केन्द्रीय विद्यालय संगठन
कोलकाता संभाग

KENDRIYA VIDYALAYA SANGATHAN
KOLKATA REGION

केन्द्रीय विद्यालय संगठन

CHEMISTRY STUDENT SUPPORT MATERIAL

CLASSES – XII

SESSION 2023-24

CHEMISTRY STUDENT SUPPORT MATERIAL

SESSION – 2023-24

OUR PATRONS

SH. Y ARUN KUMAR

DEPUTY COMMISSIONER, KVS RO KOLKATA

SH. SANJIV SINHA

SH.CH VIJAYARATNAM

SH. DIWAKAR BHOI

SH. AMIT BAIDYA

ASSISTANT COMMISSIONERS, KVS RO KOLKATA

Coordinator:

Sh. Sangram Banerjee

Principal, KV No.2 Kharagpur

CHEMISTRY STUDENT SUPPORT MATERIAL
SESSION – 2023-24

Content Review & Moderation:

Sh. Arunesh Gupta PGT Chem KV AFS Barrackpore

Sh. Robin Banerjee PGT Chem KV Sukna

Sh. Uthsek Ghosh PGT Chem KV Ishapore no. 1

Content Development Team

SR. NO.	NAME of the PGTs Chemistry	KV	CLASS	TOPIC	PAGE NO.
1	Mr. Ujjal Banerjee	Fort William	XII	**Unit II: Solutions**	73
2	Mrs B. Kamakshi	Fort William	XII	**Unit XIV: Biomolecules**	6
3	MR. DIGBIJOY MAHTO	Gangtok	XII	**Unit XIII: Amines**	73
4	Mr. S.K. Mondal	Garden Reach	XII	**Unit XIII: Amines**	66
5	Mr S K Singh	Hasimara	XII	**Unit XII: Aldehydes, Ketones and Carboxylic Acids**	66
6	Dr Hemant Kumar	Ishapore No.1	XII	**Unit IX.: Coordination Compound**	59
7	MR RAGHIB ROUSHAN	Ishapore No.2	XII	**Unit XII: Aldehydes, Ketones and Carboxylic Acids**	37
8	Mr K Barik	Kanchrapara No.2	XII	**Unit XI: Alcohols, Phenols and Ethers**	59
9	MR A K RAKSHIT	Kharagpur No.1 - IIT	XII	**Unit XI: Alcohols, Phenols and Ethers**	52
10	MR A K PRATIHAR	Kharagpur No.2 (Rly.)	XII	**Unit X: Haloalkanes and Haloarenes.**	52
11	MR MD. MOHAMUDDIN	Malda-NHPC	XII	**Unit X: Haloalkanes and Haloarenes.**	44
12	MS Kuhelika Bandyopadhyaya	Panagarh	XII	**Unit VIII: d and f Block Elements**	44
13	Ms. Sampa Ghosh	Raninagar (BSF)	XII	**Unit VIII: d and f Block Elements**	27
14	MS SUMANA CHAKRABORTY	Salt Lake No.1	XII	**Unit IV: Chemical Kinetics**	18
15	Mrs. Shubhra Chaudhuri	Salt Lake No.2	XII	**Unit III: Electrochemistry**	11
16	Mrs. Trisha Biswas	Salt Lake No.2	XII	**Unit IV: Chemical Kinetics**	18
17	Mr. Ranjit Kumar Pathak	Santragachi	XII	**Unit III: Electrochemistry**	11
18	Mr. Jatindranath Mandal	Tarakeswar	XII	**Unit II: Solutions**	6

How to use this document?

Dear Student,

- This material we have created exclusively for you!!
- Our prime focus has been to develop a content which will ensure that you will attain the minimum level of learning (MLL) required for the examinations.
- We have collected a wide range of questions from your teachers across the region and have compiled this document with the aspiration that you will come out with flying colours in Chemistry.
- You may use this chemistry study material during remedial classes where you can learn the question – answers portion of each.
- Whenever in doubt, please refer to our definitions and formula portions of each chapter, which are kept as short and lucid as possible.
- The important questions from each topic and each chapter may be used as the 'last minute look up' before the exam.
- The important rules, structures and reagents are compiled topic-wise and they should be used for daily revision.
- We have kept the essentials to the bare minimum so that the voluminous look of Chemistry doesn't scare you away.

All the Best from all of us!!!!

STUDENTS SUPPORT MATERIALS for Class XII

Unit 1: SOLUTIONS

1) Define: Molarity, Molality, Van't Hoff factor, abnormal molar mass, azeotropes.

Molality: No. of moles of solute dissolve per kg of solvent. Mathematically, $m = n_{solute}/w_{solvent}(kg)$

Molarity: No. of moles of solute dissolve per litre of solution. Mathematically, $M = n_{solute}/V_{solution}(L)$

Van't Hoff factor(i) = No. of particles after association or dissociation/ No. of particles before association / dissociation.

Abnormal molar mass: Molar mass that is either lower or higher than the expected or normal value is called abnormal molar mass.

Azeotropes: Some liquids on mixing, form **azeotropes** which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

2) State: Henry's Law, Raoult's Law for two volatile liquids, Law for one non-volatile and one volatile liquid solutions.

Henry's Law: The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution. Mathematically $p = K_H \chi$

Raoult's Law : For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Mathematically $p_A = p^o_A X_A$; $p_B = p^o_B X_B$

1. Differentiate between: Ideal solution and non-ideal solution, positive and negative deviation from Raoult's Law.

Ideal solution	**Non ideal solution**
1. The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions.*	1.When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*.
2.$\Delta_{mix}H = 0$,	2.$\Delta_{mix}H \neq 0$,
3.$\Delta_{mix}V = 0$	3.$\Delta_{mix}V \neq 0$

Positive deviation from Raoult's Law	**Negative deviation from Raoult's Law**
1. $p_A > p^o_A$; $p_B > p^o_B$ (V.P. increases)	1. $p_A < p^o_A$; $p_B < p^o_B$ (V.P. decreases)
2.$\Delta_{mix}H > 0$ Solution becomes cold, endothermic process	2. $\Delta_{mix}H < 0$ Solution becomes hot, exothermic process.
3. $\Delta_{mix}V > 0$ Volume increases om mixing	3. $\Delta_{mix}V < 0$ Volume decreases om mixing

2. Formula for easy and common numerical:

(a) Molality:	$m = n_{solute}/w_{solvent}(kg)$
(b) Henry's Law	$p = K_H x$
(c) Relative lowering of vapour pressure	$(p^o_A - p_A)/p^o_A = i X_B$
(d) elevation of boiling point	$\Delta T_b = i K_b m$
(e) depression of freezing point	$\Delta T_f = i K_f m$
(f) osmotic pressure	$\pi = i CRT$

'i' stands for van't Hoff factor.

