde without using a reducing agent? Identify the compounds A, B and C in the following reactions:

$$CH_3\text{-}Br \xrightarrow[(i)]{Mg/ether} (A) \xrightarrow{CO_2/(ii)H_2O} (B) \xrightarrow{(i)CH_3OH/H^+} (C)$$

1. How do you convert the following?

(i) Benzoic acid to benzaldehyde

(ii) Ethyne to ethanoic acid

2. (a) Account for the following-

(i) The boiling points of aldehydes and ketones are lower than their corresponding carboxylic acids.

(ii) The aldehydes and ketones undergo a number of addition reactions

(iii) In the reaction of ammonia derivatives with carbonyl compounds the pH should not be lesser than 4.5.

(b) Give chemical test to distinguish between:

(i) Acetaldehyde and benzaldehyde (ii) Propanone and propanal

3. Distinguish between the following:

(a) (i) Butanone and Butanal

(ii) Ethanal and ethanoic acid

(b) Write a suitable example of each:

(i) Rosenmund reaction

(ii) Etard reaction

MCQs

1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions.

i). $CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO$ (ii). $CH_3\text{-}CH_2\text{-}CO\text{-}CH_3$

(iii). $CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH + CO_2$ (iv). $CH_3\text{-}COOH + H\text{-}COOH$

Ans: (ii)

2. Which of the following compounds is most reactive towards nucleophilic addition reactions?

(i). CH_3-COOH ii). CH_3-CO-CH_3
(iii) C_6H_5-CHO iv). C_6H_5-CO-CH_3

Ans: (i)

3. The correct order of increasing acidic strength is _____________.

(i) Phenol < Ethanol < Chloroacetic acid < Acetic acid
(ii) Ethanol < Phenol < Chloroacetic acid < Acetic acid
(iii) Ethanol < Phenol < Acetic acid < Chloroacetic acid
(iv) Chloroacetic acid < Acetic acid < Phenol < Ethanol

Ans: (iii)

4. Compound can be prepared by the reaction of _____________.

(i) Phenol and benzoic acid in the presence of NaOH
(ii) Phenol and benzoyl chloride in the presence of pyridine
(iii) Phenol and benzoyl chloride in the presence of $ZnCl_2$
(iv) Phenol and benzaldehyde in the presence of palladium

Ans: (ii)

5. The reagent which does not react with both, acetone and benzaldehyde.

(i) Sodium hydrogensulphite
(ii) Phenyl hydrazine
(iii) Fehling's solution
(iv) Grignard reagent

Ans: (iii)

6. Cannizaro's reaction is not given by _____________.

(i). Cyclohexanone
(ii). C_6H_5-CHO
(iii) H CHO
(iv) CH_3CHO

Ans: (iv)

7. $CH_3\text{-C}\Xi\text{C-H} \xrightarrow{H_2SO_4/HgSO_4} \text{A} \xrightarrow{\text{Isomerisaion}} CH_3\text{-CO-}CH_3$

Structure of 'A' and type of isomerism in the above reaction are respectively.

(i) Prop–1–en–2–ol, metamerism
(ii) Prop-1-en-1-ol, tautomerism
(iii) Prop-2-en-2-ol, geometrical isomerism
(iv) Prop-1-en-2-ol, tautomerism

Ans: (iv)

8. Which is the most suitable reagent for the following conversion?

$CH_3\text{-CH=CH-}CH_2\text{-CO-}CH_3 \longrightarrow CH_3\text{-CH=CH-}CH_2\text{-COOH}$

(i) Tollen's reagent
(ii) Benzoyl peroxide
(iii) I_2 and NaOH solution

(iv) Sn and NaOH solution
Ans: (iii)

9. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?
(i) Butan-1-ol
(ii) Butan-2-ol
(iii) Both of these
(iv) None of these
Ans: (ii)

10. In Clemmensen Reduction carbonyl compound is treated with _____________.
(i) Zinc amalgam + HCl
(ii) Sodium amalgam + HCl
(iii) Zinc amalgam + nitric acid
(iv) Sodium amalgam + HNO_3
Ans: (i)

SHORT ANSWER QUESTIONS (1-MARK)

1. Why carboxylic acid have higher boiling point than alcohols as both have intermolecular hydrogen bonding?

Ans. Carboxylic acid forms a dimer due to double H-bonding. So it has higher boiling point than alcohols.

2. Arrange the following in increasing order of acidic character : HCOOH, $CH_2ClCOOH$, CF_3COOH , CCl_3COOH

Ans. $HCOOH < CH_2ClCOOH < CCl_3COOH < CF_3COOH$

3. Why is the boiling point of an acid anhydride higher than the acid from which it is derived?

Ans. Acid anhydrides are bigger in size than corresponding acid. These have more surface area so have strong van der Waals Force of attractions. Hence they have higher boiling point.

4. Why do carboxylic acids not give the characteristic reactions of a carbonyl group?

Ans. Due to resonance, It does not have free carbonyl.

5. Arrange the following compounds in increasing order of their boiling points.
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$

Ans. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

6. What happens when ethanoyl chloride is subjected to rosenmund reduction?

Ans. Ethanoyl chloride is converted in to Ethanal. OR

$CH_3COCl + H_2 \xrightarrow{Pd\text{-}BaSO_4/S} CH_3CHO + HCl$

7. Why does solubility decrease with increasing molecular mass in carboxylic acid?

Ans. Because with increase of molecular mass size of hydrophobic carbon chain length increases.

8. Why PCC cannot oxidize methanol to methanoic acid while $KMnO_4$ can?

Ans. This is because PCC is a mild oxidizing agent and can oxidize methanol to methanal only. while $KMnO_4$ is strong oxidizing agent which oxidizes it to methanoic acid.

9. Aromatic acids are solid while most of aliphatic acids are liquids. Why?

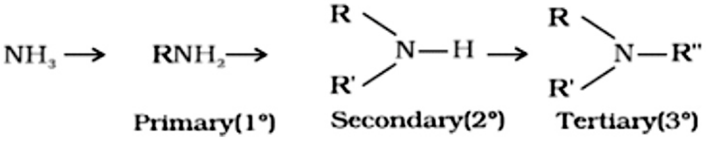
Ans. Aromatic acids have higher molecular weight and strong Van der Waals force of attraction as compared to aliphatic acids so they are solids.

10. The boiling points of aldehydes and ketones are lower than that of the corresponding acids. Why?

Ans. This is due to intermolecular hydrogen bonding in carboxylic acids.

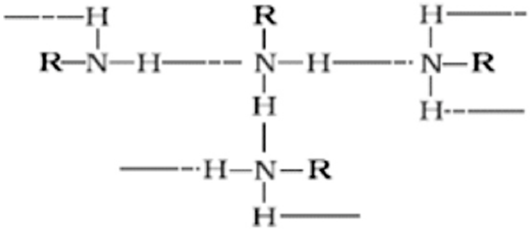
AMINES (UNIT-12)

Classification: Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three.



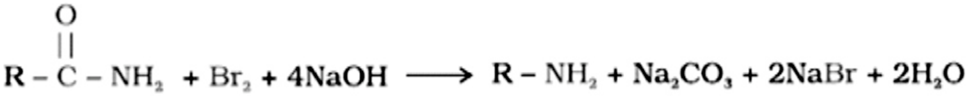
Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
2. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
3. Boiling points order: primary amine > secondary amine > tertiary amine



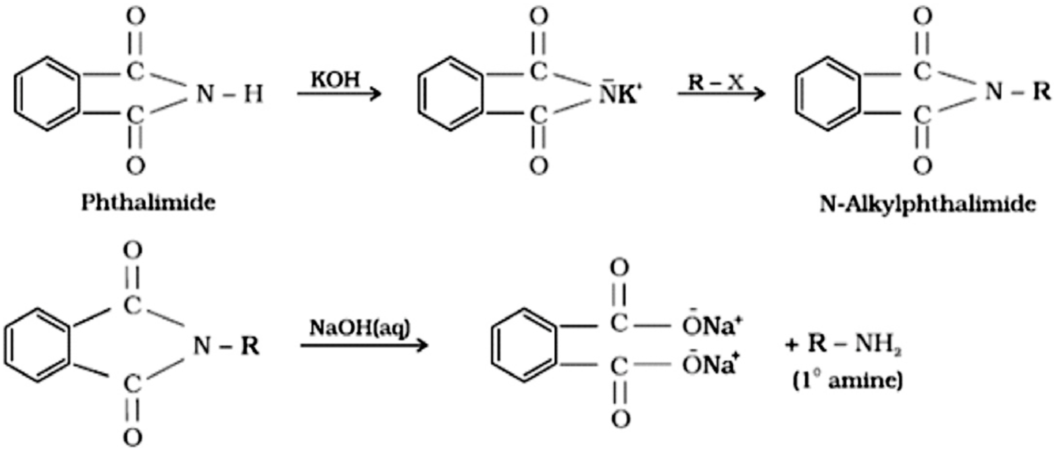
Preparation

HOFFMANN BROMAMIDE REACTION:-



$$R-\overset{O}{\overset{||}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

GABREIL PHTHALIMIDE SYNTHESIS:



Chemical Properties Basic Strength of Amines

Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom. More the K_b (dissociation constant of base), higher is the basicity of amines. Lesser the pK_b higher is the basicity of amines. Aliphatic amines ($R\text{-}NH_2$) are stronger bases than NH_3due to the electron releasing +I effect of the alkyl group. Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows:
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3\ (CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

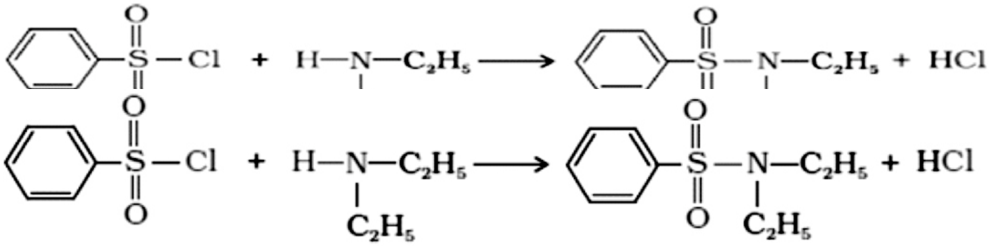
Aromatic amines are weaker bases than aliphatic amines and NH_3, due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π-electron pairs of the rin**g.**

BENZOYLATION:

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \rightarrow \underset{\text{N – Methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

CARBYLAMINE REACTION: HINSBERG'S TEST:

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R{-}NC + 3KCl + 3H_2O$$



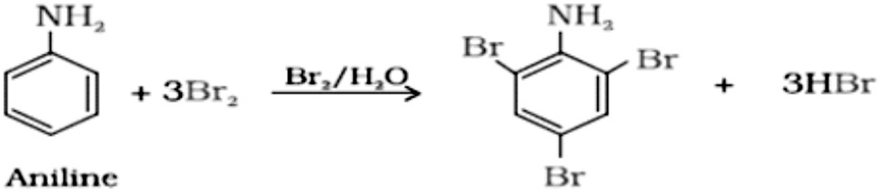
N.N-Diethylbenzenesulphonamide (Insoluble in KOH)

Tertiary amines do not react with benzene sulphonyl chloride. ELECTROPHILIC SUBSTITUTION

REACTIONS:-

BROMINATION:-

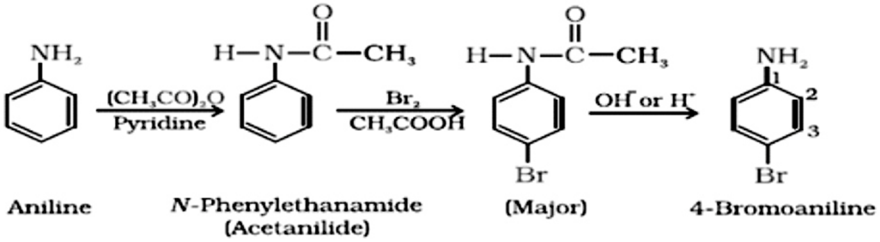
To prepare monosubstituted derivative, activating effect of $–NH_2$ group must be controlled by



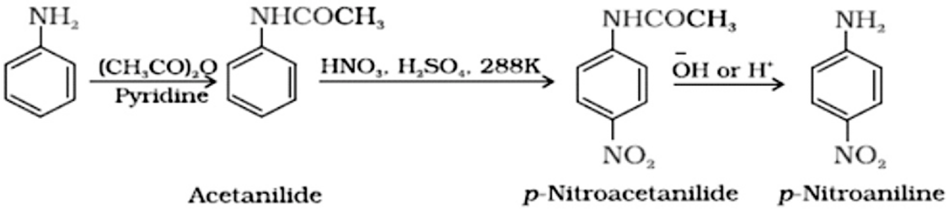
Aniline

2,4,6-Tribromoaniline

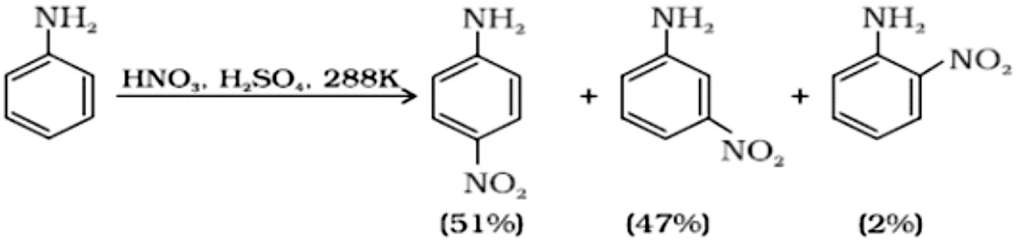
protecting–NH_2 by acetylation with acetic anhydride.



NITRATION: Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strongly acidic medium, aniline is protonated to form anilinium ion which is meta directing so it gives meta product also



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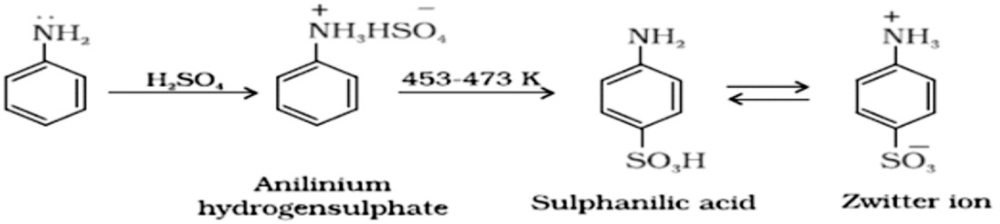


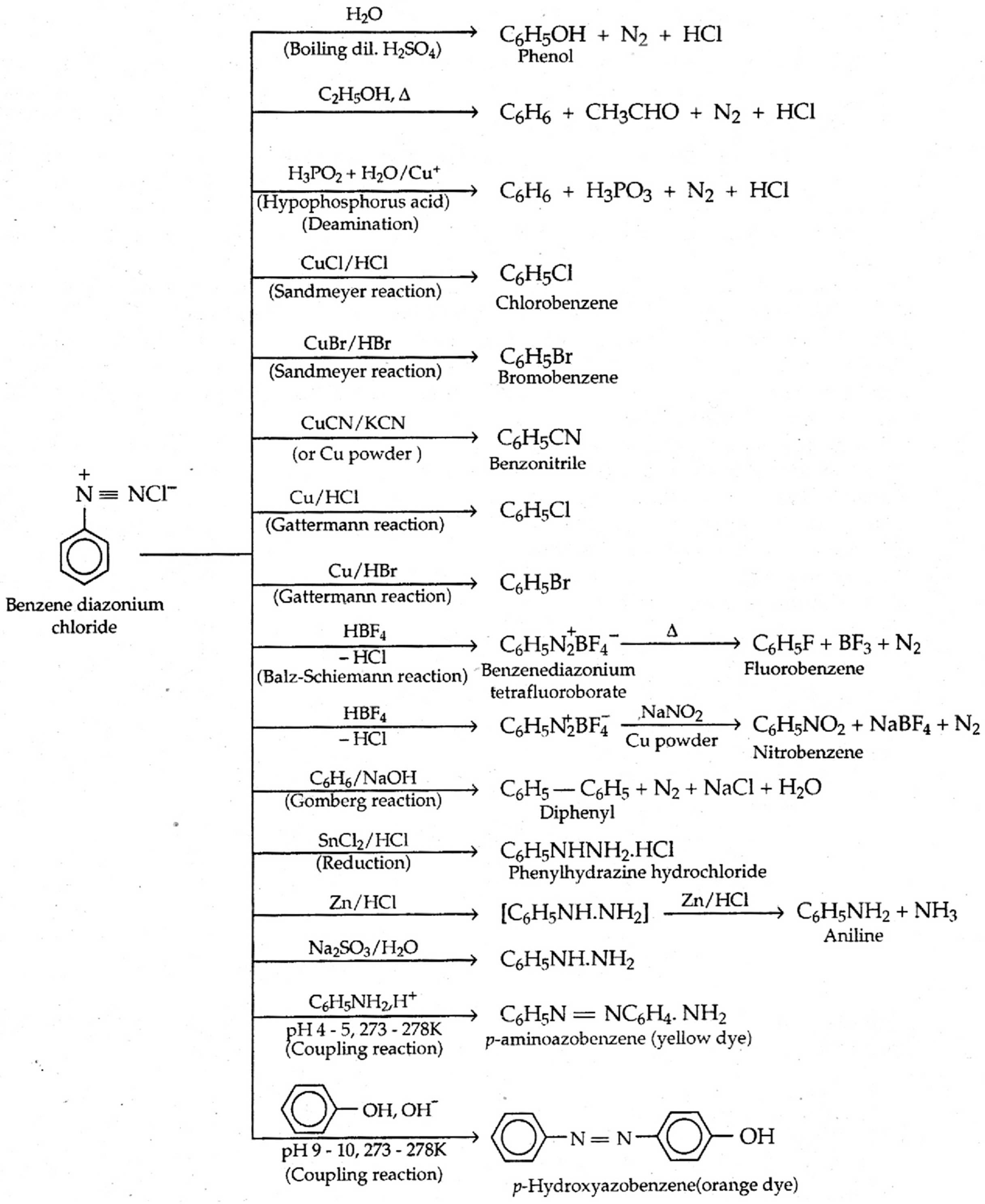
Aniline does not undergo Friedel Craft reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst.

DIAZOTISATION:

Properties of benzene diazonium chloride

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5\overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

Reactions of benzene diazonium chloride are summarised as below :



Very Short Answer questions: (1 Mark)

Q.1 What is Hinsberg's reagent? Ans. Benzene sulphonyl chloride

Q.2 Why is aniline acylated before its nitration?

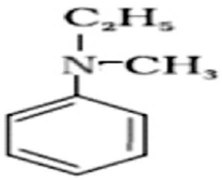
Ans. To prevent it from oxidation

Q.3 Ethylamine is soluble in water but aniline is not, why?

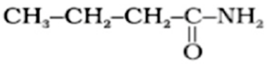
Ans. Ethylamine forms intermolecular H-bond with water, but aniline does not form H-bond to a very large extent due to the presence of large hydrophobic $–C_6H_5$ group.

Q.4 Write the structure of N-Ethyl-N-methylaniline.

Ans.



Q.5 Write structures and IUPAC names of the amide which gives propanamine by Hoffmann bromamide reaction.

Ans. 
$CH_3–CH_2–CH_2–\overset{}{\underset{\underset{O}{\|}}{C}}–NH_2$, Butanamide

ASSERTION - REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below.

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : The diazotisation reaction must be carried in ice cold solution ($0\text{-}4^oC$).
Reason : At higher temperature, benzenediazonium chloride reacts with water to give phenol. (Ans - a)

2. Assertion : In strongly acidic solution aniline becomes less reactive towards electrophilic reagents.
Reason : Due to protonation of amino group the lone pair of electrons on nitrogen is not available for resonance. (Ans - a)

3. Assertion : Gabriel phthalimide synthesis can be used to convert alkyl chlorides into primary amines.
Reason : With proper choice of reagent Gabriel synthesis can be used to prepare primary, secondary and tertiary amines. (Ans - c)

4. Assertion : N-Ethylbenzenesulphonamide is soluble in alkali.
Reason : Hydrogen attached to nitrogen in sulphonamide is strongly acidic in nature. (Ans - a)

5. Assertion : Benzenediazonium chloride can not be stored and is used immediately after its preparation.
Reason : It is very unstable and dissociates to give nitrogen. (Ans - a)

One - word answer

1. Which one is more acidic : anilinium ion or p-fluoroanilinium ion ? (Ans - p-fluoroanilinium ion)
2. Name the effect due to which nitrobenzene does not undergo Friedal Craft reaction.
3. (Ans - Deactivating)

Short Answer questions: (2 Mark)

Q.6 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $C_6H_5NHCH_3$

Ans. (i) N-Methyl aniline 2^0

(ii) $(CH_3CH_2)_2NCH_3$

(ii) N-Ethyl-N-methylethanamine 3^0

Q.7 Give plausible explanation for each of the following:

(i) Why do primary amines have higher boiling point than tertiary amines?

(ii) Why are aliphatic amines stronger bases than aromatic amines?

Ans. (i) Due to strong intermolecular H-bonding in primary amines.

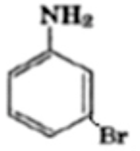
(ii) In aromatic amines lone pair is engaged with benzene in resonance.

Q.8 How can you convert an amide into an amine having one carbon less than the starting compound? Name the reaction.

Ans. By using Hoffmann bromamide reaction

Q.9 Write the structures of: (a) 3-Bromobenzenamine (b) 3-Chlorobutanamide

Ans: (a)



(b) $CH_3CH(Cl)CH_2CONH_2$

Q.10 Arrange the following:

(i) In decreasing order of the pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength: Aniline, *p*-nitroaniline and *p*-toluidine

Ans: (i) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_2H_5NH_2$, $(C_2H_5)_2NH$

(ii) *p*-Nitroaniline , aniline, *p*-toluidine

Short Answer questions: (3 Marks)

Q.11 Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamineand dimethylamine

(ii) Ethylamine and aniline

(iii) Aniline and benzylamine

Ans: (i) Carbylamine reaction

(ii) Azo dye Test

(iii) Azo dye Test

Q.12 Account for the following:

- (i) Although amino group is o, p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.
- (ii) Aniline does not undergo Friedel-Crafts reaction.
- (iii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Ans. (i) Because nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion which is meta-directing.

(ii) Friedel-Craft reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ acts as a Lewis acid, while aniline acts as a Lewis base. Thus, aniline reacts with $AlCl_3$ to form a salt.

(iii) Gabriel phthalimide synthesis results in the formation of primary amines only. Secondary and tertiary amines are not formed in this synthesis. Thus, a pure primary amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q.13 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B$ B $\xrightarrow{NaOHBr_{20}} C$

(ii) $C_6H_5N_2Cl \xrightarrow{NaCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\text{☟}]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{CuCN/KCN} A \xrightarrow{LiH_4} B \xrightarrow[0°C]{HNO_2} C$

Ans: (i) (A)CH_3CH_2CN (B)$CH_3CH_2CONH_2$ (C)$CH_3CH_2NH_2$

(ii) (A)C_6H_5CN (B)C_6H_5COOH (C)$C_6H_5CONH_2$

(iii) (A)CH_3CH_2CN (B)$CH_3CH_2CH_2NH_2$ (C)$CH_3CH_2CH_2OH$

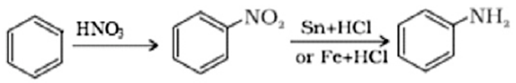
Q.14 How will you convert:

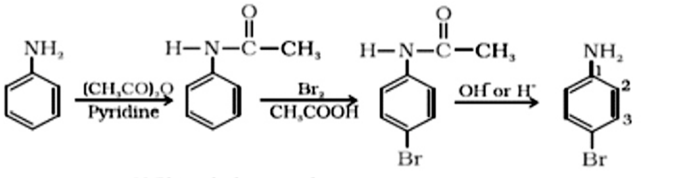
(i) Benzyl chloride to 2-phenylethanamine

(ii) Benzene to Aniline

(iii) Aniline to *p*-bromoaniline

Ans: (i) $C_6H_5CH_2Cl \xrightarrow{Ethanolic\,NaCN} C_6H_5CH_2CN \xrightarrow{H_2/N_1} C_6H_5CH_2CH_2NH$





Q.15 An organic compound [A] $C_3H_6O_2$ on reaction with ammonia followed by heating yield B. Compound B on reaction with Br_2 and alc. NaOH gives compound C (C_2H_7N). Compound C forms a foul smelling compound D on reaction with chloroform and NaOH. Identify A, B, C, D and the write the equations of reactions involved.

[Hint: (A) CH_3CH_2COOH (B) $CH_2CH_2CONH_2$ (C) $CH_3CH_2NH_2$ (D) CH_3CH_2NC.]

ASSIGNMENTS

1 MARK QUESTIONS

1. Arrange the following in decreasing order of their basic strength: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$and $C_6H_5NH_2$
2. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Why?
3. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Why?
4. Why aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis?
5. Write structures and IUPAC names of the amine produced by the Hoffmann degradation of benzamide.

2 MARKS QUESTIONS

Q1. Write short notes on the following:

(i) Carbylamine reaction

(ii) Diazotisation

(iii) Hofmann's reaction

(iv) Coupling reaction

Q2. Complete the followingreactions:

(i) $C_6H_5NH_2$+$CHCl_3$+ alc.KOH →

(ii) $C_6H_5N_2Cl$+H_3PO_2+H_2O →

Q3. Give a chemical test to distinguish between:

(a) $C_6H_5NH_2$ & CH_3NH_2

(b) CH_3NHCH_3 & $(CH_3)_3N$

Q4. Give the IUPAC names of: (a) $(CH_3)_2CHNH_2$ (b) $(CH_3CH_2)_2NCH_3$

3 MARK QUESTIONS

Q1. How will you convert?

(v) Benzene into N, N□dimethylaniline

(vi) Aniline to phenol

(vii) Aniline into benzene

Q2. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

MULTIPLE CHOICE QUESTIONS(MCQs)

1. Which of the following is a 3° amine?

(i) 1-methylcyclohexylamine

(ii) Triethylamine

(iii) tert-butylamine

(iv) N-methylaniline

Ans: (ii)

2. The correct IUPAC name for $CH_2=CHCH_2\ NHCH_3$ is

(i) Allylmethylamine

(ii) 2-amino-4-pentene

(iii) 4-aminopent-1-ene

(iv) N-methylprop-2-en-1-amine

Ans:(iv)

3. Amongst the following, the strongest base in aqueous medium is ____________.

(i) CH_3NH_2

(ii) $NCCH_2NH_2$

(iii) $(CH3)_2\ NH$

(iv) $C_6H_5NHCH_3$

Ans: (iii)

4. Benzylamine may be alkylated as shown in the following equation :

$C_6H_5CH_2NH_2 + R—X \longrightarrow C_6H_5CH_2NHR$

Which of the following alkylhalides is best suited for this reaction through S_N1 mechanism?

(i) CH_3Br

(ii) C_6H_5Br

(iii) $C_6H_5CH_2Br$

(iv) C_2H_5 Br

Ans: (iii)

5. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?

(i) H_2 (excess)/Pt

(ii) $LiAlH_4$ in ether

(iii) Fe and HCl

(iv) Sn and HCl

Ans: (ii)

6. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is ___________.

(i) Sodium amide, $NaNH_2$

(ii) Sodium azide, NaN_3

(iii) Potassium cyanide, KCN

(iv) Potassium phthalimide, $C_6H_4(CO)_2N–K+$

Ans: (iii)

7. The source of nitrogen in Gabriel synthesis of amines is _____________.

(i) Sodium azide, NaN_3

(ii) Sodium nitrite, $NaNO_2$

(iii) Potassium cyanide, KCN

(iv) Potassium phthalimide, $C_6H_4(CO)_2N–K+$

Ans: (iv)

8. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is _____.

(i) excess H_2

(ii) Br_2 in aqueous NaOH

(iii) iodine in the presence of red phosphorus

(iv) $LiAlH_4$ in ether

Ans: (iv)

9. The best reagent for converting, 2-phenylpropanamide into 1- phenylethanamine is ____.

(i) excess H_2/Pt

(ii) NaOH/Br_2

(iii) $NaBH_4$/methanol

(iv) $LiAlH_4$/ether
Ans: (ii)

10. Hoffmann Bromamide Degradation reaction is shown by __________.
(i) $ArNH_2$
(ii) $ArCONH_2$
(iii) $ArNO_2$
(iv) $ArCH_2NH_2$
Ans: (ii)

SHORT ANSWERED QUESTIONS (1-MARK)

1. What is the hybridisation of N in $(CH_3)_3N$ and shape of $(CH3)_3N$?

Ans. Hybridisation of N in $(CH_3)_3N$ is sp^3 and shape of $(CH_3)_3N$ is trigonal pyramidal.

2. Which diazonium salt is stable at room temprature.

Ans. Benzene diazonium fluoro borate($C_6H_5N_2$ F).

3. Which diazonium salt is insoluble in water at room temprature?

Ans. Benzene diazonium fluoro borate ($C_6H_5N_2$ F).

4. Out of CH_3NH_2 and $CH_3CH_2NH_2$ which has higher boiling point and why ?

Ans. $CH_3CH_2NH_2$ because bigger the alkyl group more is the surface area higher is the magnitude of van der Waals force.

5. Why are primary amines higher boiling than tertiary amines ?

Ans. Primary amines have two hydrogen atoms on the N atom and therefore form intermolecular hydrogen bonding. Tertiary amines do not have hydrogen atoms on the N atom and therefore,these do not form hydrogen bonds.

6. Write the structure and IUPAC name of t-butylamine.

Ans. 2-Methylpropan-2-amine

7. Which one is more basic CH_3NH_2 or $(CH_3)_3N$ in gaseous phase and why ?

Ans. $(CH_3)_3N$ is more basic because greater number of alkyl groups increase the magnitude of +I effect so increase the basicity .

8. Which one is more basic CH_3NH_2 or $(CH_3)_3N$ in gaseous phase and why ?

Ans. $(CH_3)_3N$ is more basic because greater number of alkyl groups increase the magnitude of +I effect so increase the basicity .

9. Out of Butan-1-ol and butan-1-amine ,which will be more soluble in water and why?

Ans. Butan-1-ol are more polar than amines and forms stronger intermolecular hydrogen bonds with water molecules than amines.

10. Why ethylamine is soluble in water whereas aniline is not ?

Ans. Ethylamine when added to water forms intermolecular H−bonds with water. Hence, it is soluble in water.

BIOMOLECULES (UNIT 13)

KEY POINTS	**EXPLANATIONS**
Monosaccharides	Cannot be hydrolyzed further.e.g.-glucose,fructose,ribose
Disaccharides	Sucrose(α-D-glucose+β-D-fructose),Maltose (α-D-glucose+ α-D- glucose) Lactose(β-D-galactose + β-D-glucose)
Polysaccharides	*Starch* (two components—Amylose and Amylopectin) polymer of α-D-glucose
Amylose	Water soluble, 15-20% of starch., unbranched chain, C1– C4 glyosidic linkage.
Amylopectin	Water insoluble , 80-85% of starch, branched chain polymer, C1–C4 & C1–C6 glyosidic linkage
Cellulose	Straight chain polysaccharide of β -D-glucose units/ joined by C1-C4 glycosidic linkage (β-link), not digestible by human / constituent of cell wall of plant cells
Glycogen	Highly branched polymer of α-D- glucose .found in liver, muscles and brain.
Reducing sugars	Aldehydic/ ketonic groups free so reduce Fehling's/ Tollen's solution and. e.g.- maltose and lactose
Non reducing sugars	Aldehydic/ ketonic groups are bonded so cannot reduce Fehling's solution and Tollen's reagent. E.g.- Sucrose
Anomers.	The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* Such isomers, i.e., α –form and β -form, arecalled anomers.
Invert sugar	Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named asinvert sugar.
Glycosidic linkage	Linkage between two mono saccharide
Importance of Carbohydrates	Major portion of our food. / used as storage molecules as starch in plants and **glycogen** in animal. Cell wall of bacteria and plants is made up of cellulose.Wood and cloth are cellulose, provide raw materials for many important industries like textiles, paper, lacquers and breweries.
Essential amino acids	Which cannot be synthesized in the body and must be obtained through diet, e.g.- Valine, Leucine

Non-essential aminoacids	Which can be synthesised in the body, eg-Glycine, Alanine
Zwitter ion.	In aqueous solution, amino acids exist as a dipolar ion known as *zwitter ion*.
Peptide linkage	peptide linkage is an amide formed between –COOH group and $-NH_2$ group of two successive amino acids in peptide chain.
1^0- str. Of proteins:	sequence of amino acids that is said to be the primary structure of protein
2^0- str. of proteins:	secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two types of structures viz. α-helix and β-pleated sheet structure.
Tertiary structure of proteins**:**	further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular.
Fibrous proteins	Polypeptide chains run parallel, held together by hydrogen and disulphide bonds, fiber– like structure. Water insoluble.Eg- are keratin (in hair, wool, silk) and myosin (present in muscles).
Globular proteins	chains of polypeptides coil around to give a spherical shape. water soluble. Eg-Insulin and albumins
Stab. forces 2°& 3°	Hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
Denaturation of Proteins	When a protein is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of protein. (During denaturation 2° and 3° structures are destroyed but 1°structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk
Fat soluble vitamins	These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues
Water soluble vitamins	B, C. these vitamins must be supplied regularly in diet because they are readily excreted in urine
Vitamins –sources- Deficiency diseases	Vit- A (Fish liver oil, carrots)- Night blindness / Vitamin B_1 (Yeast, milk,)- Beri Beri
	Vit-B_2 (Milk, egg white)- Cheilosis / Vit- B_6 (Yeast, milk,)- Convulsions/ Vit- B_{12} (Meat, fish,)- anemia
	Vit-C (Citrus fruits)-Scurvy,/ Vit-D (Exposure to sunlight, fish and egg yolk)- Rickets, osteomalacia
	Vit- E (wheat oil, sunflower oil)- fragility of RBCs / Vit - K (leafy vegetables)-Increased blood clotting time

DNA	pentose sugar (D-2-deoxyribose) + phosphoric acid + nitrogenous bases (A , G , C, T)
RNA	pentose sugar (ribose) + phosphoric acid + nitrogenous bases (A, G , C, U)
Nucleoside/tides	Nucleoside $\longrightarrow$ sugar + base Nucleotides→ sugar+base +phosphate
Phosphodiester link	Linkage between two nucleotides in polynucleotides
Functions of Nucleic Acids	DNA reserve genetic information, maintain the identity of different species is capable of self-duplication during cell division, synthesizes protein in the cell.

QUESTIONS

VSA TYPE QUESTIONS (1 - MARK QUESTIONS)

1. How many asymmetric carbon atoms are present in D (+) glucose?
2. Give the significance of (+)-sign in the name D- (+)-glucose.
3. Give the significance of prefix ‘D’ in the name D- (+)-glucose.
4. Why is sucrose called invert sugar?
5. Write the Zwitter ionic form of amino acetic acid. (H_2NCH_2COOH).
6. How would you explain the amphoteric behaviour of amino acids?
7. Which nucleic acid is responsible for carrying out protein synthesis in the cell?
8. The two strands in DNA are not identical but complementary. Explain.
9. What type of linkage holds together the monomers of DNA and RNA?
10. Mention the number of hydrogen bonds between adenine and thymine.

Answers

1. 4

2. (+) sign indicates dextrorotatory nature of glucose.

3.‘D’ Signifies that –OH group on C-5 is on the right hand side

4.When sucrose is hydrolyzed by water, the optical rotation of solution changes from positive to negative.

5.Amino acids are amphoteric due to the presence of both acidic and basic functional groups.

6.Amphoteric behavior.

7.RNA

8. complementary bases are prepared.

9.H-bonding is present between specific pairs of bases present in strands.

10.Phosphodiester linkage.

(Q.) **What is difference between reducing and non-reducing sugars or carbohydrates?** **(1 Mark)**

(**Ans**) All those carbohydrates which contain aldehydic and ketonic group in the hemiacetal or hemiketal form and reduce Tollen's reagent or Fehling's solution are called reducing carbohydrates while others which do not reduce these reagents are called non-reducing sugars.

(Q.) **Explain the term mutarotation?** **(1 Mark)**

(**Ans**) Mutarotation is the change in the specific rotation of an optically active compound with time, to an equilibrium mixture.

(Q.) **Define glycosidic linkage?** **(1 Mark)**

(**Ans**) The two monosaccharide units are joined together through an ethereal or oxide linkage formed by the loss of a molecule of H_2O. Such a linkage between two monosaccharide units through oxygen atoms is called glycosidic linkage.

(Q.) **Give a chemical equation for obtaining maltose?** **(1 Mark)**

(**Ans**) Maltose is obtained by partial hydrolysis of starch by the enzyme diastase present in malt i.e., sprouted barley seeds.

$$2(C_6H_{10}O_5)_n + nH_2O \quad \mathit{Diastase} \longrightarrow n\ C_6H_{12}O_6$$

ASSERTION - REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : All enzymes found in cells are invariably proteins which catalyse biological reactions.
   Reason : Enzymes act efficiently at a moderate temperature and pH. (Ans - b)
2. Assertion : D - glucose is dextrorotatory whereas L - glucose is laevorotatory.
   Reason : D - compounds are always dextro and L - compounds are always laevo. (Ans - b)
3. Assertion : Vitamin D cannot be stored in our body.
   Reason : Vitamin D is fat soluble vitamin and is excreted from the body in urine. (Ans - d)
4. Assertion : Purine bases present in DNA are adenine and guanine.
   Reason : The base thymine is present in RNA while base uracil is present in DNA. (Ans - c)
5. Assertion : α - Amino acids are the building blocks of proteins.
   Reason : Natural amino acids are mostly α - amino acids. (Ans - b)

One - word answer

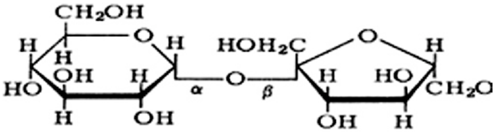
1. Name the linkage used to link different monosaccharide in a polysaccharide ? (Ans - Glycosidic)
2. Name a water soluble vitamin which is not excreted from our body? (Ans - Vitamin - B12)

(Q.) What do you understand by denaturation of proteins? (2Marks)

(**Ans**) When a protein in its native form, is subjected to physical change like in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

(Q.) Give the chemical structure of sucrose & explain why sucrose is non reducing sugar. (2 Marks)

(**Ans**)



The two monosaccharide are held together by a glycosidic linkage between C1 of ♋glucose and C2 of ♌ - fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

(Q.) Give a broad classification of vitamins? (2Marks)

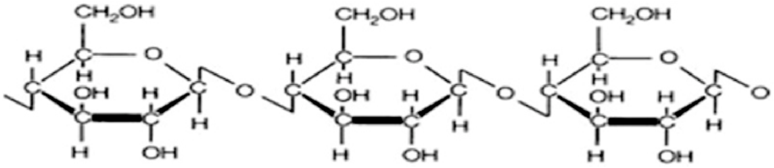
(**Ans**) Vitamins are complex organic molecules. They can be broadly classified as:

(i) **Water soluble vitamins:** These include vitamin B-complex and vitamin C.

(ii) **Fat soluble vitamins:** These are oily substances that are not readily soluble in water. However, they are soluble in fat. These include vitamins A,D,E and K.

(Q.) **Write a short note on cellulose and give its chemical structure.** **(3 Marks)**

(**Ans**)



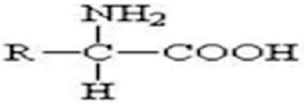
Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of α– D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit

(Q.) **Give a short note on Zwitter ion?** **(3 Marks)**

(**Ans**) Amino acids are usually colourless, crystalline solids. These are water soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxylic group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitterion.

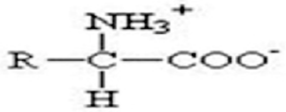
(Q.) **How are peptides formed. Show the formation of peptide bond with diagram. (3 Marks)**

(**Ans**) Peptides are amides formed by the condensation of amino group of one NH_2– amino group with the carboxyl group of another molecule of the same or different

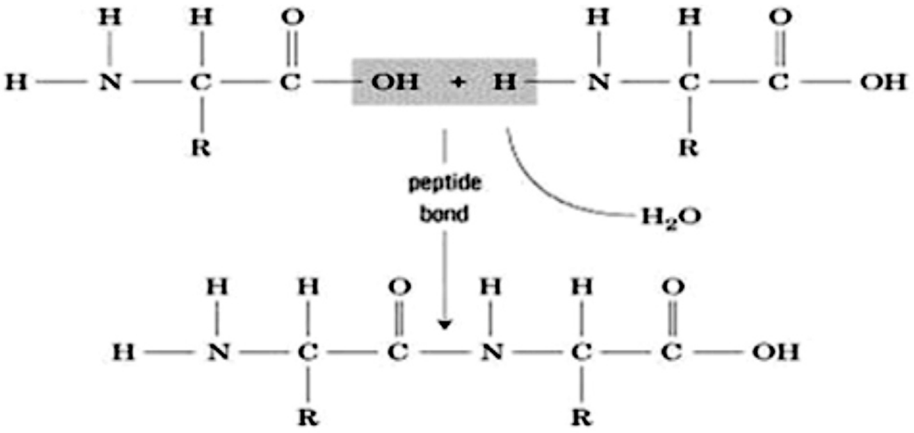


$$R-\underset{H}{\overset{NH_2}{C}}-COOH$$

R is the functional group of the amino acid



$$R-\underset{H}{\overset{NH_3^+}{C}}-COO^-$$



1-Vitamins are organic compounds which are essential for maintenance of normal growth and health of the organism. Certain vitamins cannot be stored in our body and have to be supplied regularly in diet while others can be stored in the body. Vitamins are required only in small amounts and should not be taken in excess. Answer the following questions:

(i) Out of water soluble and fat soluble vitamins which can be stored in our body?

(ii) Name any two water soluble and two fat soluble vitamins.

(iii) Which of the vitamin belonging to B-complex series can be stored in our body?

Ans. (i) Fat soluble

(ii) (Water soluble) B and C, (fat soluble) A,D,E,K

(iii) B_{12}

Biomolecules

These are the macromolecules essential for survival of life, e.g. carbohydrates, proteins, etc.

Carbohydrates

These are polyhydroxy aldehydes or ketones or their derivatives, e.g. glucose.

Sugars

These are the carbohydrates having sweet taste.
They may be reducing or non-reducing.

Glucose

- It is obtained by hydrolysing starch or cane sugar.
- Its reactions are as:

$$\text{Glucose} \xrightarrow[\Delta]{\text{HI}} n\text{-hexane}$$
$$\xrightarrow[\text{3 mol}]{\text{NH}_2\text{OH}} \text{Oxime}$$
$$\xrightarrow{\text{Br}_2 \text{ water}} \text{Gluconic acid}$$
$$\xrightarrow[\text{CH}_3\text{COCl}]{\text{Acetylation}} \text{Pentaacetate}$$
$$\xrightarrow{\text{HNO}_3} \text{Saccharic acid}$$

Sucrose

- It contains D-(+)-glucose and D(−)-fructose joined together by β-1,2-glycosidic linkage.
- It is also called invert sugar.

Starch

- It contains two components: amylose (water soluble, 20%) and amylopectin (80%, water insoluble).
- It is the reserve food of plants.

Cellulose

- Most abundant in plants and contains glucose units, joined together by β-1,4-glycosidic linkage.

Proteins

These are polymers of α-amino acids.

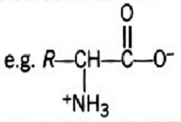
Amino Acids

These contain amino as well as carboxyl functional group.
They may be essential or non-essential.