S.No.	Questions and Answer	Marks
Type 1	Assertion and Reasoning type questions (1 Mark Each)	

	For these Questions, two statements are given one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A). (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A). (c) Assertion (A) is true, but Reason (R) is false. (d) Assertion (A) is false, but Reason (R) is true.	1
1	Assertion(A): Molarity is more preferable than molality. Reason(R): Molarity depends on volume of solution whereas molality depends on mass of solvent and hence molality remains unchanged with temperature, pressure etc.	1
2	Assertion(A): Carbon dioxide is more soluble in water than oxygen Reason (R): Gas having higher partial pressure is more soluble	1
3	Assertion(A): 0.1M NaCl will have same osmotic pressure as that of 0.1M Urea solution. Reason(R): Solution with same concentration will have same osmotic pressure	1
4	Assertion(A): When a solution is separated from pure solvent by a semi permeable membrane, the solvent passes through it form pure solvent side to solution side. Reason(R): Osmosis of solvent occurs from a region of low concentrated solution to a region of high concentration of solution through semi permeable membrane.	1
5	Assertion(A): Total vapour pressure of a solution is always lesser than the vapour pressure of pure liquid at same temperature Reason(R): Vapour pressure of a liquid is directly proportional to its mole fraction in mixture.	1
Ans.	1(D) ; 2(B) ; 3(D) ; 4(A) ; 5(D)	
Type 2	**Very short Answer Question (1 Mark each)**	
1	Define Molality.	1
Ans.	No. of moles of solute dissolve per kg of solvent. Mathematically, $m=n_{solute}/w_{solvent}(kg)$	
2	State Henry's Law.	1
Ans.	The partial pressure of the gas in vapour phase (*p*) is proportional to the mole fraction of the gas (*x*) in the solution. Mathematically $p = K_H x$	1
3	State Raoult's Law for two volatile liquids.	1
Ans.	For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. Mathematically. $p_A = p^o_A$ x $p_B = p^o_B$	1

4	Explain why aquatic species are more comfortable in cold water rather than in warm water?	1
Ans.	Solubility of gases increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.	1
5	Define Azeotropes.	1
Ans.	Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.	1
6	Define abnormal molar mass.	1
Ans.	Such a molar mass that is either lower or higher than the expected or normal value is called abnormal molar mass.	1
7	Define molarity	1
Ans.	Molarity (*M*) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution. Unit: mol / L	1
8	When ‘i’ is found to be more than one?	1
Ans.	For dissociation of solute in the solution.	1
9	When ‘i’ is found to be less than one?	1
Ans.	For association of solute in the solution.	1
10	Why is air diluted with helium in the tanks used by scuba divers?	1
Ans.	To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium.	1
11	0·1 M KCl has higher boiling point than 0·1 M Glucose. Why?	1
Ans.	Value of vant Hoff factor for KCl is 2 and that of Glucose is 1.	1
12	Meat is preserved for a longer time by salting. Why?	1
Ans.	Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.	1
13	Write the formula to determine elevation of boiling point.	1
Ans.	$\Delta T_b = iK_b m$	1
14	Write the formula to determine depression of freezing point.	1
Ans.	$\Delta T_f = iK_f m$	1
15	Write the formula to determine osmotic pressure.	1
Ans.	$\pi = i(n/v)RT$	1
TYPE 3	**MCQs (1 Mark each)**	
1	Which of the following unit is useful in relating concentration of solution with its vapour pressure? (a) Mole fraction (b) Parts per million (c) Mass percentage (d) Molality	1
2	Low concentration of oxygen in the blood and tissues of people living at high altitude is due to (a) low temperature (b) low atmospheric pressure (c) high atmospheric pressure (d) both low temperature and high atmospheric pressure	1

3	Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixture will show a positive deviation from Raoult's law? (a) Methanol and acetone (b) Chloroform and acetone (c) Nitric acid and water (d) Phenol and aniline	1
4	Which of the following aqueous solution should have the highest boiling point? (a) l.0 M NaOH (b) 1.0 M Na_2SO_4 (c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3	1
5	In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgCl_2$ solution is (a) the same (b) about twice (c) about three times (d) about six times.	1
6	An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because (a) it gains water due to osmosis (b) it loses water due to 1reverse osmosis (c) it gains water due to reverse osmosis (d) it loses water due to osmosis	1
7	The value of van't Hoff factors for KCl, NaCl and K_2SO_4, respectively are (a) 2, 2 and 2 (b) 2, 2 and 3 (c) 1, 1, and 2 (d) 1, 1 and 1	1
8	When two liquids A and B are mixed, their boiling points become greater than both. The mixture is: (a) ideal solution (b) non-ideal solution with negative deviation from Raoult's law (c) non-ideal solution with positive deviation from Raoult's law (d) normal solution	1
9	Which of the following will form an ideal solution? (a) $C_2H_5OH$and water (b) HNO_3 and water (c) $CHCl_3$ and CH_3COCH_3 (d) C_6H_6 and $C_6H_5CH_3$	1
10	A 0.6% urea solution would be isotonic with: (a) 0.1 M glucose solution (b) 0.1 MKCl solution (c) 0.6% glucose solution (d) 0.6% NaCl solution	1
	ANSWERS of MCQs	
1	(a)	1
2	(b)	1
3	(a)	1
4	(b)	1
5	(c)	1
6	(d)	1
7	(b)	1
8	(b)	1
9	(d)	1
10	(c)	1
PART 4	**SHORT ANSWER QUESTIONS (2 MARKS each)**	1
1	For a 5% solution of urea (Molar mass = 60 g/mol), calculate the osmotic pressure at 300 K. [$R = 0{\cdot}0821$ L atm K^{-1} mol^{-1}]	2

<table>
<tr><td>Ans</td><td>π= CRT (Volume of solution = 100 mL)
π = (n/v) RT [n=5/60 and v = 0.1L
π = (5/60)0.0821x300 / 0.1
π = 20.5 atm. (½ mark may be deducted for no or incorrect unit)</td><td>½
½

1</td></tr>
<tr><td>2</td><td>Write two points of differences between ideal and non-ideal solution</td><td>2</td></tr>
<tr><td>Ans.</td><td><table>
<tr><td>Ideal solution</td><td>Non ideal solution</td></tr>
<tr><td>1. The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.</td><td>1.When a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution.</td></tr>
<tr><td>2.$\Delta_{mix}H = 0$,</td><td>2.$\Delta_{mix}H \neq 0$,</td></tr>
<tr><td>3.$\Delta_{mix}V = 0$</td><td>3.$\Delta_{mix}V \neq 0$</td></tr>
</table>
Or any points</td><td>1
1</td></tr>
<tr><td>3</td><td>Write two points of differences between positive and negative deviation</td><td>2</td></tr>
<tr><td></td><td><table>
<tr><td>Positive deviation from Raoult's Law</td><td>Negative deviation from Raoult's Law</td></tr>
<tr><td>1. $p_A > p^o_A$; $p_B > p^o_B$</td><td>$p_A < p^o_A$; $p_B < p^o_B$</td></tr>
<tr><td>2. $\Delta_{mix}H > 0$</td><td>$\Delta_{mix}H < 0$</td></tr>
<tr><td>3. $\Delta_{mix}V > 0$</td><td>$\Delta_{mix}V < 0$</td></tr>
</table>
Or any suitable points.</td><td>1
1</td></tr>
<tr><td>4</td><td>Calculate the solubility of CO_2 in water at 298 K under 760 mm Hg.
(K_H for CO_2 in water at 298 K is 1.25×10^6 mm Hg)</td><td>2</td></tr>
<tr><td></td><td>$p = K_H x$
$x = p/K_H$
$x = 760 / (1.25 \times 10^6)$
$= 6.08 \times 10^{-4}$</td><td>½
½
1</td></tr>
<tr><td>5</td><td>Calculate Van't Hoff factor for (i) $K_4[Fe(CN)_6]$ 100% dissociated in water
(ii) Acetic acid dimerises in benzene(100%)</td><td>2</td></tr>
<tr><td>Ans.</td><td>(i) $1\ K_4[Fe(CN)_6] \rightarrow 4K^+ + 1\ [Fe(CN)_6]^{4-}$
i = 5/1 = 5
(ii) $2\ CH_3COOH \rightarrow 1\ (CH_3COOH)_2$ (dimerises)
i = ½</td><td>½
½
½
½</td></tr>
<tr><td>PART 5</td><td>LONG ANSWER QUESTIONS (3 MARKS)</td><td></td></tr>
<tr><td>1</td><td>A 10% solution (by mass) of sucrose in water has a freezing point of 269·15 K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273·15 K.</td><td>3</td></tr>
<tr><td>Ans.</td><td>$\Delta T_f = K_f m$
Here , $m = w_2 x\ 1000/ M_2 X M_1$
$273.15-269.15 = K_f \times 10 \times 1000/ 342 \times 90$
$K_f = 12.3$ K kg/mol
$\Delta T_f = K_f m = 12.3 \times 10 \times 1000/ 180 \times 90 = 7.6$ K
$T_f = 273.15 - 7.6 = 265.55$ K (or any other correct method)</td><td>1

1

1</td></tr>
<tr><td>2</td><td>A solution contains 5·85 g NaCl (Molar mass = 58·5 g mol^{-1}) per</td><td>3</td></tr>
</table>

	litre of solution. It has an osmotic pressure of 4·75 atm at 27^{0}C. Calculate the degree of dissociation of NaCl in this solution. *3* (Given : R = 0·082 L atm K^{-1} mol^{-1})	
Ans.	Π =iCRT 4.75 = i(5.85/58.5)0.082x300 So, i = 1.93 Degree of dissociation(α) = (i-1) / (n - 1) = (1.93 - 1) / (2 - 1) = 0.93 or 93%	1 1 1
3	The freezing point of a solution containing 5g of benzoic acid (M = 122 g mol^{-1}) in 35g of benzene is depressed by 2.94 K. What is the percentage association of benzoic acid if it forms a dimer in solution? (K_f for benzene = 4.9 K kg mol^{-1})	3
Ans	$\Delta T_f = iK_f m$ Here , m = w_2x 1000/ (M_2XM_1) 2.94= i x 4.9 x 5x1000/ (122 x 35) so, i = 0.512 Percentage association of benzoic acid in benzene α = (I - 1) / (1/n - 1) = (0.512 - 1) / (1/2 - 1) = 0.976 = 97.6%	1 1 1

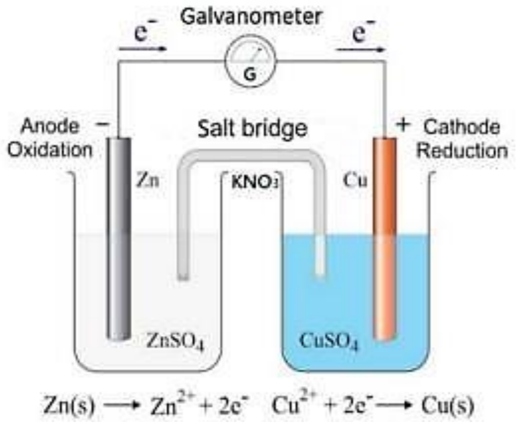
UNIT 2 ELECTROCHEMISTRY

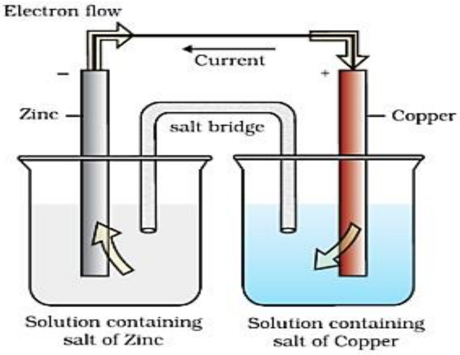
ELECTROCHEMISTRY: The branch of chemistry that deals with the relations between electrical and chemical phenomena.

Electrochemical cell: A device in which chemical energy of the redox reaction is converted into electrical energy. e.g., Daniel cell or Galvanic cell the overall cell reaction is:

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

The Daniel cell is represented as: $Zn(s)| Zn^{2+}(aq)(C_1) || Cu^{2+}(aq) (C_2)| Cu(s)$





Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

Salt Bridge and Its Functions: It consists KCl, KNO_3 or NH_4Cl. It helps in flow of ions by completing the circuit and maintains electrical neutrality.

Measurement of electrode potential: Potential of individual half-cell cannot be measured but we can measure the difference between the two half-cell potentials that gives the emf of the cell by using SHE (Standard Hydrogen electrode).