Zwitter Ion

Ion containing positive as well as negative charge is called zwitter ion.

e.g.



$$R{-}\underset{\overset{|}{^{+}NH_3}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}O^-$$

Denaturation

- It is the process of destroying 2° or 3° structure of protein by heating and by changing pH.
- Due to this, protein losts its biological activity.
- e.g. coagulation of egg white on boiling.

Structure of Proteins

Primary Structure

(It shows the sequence of amino acids in a protein).

Secondary Structure

(It is formed due to hydrogen bonding and may be α-helix or β-pleated sheet structure).

Enzymes

These are the proteins which catalyse reaction occurring in human body, so also called biocatalysts, e.g. maltase, zymase, etc.

Vitamins, Nucleic Acids and Hormones

Vitamins

These are essential but in very small amounts. Vitamins A, D, E and K are fat soluble while rest are water soluble.

Deficiency Diseases

Vitamin	Deficiency Disease
A	Xerophithalmia
B_1	Beri-beri
B_{12}	Pernicious anaemia
C	Scurvy
D	Rickets
E	Infertility

Nucleic Acids

These are the polymer of nucleotides (sugar + base + phosphoric acid).

Deoxyribonucleic Acid (DNA)

It contains pentose sugar (deoxyribose), purine base (adenine, A and guanine, G) pyrimidine base (Thymine, T and cytosine, C) and phosphoric acid.

Ribonucleic Acid (RNA)

It contains sugar (ribose), purine base (adenine and guanine) and pyrimidine base (uracil, U and cytosine) and phosphoric acid.

Hormones

These are the rea
gl

Chemicals released by endocrine glands

Steroid Hormones

e.g. sea hormones, bile acids, etc.

Non-steroid Hormones

These do not have steroid ring, e.g. insulin.

QUESTIONS/ ANSWERS

MCQ TYPE QUESTIONS (1 – MARK EACH)

1.Antibodies are –

(a) carbohydrates (b) Proteins

(c) Lipids (d) Enzymes

Ans b

2.The function of enzymes in the living system is to–

(a) Transport oxygen (b) Provide immunity (c)Catalyze biochemical reactions (d)Provide energy

Ans c

3.Vitamin A is called –

(a) Ascorbic acid (b) Retinol

(c) Calciferol (d) Tocopherol

Ans b

4.Which carbohydrate is an essential constituent of plant cells?

(a) Starch (b) Cellulose (c) Sucrose (d) Vitamins

Ans b

5.Vitamin B_1 is –

(a) Riboflavin (b) Cobalamin (c) Thiamine (d) Pyridoxine

Ans c

6.Which statement is incorrect about peptide bond?

(a) N bond length in proteins is longer than usual bond length of C – N bond

(b) Spectroscopic analysis shows planar structure of – CO – NH – group

© C – N bond length in proteins is smaller than usual bond length of C – N bond

(d) None of the above

Ans a

7.The vitamins absorbed from intestine along with fats are –

(a) A, D (b) A, B (c) A,C (d) D, B

Ans a

8.The functional group which is found in amino acid is

(a) – COOH (b) $-NH_2$ (c) $-CH_3$ (d) both (a) and (b)

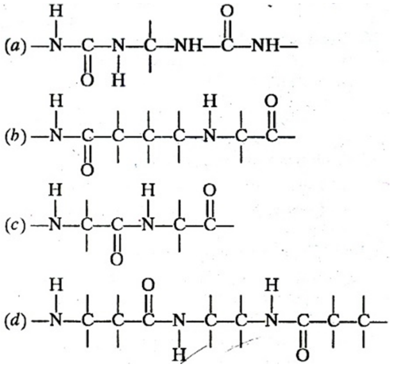
Ans d

9.Complete hydrolysis of cellulose gives –

(a) L – glucose (b) D-Fructose(c) D-ribose (d) D-glucose

Ans d

10.Which of the following structures represents the peptide chain?



Ans c

11.Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories –
(a) A coenzyme (b) a hormone (c) an enzyme (d) An antibiotic
Ans b

12.Which base is present in RNA but not in DNA?
(a) Uracil (b) Cytosine (c) Guanine (d) Thymine
Ans d

13.The nucleic acid base having two possible binding sites is –
(a) Thymine (b) cytosine (c) Guanine (d) Adenine
Ans c

14.Which functional group participates in disulphide bond formation in proteins?
(a) Thioether (b) Thiol (c) Thioester (d) Thiolactone
Ans b

15.In both DNA and RNA, heterocyclic base and phosphate ester linkages are at –
a. C_5' and C_2' respectively of the sugar molecule
b. C_2' and C_5' respectively of the sugar molecule
c. C_1' and C_5' respectively of the sugar molecule
d. C_5' and C_1' respectively of the sugar molecule
Ans c

16.The human body does not produce –
(a) Enzymes (b) DNA (c) Vitamins (d) Hormones
Ans c

17.The Pyrimidine bases presentin DNA are –
a) cytosine and adenine (b) cytosine and guanine
c) cytosine and thymine (d) cytosine, thiamine and uracil
Ans d

18.Cellulose is a straight chain polysaccharide composed of only –
a) D-glucose units joined by α - glyosidic linkage
b) D – glucose units joined by β - glyosidic linkage
c) D – galactose units joined by α - glyosidic linkage
d) D – galactose units joined by β - glyosidic linkage
Ans a

19.Which of the following vitamins is water soluble?
(a) Vitamin E (b) Vitamin K (c) Vitamin A (d) Vitamin B
Ans d

20.Cellulose is insoluble in –
a)ammoniacal cupric hydroxide solution
b)organic solvents (c) water (d) None
Ans c

HOTS

1. Fresh tomatoes are a better source of Vitamin C than which have been stored for some time. Explain.

Ans. Vitamin C is destroyed on prolonged exposure to air due to its oxidation.

Q2. Why are carbohydrates generally optically active?

Ans. It is due to the presence of Chiral Carbon atoms in their molecules

Q3. How is globular protein different from fibrous protein?

Ans–

Globular Protein	Fibrous Protein
1.they form α-helix structure. 2.they are water soluble. 3.they involve H bonding.	1. they have β-pleated structure. 2. they are water insoluble. 3. they have strong intermolecular forces of attraction.

Q4. (i) What products would be formed when a nucleotide from DNA containing thymine is hydrolyzed?

(ii)How will you distinguish 1° and 2° hydroxyl groups present in glucose?

Ans. (i) Complete hydrolysis of DNA yields a pentose sugar, phosphoric acid and thymine

(ii) On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.

Q5. Explain tertiary structure of Protein.

Ans. *Tertiary structure of proteins***:** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilize the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

POLYMERS (UNIT-14)

KEY POINTS

Polymer:

It is a very large molecule having high molecular mass (10^3 - 10^7 u). They are formed by joining of repeating structural units on large scale.

Copolymer is derived from more than one species of monomer. Copolymer is fromed by copolymerization of two monomer species.

Classification of polymers:

Based on Source

(i) **Natural:** Found in plants and animals, e.g. proteins, cellulose, natural rubber,.

(ii) **Synthetic:** Man-made e.g. nylon, polyester, neoprene, Bakelite, Teflon, PV.C, Semi-synthetic: Cellulose derivatives as cellulose acetate and cellulose nitrate**.**

(iii) **Based on structure:**

Linear polymers: This consist of long and straight chain repeating units. e.g. polythene (HDPE), PVC, nylon, polyester.

Branched polymers: This contain linear chains having some branches
e.g. amylopectin.

Cross linked polymers: Strong covalent bonds are present between various linear polymer chains.
e.g Bakelite, urea-formaldehyde polymer, melamine etc.

Based on molecular forces:

Elastomers: Forces of interaction between polymer chains is weakest, e.g. Buna -S , Buna- N, neoprene etc.

Fibers: Strong hydrogen bonds are present between the polymer chains. They have high tensile strength e.g., nylon, polyester, silk, wool, orlon, rayon etc.

Thermoplastics: They are linear/slightly branched chain molecules capable of repeatedly softening on heating and hardening on cooling, e.g. polythene, PVC, polystyrene, etc.

Thermosetting Plastics: They are coss-linked or heavily branched molecules, which on heating undergo extensive cross-linkages and become infusible, e.g, bakelite, urea- formaldehyde resin etc.

POLYMERS AT AGLANCE

Polymer	Monomer	Uses
(a) Polythene	Ethene	Insulation of wires, toys, manufacture of dustbins etc.
Polytetrafluroethene (Teflon)	Tetrafluroethene	Oil seal and gasket and non-stick kitchen Wares.
(c) Polyarcylonitrile	Acrylonitirile	Substitute for wool.
(d) Terylene or Dacron	Ethylene glycol + Terephthalic acid	Safety helmets, used in blending with cotton and wool fibers.
(e) Nylon-6,6	Hexamethylenediamine + adipic acid	Stocking, Socks, ropes, parachutes, fabrics, bristles of tooth brush.
(f) Novolac	Phenol + Formaldehyde	Used for binding glue, paints.
(g) Bakelite	Formaldehyde + Phenol	Combs, records, Switches boards
(h) Melamine	Melamine + Formaldehyde	Manufacture of unbreakable crockery.
(i) Polypropene	Propene	Ropes, toys, pipes, fibres etc.
(j) Polystyrene	Styrene	As insulator, wrapping material, radio and television cabinets.
(k) Glyptal	Ethylene glycol + phthalic acid	Manufacture of paints and lacquers.
(l) Buna-N	1,3-Butadiene+Acrylonitrile	In making oil seals, tank lining, etc.
(m) Nylon-2-Nylon6	Glycine + aminocaproic acid	it is biodegradable polymer
(n) Buna-S copolymer	1,3-Butadiene+Styrene	floor tiles foot-wear components
(o) Natural Rubber	2-methyl-1,3-butadiene	Used for tyres
(p) Neoprene	2-chloro-1,3-butadiene	Conveyor belts, gasket, hoses
(PHBV) poly-β hydroxybutyrate-co-β hydroxy valerate (Biodegradable)	3□hydroxybutanoic acid + 3-hydroxypantanoic acid	Speciality packaging, orthopaedic devices.

1 MARK QUESTIONS

Q.1 What does the designation 6,6 mean in the name nylon-6,6?

Ans. The acid and amine parts, which condense to give the polymer both contain 6 carbons each.

Q.2 Give an example of elastomers.

Ans. Buna-S, Buna-N and neoprene are examples of elastomers.

Q.3 Name the polymers used in laminated sheets and give the name of monomeric units involved in its function.

Ans. Urea-formaldehyde resins. Monomer units are Urea and formaldehyde.

Q.4 Explain the difference between Buna-N and Buna-S.

Ans. Both are copolymers. Buna-N is a copolymer of 1,3-butadiene and acrylonitrile while Buna-S is a copolymers of 1,3-butadiene and styrene.

Q.5 Why are rubbers called elastomers?

Ans. Rubbers are stretched on application of force and regain its original state after the force is removed, therefore these are called elastomers.

ASSERTION - REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below :

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

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

(c) Assertion is true but reason is false.

(d) Both assertion and reason are false.

1. Assertion : Strong interparticle forces exist in thermosetting polymers.
   Reason : These polymers are heavily cross - linked. (Ans - a)
2. Assertion : Most of the synthetic polymers are non - biodegradable.
   Reason : During polymerisation, the polymers become toxic and non - biodegradable. (Ans - c)
3. Assertion : Teflon is used for making oil seals, gaskets and non - stick surface coating.
   Reason : Teflon is chemically inert and resistant to attack by corrosive reagents. (Ans - a)
4. Assertion : Low density polythene is used in the insulation of electricity carrying wires.
   Reason : It is chemically inert, tough, flexible and poor conductor of electricity. (Ans - a)

ONE - WORD ANSWER

1. What is the commercial name of polyacrylonitrile? (Ans - orlon)
2. Name a polymer having a vinylic monomeric unit. (Ans - Polystyrene)

2 Marks Questions

Q1 Arrange the following polymers in increasing order of their intermolecular forces.

(i) Nylon 6,6, Buna-S, polythene.

(ii) Nylon 6, neoprene, polyvinyl chloride.

Ans. The increasing intermolecular forces of attraction follows the order : Elastomer, Thermo plastic, Fibre.

(i) Buna-S, polythene, Nylon 6, 6.

(ii) Neoprene, polyvinyl chloride, Nylon 6.

Q.2 Distinguish between the terms homopolymers and copolymers and give an example of each.

Ans. Homopolymers :- Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers. For example, Polythene, PVC, PAN, teflon, etc.

Copolymers :- Polymers whose repeating structural units are derived from different types of monomer molecules. For examples, Buna-S, nylon 6,6, polyester, bakelite, etc.

Q.3 Differentiate the following pairs of polymers based on the property mentioned against each

(i) Novolac and bakelite (structure)

(ii) Buna-S and terylene (intermolecular force of attraction)

Ans. (i) Novolac is a linear condensation polymer formed by reaction between phenol and formaldehyde. Bakelite is a cross linked condensation polymer formed by reaction between phenol and formaldehyde.

(ii) Buna-S has weak intermolecular forces of attraction. terylene has stronger intermolecular force of attraction (dipole- dipole attraction).

Q.4 Write the name of monomers used for getting the polymers PVC and PMMA. State one use for each of these polymers.

Ans. **PVC:-** Vinylchloride is the monomer used in PVC. It is used for making pipes and electrical insulators.

PMMA:- Polymethyl methacrylate is the monomer used in PMMA. It is used as substitute of glass.

Q.5 Write one difference between chain growth and step growth polymerisation. Give one example of each.

Ans. Chain growth polymerisation involves addition of monomers by free radical mechanism. Generally unsaturated monomers react by this mode of polymerisation to give polymers. Example Polythene, polypropene.

Step growth polymerisation involves repetitive condensation reaction between two bifunctional monomers. Ex Terylene.

3 Marks questions

Q.1 How does the presence of double bonds in rubber molecules influence their structure and reactivity?

Ans. Natural rubber is cis-1,4-polyisoprene and is obtained by linear polymerisation of isoprene units. The cis-configuration at double bonds does not allow the polymer chains to come closer for effective interactions and hence intermolecular forces are quite weak. As a result, natural rubber i.e, cis-polyisoprene has a randomly coiled structure and hence shows elasticity.

Q.2 How is bakelite made and what is its major use? Why Is bakelite a thermosetting polymer?

Ans. Bakelite is obtained by condensation reaction of phenol and formaldehyde. It is used in making electrical switches and switch boards. It is thermosetting polymer because on heating it undergoes extensive cross linking in the mould.

Q.3 Draw the structures of the monomers of the following polymers:

(i) Polythene (ii) PVC (iii) Teflon Ans (i) Polythene:-The structure of the monomer of polythene is :

$CH_2= CH_2$

(ii) PVC(polyvinylchloride) :-The structure of monomer of PVC is given below:

$CH_2=CH-Cl$

Teflon:-The structure of the monomer of teflon is: $CF_2=CF_2$

Q.4 (a) Give an example of synthetic rubber and mention its main advantages.

Write the monomers of Dacron.

Arrange the following polymers in increasing order of tensile strength : Nylon-6, Buna-S, Polythene.

Ans. (a) An example of synthetic rubber is Buna-S. Main Advantage : It is resistant to the action of petrol, lubricating oil and organic solvents.

(b) Monomers of dacron are: Ethylene glycol and Terephthalic acid

(c) Increasing order of tensile strength of the given polymers : Buna-S < Polythene < Nylon -6

Q.5 Write the names of monomers of the following polymers and classify them as addition or condensation polymers (a) Teflon (b) Bakelite (c) Natural rubber

Ans. (a) Monomer of Teflon is tertraflouroethene ($CF_2=CF_2$). It is an addition polymer.

(b) Monomer of bakelite are formaldehyde and phenol. It is a condensation polymer.

(c) Monomer of natural rubber is isoprene (2-methyl-1 , 3-butadience). It is an addition polymer.

ASSIGNMENT QUESTIONS

1. Name a synthetic polymer which is an amide.
2. How are addition polymers different from condensation polymers?
3. What is the basic difference between following pairs:
   (a) Elastomers and fibres
   (b) Thermo setting polymer & thermo plastic polymers.
4. Explain the mechanism of polymerisation of ethene.
5. Differentiate between LDP and HDP.
6. Give preparation of polyacrylonitrile.
7. Write one use of each – Teflon and polyacrylonitrile.
8. Give monomers and preparation of Nylon – 6, 6 and Dacron.
9. How is Nylon – 6, 6 different from Nylon -6?
10. Write uses of bakelite and melamine.
11. How are neoprene & Buna – N prepared? Which one is a copolymer?
12. Classify following on homopolymer and copolymer- PVC, Polystyrene, Buna–S, Neoprene, Buna–N, Teflon.
13. Classify following an addition and condensation polymer- Bakelite, Polythene, Nylon–6, 6, Polyacrylonitrile
14. Write monomers of polystyrene and PVC.

MCQ (ONE MARK)

1. Which of the following polymers of glucose is stored by animals?

(i) Cellulose
(ii) Amylose
(iii) Amylopectin
(iv) Glycogen

Ans (iv)

2. Which of the following is not a semisynthetic polymer?

(i) *cis*-polyisoprene
(ii) Cellulose nitrate
(iii) Cellulose acetate
(iv) Vulcanised rubber

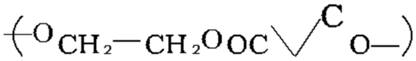
Ans (i)

3. The commercial name of polyacrylonitrile is ______________.

(i) Dacron
(ii) Orlon (acrilan)
(iii) PVC
(iv) Bakelite

Ans (ii)

4. In which of the following polymers ethylene glycol is one of the monomer units?

(i) 

(ii) $\left(CH_2 - CH_2 \right)$

(iii) $\left(CH_2 - CH{=}{=}CH - CH_2 - CH - CH_2 \right)$

(iv) $\left(O - CH - CH - C - O - CH - CH - C \right)$

Ans (i)

5. Which of the following statements is not true about low density polythene?

(i) Tough
(ii) Hard
(iii) Poor conductor of electricity
(iv) Highly branched structure

Ans (iii)

6. Which of the following polymer, need at least one diene monomer for their preparation?

(i) Bakelite
(ii) Buna-S
(iii) Neoprene
(iv) Novolac

Ans (ii)

7. Which of the following monomers form biodegradable polymers?

(i) 3-hydroxybutanoic acid + 3-hydroxypentanoic acid

(ii) Formaldehyde + Phenol

(iii) Ethylene glycol + phthalic acid

(iv) Caprolactum

Ans (ii)

8. Which of the following polymers have no vinylic monomer units?

(i) Acrolein

(ii) Polystyrene

(iii) Nylon

(iv) Teflon

Ans (iii)

9. Vulcanisation of rubber is done by adding _____________.

(i) oxygen

(ii) sulphur

(iii) silicon

(iv) sulphates

Ans (ii)

10. Caprolactum is the monomer unit of

(i) Nylon 6,6

(ii) Buna- S

(iii) Nylon-6

(iv) Teflon

Ans (iii)

CHEMISTRY IN EVERYDAY LIFE (UNIT 15)

KEY CONCEPTS

1. DRUGS- Drugs are chemical of low molecular masses, which interact with macromolecular targets and produces a biological response.
2. CHEMOTHERAPY- The use of chemicals for therapeutic effect is called chemotherapy.
3. CLASSIFICATION OF DRUGS-

a) ON THE BASIS OF PHARMACOLOGICAL EFFECT- Useful for doctors as it provides whole range of drugs for treatment of particular kind of disease.

b) ON THE BASIS OF DRUG ACTION- Action of drug on a particular biochemical process.

c) ON THE BASIS OF CHEMICAL STRUCTURE- Drugs having similar chemical structure.

d) ON THE BASIS OF MOLECULAR TARGETS- Drugs interacting with biomolecules as lipids, proteins.

4. ANTAGONISTS- The drugs that bind to the receptor site and inhibit its natural function.
5. AGONISTS- Drugs mimic the natural messenger by switching on the receptor.
6. HORMONES- They are molecules that act as intercellular messengers.These are produced by endocrine glands in the body and are released directly in the blood stream.
7. ANTACIDS- These are compounds which neutralize excess acid of stomach. eg-Aluminium Hydroxide, Magnesium Hydroxide.
8. ANTIHISTAMINES – The drugs which interfere with the natural action of histamines and prevent the allergic reaction e.g.- Ranitidine, Brompheniramine.
9. TRANQUILIZERS- The class of chemical compound used for the treatment of stress,mild or even severe mental diseases e.g.- derivatives of Barbiturates, Luminal, Equanil.
10. ANALGESICS- They reduce pain without causing impairment of consciousness, mental confusion or some other disturbance of the nervous system. E.g.- Aspirin, Phenacetin.
11. ANTIMICROBIALS – They tend to prevent / destroy or inhibit the pathogenic action of microbes as bacteria, virus, fungi etc. They are classified as :

(i) ANTIBIOTICS – those are the chemicals which are produced by the micro-organisms e.g. – Penicillin, Ofloxacin.

NARROW SPECTRUM ANTIBIOTICS – These are effective mainly against gram positive and gram negative bacteria. Eg. Penicillin, streptomycin.

BROAD SPECTRUM ANTIBIOTICS – They kill or inhibit a wide range of gram positive and gram -ve bacteria. Eg. Chloramphenicol, tetracycline.

(ii) ANTISEPTICS OR DISINFECTANT—These are which either kill/inhibit the growth of micro-organisms. Antiseptic are applied to the living tissues such as wounds, cuts, ulcers etc.

Eg. Boric acid, terpineol (Dettol). Disinfectant are applied to inanimate objects such as floors, drainage system. Eg. Cl_2 , SO_2 (0.2% solution of phenol is an antiseptic while 1% solution is disinfectant.)

12. ANTIFERTILITY DRUGS – These is the chemical substances used to control pregnancy. They are also called oral contraceptives or birth control pills. Eg. Mifepristone, norethindrone.

13. ARTIFICIAL SWEETING AGENTS – These are the chemical compounds which give sweetening effect to the food without increasing calories to the body. They are good for diabetic people. Eg. Aspartame, saccharin, alitame, sucralose.