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

Nernst equation: It is an equation which gives the relationship between electrode potential and the concentration of ions. For an electrode reaction (reduction reaction),

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

Nernst equation can be written as:

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

where, $E^{o}_{Mn+/M}$ = Standard electrode potential, R= 8.314JK /mol, T = Temperature in kelvin,

n = No. of electrons gained, F = Faraday constant (96500 C /mol)

Nernst equation can be written as for a general reaction- aA+ bB → cC + dD

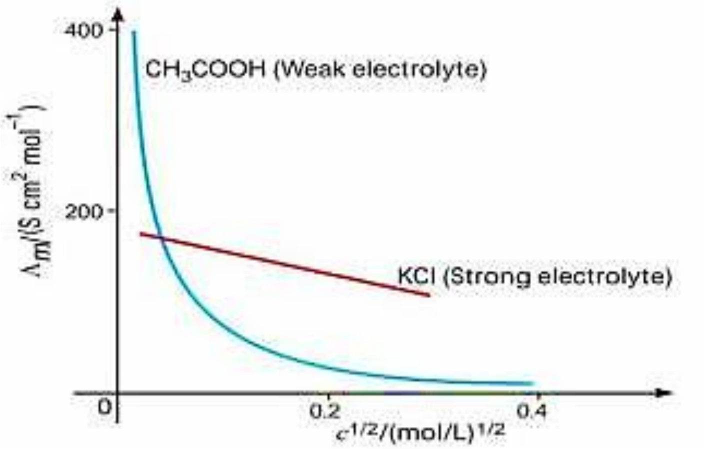
$E_{cell} = E^{0}_{cell} - 2.303RT/nF \log [Products]/[Reactants]$

$E_{cell} = E^{0}_{cell} - 0.0591/n \log [P]/[R]$ (at 298K)

Electrochemical cell and Gibbs Free Energy: The work done by a reversible galvanic cell is equal to decrease in its free energy. Mathematically, $\Delta G = -nFE_{cell}$

Limiting molar conductivity: When concentration approaches zero i.e., at infinite dilution, the molarconductivity is known as limiting molar conductivity (Λ°_{m}).

Variation of Conductivity and Molar Conductivity with Concentration:



For strong and weak electrolytes: Λ_m increases as concentration decreases but does not reach a constant value even at infinite dilution. Hence, their Λ°_{m} cannot be determined experimentally.

Kohlrausch's Law: It states that the limiting molarconductivity of an electrolyte can be represented asthe sum of the individual contributions of the anionand cation of the electrolyte. $\Lambda^{o} = v_{+}\lambda^{\circ}_{+} + v_{-}\lambda^{\circ}_{-}$

Applications of Kohlrausch's law:

Calculation of molar conductivities of weak electrolyte at infinite dilution.
i.e.,$\Lambda^{\circ}_{m}(CH_3COOH) = \Lambda^{\circ}_{m}(CH_3COONa) + \Lambda^{\circ}_{m}(HCl) - \Lambda^{\circ}_{m}(NaCl)$

Determination of degree of dissociation of weak electrolytes: Degree of dissociation (α) = $\Lambda m / \Lambda^{\circ} m$

Faraday's first law of electrolysis: The amount of chemical reaction which occurs at any electrode duringelectrolysis is proportional to the quantity of electricity passed through the electrolyte.

$m = Z \times I \times t$ where Z = Electrochemical equivalent.

Faraday's second law of electrolysis: Amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

$$W_1 / E_1 = W_2 / E_2$$

Battery: Combination of galvanic cells in series and used as a source of electrical energy.

(i) Primary batteries are non-chargeable batteries such as Leclanche cell and Dry cell. Secondary batteries are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.

Dry cell (Leclanche cell): The anode consists of a zinc container and the cathode is a graphite electrodesurrounded by powdered MnO_2 and C. The space is filled with paste of NH_4Cl and $ZnCl_2$.

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

At cathode: $MnO_2(s) + NH_4^+(aq) + 2e^- \rightarrow MnO(OH) + NH_3$

The net reaction: $Zn + NH_4^+(aq) + MnO_2 \rightarrow Zn^{2+} + MnO(OH) + NH_3$.

Fuel cells: Electrical cells that are designated to convert the energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells. the cell reactionsare:

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

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

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

Multiple Choice Questions (MCQs) (1 Mark each)

1. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is
   (a) 4 F (b) 3 F (c) 3.5 F (d) 5 F

2. Which of the following does not belong in the category of electrochemical cell?
   a) voltaic cell b) photovoltaic cell c) electrolytic cell d) fuel cell.

3. Conductivity of aqueous solutions of an electrolyte depend on:
   a) molecular mass of the electrolyte b) boiling point of the solvent.
   c) degree of ionization d) volume of the solvent.

4.The conductivity of electrolytic conductors is due to:
   a) flow of free mobile electrons b) movement of ions
   c) either movement of electrons or ions d) cannot be said.

5. In a fuel cell, which of the following can be utilized as a fuel?
   a) nitrogen b) argon c) hydrogen d) helium.

6. Galvanised iron sheets are coated with (a) Carbon (b) Copper (c) Zinc (d) Nickel.

7. The standard reduction potentials of X, Y, Z metals are 0.52, -3.03, -1.18 respectively. The order of reducing power of the corresponding metals is:
(a) Y > Z > X (b) X > Y > Z (c) Z > Y > X (d) Z > X > Y.

8.Which of the following is not a good conductor?
(a) Cu (b) NaCl (aq) (c) NaCl (molten) (d) NaCl(s)

9. Which of the following is a secondary cell?
(a) Leclanche cell (b) Lead storage battery
(c) Concentration cell (d) All of these.

10.Which of the following is supplied to the cathode of a fuel cell?
a) Hydrogen b) Nitrogen c) Oxygen d) Chlorine.

11. Out of the following which one is an example of primary cell
a) fuel cell b) lead storage cell c) dry cell d) all of the above.

12. The standard hydrogen electrode potential is zero, because
a) hydrogen oxidized easily b) electrode potential is considered as zero
c) hydrogen atom has only one electron d) hydrogen is a very light element.

13. Faraday's law of electrolysis are related to the
a) atomic no. of the cation b) atomic no. of the anion
c) equivalent weight of the electrolyte d) speed of the cation.

ANSWERS of MCQs: 1.(b) 2.(b) 3(c) 4(b) 5(c) 6(c) 7(a) 8(d) 9(b) 10(c) 11(c) 12(b) 13(c)

ASSERTION & REASON TYPE OF QUESTIONS (1mark)

The question given below consist of an assertion and a reason use the following key to choose appropriate answer.
a) Both assertion and reason are correct and reason is the correct explanation of the assertion
b) Both assertion and reason are correct and reason is not the correct explanation of the assertion
c) Assertion is correct but reason is incorrect
d) Assertion is wrong but reason is correct.

1. Assertion: Conductivity of all electrolytes decreases on dilution.
Reason: On dilution, number of ions per unit volume decreases.

2. Assertion: Mercury cell does not give steady potential.
Reason: In the cell reaction, ions are not involved in solution.

3. Assertion: Molar conductivity of strong electrolytes increases with dilution.
Reason: On dilution inter ionic interaction increases.

4. Assertion: Electrolytic conduction increases with temperature
Reason: On increasing the temperature mobility of ion increases.

5) Assertion: Current stops flowing when $E_{cell} = 0$
Reason: Equilibrium of the cell reaction is attained.

6) Assertion: Galvanic cell containing hydrogen, methane, methanol etc as fuels are called fuel cells.
Reason: They are designed to convert the energy of combustion of fuels directly into electrical energy.

Answers of Assertion-reason questions.: 1-a, 2-d, 3-c, 4-a, 5-a, 6-a

Very Short Answer type Question (1 Mark)

Q1) What is meant by 'limiting molar conductivity'?
Ans. The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ_m^0.

Q2. Express the relation between conductivity and molar conductivity of a solution held in a cell.
Ans. $\Lambda_m = 1000K/ C$

Q3.Define Fuel cell
Ans. Fuel cells : These cells are the devices which convert the energy produced during combustion of fuels like H_2, CH_4, etc. directly into electrical energy.

Q4. How much charge in Faraday is required for the reduction of 1 mol of Ag^+ to Ag?
Ans. $Ag^+ + e^- \longrightarrow Ag(s)$
1 Faraday of charge is required (charge on 1 mole of electrons).

Q5. Accounts for the following:
(i) Rusting of iron is quicker in saline water than in ordinary water.
Ans (i) Electrolytes present in sea water favour the formation of more electrochemical cells on the surface of iron leading to increase in the rate of rusting.

Q6. Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn
Ans: The following is the order in which the given metals displace each other from the solution of their salts. Mg, Al, Zn, Fe, Cu.

Q7. Define Molar conductivity (Λ_m)
Ans: (i) Molar conductivity: It is defined as the conductance of solution containing 1 mole of electrolyte placed in a cell having electrodes unit distance apart having sufficient area of cross-section to hold electrolyte.

Q8. What are Secondary batteries?
Ans. Secondary battery: Those batteries which can be recharged are called secondary batteries, e.g., lead storage battery, Nickel-cadmium battery.
Q9. What is the emf of a cell?
Ans. The electromotive force or emf of a cell refers to the maximum potential difference between the two electrodes of a cell.

Q10. What is used in a dry cell as an electrolyte?
Ans. A paste of NH_4Cl, $ZnCl_2$ (MnO_2 and Carbon) is used as an electrolyte in a dry cell.

Q11. Which metal is used in a hydrogen electrode?
Ans. Platinum foils are used in hydrogen electrodes.

Q12. What is the purpose of using salt bridges in galvanic cells?
Ans. Salt bridges are used in galvanic cells to complete the inner circuit and to maintain the electrical neutrality of the solution.

Q13. What is corrosion?
Ans. Corrosion can be defined as the process of deterioration of metals because of their reaction with air and water. In this process, sulphides, oxides, carbonates, hydroxides, etc. are produced that slowly damage the metals. Rusting of iron is an example of corrosion. Rust is an oxide of iron (Fe_2O_3, x H_2O).

Q14. When does the emf of a cell become zero?
Ans. When the cell reaction attains the stage of equilibrium, the emf of the cell becomes zero.

Q15. What is the significance of the internal circuit in a galvanic cell?
Ans. Ions flow in the internal circuit of a galvanic cell.

Short Answer Type Question (2 Marks)

Q1. A cell reaction is considered spontaneous if the overall emf of the cell is positive. Comment.
Ans. When the emf of a cell is positive, then the Gibbs free energy of the overall reaction is less than zero.
$\Delta G = -nFEcell$
Hence, the cell reaction is considered spontaneous.

Q2. Can you store copper sulphate solutions in a zinc pot?
Ans. Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution. $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$
Hence, copper sulphate solution cannot be stored in a zinc pot.

Q.3 Calculate the emf of the cell in which the following reaction takes place:

$$Ni_{(s)} + 2Ag^{+}(0.002\ M) \rightarrow Ni^{2+}(0.160\ M) + 2Ag_{(s)}$$

Given that $E^{o}_{cell} = 1.05$ V
Ans. Applying Nernst equation, we have:

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$

$$= 1.05 - \frac{0.0591}{2}\log\frac{(0.160)}{(0.002)^{2}}$$

$$= 1.05 - 0.02955\ \log\frac{0.16}{0.000004}$$

$= 1.05 - 0.02955 \log 4 \times 104$
$= 1.05 - 0.02955 (\log 10000 + \log 4)$
$= 1.05 - 0.02955 (4 + 0.6021)$
$= 0.914$ V

Q4. State one merit and one demerit of nickel-cadmium cell over lead storage cell.
Ans. Nickel-Cadmium cell has longer life than the lead storage cell but more expensive to manufacture.

Q5 Suggest two materials other than hydrogen that can be used as fuels in fuel cells.
Ans. Methane and methanol can be used as fuels in fuel cells.

Q6. Define electrochemical cell. What happens when applied external potential becomes greater than E^{θ} cell of electrochemical cell?
Ans. Electrochemical cell is a device that converts the chemical energy of a spontaneous redox reaction into electrical energy. If the external applied potential becomes greater than Eθ cell of electrochemical cell, the reactions get reversed and electrochemical cell now function as an electrolytic cell.

LONG Answer Type Questions (3 marks)
Q.1) Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show: (i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell. (iii) Individual reaction at each electrode.
Ans. The galvanic cell in which the given reaction takes place is depicted as:

$$Zn_{(s)}\left|Zn^{2+}{}_{(aq)}\right\|Ag^{+}{}_{(aq)}\left|Ag_{(s)}\right.$$

(i) Zn electrode (anode) is negatively charged.
(ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.
(iii) The reaction taking place at the anode is given by,

$$Zn_{(s)} \longrightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

The reaction taking place at the cathode is given by,

$$Ag^{+}{}_{(aq)} + e^- \longrightarrow Ag_{(s)}$$

2. From the given cells,
Lead storage cell, Mercury cell, Fuel cell and Dry cell,
Answer the following:
i) Which cell is used in hearing aids?
ii) Which cell was used in Apollo space programme?
iii) Which cell is used in automobiles and inverters?
iv) Which cell does not have long life?
Ans. Mercury Cell ii) Fuel cell iii) Lead Storage cell iv) Dry cell.

Q 3. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1}. Calculate its molar conductivity?
Ans. Given, $\kappa = 0.0248\ S\ cm^{-1}$ $c = 0.20\ M$

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

∴ Molar conductivity, $\Lambda_m = \frac{0.0248\ x\ 1000}{0.2}$ = = 124 $S\ cm^2\ mol^{-1}$

Q4. What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a Lead Storage battery when current is drawn from it.

Ans. It is secondary battery. The cell reactions when the battery is in use are given below:
Anode: $Pb(s)+SO_4^{2-}(aq)$ -----> $PbSO_4$ (s) + $2e^-$
Cathode : PbO_2 (s) + SO_4^{2-}(aq) + 4 H^+ (aq) + $2e^-$ → $PbSO_4$ (s) + $2H_2O$ (l)
Overall Reaction:
Pb (s) + PbO_2 (s) + $2H_2SO_4$ (aq) ----→ $2PbSO_4$ (s) + $2H_2O$ (l)

Q.5) State Kohlrausch’s law of independent migration of ions. Why does the conductivity of a solution decreases with dilution?
Ans. The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
The conductivity of a solution is related with the number of ions present per unit volume of the solution. When the solution is diluted, the number of ions per unit volume decreases. Hence , conductivity of the solution decreases.