14. FOOD PRESERVATIVES – They prevent spoilage of food to microbial growth. Eg. Salt, sugar and sodium benzoate.

15. ANTIOXIDANTS IN FOOD- They help in food preservation by retarding the action of oxygen on food. For example butylated hydroxyl toluene (BHT) and butylated hydroxyl anisole(BHA)

16. CLEANSING AGENTS-

(i) SOAPS- They are sodium or potassium salts of long chain fatty acids. They are obtained by the saponification reaction, when fatty acids are heated with aqueous sodium hydroxide.

17. SYNTHETIC DETERGENTS – They are cleaning agent having properties of soaps, but actually contain no soap. They can be used in both soft and hard water. They are-

(i) ANIONIC DETERGENT – They are sodium salts of sulphonated long chain alcohols or hydrocarbon. E.g. –sodium lauryl sulphonate. They are effective in acidic solution.

$CH_3(CH_2)_{10}CH_2OH \qquad H_2SO_4 \rightarrow CH_3(CH_2)_{10}CH_2OSO_3H$ (laurylalchol)

(ii) CATIONIC DETERGENTS- They are Quaternary NH_4 salts of amines with acetates, Cl^{-} or Br^{-}. They are expensive. E.g.- Cetyltrimethylammonium bromide.

(iii) NON-IONIC DETERGENTS – They do not contain any ions, some liquid dish washing detergents which are of non-ionic type.

18. NON-BIODEGRADABLE – The detergents which are branched and cannot be decomposed by microorganisms are called non-biodegradable. It creates water pollution.

E.g. - sodium-4(1,3 -tetramethyloctyl)-benzene sulphonate.

FAQ

Q.1. What is meant by narrow spectrum antibiotics?

Ans. Those antibiotics which are effective against only one particular micro organisms are called narrow spectrum antibiotics.

Q.2. Define the term Chemotherapy?

Ans. The branch of chemistry which deals with the treatment of disease using chemicals is called chemotherapy.

Q.3. What is tincture of iodine?

Ans. A 2-3% solution of iodine in alcohol – water mixture is known as tincture of iodine. It is used as an antiseptic.

Q.4. Name the substance that can be used as an antiseptic as well as disinfectant.

Ans. 0.2% solution of phenol act as an antiseptic and 1% of the solution acts as a disinfectant.

Q.5. What is BHA and BHT?

Ans. BHA is butylated hydroxyl anisole whereas BHT is butylated hydroxyl toluene. Both are used as antioxidant in food.

ASSERTION - REASON TYPE

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Both assertion and reason are false.

1. Assertion : Penicillin(G) is an antihistamine.
   Reason : Penicillin (G) is effective against gram positive as well as gram negative bacteria.
   (Ans - c)
2. Assertion : Receptors are crucial to body's communication process.
   Reason : Receptors are proteins. (Ans - a)
3. Assertion : Sodium chloride is added to precipitate soap after saponification.
   Reason : Hydrolysis of esters of long chain fatty acids by alkali produces soap in colloidal form.
   (Ans - a)
4. Assertion : Preservatives are added to food items.
   Reason : Preservatives inhibit the growth of micro organisms. (Ans -b)
5. Assertion : Artificial sweetners are added to the food to control the intake of calories.
   Reason : Most of the artificial sweetners are inert and do not metabolise in the body. (Ans - b)

One - word answer

1. Name the artificial sweetner which can be added to cold food items. (Ans -Aspartame)
2. Name the drug which is effective in curing typhoid and dysentry? (Ans - Chloramphenicol)

2 Marks

Q.1. Why are cimetidine and ranitidine better antacids than sodium bicarbonate or aluminium hydroxide?

Ans. $NaHCO_3$ or $Mg(OH)_2$ or $Al(OH)_3$; if taken in excess makes the stomach alkaline and thus triggers the release of even more HCl causing ulcers in stomach , whereas cimetidine and ranitidine prevent the interaction of histamine with the receptor cells in the stomach wall, resulting in release of lesser amount of HCl.

Q. 2. What are analgesics? How are they classified?

Ans. The drugs which give relief from the pain are known as analgesics. They are classified as

1.) Non-Narcotics: They do not cause addiction. eg. Aspirin

2.) Narcotics: They are habit forming. eg. Morphine

Q. 3. What are biodegradable and non-biodegradable detergents ? Give one example each.

Ans. Biodegradable detergents are decomposed by microorganisms like bacteria into harmless product. They do not create water pollution. Detergents having linear alkyl chains are biodegradable. Eg. Sodium lauryl sulphate.

Non-Biodegradable are not decomposed by microorganisms. They create water pollution.eg. Cetymethyl, Ammonium bromide.

Q. 4. How antiseptics are different from disinfectant. Give one example of each.

Antiseptics	**Disinfectant**
Do not harm the living tissues.	Tonic to living tissues.
Applied to wounds, Ulcers, diseased skin etc.	Used for disinfecting instruments, floors, toilet, drains etc.
Examples. Phenol(0.2%), Boric acid, Tincture of Iodine	Example. Phenol(1%), Chlorine, DDT etc.

Q. 5. A) Why is Bithional added to soap?

B) Give the composition of Dettol.

Ans. A) Bithional is an antiseptic which reduces the odour produced by bacteria decomposition of organic matter on skin.

B) Dettol is a mixture of chloroxyenol and terpineol.

3 marks

1. Explain the following terms with suitable examples (a) cationic detergents (b) anionic detergents (c) neutral detergents.

Ans. (a) Cationic detergents are generally quaternary Ammonium salts as Chlorides, Bromides or acetates. These detergents are quite expensive and find limited use. Some of these detergents have germicidal properties and are used as germicides.

(b) Anionic detergents: - A detergent whose hydrophilic activity hinges on an anionic group. Fatty acids are natural anionic detergents (AD), but are neither used as detergents nor functional in biological systems; the main synthetic ADs are aliphatic Sulphate esters (e.g., Sodium dodecyl sulphate).

(c) **Neutral Detergent**s the most common measure of fibre used for animal feed analysis, but it does not represent a unique class of chemical compounds. NDF measures most of the structural components in plant cells (i.e. Lignin, Hemicellulose and Cellulose)

Q. 2. What are the following substances, give one example of each.

(a) Tranquilizers (b) Food preservatives (c) Antihistamines.

Ans. (a) Tranquilizers: - These chemicals are used for the treatment of stress, fatigue and mental diseases. They release anxiety, stress irritability, etc.

example- Equanil, Luminal.

(b) Food preservatives: - These chemical substances are added to the food materials to prevent their spoilage due to microbial growth.

example: - Sodium benzoate, Sodium chlorate.

(c) Antihistamines: - These drugs interfere with the natural action of histamine by competing with histamine for bonding sites of receptor with histamine exerts its effects.
example: -Cetrizine

Q. 3. Define: (a) Receptors (b) Agonists (c) Antagonists.

Ans. (a) Receptors: - Proteins which are crucial to communication system in the body are called receptors. Receptors are embedded in cell membrane.

(b) Agonists: - Drugs that mimic the natural messenger by switching on the receptor are called agonists.

(c) Antagonists: - Drugs that bind the receptors site and inhibit its natural function are called antagonist.

Q. 4. (a) Name two artificial sweetness used in food materials.

(b) Give one examples of (i) bactericidal antibiotic (ii) bacteriostatic antibiotic

(c) Give an example of sulpha drug.

Ans. (a) Aspartame and Alitame

(b) (i) Penicillin (ii) Tetracycline

(c) Sulpha pyridine or Sulpha guanidine

ASSIGNMENT

1. Which site of an enzyme is called allosteric site?
2. Which class of drugs is used in sleeping pills?
3. Explain soaps do not work in hard water.
4. Why is the use of sweetener aspartame limited to cold food and drinks only?
5. Mention one important use of each of the following: (i) Equanil (ii) Sucralose.
6. What is the cause of a feeling of depression in human beings? Name a drug which can be useful in treating this depression.
7. Account for the following : -

(i) Aspirin drug helps in prevention of heart attack.

(ii) Diabetic patients are advised to take artificial sweeteners instead of natural sweeteners.

MIND MAP

Chemistry in healthcare	**Classes of drugs**	**Chemicals in otherindustries**
DRUGS-Chemicals of low molecular masses.(n=100-500u)	Antacids- removes excess acid and raise pH to an appropriate level.Eg: $Mg(OH)_2$, Histamine	**Chemicals in food** Artificial sweeteners- provide sweetness without calories. Eg: Aspartame, Alitame.
Medicines are drugs which produce useful biological response.	Antihistamines- interfere with natural action of histamine.Eg: Chlorophenirамine	Food preservatives- prevent spoilage of food.Eg: Sodium Benzoate.
Chemotherapy-disease is treated with chemicals.	Analgesics- drugs used to reduce body pain. Eg: aspirin, paracetamol.	Antioxidants-retard the oxidation of food. Eg: BHT, BHA.
Drug target interactions	Antimicrobials- prevent development of micro organisms.	Cleansing agents- improve the cleansing property of water.

Receptors-proteins used for communication in body.	Antibiotics-inhibit the growth of microorganisms or may destroy it.Eg:Penicillin, tetracycline	Soaps- Na or K salts of long chain fatty acids.
Inhibitors-drugs that block binding site of enzymes.	Antiseptics-check the growth of micro organisms.Eg: Furacin, Iodine tincture.	Synthetic detergents□ soapless soaps.
Antagonists- drugs that bind the receptor site.	Antifertility drugs-used to prevent unwanted pregnancies. Eg:progesterone	Anionic Detergents- Na salt of sulphonated long chain alcohol or hydrocarbon.Eg: Sodium Lauryl Sulphates.
Agonists- drugs which mimic the natural messengers.	Disinfectant-applied to inanimate objects like floors, drainage.Eg: 100% solution of phenol	Non ionic detergents-don't contain ions. Eg:detergents obtained from steric acids and polyethylene glycol. Cationic detergents□quaternary ammonium salts Eg: Cetyltrimethyl ammonium bromide.

MULTIPLE CHOICE QUESTION

.1Which of the following statements is not correct?
i). Some antiseptics can be added to soaps.
ii) Dilute solutions of some disinfectants can be used as antiseptic.
iii) Disinfectants are antimicrobial drugs.
iv) Antiseptic medicines can be ingested.
Ans (iv)

.2Which is the correct statement about birth control pills?
i) Contain estrogen only.
ii) Contain progesterone only.
iii) Contain a mixture of estrogen and progesterone derivatives.
iv) Progesterone enhances ovulation.
Ans (iii)

.3Which statement about aspirin is not true
i) Aspirin belongs to narcotic analgesics.
ii) It is effective in relieving pain.
iii) It has antiblood clotting action.
iv) It is a neurologically active drug.
Ans (i)

.4Which of the following chemicals can be added for sweetening of food items at cooking temperature and does not provide calories?
i) Sucrose
ii) Glucose
iii) Aspartame
iv) Sucralose
Ans (iv)

.5Which of the following will not enhance nutritional value of food?
i) Minerals
ii) Artificial sweeteners
iii) Vitamins
iv) Amino acids
Ans (ii)

.6Salvarsan is arsenic containing drug which was first used for the treatment of_______.
i) syphilis
ii) typhoid
iii) meningitis
iv) dysentery
Ans (i)

.7A narrow spectrum antibiotic is active against ________________.
i) gram positive or gram negative bacteria.
ii) gram negative bacteria only.
iii) single organism or one disease.
iv) both gram positive and gram negative bacteria.
Ans (ii)

.8The compound that causes general antidepressant action on the central nervous system belongs to the class of ______________.
i) analgesics
ii) tranquilizers
iii) narcotic analgesics
iv) antihistamines
Ans (ii)
.9Compound which is added to soap to impart antiseptic properties is __________.
i) sodium lauryl sulphate
ii) sodium dodecylbenzenesulphonate
iii) rosin
iv) bithional
Ans (iv)

10 .Equanil is ___________.
i) artificial sweetener
ii) tranquilizer
iii) antihistamine
iv) antifertility drug
Ans (ii)
.11Which of the following enhances leathering property of soap?
i) Sodium carbonate
ii) Sodium rosinate
iii) Sodium stearate
iv) Trisodium phosphate
Ans (ii)
.12Glycerol is added to soap. It functions _______________.
i) as a filler.
ii) to increase leathering.
iii) to prevent rapid drying.
iv) to make soap granules.
Ans (iii)

.13Which of the following compounds are administered as antacids?
i) Sodium carbonate
ii) Sodium hydrogen carbonate
iii) Aluminium carbonate
iv) Sodium Chloride
Ans (ii)

.14Polyethylene glycols are used in the preparation of which type of detergents?
i) Cationic detergents
ii) Anionic detergents
iii) Non-ionic detergents
iv) Soaps
Ans (iii)

.15Which of the following is not a target molecule for drug function in body?
i) Carbohydrates
ii) Lipids
iii) Vitamins
iv) Proteins
Ans (iii)

QUESTIONS (1 mark)

1. What is the average molecular mass of drugs?
2. Write the uses of medicines.
3. What are antiseptics?
4. Which type of drugs come under antimicrobial drugs?
5. Where are receptors located?
6. What is the harmful effect of hyperacidity?
7. Which site of an enzyme is called allosteric site?
8. What type of forces are involved in binding of substrate to the active site of enzyme?
9. What is the commonality between the antibiotic arsphenamine and azodye?
10. Which class of drugs is used in sleeping pills?

ANSWER

1.~100–500u.

2. Medicines are used in diagnosis, prevention and treatment of diseases.

3. Antiseptics are chemicals which either kill or prevent the growth of microorganisms and

are applied to living tissues.

4. Antiseptics, antibiotics and disinfectants.

5. Receptors are embedded in cell membrane.

6. Ulcer development in stomach.

7. Sites different from active site of enzyme where a molecule can bind and affect the active site is called allosteric site. Some drugs may also bind at this site.

8. Ionic bonding, hydrogen bonding, van der Waals interaction, dipole-dipole interaction.

9. Arsphenamine possesses —As=== As— linkage that resembles —N=== N— linkages in azodyes.

10. Tranquilizers

APPENDIX –A

Important formula (from unit 1 - 3)

UNIT- 1 SOLUTIONS

HENRY'SLAW $P = K_H X$ K_H is Henry's law constant .

RAOULT'SLAW:- $P_A = P^0_A X_A$; $P_B = P^0_B X_B$ $P_{total} = P_A + P_B$

5. RELATIVE LOWERING OF VAPOUR PRESSURE

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

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

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

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

6. ELEVATION OF BOILING POINT

$\Delta T_b = k_b m$

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

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

7. DEPRESSION IN FREEZING POINT

$\Delta T_f = K_f m$

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

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

8. OSMOTIC PRESSURE

$\Pi = CRT$ $\Pi = n/VRT$

R= 0.0821 Latm mol^{-1} ;

i = normal molecular mass/ observed molecular mass

VAN'T HOFF FACTOR (i)

i = observed colligative properties/ calculated value of colligative properties i<1 (for association)

i>1 (for dissociation)

MODIFIED FORMS OF COLLIGATIVE PROPERTIES

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

6) $\Delta T_b = i\ K_b m$

7) $\Delta T_f = i\ K_f m$

8) $\Pi = i\ CRT$

UNIT2 ELECTROCHEMISTRY

1.) ρ= Ra\l

2.) K =1\ρ

3.) K = 1\R l\a

4.) Λ_m = k100\c

5.) $E_{cell} = E^0_{cell} -$ 2.303R.T\nF log K

6.) At 25^0 C $E_{cell} = E^0_{cell} -$ 0.0591\n log K 7.) At equilibrium

E^0_{cell} = 0.0591\n log K

8.) $\Delta G = -nFE^0$

UNIT 3 CHEMICAL KINETICS

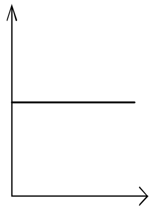
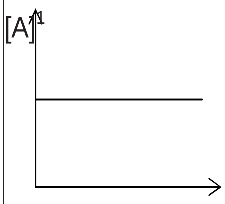
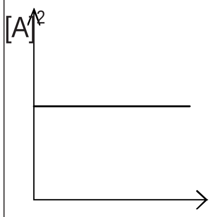
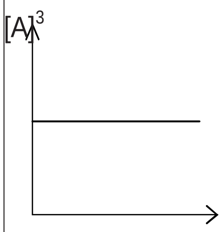
1. **1. Rate of reaction**:- For a reaction $R \rightarrow P$,

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

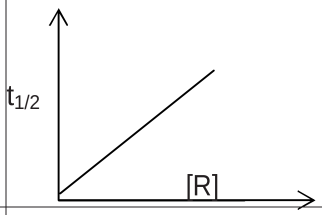
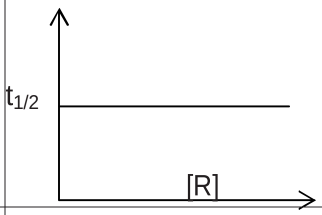
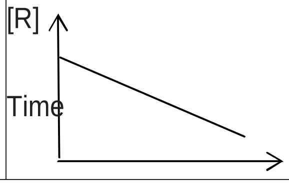
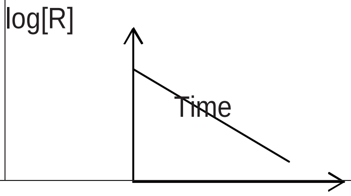
2. **Order ofreaction:** 2. For the reaction $aA + bB \rightarrow cC + d\boxed{D}$

3. $= \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$ Rate = $K[A]^x[B]^y$

4. **Units of rate constants and graph between rate and conc. of reactat**

Order of reaction	**zero**	**first**	**second**	**third**
Unit of rate constt.	$molL^{-1}s^{-1}$	s^{-1}	$mol^{-1}L^{+1}s^{-1}$	$mol^{-2}L^{+2}s^{-1}$
Relation b/w rate&concof **Reactant**	R α $[A]^0$	R α $[A]^1$	R α $[A]^2$	R α $[A]^3$
Graph b/w rate & conc of Reactant	R  [A]	R 	R 	R 

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

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

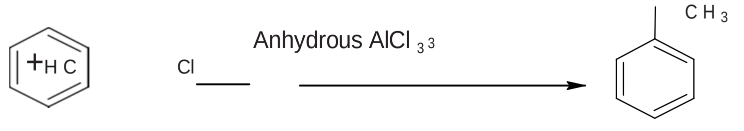
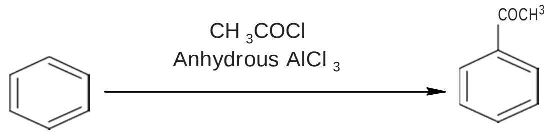
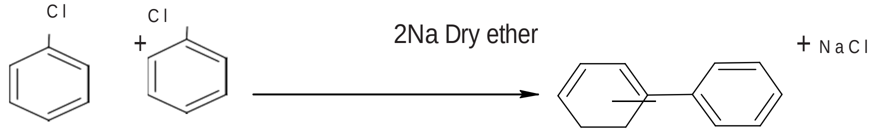
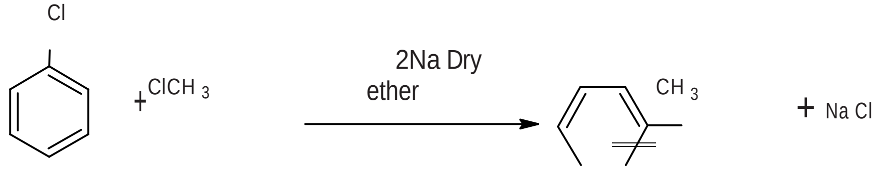
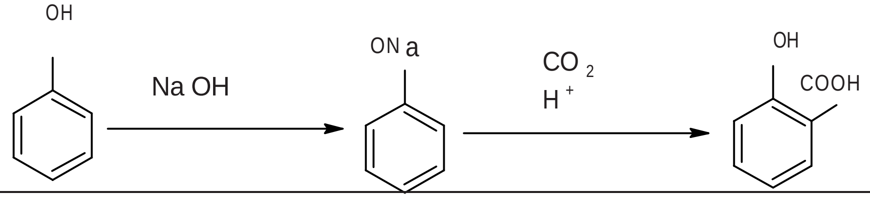
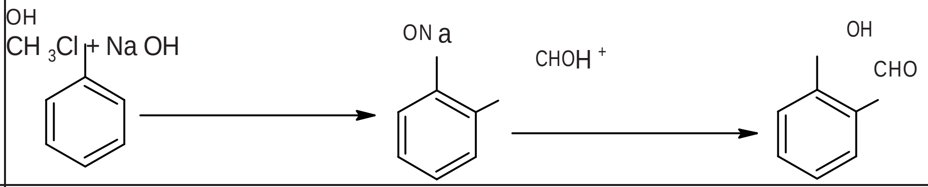
6. $t_{1/2} \propto [conc]^{1-n}$ where n = order of reaction.