3. CHEMICAL KINETICS

MINIMUM LEVEL OF LEARNING: Important terms and Concepts

***Rate of reaction**-The change in concentration of any one of the reactant or product per unit time. eg- R ---→ P, then Rate= $-\Delta[R] / \Delta t = +\Delta[P] / \Delta t$
***Unit of Rate-** mol / L / s or mol / L / min
Example: $N_2(g) + 3H_{2(g)} \rightarrow 2NH_3(g)$
Rate of reaction of N_2 = $r_{N_2} = -\frac{\Delta[N_2]}{\Delta t}$ & Rate of reaction of H_2 = $r_{H_2} = -\frac{\Delta[H_2]}{\Delta t}$
Rate of formation of NH_3 = $r_{NH_3} = +\frac{\Delta[NH_3]}{\Delta t}$
General rate of reaction: $r = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$
For a chemical reaction:

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

Average rate of reaction: $(r_{av}) = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$

where rate of disappearance of A, $r_A = -\frac{\Delta[A]}{\Delta t}$, rate of disappearance of B, $r_B = -\frac{\Delta[B]}{\Delta t}$

and rate of formation of C, $r_C = +\frac{\Delta[C]}{\Delta t}$ and rate of formation of D, $r_D = +\frac{\Delta[D]}{\Delta t}$

***Rate Law**-It relates rate with concentration of reactants.eg- A +B → P, then $dx/dt= k\{A\}^x\{B\}^y$
***Factors affecting rate of a reaction**- a) greater concentration -rate faster,
b) greater surface area-rate faster,
c) higher temperature-higher rate,
d) lower activation energy-higher rate of reaction.

***Molecularity-**Number of molecules which collide simultaneously to form products.
Eg. $H_{2(g)} + Cl_2$ (g) → 2HCl(g), is bimolecular reaction.

* **Elementary step in a reaction:** Those reactions which take place in one step are called elementary reactions. Example: Reaction between H_2, and I_2 to form 2HI ($H_2 + I_2 \rightarrow 2HI$)
***A complex reaction** is a multiple steps reaction. It involves an intermediate and multiple transition.

In general; $aA + bB \rightarrow$ Products, where a & b are stoichiometric coefficients of reactants A & B.

From experiments of kinetic studies, the rate law expression is found to be

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

Or, $r = -\frac{d[R]}{dt} = k\,[A]^x.[B]^y$ where values x & y are determined experimentally.

These may or may not be equal to a & b respectively. (**k is called rate constant or specific rate constant**)

The rate law or rate law expression may be defined as " the mathematical expression in which the rate of a reaction is given in terms of molar concentration of reactants with each term raised to same power which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation".

Order of a reaction: It is defined as the sum of the powers to which the concentration terms are raised in the rate law equation to express the observed rate of the reaction.

The sum of power of the concentration terms in the rate law equation is called order of a reaction.

In general, $aA + bB \rightarrow$ Products, Rate law expression is determined experimentally as

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

Hence, order in respect to reactant A is x. order of reactant B is y, so overall order of reaction 'n' = x + y.

This is to note that (i) order of a reaction is determined experimentally which cannot be predicted from the chemical reaction. (ii) Order (n) can be 0,1, 2, 3, fractional and negative.

Examples:

(i) First order reaction: A → product, Rate law expression: $r = -\frac{d[R]}{dt} = k\,[A]$ Here, n = 1 (order=1)

(a) $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ Rate law expression: $r = k\,[N_2O_5]$ [or $r = k\,[A]$]

Unit of rate constant $k = \frac{r}{[A]} = \frac{mol\,L^{-1}s^{-1}}{mol\,L^{-1}} = s^{-1}$ or time^{-1}

(ii) Second order reaction A + B → product or 2A → product

Rate law expression: $r = -\frac{d[R]}{dt} = k\,[A]^2$ or $k[A].[B]$ Here, n = 2. (order=2)

Example: $2NO_2 \rightarrow 2NO + O_2$ Rate law expression: $r = k\,[NO_2]^2$ Here, n = 2.

Unit of rate constant $k = \frac{r}{[A]^2} = \frac{mol\,L^{-1}s^{-1}}{(mol\,L^{-1})^2} = L\,mol^{-1}s^{-1}$.

*Example for ZERO ORDER REACTION

Example: (a) $2NH_3(g) \xrightarrow{Pt,\ 1130K} N_2(g) + 3H_2(g)$:

Rate law: $r = -\frac{d[R]}{dt} = k\,[NH_3]^0$ or rate $r = k$

.

Reactions	**Units of k, reaction rate in solution**	**Units of k in gaseous reactions**
Zero order	**mol L^{-1} s^{-1}**	**atm s^{-1}**
First order	**s^{-1}**	**s^{-1}**
Second order	**L mol^{-1} s^{-1}**	**atm^{-1} s^{-1}**
Third order	**$L^2 mol^{-2}$ s^{-1}**	**atm^{-2} s^{-1}**
nth order	**$(mol\ L^{-1})^{1-n}$ s^{-1}**	**$(atm)^{1-n}$ s^{-1}**

	Order of a reaction	Molecularity of a reaction
1	Order of a reaction is defined as the sum of the exponents of molar concentrations of reactants in the rate law equation.	Molecularity of a reaction is the number of atoms, ions or molecules that must collide with one another to form products in a chemical reaction.
2	It can be fractional as well as zero	It can not be fractional or zero.
3	It is determined experimentally.	It is determined theoretically from the chemical eqn.
4	Order of reaction is applicable to elementary as well as complex reaction.	Molecularity is applicable only to elementary reaction. It has no meaning for a complex reaction
5	Negative order of a reaction is possible. e.g. $2O_3 \rightarrow 3O_2$ Rate = $k[O_3]^2[O_2]^{-1}$ Order with respect to O_2 is -1.	Molecularity can never be negative.

Pseudo unimolecular reaction or pseudo first order reactions:

The order of a reaction can be altered by different conditions. Some higher order reactions may behave as first order reaction if except one reactant, the concentration of other reactants are taken in large excess as constant such that rate of reaction depends upon the concentration of one reactant only.