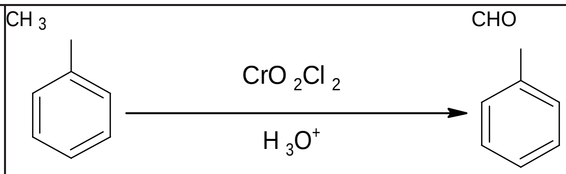
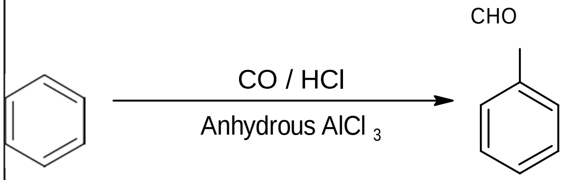
7. Arrhenius equation

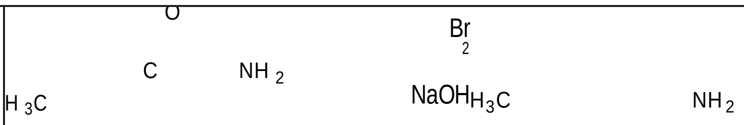
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

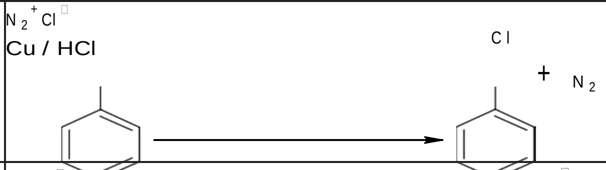
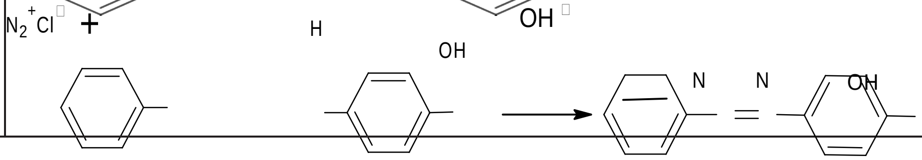
$\log K = \log A - E_a/2.303RT$

APPENDIX –B
NAME REACTIONS

1.	Finkelstein	$CH_3Br + NaI \xrightarrow{\text{Acetone}} CH_3\text{-}I + NaBr$
2.	Swarts	$CH_3Br + AgF \longrightarrow CH_3F + AgBr$
3.	Friedel-Crafts Alkylation	
4.	Friedel-Crafts Acylation	
5.	Wurtz	$H_3C - Cl + Cl\ CH_3 \xrightarrow{\text{2Na Dry ether}} H_3C - CH_3 + NaCl$
6.	Fittig	
7.	Wurtz-Fittig	
8.	Kolbe	
9.	Reimer–Tiemann	
10.	Williamson	$CH_3\text{-}Br + CH_3\text{-}ONa \longrightarrow CH_3\text{-}O\text{-}CH_3 + NaBr$
11.	Stephen	$H_3C - CN + SnCl_2 + HCl \longrightarrow H_3C - CH = NH \xrightarrow{H_3O^+} H_3C - CHO$

12.	Etard	
13.	*Gatterman – Koch*	
14.	Rosenmund reduction	$H_3C-\overset{O}{\overset{\parallel}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} H_3C-\overset{O}{\overset{\parallel}{C}}-H$
15.	Clemmensen reduction	$H_3C-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn - Hg}} H_3C-CH_2CH_3$
16.	Wolff-Kishner reduction	$H_3C-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow[\text{ii) KOH/Ethyleneglycol}]{\text{i) } NH_2-NH_2} H_3C-CH_2CH_3$
17.	*Tollens' test*	$R-CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R-COO^- + 2Ag\downarrow + 2H_2O + 4NH_3$
18.	*Fehling's test*	$R-CHO + 2Cu^{2+} + 5OH^- \longrightarrow R-COO^- + Cu_2O\downarrow + 3H_2O$
19.	*Iodoform*	$H_3C-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow[\text{OR, NaOI}]{I_2/NaOH} CHI_3\downarrow + CH_3COO\,Na$
20.	*Aldol condensation*	$2\,H_3C-CHO \xrightarrow{\text{dil NaOH}} H_3C-\overset{OH}{\overset{\vert}{CH}}-CH_2-CHO \longrightarrow CH_3-CH=CHCHO$
21.	*Cannizzaro*	$HCHO + HCHO \xrightarrow{\text{Conc. NaOH}} HCOONa + H_3C-OH$
22.	Hell-Volhard-Zelinsky (HVZ)	$H_3C-COOH \xrightarrow[H_2O]{Cl_2/\text{Red Phosphorus}} \underset{Cl}{\underset{\vert}{H_2C}}-COOH$

23.	*Hoffmann bromamide degradation*	

24.	*Carbylamine*	$R-NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\Delta} R-NC + 3\ KCl + 3\ H_2O$
25.	*Diazo*	
26.	*Sandmeyer.*	
27.	*Gatterman*	
28.	*Coupling*	

APPENDIX –C

Distinguish By a Single Chemical Test

1. All aldehydes (R–**CHO**) give **Tollens' Test** and produce silver mirror.

   $RCHO + 2\ [Ag(NH_3)_2]^+ + 3\ OH^- \rightarrow RCOO^- + 2\ Ag\downarrow + 2H_2O + 4\ NH_3$

   Tollens' Reagent silver ppt

   Note: HCOOH (methanoic acid) also gives this test, ketones (RCOR) do not give this test

2. All aldehydes (R–**CHO**) and ketones (R**CO**R) give **2,4–DNP test**

   RCOR + 2,4–DNP → Orange ppt R–CHO + 2,4–DNP → Orange ppt

3. Aldehydes and ketones having **CH_3CO–** (keto methyl) group give Iodoform Test. Alcohols having CH_3CH– OH group also give **Iodoform Test**.

   $CH_3CHO + 3I_2 + 4\ NaOH \rightarrow CHI_3\downarrow + HCOONa + 3\ NaI + 3H_2O$

   Yellow ppt

4. The following compounds give Iodoform Test: ethanol (C_2H_5OH), propan–2–ol ($CH_3CH(OH)CH_3$), ethanal (CH_3CHO), propanone (CH_3COCH_3), butanone ($CH_3COCH_2CH_3$), pentan–2–one ($CH_3COCH_2CH_2CH_3$), acetophenone ($PhCOCH_3$)

5. All carboxylic acids (R–**COOH**) give **Bicarbonate Test**

   $RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2\uparrow + H_2O$

   effervescence

6. **Phenol** gives **$FeCl_3$** Test

   $C_6H_5OH + FeCl_3 \rightarrow (C_6H_5O)_3Fe + 3\ HCl$(neutral) (violet color)

7. All primary amines (R/Ar –**NH_2**) give **Carbyl Amine Test**

$R-NH_2 + CHCl_3 + KOH(alc) \rightarrow R-NC + KCl + H_2O$

offensive smell

8. Aniline gives Azo Dye Test (Only for aromatic amines)

$C_6H_5NH_2 + NaNO_3 + HCl \rightarrow C_6H_5N_2^+Cl^-$; then add β–naphthol orange dye

9. All alcohols (R**OH**) give **Na–metal test**

$R-OH + Na \rightarrow R-ONa + H_2$

bubbles

10. For esters (RCOOR) : Hydrolyses first. Then see the products (acid & alcohol) and give a test to identify them.

11. All alkenes (C=C) and alkynes (C≡C) decolorizes Br_2 – water from red to colourless

12. Lucas Test to distinguish primary, secondary and tertiary alcohols

Lucas reagent: $ZnCl_2/HCl$

3^0–alcohol + Lucas reagent $\rightarrow$ immediate turbidity 2^0–alcohol + Lucas reagent $\rightarrow$ turbidity after sometime

1^0–alcohol + Lucas reagent $\rightarrow$ no turbidity

APPENDIX –D

ORGANIC CHEMISTRY CONCEPT BASED QUESTION & ANSWER

1 Bond enthalpy decreases as: CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I Because C-X bond length increases from F to I due to greater size

2 Phenol can not be converted into chlorobenzene by using HCl
Because C-O bond in phenol has partial double bond character and -OH gr is attached to sp^2 carbon

3 Thionyl chloride is preferred to convert ROH into RCl
Because the side products are gases and the product can be obtained as pure

4 3^0 alcohol easily can be converted into alkyl halide Because 3^0 carbocations are stable

5 Benzene Is converted into iodobenzene in presence of oxidizing agent like HNO_3 or HIO_3
$C_6H_6 + I_2/Fe \rightleftharpoons C_6H_5I + HI$ Because HNO_3 or HIO_3 oxidises HI and prevent backward reaction

6 ROH is converted into RI by using KI in presence of H_3PO_4 not H_2SO_4 H_2SO_4 converts KI into HI and than into I_2

7 B.pt. Of alkyl halides (RX) is higher than hydrocarbons Because R-X is polar so there is dipole- dipole attraction

8 B.pt : R-I > R-Br > R-Cl > R-F
Because molecular mass decreases so Van der Waals force decreases from RI to RF

9 B.pt : CH_3-CH_2-CH_2-CH_2-Br > CH_3-CH_2-CH(Br)-CH_3 > (CH_3)CBr
Because as the branching increases surface area decreases so Van der Waals force of attraction decreases

10 P-dichloro benzene has higher m.pt than ortho and meta isomer
Because p-dichloro benzene has symmetrical structure so it fits well in the crystal lattice

11 Alkyl halide (RX) with KCN gives alkyl cyanide (RCN) where as with AgCN it gives isocyanide(RNC) KCN is ionic and CN^- is ambident nucleophile but it link through C because C-C bond is more stable than C-N. In the other hand AgCN is covalent and links through N only.

12 S 2 reactivity : $(1^0 > 2^0 > 3^0)$
Due to stearic hindrance nucleophile can not approach easily. In S_N2 path release of X and linking of Nu^- take place simultaneously

13 S_N1 reactivity : $(1^0 < 2^0 < 3^0)$
Because S_N1 path involves formation of carbocation intermediate. And stability of Carbocation is in the order : $(1^0 < 2^0 < 3^0)$

14 S_N1 reactivity : R-I > R-Br > R-Cl > R-F
Because as the size of halogen increases C-X bond becomes weaker

15 Aryl halides (C_6H_5–X) are less reactive than alkyl halides(R–X) towards nucleophilic substitution
Because in aryl halide C-X bond has partial double bond character and X is attached to sp^2 C, there is also the repulsion between Nu^- and benzene ring which is electron rich.

16 Chloroform is stored in dark coloured bottle as closed and completely filled, because in air and light it converts into poisonous phosgene gas($COCl_2$).

17 In many countries DDT has been banned now, because of its slow metabolism and it has toxic effect on aquatic animals.

18 Cyclohexyl chloride has greater dipole moment than chloro benzene.

19 Alkyl halides are immiscible in water although they are polar, in water there is intermolecular H-bonding but there is less attraction between R-X and H_2O.

20 Grignard reagent (RMgX) should be prepared in anhydrous condition because RMgX reacts with water and gives corresponding alkane.

21 Alkyl halides undergo substitution when treated with aq KOH but in presence of alc KOH elimination takes place Alcohol + KOH produces RO^- which is a strong base so it extract H^+ and elimination takes place.

22 C-O-H bond angle in alcohol is less than regular tetrahedral angle due to lp-lp repulsion.

23 In phenol the C-O bond length is less

Due to i) partial double bond character ii) O is attached to sp^2 carbon.

24 In ether the R-O-R bond angle is greater, due to repulsion between two bulkier R-group

25 To convert acid into alcohol $LiAlH_4$ is not used, because it is expensive so: RCOOH → RCOOR' then ester is reduced into RCH_2OH by Hg_2/Pd.

26 b.pt of alcohol(ROH) is higher than alkane(RH), ether(R-O-R), alkyl halide(R-X) and aryl halide(Ar-X), due to inter molecular H-bonding in R-O-H.

27 b.pt : n-butyl alcohol > sec. butyl alcohol > tert. Butyl alcohol, because as the branching increases surface area decreases so Van der Waals force of attraction decreases.

28 Alcohols are highly miscible in water, due to H-bonding with water.

29 Acidity of alcohol : $R\text{-}CH_2\text{-}OH > R_2CH\text{-}OH > R_3C\text{-}OH$

Because as the R gr increases +I effect increases so alkoxide ion becomes less stable.

30 Alcohol is weaker acid than water, because $R\text{-}O^-$ is less stable than HO^-

31 Phenol (Ph-OH) is acidic in nature

Because phenoxide ion($Ph\text{-}O^-$) is resonance stabilized.

32 Acidity: nitrophenol>phenol>methylphenol.

Because $-NO_2$ group is electron withdrawing it further increases the stability of phenoxide ion where as -CH_3 group is electron donating it destabilizes phenoxide ion.

33 Esterification is carried out in presence of small amount of conc. H_2SO_4 because it absorbs the water produced and accelerate the forward reaction.

34 $R'COCl + R\text{-}OH \rightarrow R'COOR + HCl$. Pyridine is used in this reaction. It is to remove HCl produced and to prevent the backward reaction.

35 Tert. Alcohols are easier to dehydrate

Because the intermediate tert. carbo cation is stable.

36 -OH group in benzene ring is ortho and para directing for electrophilic substitution, due to + R effect it increases the electron density at ortho and para positions.

37 O-nitro phenol is steam volatile(low b.pt) but p-nitro phenol is not

In o-nitro phenol there is intra molecular H-bonding. But in p-nitro phenol there is inter molecular H-bonding so molecules get associated and hence it has comparatively higher b.pt.

38 Phenol with aq bromine gives 2,4,6-tribromophenol but in non polar medium mono -substitution takes place.

39 $CuSO_4$ and pyridine are mixed with ethanol used for industrial purpose, to prevent its misuse. $CuSO_4$ gives colour pyridine gives smell.

40 Ethers (R-O-R) are polar.

41 Ethers are soluble in water, due to H-bond with water and ether.

42 Aldehydes (R-CHO) and ketones (R-CO-R) have higher b.pt than hydrocarbon and ether, because they are polar so there is dipole-dipole attraction in aldehyde and ketones.

43 Lower aldehydes and ketones are miscible with water, because they form hydrogen bond with water

44 Aldehydes (R-CHO) are more reactive than ketones (R-CO-R) in nucleophilic addition, in ketone the two alkyl groups (R) have +I effect so they reduce the electrophilicity

carbonyl carbon. Also there is stearic hindrance in ketone.

45 Benzaldehyde (C_6H_5CHO) is less reactive than propanal (CH_3CH_2CHO)
due to resonance the electrophilicity of carbonyl carbon is less in benzaldehyde.

46 $NaHSO_3$ is used for separation of aldehydes.
It forms a soluble compound with aldehyde which on hydrolysis gives back the aldehyde.

47 A-H of aldehyde and ketone is acidic in nature, because the corresponding carbanion is resonance stabilized.

48 Carboxylic acids (R-COOH) do not give nucleophilic addition reaction like RCHO & RCOR although it has >C=O due to resonance the carbonyl carbon looses its electrophilicity.

49 Carboxylic acids have higher b.pt than aldehyde, ketones and even than alcohols.
There is extensive inter molecular H-bonding in carboxylic acid (RCOOH). Even in vapour phase it exists as dimer.

50 Carboxylic acids are miscible in water, due to H-bonding with water.

51 R-COOH is acidic in nature, because the conjugate base $R\text{-}COO^{-}$ (carboxylate ion) is stable due to resonance

52 Acidic Strength : $Cl\text{-}CH_2\text{-}COOH > CH_3\text{-}COOH > CH_3CH_2\text{-}COOH$
Because Cl has –I effect which stabilizes the conjugate base and ethyl gr has +I effect.

53 In amines the C-N-H/C bond angle is less than 109.5^{o}, due to lp-bp repulsion.

54 For reduction of nitro compounds into amines Fe/HCl is preferred instead of Sn/HCl, because $Fe + HCl \rightarrow FeCl_2$. On hydrolysis $FeCl_2$ gives HCl, so just small quantity of HCl is required to initiate the reaction.

55 To convert alkyl halide(R-X) into amines ($R\text{-}NH_2$) ammonolysis is not suitable,
because on ammonolysis a mixture of pri, sec, tert and quaternary amine will be produced.

56 Aniline on exposure to air and light turns into coloured, due tto atmospheric oxidation.

57 Lower amines are soluble in water, due to H-bonding with water. In case of higher amine alkyl group is larger which is hydrophobic.

58 Amines ($R\text{-}NH_2$) are less soluble than alcohols (R-OH), in alcohol the H-bonding with water is stronger because O is more electronegative than N.

59 Amines ($R\text{-}NH_2$) are lower boiling than alcohols (R-OH), in alcohol the intermolecular H-bonding is stronger because O is more electronegative than N.

60 Order of b.pt : primary amine > sec. amine > tert. amine
The no. of N-H bond decreases so extent of H-bonding also decreases.

61 In gaseous phase the order of basic strength : 3^0-amine > 2^0-amine > 1^0-amine > NH_3

Due to +I effect of alkyl groups the electron density on N increases. So 3° is strongest as it has 3 alkyl groups.

62 In aqueous state the base strength order : (2^0>3^0>1^0> NH_3) : (2^0> 1^0> 3^0> NH_3)

In aqueous state +I effect, steric effect and solvation effect interplay. So the order is not regular

63 R-NH_2 is stronger base than NH_3

Due to +I effect of alkyl group electron density on N increases in R-NH_2

64 Aniline (C_6H_5-NH_2) is weaker base than NH_3 and R-NH_2

In aniline the lone pair of electron of N is involved in resonance. So it is less available.

65 Base strength : p-methoxy aniline > aniline > p-nitro aniline

Methoxy group (-OCH_3) has +R effect where as –NO_2 group has –R effect so electron density in the first case increases but in the second case it decreases.

66 Acylation of aniline is carried out in presence of pyridine .Pyridine removes HCl produced and favours forward reaction.

67 -NH_2 group in benzene ring is ortho –para directing for electrphilic substitution Due to +R effect it increases the electron density at ortho and para position.

68 Bromination of aniline gives 2,4,6-tribromo aniline

Because –NH_2 group activates benzene ring by +R effect. So for mono substitution –NH_2 group is acylated.

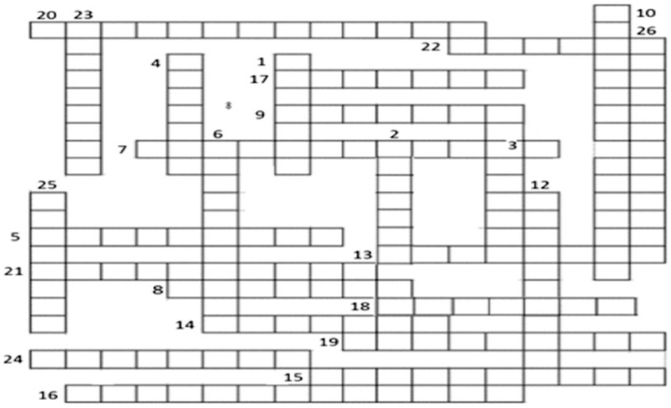
69 Nitration of aniline gives un usual meta□nitro aniline although –NH_2 group is ortho□para directing

In presence of acid –NH_2 is converted into –NH_3^+ which is meta directing

70 Aniline does not undergo Friedel Craft reaction

Aniline is base and reacts with anhydrous $AlCl_3$ so N becomes positive which deactivates benzene ring.

APPENDIX E



TOP TO BOTTOM

1. Biological macromolecules with which drugs usually interact.
2. An analgesic prepared from salicylic acid.
3. The building blocks of a polymer are small molecules.
4. Natural Catalyst.
6. Nucleic acids are polymers in which _________ are the monomers.
12. Monomer of nylon 6 is –
23. Proteins embedded in the cell membrane to receive Chemical messenger□
25. Cetyltrimethyl ammonium chloride is an example of _____________Detergent.
26. Soaps are safer to use from the environmental point of View because they are□

LEFT TO RIGHT

5. This type of polymer has extensive cross links between its chains.
7. Globular proteins on heating or due to pH change undergoes coagulation & loose biological activity. The Phenomenon is-
8. In DNA thymine pairs with -
9. Optically inactive amino acid –
11. Commercial name of poly totrafluroethylene is
13. Polymerization of chloroprene forms -
14. Element with Which natural rubber is heated for vulcanization-
15. The polymers in which polymer chains are held together by vander waal's forces are known as –
16. ____________And a terpineol are the main constituents of an antiseptic Dettol.
17. Ranitidine is an-
18. A high potency artificial sweeter -
19. A sweeter that decomposes at looking temperature-
20. Drugs which reduce anxiety and produce feeling of well Being –
21. It is added to soaps to impart antiseptic properties-
22. Chloramphenicol is a___________Spectrum Antibiotic.
24. Medicines used for the relief of post□operative pain & Cardiac pain –

APPENDIX-F

SYLLABUS

CLASS XII (2019-20)
THEORY
Total Periods (Theory 160 + Practical 80)
Time: 3 Hours Max. Marks 70

Unit I: Solutions 10 Periods

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties - relative lowering of vapour pressure, Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit II: Electrochemistry 12 Periods

Redox reactions, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and

Unit No. Title No. of
Periods
Marks
Unit I Solutions 10
Unit II Electrochemistry 12 23
Unit III Chemical Kinetics 10
Unit IV Surface Chemistry 08
Unit V General Principles and Processes of Isolation of Elements 08
Unit VI p -Block Elements 14
Unit VI d -and f -Block Elements 12 19
Unit VII Coordination Compounds 12
Unit VIII Haloalkanes and Haloarenes 12
Unit IX Alcohols, Phenols and Ethers 12
Unit X Aldehydes, Ketones and Carboxylic Acids 14
Unit XI Organic Compounds containing Nitrogen 12
Unit XII Biomolecules 12
Unit XIII Polymers 06
Unit XIV Chemistry in Everyday Life 06
Total 160 70

Galvanic cells, lead accumulator, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, fuel cells, corrosion.

Unit III: Chemical Kinetics 10 Periods

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment). Activation energy, Arrhenius equation.

Unit IV: Surface Chemistry 08 Periods

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, catalysis, homogenous and heterogenous activity and selectivity; enzyme catalysis colloidal state distinction between true solutions, colloids and suspension; lyophilic, lyophobic multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.

Unit V: General Principles and Processes of Isolation of Elements 08 Periods

Principles and methods of extraction - concentration, oxidation, reduction - electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron

Unit VI: p -Block Elements 14 Periods

Group 16 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: Preparation, Properties and uses, classification of Oxides, Ozone, Sulphur - allotropic forms; compounds of Sulphur: Preparation Properties and uses of Sulphur-dioxide, Sulphuric Acid: industrial process of manufacture, properties and uses; Oxoacids of Sulphur (Structures only).

Group 17 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation, properties and uses of Chlorine and Hydrochloric acid, interhalogen compounds, Oxoacids of halogens (structures only).

Group 18 Elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.

Unit VII: 'd' and 'f' Block Elements 12 Periods

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals - metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and KM_nO_4.

Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and

lanthanoid contraction and its consequences.
Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit VIII: Coordination Compounds 12Periods

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative inclusion, extraction of metals and biological system).