Example: (1) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ (molecularity = 2)
(sucrose) (excess) (glucose) (fructose)

The expected rate law equation: rate (r) = k[sucrose][water]

Here, [water] = constant , being large excess, so, k[water] = k´ (a new constant)

Hence, the rate law equation becomes rate (r) = k´[sucrose] & order = 1

(i.e. pseudo unimolecular reaction, as the rate depends on the concentration of sucrose only)

Table for zero and first order reactions:

Order	**Rate law**	**Integrated rate law**	**Straight line plot**	**Half life ($t_{½}$)**	**Unit of rate constant (k)**
0	**r = $-\frac{d[R]}{dt}$ = k**	**k = $\frac{[R]_0-[R]}{t}$**	**[R] vs t**	$\frac{[R]_0}{2k}$	**Conc. $time^{-1}$ or mol L^{-1} s^{-1}**
1	**r = $-\frac{d[R]}{dt}$ = k [A]**	**k = $\frac{2.303}{t}$ log_{10} $\frac{[R]_0}{[R]}$**	**ln[R] vs t**	$\frac{0.693}{k}$	**time $^{-1}$ or s^{-1}**

ACTIVATION ENERGY: Activated complex in the complex is formed on collision of reactants with maximum energy and least stability. The minimum energy over and above the average energy of the reactants required to form activated complex is called **activation energy (E_a).**

Higher the value of activation energy (E_a), the reaction is slow.

Lower the value of activation energy (E_a) the reaction is fast.

Arrhenius equation:

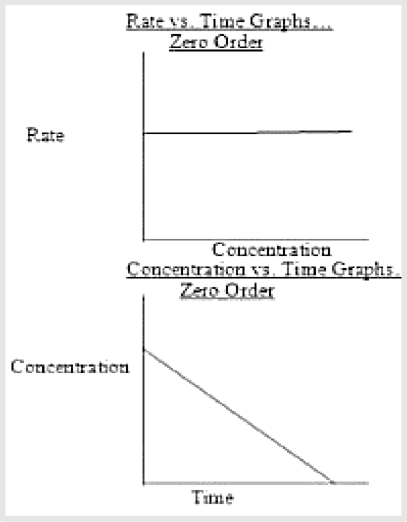
$$k = A\,e^{\frac{-E_a}{RT}}$$

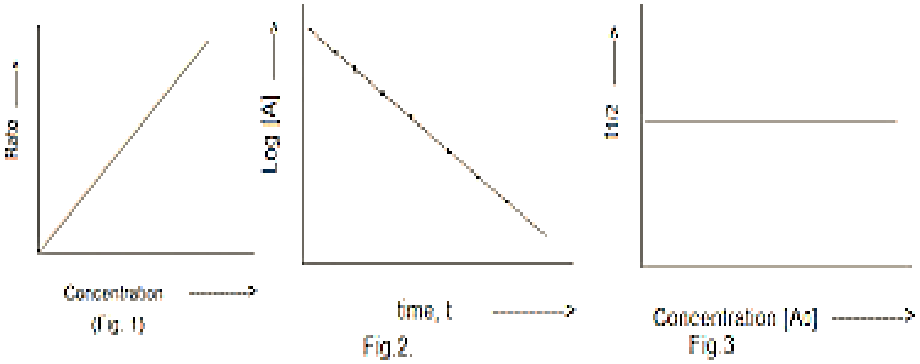
This equation is known as Arrhenius equation.

Here, A is called pre exponential factor or frequency factor or Arrhenius factor. & E_a is called activation energy at T kelvin..

And $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$ Here $T_2 > T_1$ or $k_2 > k_1$

GRAPH OF ZERO ORDER and FIRST ORDER REACTIONS-





First order reactions

QUESTIONS & ANSWERS

<u>MCQ QUESTIONS - (1 mark each)</u>

1. Which of the following factors does NOT affect the rate of a chemical reaction?
   a. Temperature b. Concentration of reactants
   c. Nature of reactants d. Volume of the reaction vessel

Ans. d.

2. The rate of a chemical reaction can be determined by measuring:
   a. The change in enthalpy (∆H) of the reaction
   b. The change in Gibbs free energy (∆G) of the reaction
   c. The change in concentration of reactants or products with time
   d. The change in entropy (∆S) of the reaction

Ans. c.

3. In a reaction, if the concentration of reactants is doubled, how will it affect the reaction rate?
   a. The rate will remain the same b. The rate will decrease by half
   c. The rate will double d. The rate will quadruple

Ans. c.

4. Which of the following is an example of a first-order reaction?
   a. Radioactive decay b. First-aid medical kit expiration
   c. Rusting of iron d. Digestion of food

Ans. a.

5. The rate constant (k) of a reaction depends on:

a. Temperature only b. Temperature and concentration of reactants
c. Nature of reactants only d. Pressure and volume of the reaction vessel

Ans. b.

6. A reaction has a rate constant of 0.05 s^{-1}. What is the half-life of the reaction?
a. 5 seconds b. 10 second c. 20 seconds d. 50 seconds

Ans. b.

7. Which of the following factors can increase the rate of a reaction?
a. Decreasing the temperature b. Decreasing the surface area of reactants
c. Adding a catalyst d. Decreasing the concentration of reactants

Ans. c

8. The activation energy of a reaction is a measure of:
a. The energy released during the reaction b. The energy of the products
c. The energy barrier that must be overcome for the reaction to occur
d. The total energy change in the reaction

Ans c.

9.In a chemical reaction X--→Y it is found that the rate of a reaction doubles when the concentration of X is increased four times. The order of the reaction with respect to X is
a.1 b.0 c.2 d.1/2

Ans. d.

10.The half-life for a chemical reaction is 30min.The time taken for 90% reaction to complete will be a.100min b.200 min c.300 min d.400 min

Ans. a.

11.For a zero-order reaction, the slope of plot of {R} vs time is
a. –k/2.303 b. –k c. 2.303/k d. $R_0/2k$

Ans. b.

12. The unit of rate constant for a first order reaction A+B→C
a. Mol / L / s b. s^{-1} c. mol /L d. L / mol / s

Ans. b.

ASSERTION-REASON QUESTIONS (1MARK)

The question given below consist of an assertion and a reason use the following key to choose appropriate answer.

a. Both the assertion and reason are correct, and the reason is a correct explanation of the assertion.

b. Both the assertion and reason are correct, but the reason is not a correct explanation of the assertion.

c. The assertion is correct, but the reason is incorrect.

d. Both the assertion is in correct and reason are correct.

13. **Assertion**: The rate of a chemical reaction increases with an increase in the temperature.
Reason: An increase in temperature provides reactant molecules with more kinetic energy, leading to a greater number of effective collisions.

Ans-a.

14. **Assertion**: Catalysts increase the rate of a chemical reaction.
Reason: Catalysts lower the activation energy required for the reaction to proceed.
Ans- a.

15.**Assertion**-All collisions of reactant molecules lead to product formation.
Reason-Only those collisions in which molecules have correct orientation and sufficient energy lead to compound formation.
Ans- d.

16. **Assertion**-For a complex reactions, molecularity and order are not the same.
Reason-Order of reaction may be zero.
Ans-b.