Unit IX: Haloalkanes and Haloarenes 12 Periods

Haloalkanes: Nomenclature, nature of C-X bond, physical and chemical properties, mechanism of substitution reactions, optical rotation.
Haloarenes: Nature of C-X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).
Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit X: Alcohols, Phenols and Ethers 12 Periods

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.
Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols.
Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit XI: Aldehydes, Ketones and Carboxylic Acids 14 Periods

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.
Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit XII: Organic compounds containing Nitrogen 12 Periods

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.
Cyanides and Isocyanides - will be mentioned at relevant places in text.
Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit XIII: Biomolecules 12 Periods

Carbohydrates - Classification (aldoses and ketoses), monosaccahrides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates.
Proteins -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure.
Vitamins - Classification and functions.
Nucleic Acids: DNA and RNA.

Unit XIV: Polymers 06 Periods

Copolymerization, some important polymers: natural and synthetic like polythene, nylon polyesters, bakelite, rubber. Biodegradable and nonbiodegradable polymers.

Unit XV: Chemistry in Everyday life 06 Periods

Chemicals in medicines - analgesics, tranquilizers antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines.

Chemicals in food - preservatives, artificial sweetening agents, elementary idea of antioxidants.Cleansing agents- soaps and detergents, cleansing action.

PRACTICALS

Micro-chemical methods are available for several of the practical experiments. Wherever possible, such techniques should be used.
A. Surface Chemistry
(a) Preparation of one lyophilic and one lyophobic sol Lyophilic sol - starch, egg albumin and gum
Lyophobic sol - aluminium hydroxide, ferric hydroxide, arsenous sulphide.
(b) Dialysis of sol-prepared in (a) above.
(c) Study of the role of emulsifying agents in stabilizing the emulsion of different oils.
B. Chemical Kinetics
(a) Effect of concentration and temperature on the rate of reaction between Sodium Thiosulphate and Hydrochloric acid.
(b) Study of reaction rates of any one of the following:
(i) Reaction of Iodide ion with Hydrogen Peroxide at room temperature using different concentration of Iodide ions.
(ii) Reaction between Potassium Iodate, (KIO_3) and Sodium Sulphite: (Na_2SO_3) using starch solution as indicator (clock reaction).

Evaluation Scheme for Examination Marks

Volumetric Analysis	08
Salt Analysis	08
Content Based Experiment	06
Project Work	04
Class record and viva	04
Total	30

C. Thermochemistry

Any one of the following experiments

i) Enthalpy of dissolution of Copper Sulphate or Potassium Nitrate.

ii) Enthalpy of neutralization of strong acid (HCl) and strong base (NaOH).

iii) Determination of enthaply change during interaction (Hydrogen bond formation) between Acetone and Chloroform.

D. Electrochemistry

Variation of cell potential in Zn/Zn^{2+}|| Cu^{2+}/Cu with change in concentration of electrolytes ($CuSO_4$or $ZnSO_4$) at room temperature.

E. Chromatography

i) Separation of pigments from extracts of leaves and flowers by paper chromatography and determination of Rfvalues.

ii) Separation of constituents present in an inorganic mixture containing two cations only (constituents having large difference in Rf values to be provided).

F. Preparation of Inorganic Compounds

i) Preparation of double salt of Ferrous Ammonium Sulphate or Potash Alum.

ii) Preparation of Potassium Ferric Oxalate.

G. Preparation of Organic Compounds

Preparation of any one of the following compounds

i) Acetanilide

ii) Di -benzal Acetone

iii) p-Nitroacetanilide

iv) Aniline yellow or 2 - Naphthol Aniline dye.

H. Tests for the functional groups present in organic compounds:

Unsaturation, alcoholic, phenolic, aldehydic, ketonic, carboxylic and amino (Primary) groups.

I. Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in given food stuffs.

J. Determination of concentration/ molarity of $KMnO_4$ solution by titrating it against a standard solution of:

i) Oxalic acid,

ii) Ferrous Ammonium Sulphate

(Students will be required to prepare standard solutions by weighing themselves).

K. Qualitative analysis

Determination of one cation and one anion in a given salt.
Cation - Pb^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+},
Mg^{2+},$[NH_4]^+$

Anions – $[CO_3]^{2-}$, S^{2-}, $[SO_3]^{2-}$, $[SO_4]^{2-}$, $[NO_2]^-$, Cl^-,Br^-, I^-, $[PO_4]^{3-}$, $[C_2O_4]^{2-}$, CH_3COO^-
(Note: Insoluble salts excluded)

PROJECT

Scientific investigations involving laboratory testing and collecting information from other sources.

A few suggested Projects.

- Study of the presence of oxalate ions in guava fruit at different stages of ripening.
- Study of quantity of casein present in different samples of milk.
- Preparation of soybean milk and its comparison with the natural milk with respect to curd formation, effect of temperature, etc.
- Study of the effect of Potassium Bisulphate as food preservative under various conditions (temperature, concentration, time, etc.)
- Study of digestion of starch by salivary amylase and effect of pH and temperature on it.
- Comparative study of the rate of fermentation of following materials: wheat flour, gram flour, potato juice, carrot juice, etc.
- Extraction of essential oils present in Saunf (aniseed), Ajwain (carum), Illaichi (cardamom).
- Study of common food adulterants in fat, oil, butter, sugar, turmeric power, chilli powder and pepper.

Note: Any other investigatory project, which involves about 10 periods of work, can be chosen with the approval of the teacher.

Practical Examination for Visually Impaired Students of Classes XI and XII

Evaluation Scheme

Time Allowed: Two hour Max.Marks: 30

Identification/ Familiarity with the apparatus 5 marks
Written test (based on given/ prescribed practicals 10 marks
Practical Record 5 marks
Viva 10 marks
Total 30 marks

General Guidelines

- The practical examination will be of two hour duration.
- A separate list of ten experiments is included here.
- The written examination in practicals for these students will be conducted at the time of practical examination of all other students.
- The written test will be of 30 minutes duration.
- The question paper given to the students should be legibly typed. It should contain a total of 15practical skill based very short answer type questions. A student would be required to answer any 10 questions.
- A writer may be allowed to such students as per CBSE examination rules.
- All questions included in the question papers should be related to the listed practicals. Every question should require about two minutes to be answered.
- These students are also required to maintain a practical file. A student is expected to record at least five of the listed experiments as per the specific instructions for each subject. These practicals should be duly checked and signed by the internal examiner.
- The format of writing any experiment in the practical file should include aim, apparatus required, simple theory, procedure, related practical skills, precautions etc.
- Questions may be generated jointly by the external/internal examiners and used for assessment.
- The viva questions may include questions based on basic theory/principle/concept, apparatus/materials/ chemicals required, procedure, precautions, sources of error etc.

A. Items for Identification/Familiarity of the apparatus for assessment in practicals (All experiments)

Beaker, glass rod, tripod stand, wire gauze, Bunsen burner, Whatman filter paper, gas jar, capillary tube, Pestle and mortar, Test tubes, tongs, test tube holder, test tube stand, burette, Pipette, conical flask, standard flask, clamp stand, Tripod stand, burner, wire gauze, funnel, filter paper

Hands-on Assessment

- Identification/familiarity with the apparatus
- Odour detection in qualitative analysis

B. List of Practicals

The experiments have been divided into two sections: Section A and Section B. The experiments mentioned in Section B are mandatory.

CHEMISTRY

SECTION- A

A. Surface Chemistry
(1) Preparation of one lyophilic and one lyophobic sol
Lyophilic sol - starch, egg albumin and gum
(2) Preparation of one
lyophobic sol Lyophobic
sol - Ferric hydroxide
B. Chromatography
(1) Separation of pigments from extracts of leaves and flowers by paper chromatography and determination of Rf values (distance values may be provided).
C. Tests for the functional groups present in organic compounds:
(1) Alcoholic and Carboxylic groups.
(2) Aldehydic and Ketonic
D. Characteristic tests of carbohydrates and proteins in the given food stuffs.
E. Preparation of Inorganic Compounds- Potash Alum

SECTION-B (Mandatory)

F. Quantitative analysis
(1) (a) Preparation of the standard solution of Oxalic acid of a given volume
(b) Determination of molarity of $KMnO_4$solution by titrating it against a standard solution ofOxalic acid.
(2) The above exercise [F 1 (a) and (b)] to be conducted using Ferrous ammonium sulphate (Mohr's salt)
G. Qualitative analysis:
(1) Determination of one cation and one anion in a given salt.
Cations- $[NH]_4^+$
Anions – $[CO_3]^{2-}$, S^{2-}, $[SO_3]^{2-}$, Cl^-, CH_3COO^- (Note: Insoluble salts excluded)
Note: The above practicals may be carried out in an experiential manner rather than recording observations.
Prescribed Books:
1. Chemistry Part -I, Class-XII, Published by NCERT.
2. Chemistry Part -II, Class-XII, Published by NCERT.
3. Chemistry Lab Manual, Class XII , Published by NCERT

Blue Print

Class XII

Subject: Chemistry

Unit No.	Title/ chapter	VSA (1mark)	SA-I (2marks)	SA-II (3marks)	Long answer questions (5)	Total
1	Solutions	3(1)	-	1(3)	-	6
2	Electro Chemistry	1(1)	-	-	1(5)	6
3	Chemical Kinetics	-	-	2(3)	-	6
4	Surface Chemistry	1(1)	-	1(3)	-	4
5	Principles And processes of Isolation of elements	1(1)	1(2)	-	-	3
6	p-block elements	5(1)	-	1(3)	-	8
7	d and f block elements	-	-	-	1(5)	5
8	Coordination compounds	1(1)	1(2)	-	-	3
9	Haloalkanes and Haloarenes	-	2(2)	-	-	4
10	Alcohols, Phenols and Ethers	1(1)	-	1(3)	-	4
11	Aldehydes, ketones and carboxylic acids	1(1)	-	-	1(5)	6
12	Organic compounds containing nitrogen	2(1)	1(2)	-	-	4
13	Biomolecules	2(1)	-	1(3)	-	5
14	Polymers	1(1)	1(2)	-	-	3
15	Chemistry in everyday Life	1(1)	1(2)	-	-	3
		20(1)	7(2)	7(3)	3(5)	70

SAMPLE PAPER (2019 -20)
CLASS : XII
SUBJECT : CHEMISTRY
Time allowed: 3 hours
M.Marks : 70

General Instruction:-

(1) All questions are compulsory.
(2) Question no. 1 to 20 are VSA / objective type questions and carry 1 mark each.
(3) Question no. 21 to 27 are short answer questions and carry 2 marks each.
(4) Question no 28 to 34 are also short answer questions and carry 3 marks each.
(5) Question no. 35 to 37 are long answer questions and carry 5 marks each.
(6) Use log tables if necessary. Use of calculators not allowed.

Section A

	Read the given passage and answer the questions 1 to 5 that follow:	
1	The p-block elements have non-metals, metals and semi metals. The second period elements show markedly different properties in comparison to the remaining members of p-block. The lowest members of each group present in p-block show increasing trend of metallic characters. SF_4 is easily hydrolysed whereas SF_6 is not easily hydrolysed.Why?	1
2	Fluoride ion has higher hydration enthalpy than chloride ion. Why?	1
3	Why oxygen is gas but sulphur is solid at room temperature?	1
4	Why noble gases form compounds with fluorine and oxygen only?	1
5	Fluorine exhibits only -1 oxidation state whereas other halogens show +1,+3,+5 oxidation states also. Explain.	1
	Give one word answers to question no. 6 to 10	
6	Out of o-nitrophenol, o-cresol which is more acidic and why?	1
7	Two liquids A and B boil at 145^0C and 190^0c respectively. Which of them has higher vapour pressure at 80^0C ?	1
8	Write IUPAC name of the following:- $CH_3CH_2N\ (CH_2CH_3)CH_3$	1
9	Write the name of only monosaccharide units obtained on hydrolysis of maltose sugar. **Or** How many amino acids are present in a polypeptide having 100 peptide bonds?	1
10	Name the process used to obtain demineralised water.	1

	Question numbers 11 to 15 are multiple choice questions :	
11	The amount of solute required to prepare 10 litres of decimolar solution is (a) 0.01 mole (b) 0.2 mole (c) 0.05 mole (d) 1.0 mole	1
12	The process used for concentration of bauxite ore is (a) Magnetic separation (b) froth floatation (c) chemical separation (d) hydraulic washing	1
13	Which of the following fibres is made of polyamides? (a) Dacron (b) Orlon (c) Nylon (d) Rayon **OR** Which of the following is a condensation polymer? (a) Teflon (b) PVC (c) polyester (d) neoprene	1
14	How many coulombs of electricity are required for oxidation of 1 mole of H_2O to O_2 ? (a) 3F (b) 1F © 2F (d) None of these	1
15	Which one has lowest pK_b value: (a)$C_2H_5NH_2$ (b) $C_6H_5NHCH_3$ (c)$C_6H_5NH_2$ (d) $(C_2H_5)_2NH$	1
	Questions 16 to 20 (a) Both assertion and reason are correct statements and reason is 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.	
16	Assertion:$[Co(SO_4)(NH_3)_5]Br$ and $[Co(Br)(NH_3)_5]SO_4$ exhibit ionisation isomerism. Reason : They are isomeric pairs in which ionic groups have exchanged within the primary coordination sphere.	1
17	Assertion: Aldehydes have less reactivity than ketones towards nucleophilic addition reaction. Reason : Ketones show steric hinderance towards nucleophilic attack and its carbonyl carbon shows less positive charge.	1
18	Assertion : Hydrolysis of ester is an example of autocatalytic reaction. Reason: A catalyst speeds up the process without participating in the reaction.	1
19	Assertion : A colloidal sol scatters light but a true solution does not. Reason : The particles in colloidal sol move slowly than in a true solution.	1
20	Assertion : The chemical massengers are received at the binding site of receptor proteins. Reason : Chemical massenger gives messages to the cell without entering the cell.	1
	Section B	

21	(a) Arrange the compounds in order of increasing boiling point:- bromomethane, bromoform , chloromethane, dibromomethane (b) Which compound in each of the following pairs will react faster in SN^1 reaction with OH$^-$? (i) CH_3Br & CH_3I (ii) $(CH_3)_3CCl$ & CH_3Cl	2
22	How is leaching carried out in case of low grade Copper ores? **OR** Write the principle involved in the following methods of refining of metals: - (a) Zone refining (b) Electrolytic refining	2
23	$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic although both are tetrahedral. Why ?	2
24	Give reasons-: (a) Haloalkanes react with potassium cyanide to give alkyl cyanide but gives alkyl isocyanide with silver cyanide. (b) Grignard reagent should be prepared under anhydrous condition.	2
25	Write the structure of the monomers of the following polymers: - (i)Dacron (ii) Neoprene OR (i) Distinguish between addition and condensation polymerisation (ii) Write the monomeric unit of Buna -N.	2
26	Explain the following:- (a) Although $–NH_2$ group is ortho and para directing group, nitration of aniline meta derivative also in addition to ortho and para derivative. (b) Aniline does not undergo Friedal Crafts alkylation.	2
27	(i) Explain Cationic detergents. (ii) What are artificial sweetening agents? Give examples.	2
	Section C	
28	30 gm of urea (molecular mass = 60g mol^{-1}) is dissolved in 846gm of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg. **OR** How much glucose ($C_6H_{12}O_6$) per litre should be used for an intravenous solution to match the 7.65 atm osmotic pressure of blood at 37 ^{0}C ? (R = 0.08206L atm/mol/K)	3
29	The rate constant of a first order reaction increases by four times when the temperature changes from 293K to 313K. Calculate the energy of activation.	3
30	What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?	3

	OR a)What is the difference between promoter and poison? b) Action of soap is due to emulsification and micelle formation.Explain. C) What is the role of ZSM-5?	
31	How D-Glucose reacts with 1. HI 2. HCN 3. Conc. HNO_3	3
32	(a) In a reaction 2A---$\rightarrow$Products , the concentration of A decreases from 0.5 mol L^{-1} to 0.4molL^{-1}in 10 minutes. Calculate the rate during this time interval. (b)A reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.	3
33	Give chemical tests to distinguish between the following pair of Organic compounds:- Propan-1-ol and Propan-2-ol. Phenol and Benzyl alcohol. Ethanol and Phenol. Or Write short notes on:- Reimer Tiemann reaction. Kolbe's reaction Williamson synthesis	3
34	Complete the following reactions:- NaOH + Cl_2----$\rightarrow$ &conc) I_2 + HNO_3----$\rightarrow$) CaF_2 + H_2SO_4----$\rightarrow$ Or Arrange the following in the order of property indicated against each set:- H_2O ,H_2S , H_2Se ,H_2Te (increasing boiling point) $HClO_3$, HClO, $HClO_2$, $HClO_4$ (increasing acid strength) HF, HCl, HI, HBr (decreasing reducing character)	3
	Section D	
35	(a) The cell in which the following reaction occurs:- $2Fe^{3+}(aq) + 2I^{-}(aq) \text{----}\rightarrow 2Fe^{2+}(aq) + I_2(s)$ has E^0= 0.236 V at 298k. Calculate the standard Gibb's energy and the equilibrium constant of the cell reaction. (b) The resistance of a conductivity cell containing 0.001M KCl solution at 298 k is 1500	5

	Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298k is 0.146 x 10^{-3}S cm^{1}? or Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging. A solution of $Ni(NO_3)_2$is electrolysed between platinum electrodes using a current a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?	
36	(a) Describe the preparation of Potassium dichromate from iron chromite ore. What is the effect of increasing p^H on a solution of potassium dichromate? (b) Complete and balance the following equations:- $Cr_2O_7^{2-}(aq) + H^+ + H_2S$ ----→ $MnO_4^-(aq) + H^+ + Fe^{2+}$ ----→ Or (a) Give reasons for the following:- Transition metals and many of their compounds show paramagnetic behaviour. (ii) The enthalpies of atomization of the transition metals are high. (iii) The transition metals generally form coloured Compounds. What is lanthanoid contraction? Write its consequences	5
37	a) Give reasons for the following:- Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not. There are two $–NH_2$ groups in semicarbazide, however only one is involved in the formation of semicarbazone. (iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester formed should be removed as soon as it is formed. (b) How will you bring the following conversions:- (i) Propanone to Propene. (ii) Ethanol to 3-Hydroxybutanal Or An organic compound (A) has molecular formula($C_5H_{10}O$).It does not reduce Tollen's reagent but forms an orange precipitate with 2,4-DNPreagent. It forms a carboxylic acid(B) with molecular formula($C_3H_6O_2$) when heated with alkaline $KMnO_4$, yellow precipitate on treatment with NaOH and I_2,under vigorous conditions. On oxidation it gives ethanoic acid and propanoic acid. Sodium salt of (B) gave a hydrocarbon (C) in Kolbe's electrolytic reduction. Identify (A),(B) and (C) and write the reactions involved. (3) (b) Write notes on:- Aldol condensation. (ii)Clemmensen's reduction.	5

MARKING SCHEME
Class XII
Subject: Chemistry

Q**.No.1** In SF_6, sulphur atom is stearically protected by six F atoms & hence does not allow H_2O molecules to attack the S atom whereas in SF_4, Sulphur atom is surrounded by four f atoms. So, attack of H_2O molecule on sulphur atom can take place. (1)

Q**.No.2** High charge density of F^- or due to smaller size of fluoride ion . (1)

Q**.No.3** Due to small size and high electronegativity, oxygen exists as diatomic molecule. These molecules are held together by weak van der Waal's forces. Hence O_2 is gas at room temperature. Sulphur, Because of its bigger size and lower electronegativity prefers to form S-S single bond and Greater tendency for catenation than oxygen. (1)

Q **No.4** Fluorine and Oxygen are the most electronegative elements and hence are very reactive. So, they form compounds with noble gases, particularly Xenon. (1)

Q**.No.5** Fluorine is the most electronegative element and cannot exhibit any positive oxidation states. Other halogens have d-orbitals and therefore can expand their octet and show +1, +3, +5 and +7 oxidation states (1)

Q**.No.6** o- nitrophenol (1)
Q**.No.7** A (1)
Q**.No.8** N – ethyl – N-methyl ethanamine (1)
Q**.No.9** Glucose **OR** 101 (1)
Q**.No.10** Reverse osmo (1)
Q**.No.11** d (1)
Q**.No. 12** c (1)
Q**.No.13** c
OR d (1)
R. No.14 c (1)
Q.No 15 d (1)
Q**.No.16** a (1)
Q**.No.17** a (1)
Q**.No 18 c** (1)
Q**.No 19** b (1)
Q**.No 20 a** (1)
Q **No 21** a)Chloromethane<Bromomethane<Dibromomethane<Bromoform (1)

(b)(i) CH_3I, because I^- ion is better leaving group than Br^-
(ii) CH_3Cl , because of stearic hinderance in case of $(CH_3)_3CCl$. (1/2 +1/2)

Q **No 22** Copper is leached out from low grade copper by using acid in the presence of

Air, when copper goes into the solution of Cu^{2+} (1)

$Cu(S)+2H^{+}+(aq)+1/2\ O2\ (g)\text{-------------}\rightarrow Cu^{2+}(aq) + H_2O\ (l)$

The solution containing Cu^{2+} ions is treated which scrap iron or H_2

$Cu^{2+}(aq)+ H_2\ (g)\text{--------------}\rightarrow Cu\ (S)+ 2H^{+}\ (aq)$ (1)

Or

Zone Refining-

This method is based on the principal that impurities are more soluble in the melt than In the solid state of the metal. (1)

Electrolytic refining-

This method is based on the phenomenon of electrolysis. In this method, impure metal Is made to act as anode. A strip of the same metal in pure form is used as cathode (1)

Q.**No 23**$[NiCl_4]^{2-}$ has two unpaired electrons and is paramagnetic while $[Ni(CO)_4]$ has all paired electron and hence is diamagnetic (1+1)

Q **No 24(a**) Cyanide ion is an ambident nucleophile.KCN are predominantly ionic. So attack occurs through carbon atom, hence Cyanide is formed. WhereasAgCN is Covalent. So, bond between Ag &CN does not breakand attack occurs through Nitrogen(1)

(b) Grignard reagents are very reactive. They react with moisture present in the apparatus or the starting material.

R---MgX + H---OH-------→ R---H + Mg(OH)X

Therefore Grignard reagents must be prepared under anhydrous conditions. (1)

Q **No. 25 (a)** Dacron:-Ethylene Glycol &Terephthalic acid.

(1)

(b)Chloroprene (1)

OR

(a) Addition polymerisation - chain group polymerisation

Condensation polymerisation - step - growth polymerisation (1/2 + 1/2)

(b) Buna - N : Butadiene and acrylonitirile (1)

No 26.(a) The reason of formation of larger amount of unexpected m-nitroaniline is that under strongly acidic conditions of nitration, most of the Aniline is converted into anilinium ion which is am-directing group therefore an unexpected m-nitroaniline is obtained. (1)

(b) Aniline is a lewis base while $AlCl_3$ is a lewis acid. They combine with each other toform salt. Due to the presence of a positive charge on N-atom in the salt, the group $–N^{+}H_2AlCl_3^{-}$ acts as a strong electron withdrawing group. As a result, it reduces the electron density in the benzene ring and hence aniline does not undergoes Friedel –Crafts reactions. (1)

Q **No 27** (i) Cationic detergents :- These are so called because large part in their molecules are cations which is involved in the cleansing action. Cationic detergents are quaternary ammonium salts of amines with chlorides or bromides as anion .Cetyltrimethylammonium bromide is a cationic detergent and is used in hair conditioners. (1)

(ii)Artificial sweetening agent:- These are chemical substances which are sweet in taste but do not add any calories to our body. For example,,saccharin, alitame, aspartame etc. (1)

Q **No 28** W_A=30g, M_A=60g, W_B=846g, M_B=18g, p_A^o=23.8mm Hg, p_s=?

Now, $\frac{p_{A-P_S}^0}{P_A^0} = \frac{W_B}{W_A} \times \frac{M_B}{M_A}$

(1)

$\frac{23.8-P_S}{23.8} = \frac{30/_{60}}{846/_{18}}$

(1)

$$\frac{23.8 - P_S}{23.8} = \frac{30 \times 18}{846 \times 60}$$

$$\frac{23.8 - P_S}{23.8} = 0.0106$$

23.8 – P_S =0.2531

P_S = 0.2531 -23.8 =23.54 mm Hg (1)

OR

Π = icRT; i=1 (1/2, 1/2)

C =7.65 / 1x .08206x 310 = .301mol/L (1/2, 1/2)

n =.301 mol; mass of glucose = 54.1g (1/2, 1/2)

Q **No 29.**

$K_2 = 4k_1$ => $\frac{k_2}{k_1} = 4$

Log $\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_{2-T_1}}{T_1 T_2}\right)$(1)

Log 4=$\frac{E_a}{2.303 \times 8.34}\left(\frac{313-293}{293 \times 313}\right)$ (1)

2×Log2=$\frac{E_a}{19.147}\left(\frac{20}{91709}\right)$

E_a=$\frac{2 \times 0.3010 \times 19.147 \times 91709}{20}$= **52.85 KJ/mol**

(1)

Q**.No.30** The important difference between multimolecular& macromolecular colloids are:-

Multimolecular colloids	Macromolecular colloids
The colloidal particles consist of aggregate of a large no. of atoms or molecules having diameter less than 1 nm	The colloidal particles are macromolecules having very large molecular mass.
Particles are held by weak van der waals forces.	Particles are held by chemical bonds.

The common example of multimolecular colloid is sulphur sol, which consists of particles of S_8 molecules. The common example of macromolecular colloid is starch.

The associated colloids differ from multimolecular and macromolecular colloids in the sense that they behave as normal electrolytes at low concentrations but exhibit colloidal state properties at higher concentrations due to the formation of aggregated particles called micelles. (1+1+1)

OR

a) Promoter helps in facilitating action of a catalyst whereas poison increases the activation energy of a reaction and retards or slows down the rate of reaction.

b) Soap molecules adsorb on to the dirt surface and try to emulsify it by forming micelles. Soap miceele thus convert dirt into colloidal form so that it gets washed away by water.

c) It converts alcohols directly into gasoline by dehydrating them to produce mixture of hydrocarbons. (1+1+1)

Q **No 31**

(i) $OHC\text{-----}(CHOH)_4\text{----}CH_2OH + HI(excess) \text{----------}\rightarrow CH_3(CH_2)_4CH_3$ (1)
n-Hexane

(ii) $OHC\text{-}(CHOH)_4\text{-}CH_2OH + HCN\text{--------}\rightarrow CH(CN)OH\text{-}(CHOH)_4\text{-}CH_2OH$ (1)

(iii) $OHC\text{-}(CHOH)_4\text{-}CH_2OH$ + Con. $HNO_3\text{-------}\rightarrow HOOC\text{-}(CHOH)_4\text{-}COOH$ (1)

Q **No 32**.a) Rate = $-1/2\ \Delta[A]/\Delta t = -1/2\ (0.4-0.5)\text{mol } L^{-1}/10 \text{ min} = 5\text{x}10^{-3}\text{mol } L^{-1} \text{ min}^{-1}$ (1)

b) t= 20 minutes let[a]=100

a-x=100-25=>75

$k= \frac{2.303}{t} \log\frac{a}{a-x}$ --1/2

$k=\frac{2.303}{20} \log \frac{100}{75}= \frac{2.303}{20} \log\frac{4}{3}$

=0.0143/min (1/2)

Now, a-x=100-75=>25

$T=\frac{2.303}{k} \log \frac{a}{a-x}$

$=\frac{2.303}{0.0143} \log \frac{100}{25}$ (1/2)

$=\frac{2.303}{0.0143}\log 4$

=96.96 minutes (1/2)

Q.**No.33** (i) Lucas test or victor meyer's test or iodoform test (1)

(ii) Neutral $FeCl_3$ test or Bromine water test or any other test. (1)

(iii)Lucas test or Neutral $FeCl_3$ test or any other test. (1)

Or

Correct reactions (1+1+1)

Q.**No 34** (i) $6NaOH + 3Cl_2\text{----}\rightarrow 5NaCl + NaClO_3 + 3H_2O$
(hot&conc)

(ii) $I_2 + 10\ HNO_3\text{----}\rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(iii)$CaF_2 + H_2SO_4 \text{----}\rightarrow CaSO_4 + 2HF$ (1+1+1)

Or

(i) $H_2S < H_2Se < H_2Te < H_2O$

(ii) $HClO < HClO_2 < HClO_3 < HClO_4$

(iii) $HI > HBr > HCl > HF$ (1+1+1)

Q.**No.35**(a) $2Fe^{3+} + 2e^- \text{----}\rightarrow 2Fe^{2+}$ & $2I^- \text{----}\rightarrow I_2 + 2e^-$

Thus, for the given cell reaction, n = 2.

$\Delta G^0 = -nFE^0cell = 2 \times 96500 \times 0.236 \text{ J} = -45548 \text{ J mol}^-$

$= -45.55 \text{kJ mol}^-$ (1)

$\Delta G^0 = -2.303 \text{ RT} \log K_c$ (1)

$\log K_c = -\Delta G^0/2.303RT = 7.983$

$K_C = \text{Antilog}(7.983) = 9.166 \times 10^7$ (1)

(b) Conductivity (k) =Cell constant/Resistance (1/2)

0.146×10^{-3}=cellconstant/1500 (1/2) cellconstant=$0.146 \times 10^{-3} \times 1500 = 0.219 \text{cm}^{-1}$
(1)

Or

(a) During recharging, electrical energy is supplied to the cell from an external source. The reactions are reversed of those that takes place during discharge. (1)

At anode:$PbSO_4(s) + 2H_2O \text{---}\rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

At cathode: $\underline{PbSO_4(s) + 2e^- \text{---}\rightarrow Pb(s) + SO_4^{2-}(aq)}$

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

(1/2+1/2+1)

(b) Quantity of electricity passed= Ixt =5X20X60s=6000C (1)

The electrode reaction is: $Ni^{2+} + 2e^- \text{--}\rightarrow Ni$

2x96500 C deposit Ni =58.7g

6000Cwill deposit Ni = 58.7x6000/2x96500 =1.825g (1)

Q.**No.36** (a) Potassium dichromate is prepared from chromite ore ($FeCr_2O_4$)

(i) $4FeCr_2O_4 + 16\,NaOH + 7O_2 \text{--}\rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$

Or

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \text{--}\rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ (1)

(ii)$Na_2CrO_4 + H_2SO_4 \text{----}\rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ (1)

(iii) $Na_2Cr_2O_7 + 2KCl \text{---}\rightarrow K_2Cr_2O_7 + 2NaCl$ (1)

(b)

(i)$Cr_2O_7^{2-}(aq) + 8H^+ + 3\,H_2S \text{----}\rightarrow 2Cr^{3+} + 3S + 7H_2O$ (1)

(ii)$MnO_4^-(aq) + 8H^+ + 5\,Fe^{2+} \text{----}\rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (1)

Or

(a) (i) Transition metals and their compound show paramagnetic behavior due to presence of unpaired electrons in them. (1)

(ii)Transition metals exhibits high enthalpies of atomization because they have large number of unpaired electrons in their atoms. Due to this, they have stronger interatomic interactions. (1)

(iii)Due to d-d transition (1)

(b) The steady decrease in atomic and ionic sizes of lanthanoid elements with increasing atomic numbers is called lanthanoid contractions. (1/2)

Following are the consequences of lanthanoid contractions

(i) The size of second and third row of transition elements are nearly same. (1/2)

(ii) Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$ (1/2)

(iii) Lanthanoid contraction makes separation of lanthanoids possible (1/2)

Q.**No.37** (a)(i) Because of presence of three methyl groups in 2,2,6- trimethylcyclohexanone, the nucleophilic attack by the CN^- ion does not occur due to steric hindrance. Since there is no steric hindrance in cyclohexanone, therefore nucleophilic attack by the CN^-ion occurs readily and hence cyclohexanone cyanohydrin is obtained in good yield. (1)

(ii)Although semicarbazide has to $–NH_2$ groups, but one of them (which is directly attached to C=O) is involved in resonance. As a result, electron density on this$–NH_2$ group decreases and hence it does not act as nucleophile. In constrast, the lone pair of electrons on the other $–NH_2$ group is not involved in resonance and hence is available for nucleophilic attack on the C=O group of carbonyl compounds. (1)

(iii) The formation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst is a reversible reaction. To shift the equilibrium in the forward direction, the water or ester formed should be removed as soon as it id formed. (1)

(b) (i)CH_3COCH_3----→ $CH_3CH(OH)CH_3$-----→$CH_3CH=CH_2$ (1)

(ii) CH_3CH_2OH---→ CH_3CHO------→ $CH_3CH(OH)CH_2CHO$ (1)

Or

(a) A is $CH_3COCH_2CH_2CH_3$

B is CH_3CH_2COOH

C is $CH_3CH_2CH_2CH_3$

Reactions involved:-

$CH_3COCH_2CH_2CH_3 \xrightarrow{\text{alk KMnO4}} CH_3CH_2COOH$ (1)

(B) $CH_3COCH_2CH_2CH_3 + I_2 + 4NaOH \rightarrow CHI_3 + CH_3CH_2CH_2COONa +$

(A) $3NaI + 2H_2O$

$CH_3COCH_2CH_2CH_3 \xrightarrow{K2Cr2O7/H^+} CH_3CH_2COOH + CH_3COOH$ (1)

(A)

$2CH_3COONa + 2H_2O \rightarrow CH_3CH_2CH_2CH_3 + CO_2 + H_2 + 2NaOH$ (1)

© Kolbe‘s electrolysis

(b) Correct reactions (1+1)

EXAMINATION TIPS FOR STUDENTS

Self motivation- Honestly write down your aim and all the desires in your life. It will propel you towards success.

Set up a routine- Prepare smart and successful studying programme.

Find a **quiet place**, away from distractions and figure out time of the day you can contribute best and that fits into your schedule.

Make a good time table-A schedule of every subject should be made with different priorities like tough subjects and the one in which you are week should be given more hours. Study at the same place & at the same time every day.

Sit in an **alert posture**.

Stay **healthy** mentally and physically get adequate rest, exercise and balanced nutrition.

Manage distractions like cellphones, friends, sms, TV, video games, surfing etc which are biggest time drains.

Avoid doing "marathon" session (i.e. larger than 1 hour) as it is least productive. Our attention span ranges from 30-60 minute.

Unwind and relax- 10 to 15 min break after every study session.

Study difficult topics first. When mentally fresh, brain can process information more quickly. Short term planning is more achievable than long term plans.

Don't spend more than three days a week in coaching/tution as **self study is the only real study**. **Therefore atleast** four days for uninterrupted self study.

Prepare a competitive study group- share useful concepts and questions, your knowledge, skills and resources, clarify doubts, take help of a friend who is an expert in that topic/unit.

Give yourself enough time to study. dont leave until the last minute. Use flow charts & mind maps.

Test yourself before actual test–practice previous year's examination papers.

Review clear doubts revise-attempt questions of textbook and previous year CBSE papers.

NIGHT BEFORE THE EXAM - don't cram.

Reduce stress and anxiety.. avoid stressful friends....relax.. eat some brain snacks.. sleep..review main points.

Prepare to be prepared: before going to bed before an exam make sure to collect everything that you will need for exam–stationery , admit card, wrist watch....

Ensure location of exam centre.

ON EXAMINATION DAY.. leave home in time and ensure your arrival at centre in time..so that you go into your exam calmly rather than in a frantic rush sweaty.

DURING TEST-

Focus on your exam and not on what other students are doing

Start strategically..begin your exam by skimming through the question quickly and note down any initial thoughts or related memorised facts beside each question.

Start with the question you know best. This will boost your confidence and give you a good start.

- Read the instructions carefully and follow.
- Answer as per marking scheme.
- Write neat and present well.
- Attempt the easiest part and the units you are most confident. Manage time so that time can be allotted to difficult portion.
- Attempt complete question paper.
- Never cheat
- Review and make sure you have not left out any question unattempted.

CHASE YOUR GOALS. ALL THE BEST

SET-1

Series BVM/2

कोड नं.
Code No. **56/2/1**

रोल नं.
Roll No. ☐☐☐☐☐☐☐

परीक्षार्थी कोड को उत्तर-पुस्तिका के मुख-पृष्ठ पर अवश्य लिखें ।
Candidates must write the Code on the title page of the answer-book.

- कृपया जाँच कर लें कि इस प्रश्न-पत्र में मुद्रित पृष्ठ **15** हैं ।
- प्रश्न-पत्र में दाहिने हाथ की ओर दिए गए कोड नम्बर को छात्र उत्तर-पुस्तिका के मुख-पृष्ठ पर लिखें ।
- कृपया जाँच कर लें कि इस प्रश्न-पत्र में **27** प्रश्न हैं ।
- **कृपया प्रश्न का उत्तर लिखना शुरू करने से पहले, प्रश्न का क्रमांक अवश्य लिखें ।**
- इस प्रश्न-पत्र को पढ़ने के लिए 15 मिनट का समय दिया गया है । प्रश्न-पत्र का वितरण पूर्वाह्न में 10.15 बजे किया जाएगा । 10.15 बजे से 10.30 बजे तक छात्र केवल प्रश्न-पत्र को पढ़ेंगे और इस अवधि के दौरान वे उत्तर-पुस्तिका पर कोई उत्तर नहीं लिखेंगे ।
- Please check that this question paper contains **15** printed pages.
- Code number given on the right hand side of the question paper should be written on the title page of the answer-book by the candidate.
- Please check that this question paper contains **27** questions.
- **Please write down the Serial Number of the question before attempting it.**
- 15 minute time has been allotted to read this question paper. The question paper will be distributed at 10.15 a.m. From 10.15 a.m. to 10.30 a.m., the students will read the question paper only and will not write any answer on the answer-book during this period.

रसायन विज्ञान (सैद्धान्तिक)

CHEMISTRY (Theory)

निर्धारित समय : 3 घण्टे *अधिकतम अंक : 70*

Time allowed : 3 hours *Maximum Marks : 70*

सामान्य निर्देश :

(i) *__सभी__ प्रश्न अनिवार्य हैं ।*

(ii) *खण्ड अ : प्रश्न संख्या **1** से **5** तक अति लघु-उत्तरीय प्रश्न हैं और प्रत्येक प्रश्न के लिए **1** अंक है ।*

(iii) *खण्ड ब : प्रश्न संख्या **6** से **12** तक लघु-उत्तरीय प्रश्न हैं और प्रत्येक प्रश्न के लिए **2** अंक हैं ।*

(iv) *खण्ड स : प्रश्न संख्या **13** से **24** तक भी लघु-उत्तरीय प्रश्न हैं और प्रत्येक प्रश्न के लिए **3** अंक हैं ।*

(v) *खण्ड द : प्रश्न संख्या **25** से **27** तक दीर्घ-उत्तरीय प्रश्न हैं और प्रत्येक प्रश्न के लिए **5** अंक हैं ।*

(vi) *प्रश्न पत्र में समग्र विकल्प नहीं दिया गया है । फिर भी एक अंक वाले दो प्रश्नों में, दो अंकों वाले दो प्रश्नों में, तीन अंकों वाले चार प्रश्नों में तथा पाँच अंकों वाले तीनों प्रश्नों में विकल्प दिया गया है । ऐसे सभी प्रश्नों में से आपको एक ही विकल्प का उत्तर देना है ।*

(vii) *यदि आवश्यकता हो, तो आप लघुगणकीय सारणियाँ माँग सकते हैं । कैल्कुलेटरों के प्रयोग की अनुमति __नहीं__ है ।*

General Instructions :

(i) *__All__ questions are compulsory.*

(ii) *Section A : Questions number **1** to **5** are very short answer questions and carry **1** mark each.*

(iii) *Section B : Questions number **6** to **12** are short answer questions and carry **2** marks each.*

(iv) *Section C : Questions number **13** to **24** are also short answer questions and carry **3** marks each.*

(v) *Section D : Questions number **25** to **27** are long answer questions and carry **5** marks 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 choices in such questions.*

(vii) *Use of log tables, if necessary. Use of calculators is __not__ allowed.*

खण्ड अ

SECTION A

1. KCl और AgCl में से कौन शॉट्की दोष दर्शाता है और क्यों ? *1*

अथवा

गरम करने पर ZnO पीला क्यों प्रतीत होता है ? *1*

Out of KCl and AgCl, which one shows Schottky defect and why ?

OR

Why does ZnO appear yellow on heating ?

2. निम्नलिखित को क्षारीय लक्षण के घटते हुए क्रम में व्यवस्थित कीजिए : *1*

$C_6H_5NH_2$, $(CH_3)_3N$, $C_2H_5NH_2$

Arrange the following in decreasing order of basic character :

$C_6H_5NH_2$, $(CH_3)_3N$, $C_2H_5NH_2$

3. किस प्रकार का कोलॉइड बनता है जब किसी ठोस को द्रव में परिक्षिप्त किया जाता है ? एक उदाहरण दीजिए । *1*

What type of colloid is formed when a solid is dispersed in a liquid ? Give an example.

4. क्लोरोबेन्ज़ीन और साइक्लोहेक्सिल क्लोराइड में से कौन नाभिकस्नेही प्रतिस्थापन अभिक्रिया के प्रति अधिक अभिक्रियाशील है और क्यों ? *1*

Out of Chlorobenzene and Cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why ?

5. स्टार्च और सेलुलोस में मूलभूत संरचनात्मक अंतर क्या है ? *1*

अथवा

DNA के जल-अपघटन से प्राप्त उत्पाद लिखिए । *1*

What is the basic structural difference between starch and cellulose ?

OR

Write the products obtained after hydrolysis of DNA.

खण्ड ब

SECTION B

6. निम्नलिखित प्रक्रमों के लिए संतुलित रासायनिक समीकरण लिखिए : *2*

(a) बुझे चूने से Cl_2 प्रवाहित की जाती है ।

(b) Fe(III) लवण के जलीय विलयन से SO_2 गैस प्रवाहित की जाती है ।

अथवा

(a) क्लोरीन गैस से बनाई गई दो विषैली गैसों के नाम लिखिए ।

(b) अमोनिया से अभिक्रिया करने पर Cu^{2+} विलयन नीला रंग क्यों देता है ? *2*

Write balanced chemical equations for the following processes :

(a) Cl_2 is passed through slaked lime.

(b) SO_2 gas is passed through an aqueous solution of Fe(III) salt.

OR

(a) Write two poisonous gases prepared from chlorine gas.

(b) Why does Cu^{2+} solution give blue colour on reaction with ammonia ?

7. कारण दीजिए : 2

(a) खाना बनाने के बर्तन की अपेक्षा प्रेशर कुकर में खाना अधिक शीघ्रता से पक जाता है ।

(b) लाल रुधिर कोशिकाएँ (RBC) लवणीय जल में रखे जाने पर संकुचित हो जाती हैं परन्तु आसुत जल में फूल जाती हैं ।

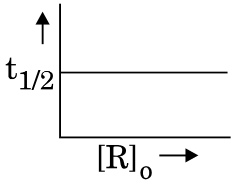
Give reasons :

(a) Cooking is faster in pressure cooker than in cooking pan.

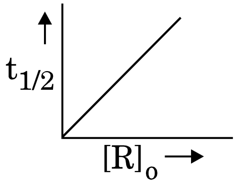
(b) Red Blood Cells (RBC) shrink when placed in saline water but swell in distilled water.

8. अभिक्रिया की कोटि परिभाषित कीजिए । दिए गए आलेखों में अभिक्रिया की कोटि की प्रागुक्ति कीजिए : 2

(a)



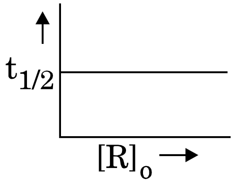
(b)



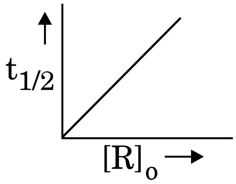
जहाँ $[R]_o$ अभिकर्मक की प्रारम्भिक सान्द्रता है और $t_{1/2}$ अर्ध आयु है ।

Define order of reaction. Predict the order of reaction in the given graphs :

(a)



(b)



where $[R]_o$ is the initial concentration of reactant and $t_{1/2}$ is half-life.

9. जब $FeCr_2O_4$ को वायु की उपस्थिति में Na_2CO_3 के साथ संगलित किया जाता है तो यौगिक (A) का पीला विलयन प्राप्त होता है । यौगिक (A) अम्लीकरण किए जाने पर यौगिक (B) देता है । यौगिक (B) KCl के साथ अभिक्रिया करके एक नारंगी रंग का यौगिक (C) बनाता है । यौगिक (C) का अम्लीय विलयन Na_2SO_3 को (D) में ऑक्सीकृत कर देता है । (A), (B), (C) और (D) की पहचान कीजिए । *2*

When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured compound (C). An acidified solution of compound (C) oxidises Na_2SO_3 to (D). Identify (A), (B), (C) and (D).

10. संकुल $[Co(en)_2(NO_2)Cl]^+$ का IUPAC नाम लिखिए । इस संकुल द्वारा किस प्रकार की संरचनात्मक समावयवता दर्शाई जाती है ? *2*

अथवा

IUPAC मानदण्डों का उपयोग करते हुए निम्नलिखित संकुलों के सूत्र लिखिए : *2*

(a) हेक्साएक्वाक्रोमियम(III) क्लोराइड

(b) सोडियम ट्राइऑक्सैलेटोफेरेट(III)

Write IUPAC name of the complex $[Co(en)_2(NO_2)Cl]^+$. What type of structural isomerism is shown by this complex ?

OR

Using IUPAC norms, write the formulae for the following complexes :

(a) Hexaaquachromium(III) chloride

(b) Sodium trioxalatoferrate(III)

11. (a) यद्यपि $[NiCl_4]^{2-}$ और $[Ni(CO)_4]$ दोनों में sp^3 संकरण होता है फिर भी $[NiCl_4]^{2-}$ अनुचुम्बकीय है और $[Ni(CO)_4]$ प्रतिचुम्बकीय है । कारण दीजिए । (Ni का परमाणु क्रमांक = 28)

(b) क्रिस्टल क्षेत्र सिद्धान्त के आधार पर d^5 का इलेक्ट्रॉनिक विन्यास लिखिए जबकि

(i) $\Delta_o < P$ और

(ii) $\Delta_o > P$ *2*

(a) Although both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ have sp^3 hybridisation yet $[NiCl_4]^{2-}$ is paramagnetic and $[Ni(CO)_4]$ is diamagnetic. Give reason. (Atomic no. of Ni = 28)

(b) Write the electronic configuration of d^5 on the basis of crystal field theory when

(i) $\Delta_o < P$ and

(ii) $\Delta_o > P$

12. निम्नलिखित प्रत्येक अभिक्रिया में मुख्य यौगिकों A और B की संरचनाएँ लिखिए : *2*

(a) $C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd-BaSO_4} B$

(b) $CH_3CN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} A \xrightarrow{\text{Zn(Hg)/सान्द्र HCl}} B$

Write structures of main compounds A and B in each of the following reactions :

(a) $C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd-BaSO_4} B$

(b) $CH_3CN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} A \xrightarrow{\text{Zn(Hg)/conc. HCl}} B$

खण्ड स

SECTION C

13. अभिक्रिया $A + 2B \longrightarrow C$ के लिए निम्नलिखित आँकड़े प्राप्त हुए : *3*

प्रयोग	[A]/M	[B]/M	C के विरचन का प्रारम्भिक वेग /M min^{-1}
1	0·2	0·3	$4{\cdot}2 \times 10^{-2}$
2	0·1	0·1	$6{\cdot}0 \times 10^{-3}$
3	0·4	0·3	$1{\cdot}68 \times 10^{-1}$
4	0·1	0·4	$2{\cdot}40 \times 10^{-2}$

(a) A और B के प्रति अभिक्रिया की कोटि ज्ञात कीजिए ।

(b) वेग नियम और अभिक्रिया की कुल कोटि लिखिए ।

(c) वेग स्थिरांक (k) परिकलित कीजिए ।

The following data were obtained for the reaction :

$$A + 2B \longrightarrow C$$

Experiment	[A]/M	[B]/M	Initial rate of formation of C /M min^{-1}
1	0·2	0·3	$4{\cdot}2 \times 10^{-2}$
2	0·1	0·1	$6{\cdot}0 \times 10^{-3}$
3	0·4	0·3	$1{\cdot}68 \times 10^{-1}$
4	0·1	0·4	$2{\cdot}40 \times 10^{-2}$

(a) Find the order of reaction with respect to A and B.

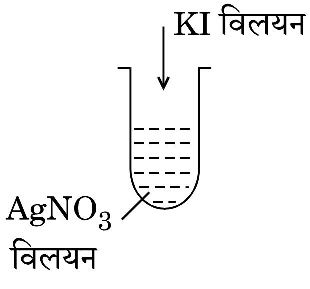
(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k).

14. (a) धूल की परिक्षिप्त प्रावस्था और परिक्षेपण माध्यम लिखिए ।

(b) भौतिक अवशोषण उत्क्रमणीय जबकि रसोशोषण अनुत्क्रमणीय क्यों है ?

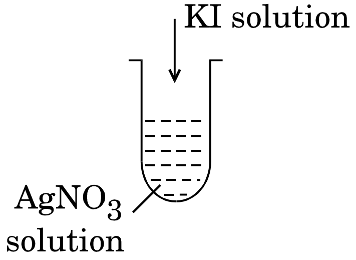
(c) चित्र में दी गई विधि द्वारा एक कोलॉइडी सॉल बनाया गया । परखनली में बने AgI कोलॉइडी कणों के ऊपर क्या आवेश है ? यह सॉल कैसे निरूपित किया जाता है ? *3*



(a) Write the dispersed phase and dispersion medium of dust.

(b) Why is physisorption reversible whereas chemisorption is irreversible ?

(c) A colloidal sol is prepared by the method given in the figure. What is the charge on AgI colloidal particles formed in the test tube ? How is this sol represented ?



15. परमाणु द्रव्यमान 81 u के किसी तत्त्व X का घनत्व 10·2 g cm^{-3} है । यदि एकक कोष्ठिका का आयतन $2{\cdot}7 \times 10^{-23}$ cm^3 है, तो घनीय एकक कोष्ठिका के प्रकार की पहचान कीजिए । (दिया गया है : $N_A = 6{\cdot}022 \times 10^{23}$ mol^{-1}) *3*

An element X with an atomic mass of 81 u has density 10·2 g cm^{-3}. If the volume of unit cell is $2{\cdot}7 \times 10^{-23}$ cm^3, identify the type of cubic unit cell. (Given : $N_A = 6{\cdot}022 \times 10^{23}$ mol^{-1})

16. 1·9 g प्रति 100 mL KCl (M = 74·5 g mol^{-1}) का विलयन 3 g प्रति 100 mL यूरिया (M = 60 g mol^{-1}) के साथ समपरासरी है । KCl विलयन की वियोजन की मात्रा परिकलित कीजिए । मान लीजिए कि दोनों विलयन समान ताप पर हैं । *3*

A solution containing 1·9 g per 100 mL of KCl (M = 74·5 g mol^{-1}) is isotonic with a solution containing 3 g per 100 mL of urea (M = 60 g mol^{-1}). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature.

17. (a) ज़िंक, (b) जर्मेनियम, (c) टाइटेनियम के लिए प्रयुक्त परिष्करण विधि का नाम और सिद्धान्त लिखिए । *3*

Write the name and principle of the method used for refining of (a) Zinc, (b) Germanium, (c) Titanium.

18. निम्नलिखित के लिए कारण दीजिए : *3*

(a) संकरण धातुएँ संकुल यौगिक बनाती हैं ।

(b) (Zn^{2+}/Zn) और (Mn^{2+}/Mn) के लिए E^o के मान अपेक्षित मानों से अधिक ऋणात्मक होते हैं ।

(c) ऐक्टिनॉयड ऑक्सीकरण अवस्थाओं का अधिक परास दर्शाते हैं ।

Give reasons for the following :

(a) Transition metals form complex compounds.

(b) E^o values for (Zn^{2+}/Zn) and (Mn^{2+}/Mn) are more negative than expected.

(c) Actinoids show wide range of oxidation states.

19. निम्नलिखित बहुलकों को प्राप्त करने के लिए प्रयुक्त एकलकों की संरचनाएँ लिखिए : *3*

(a) नाइलॉन-6

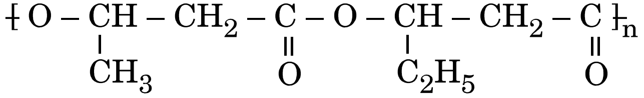
(b) टेरीलीन

(c) ब्यूना-N

अथवा

(a) क्या $\left[CH_2 - CH(C_6H_5) \right]_n$ एक समबहुलक अथवा सहबहुलक है ? कारण दीजिए ।

(b) निम्नलिखित बहुलक के एकलक लिखिए :



$$\left[O - \underset{\substack{| \\ CH_3}}{CH} - CH_2 - \underset{\substack{\| \\ O}}{C} - O - \underset{\substack{| \\ C_2H_5}}{CH} - CH_2 - \underset{\substack{\| \\ O}}{C} \right]_n$$

(c) एथीन के बहुलकन में बेन्ज़ॉयल परॉक्साइड की भूमिका लिखिए । *3*

Write the structures of monomers used for getting the following polymers :

(a) Nylon-6

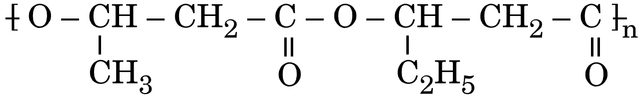
(b) Terylene

(c) Buna-N

OR

(a) Is $\left[CH_2 - CH(C_6H_5) \right]_n$ a homopolymer or copolymer ? Give reason.

(b) Write the monomers of the following polymer :



$$\left[O - \underset{\substack{| \\ CH_3}}{CH} - CH_2 - \underset{\substack{\| \\ O}}{C} - O - \underset{\substack{| \\ C_2H_5}}{CH} - CH_2 - \underset{\substack{\| \\ O}}{C} \right]_n$$

(c) Write the role of benzoyl peroxide in polymerisation of ethene.

20. (a) निम्नलिखित में से उनके चिकित्सीय गुणों के आधार पर एक विषम को छाँटिए :

इक्वैनिल, सेकोनल, बाइथायोनल, ल्यूमिनल

(b) बर्तन धोने के उपयोग में आने वाले द्रव अपमार्जक किस प्रकार के अपमार्जक होते हैं ?

(c) ऐस्पार्टेम का उपयोग केवल ठंडे खाद्य पदार्थों तक ही सीमित क्यों है ? *3*

अथवा

प्रत्येक के लिए उचित उदाहरण सहित निम्नलिखित पदों को परिभाषित कीजिए : *3*

(a) प्रतिजैविक (एन्टिबायोटिक)

(b) पूतिरोधी (एन्टिसेप्टिक)

(c) ऋणायनी अपमार्जक

(a) Pick out the odd one from the following on the basis of their medicinal properties :

Equanil, Seconal, Bithional, Luminal

(b) What type of detergents are used in dishwashing liquids ?

(c) Why is the use of aspartame limited to cold foods ?

OR

Define the following terms with a suitable example of each :

(a) Antibiotics

(b) Antiseptics

(c) Anionic detergents

21. अणुसूत्र C_4H_9Br के सभी समावयवों में से, पहचानिए

(a) एक समावयव जो ध्रुवण घूर्णक है ।

(b) एक समावयव जो S_N2 के प्रति अत्यधिक अभिक्रियाशील है ।

(c) ऐसे दो समावयव जो ऐल्कोहॉली पोटैशियम हाइड्रॉक्साइड द्वारा विहाइड्रोजनन के फलस्वरूप एक जैसा उत्पाद देते हैं । *3*

Among all the isomers of molecular formula C_4H_9Br, identify

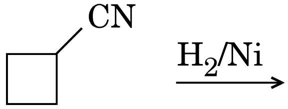
(a) the one isomer which is optically active.

(b) the one isomer which is highly reactive towards S_N2.

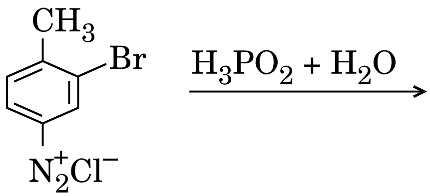
(c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH.

22. निम्नलिखित अभिक्रियाओं को पूर्ण कीजिए : *3*

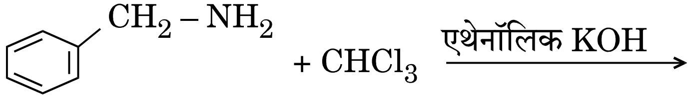
(a)



(b)



(c)



अथवा

आप निम्नलिखित रूपांतरण कैसे करेंगे : *3*

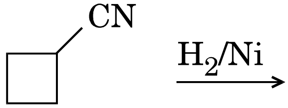
(a) N-फेनिलएथेनेमाइड से p-ब्रोमोऐनिलीन

(b) बेन्ज़ीन डाइएज़ोनियम क्लोराइड से नाइट्रोबेन्ज़ीन

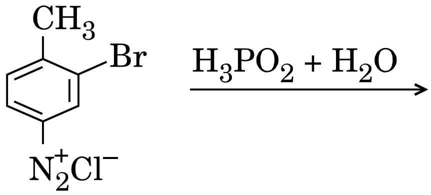
(c) बेन्ज़ोइक अम्ल से ऐनिलीन

Complete the following reactions :

(a)



(b)



(c)

OR

How do you convert the following :

(a) N-phenylethanamide to p-bromoaniline

(b) Benzene diazonium chloride to nitrobenzene

(c) Benzoic acid to aniline

23. (a) कारण दीजिए :

(i) ऐसीटिक अम्ल की अपेक्षा बेन्ज़ोइक अम्ल प्रबलतर अम्ल होता है ।

(ii) एथेनेल की अपेक्षा मेथैनेल नाभिकस्नेही योगज अभिक्रियाओं के प्रति अधिक अभिक्रियाशील होता है ।

(b) प्रोपेनैल और प्रोपेनोन के बीच विभेद करने के लिए एक सरल रासायनिक परीक्षण दीजिए । *3*

(a) Give reasons :

(i) Benzoic acid is a stronger acid than acetic acid.

(ii) Methanal is more reactive towards nucleophilic addition reaction than ethanal.

(b) Give a simple chemical test to distinguish between propanal and propanone.

24. (a) माल्टोस के जल-अपघटन के उत्पाद क्या हैं ?

(b) प्रोटीन की α-हेलिक्स संरचना को किस प्रकार का आबन्धन स्थायित्व प्रदान करता है ?

(c) उस विटामिन का नाम लिखिए जिसकी कमी से प्रणाशी रक्ताल्पता हो जाती है । *3*

अथवा

निम्नलिखित पदों को परिभाषित कीजिए : *3*

(a) प्रतीप शर्करा

(b) प्राकृत प्रोटीन

(c) न्यूक्लिओटाइड

(a) What are the products of hydrolysis of maltose ?

(b) What type of bonding provides stability to α-helix structure of protein ?

(c) Name the vitamin whose deficiency causes pernicious anaemia.

OR

Define the following terms :

(a) Invert sugar

(b) Native protein

(c) Nucleotide

खण्ड द

SECTION D

25. (a) $0{\cdot}001$ mol L^{-1} ऐसीटिक अम्ल की चालकता $4{\cdot}95 \times 10^{-5}$ S cm^{-1} है । यदि ऐसीटिक अम्ल के लिए $\wedge_m^o$ का मान $390{\cdot}5$ S cm^2 mol^{-1} है, तो इसके वियोजन स्थिरांक का परिकलन कीजिए ।

(b) अभिक्रिया

$$2\,Al\,(s) + 3\,Cu^{2+}\,(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 3\,Cu\,(s)$$

के लिए 25°C पर नेर्न्स्ट समीकरण लिखिए ।

(c) संचायक बैटरियाँ क्या हैं ? एक उदाहरण दीजिए । *5*

अथवा

(a) उस सेल को निरूपित कीजिए जिसमें निम्नलिखित अभिक्रिया होती है :

$$2\,Al\,(s) + 3\,Ni^{2+}\,(0{\cdot}1\,M) \longrightarrow 2\,Al^{3+}\,(0{\cdot}01\,M) + 3\,Ni\,(s)$$

इसका वि.वा.बल (emf) परिकलित कीजिए यदि $E^o_{\text{सेल}} = 1{\cdot}41$ V है ।

(b) प्रबल और दुर्बल विद्युत्-अपघट्य के लिए सान्द्रता बढ़ने के साथ मोलर चालकता किस प्रकार परिवर्तित होती है ? आप दुर्बल विद्युत्-अपघट्य के लिए सीमांत मोलर चालकता ($\wedge_m^o$) कैसे प्राप्त कर सकते हैं ? *5*

(a) The conductivity of $0{\cdot}001$ mol L^{-1} acetic acid is $4{\cdot}95 \times 10^{-5}$ S cm^{-1}. Calculate the dissociation constant if $\wedge_m^o$ for acetic acid is $390{\cdot}5$ S cm^2 mol^{-1}.

(b) Write Nernst equation for the reaction at 25°C :

$$2\,Al\,(s) + 3\,Cu^{2+}\,(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 3\,Cu\,(s)$$

(c) What are secondary batteries ? Give an example.

OR

(a) Represent the cell in which the following reaction takes place :

$$2\,Al\,(s) + 3\,Ni^{2+}\,(0{\cdot}1\,M) \longrightarrow 2\,Al^{3+}\,(0{\cdot}01\,M) + 3\,Ni\,(s)$$

Calculate its emf if $E^o_{cell} = 1{\cdot}41$ V.

(b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte ? How can you obtain limiting molar conductivity ($\wedge_m^o$) for weak electrolyte ?

26. (a) निम्नलिखित अभिक्रियाओं के लिए समीकरण दीजिए :

(i) फ़ीनॉल की सान्द्र HNO_3 के साथ अभिक्रिया की जाती है ।

(ii) प्रोपीन की B_2H_6 से अभिक्रिया करके H_2O_2/OH^- से अभिक्रिया की जाती है ।

(iii) सोडियम तृतीयक-ब्यूटॉक्साइड की CH_3Cl के साथ अभिक्रिया की जाती है ।

(b) ब्यूटेन-1-ऑल और ब्यूटेन-2-ऑल के बीच आप कैसे विभेद करेंगे ?

(c) निम्नलिखित को अम्लीयता के बढ़ते हुए क्रम में व्यवस्थित कीजिए :

फ़ीनॉल, एथेनॉल, जल *5*

अथवा

(a) (i) क्यूमीन, (ii) बेन्ज़ीन सल्फोनिक अम्ल, (iii) बेन्ज़ीन डाइएज़ोनियम क्लोराइड से आप फ़ीनॉल कैसे प्राप्त कर सकते हैं ?

(b) 3-मेथिलफ़ीनॉल के द्विनाइट्रोकरण से प्राप्त मुख्य उत्पाद की संरचना लिखिए ।

(c) कोल्बे अभिक्रिया से सम्बद्ध अभिक्रिया लिखिए । *5*

(a) Give equations of the following reactions :

(i) Phenol is treated with conc. HNO_3.

(ii) Propene is treated with B_2H_6 followed by H_2O_2/OH^-.

(iii) Sodium t-butoxide is treated with CH_3Cl.

(b) How will you distinguish between butan-1-ol and butan-2-ol ?

(c) Arrange the following in increasing order of acidity :

Phenol, ethanol, water

OR

(a) How can you obtain Phenol from (i) Cumene, (ii) Benzene sulphonic acid, (iii) Benzene diazonium chloride ?

(b) Write the structure of the major product obtained from dinitration of 3-methylphenol.

(c) Write the reaction involved in Kolbe's reaction.

27. (a) निम्नलिखित के कारण दीजिए :

(i) वर्ग 15 में N से Bi तक -3 ऑक्सीकरण अवस्था दर्शाने की प्रवृत्ति घटती है ।

(ii) H_2O से H_2Te तक अम्लीय लक्षण बढ़ता है ।

(iii) ClF_3 की अपेक्षा F_2 अधिक अभिक्रियाशील है, जबकि Cl_2 की अपेक्षा ClF_3 अधिक अभिक्रियाशील है ।

(b) (i) XeF_2, (ii) $H_4P_2O_7$ की संरचना खींचिए । 5

अथवा

(a) फ्लुओरीन की असामान्य अभिक्रिया दर्शाने के लिए एक उदाहरण दीजिए ।

(b) श्वेत फ़ॉस्फ़ोरस और लाल फ़ॉस्फ़ोरस के बीच एक संरचनात्मक अन्तर क्या है ?

(c) क्या होता है जब XeF_6, NaF से अभिक्रिया करता है ?

(d) H_2O की अपेक्षा H_2S एक बेहतर अपचायक क्यों है ?

(e) निम्नलिखित अम्लों को उनके अम्लीय लक्षण के बढ़ते हुए क्रम में व्यवस्थित कीजिए :

HF, HCl, HBr और HI 5

(a) Account for the following :

(i) Tendency to show −3 oxidation state decreases from N to Bi in group 15.

(ii) Acidic character increases from H_2O to H_2Te.

(iii) F_2 is more reactive than ClF_3, whereas ClF_3 is more reactive than Cl_2.

(b) Draw the structure of (i) XeF_2, (ii) $H_4P_2O_7$.

OR

(a) Give one example to show the anomalous reaction of fluorine.

(b) What is the structural difference between white phosphorus and red phosphorus ?

(c) What happens when XeF_6 reacts with NaF ?

(d) Why is H_2S a better reducing agent than H_2O ?

(e) Arrange the following acids in the increasing order of their acidic character :

HF, HCl, HBr and HI

तत् त्वं पूषन् अपावृणु

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