17. **Assertion**-Half-life of a zero order reaction doubles if initial concentration is doubled.
Reason- Rate of a zero order doubles if the initial concentration is doubled.
Ans- c.

VERY SHORT ANSWER QUESTIONS (VSA) – 1 MARK each

18. State a condition where a bimolecular reaction is kinetically first order.
Ans. In pseudo-unimolecular reaction.

19. Give an example of fractional order reaction.
Ans. Decomposition of acetaldehyde.

20. Will the rate constant depend on T if the activation energy is zero?
Ans. Temperature have no effect on rate constant.

21.It is found that large number of colliding molecules have energy more than threshold value yet the reaction is slow?
Ans. due to improper orientation of colliding molecules.

22.Why equilibrium constant does not change in the presence of catalyst?
Ans. As catalyst speeds up the forward reaction, hence equilibrium is attained quickly only.

23.What is the rate determining step of a reaction?
Ans. The slowest step is the rate determining step.

24.Give one axample of a reaction where molecularity and order are the same.
Ans. Decomposition of HI(g) on Pt surface.

25.The rate of a reaction at 30^0C is x, then what will be the rate of reaction at 60^0C?
Ans- For every 10^0C rise the rate of reaction doubles. therefore $2^3x = 8x$ ie.8 times approximately.

26.For a reaction, A +B-→Product, the rate law is given by $r = k[A]^{1/2}[B]^2$. What is the order of reaction?
Ans. Order= ½ + 2 = 2.5

27.In a reaction if the concentration of reactant A is tripled,the rate of reaction becomes twenty seven times. what is the order?
Ans. $r_1 = k[A]^x$,$r_2 = k[3A]^x$, $r_2 / r_1 = 3^x = 27$, $x=3$

28.Define Specific reaction rate?

Ans. It is the rate of a reaction when molar concentration of each reactants is unity.

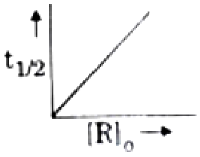
29.Express the rate in terms of disappearance of hydrogen in the reaction-
$3H_2$(g+ N_2(g) $\dashrightarrow$ $2NH_3$(g)
Ans. $r = -1/3\ d[H_2]/dt$

30. Oxygen is available plenty in air, yet fuels do not burn by themselves. why?
Ans. the activation energy for fuels is very high at room temperature.

31. In redox titration between $KMnO_4$ and oxalic acid, we heat oxalic acid solution before titration. why?
Ans. On heating reaction becomes faster.

32.Draw a plot between half-life and R_0 in the case of zero order reaction.

Ans.



SHORT ANSWER QUESTIONS-(SA)- (2MARKS each)

33. A first order reaction has a $k=1\times10^{-3}$/s. How long will 5 g of this reactant take to reduce to 3 g? (Hint- t=2.303/k log(A0/A), log5=0.6989, log3=0.4771)
Ans, $t = 2.303/1\times 10^{-3}$ [log(5)/log(3)] = 511 s

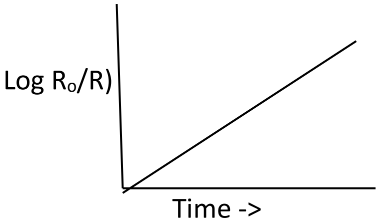
34.Distinguish between order and molecularity.
Ans-

ORDER	MOLECULARITY
i) It is experimentally determined value ie.graphically.	i) It is determined from balanced equation
ii)It can take any value from zero integer, fractional, positive, negative	ii) It can have whole number integer value

35.In a reaction, $2N_2O_{5(g)} \dashrightarrow 4NO_2(g) + O_2(g)$, the concentration of N_2O_5 decreases from 0.5mol /L to 0.4 mol / L in 10min. Calculate the average rate of this reaction and rate of production of NO_2 during this period.

Ans. Average rate= $-1/2\ \Delta[N_2O_5]/\Delta t$ = -(0.4-0.5)/(2x 10 min) = 0.005mol /L / min
For given equation,
½ x rate of disappearance of N_2O_5= ¼ x rate of formation of NO_2
=> rate of formation of NO_2 = $\dfrac{4\times -\Delta(N_2O_5)}{2\times \Delta t}$ = 4 x0.005 =0.02 mol / L / min

36. Observe the graph and answer the following questions-



i) What is the order of reaction?
ii) What is the slope of curve?

Ans. i) first order (ii) slope = k/2.303

37. . At E_{a1} and E_{a2} of two reactions are 40j/mol and 80j/mol. Which of the two has a larger value of rate constant.
Ans. (hint- lower E_a → faster rate → greater k)
k= A $e^{-(Ea/RT)}$. Hence E_{a1} has larger rate constant.

38. For the reaction in a closed vessel: $2NO (g) + O_2(g) \rightarrow 2NO_2(g)$; Rate = k $[NO]^2 [O_2]$
If the volume of the reaction vessel is doubled, how would it affect the rate of the reaction?
Ans. If volume is doubled conc. of each reactant will be halved so rate will be 1/8 volume of initial value.

LONG ANSWER QUESTIONS(LA)-(3MARKS)

39. .i) Find 2/3rd life of a first order reaction where $k=5.4x10^{-14}/s$.
Given-log3=0.4771
Ans. (Hint- t = 2.303 / k log (A_0 / (A_0/3) = 2.303 / 5.4 x 10^{-14} log (3)
= 2 x10^{13}s

(ii) For the reaction the proposed mechanism is (i) $NO_2 + NO_2 \text{-----}\rightarrow NO + NO_3$ (slow)
(ii) $NO_3 + CO \text{-----}\rightarrow CO_2 + NO_2$ (fast)
Write the rate law for the above.
Ans. it is the slowest rate determining step. hence, rate = k $[NO_2]^2$

40. (i) For a reaction A+B---→Products, the rate law is Rate=k(A)$(B)^{3/2}$, Can the reaction be elementary?
Ans. order w.r.t. B should have been 1, so not elementary)

(ii) A reaction is 50% complete in 2 hours and 75% complete in 4hours.What is the order of the reaction.
Ans. Half-life remains a constant so first order.ie. (The amount left after one half period is half the original amount and amount left after two half periods is one fourth.)

41. A first order reaction is 50% complete in 25mins.Calculate the time for 80% completion of the reaction. Given log 5=0.6990
Ans. k = 0.693 / $t_{1/2}$, $t_{80\%}$ = 2.303 / k log (A^0/A),
k = 0.693/25 min = 0.277 min
= 2.303/0.277 log(100/20)
= 58.113 mins

42. The initial concentration of N_2O_5 in the following 1st order reaction $N_2O_5(g) \rightarrow 2 NO_2(g) + ½ O_2 (g)$ was 1.24 × 10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20 × 10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.
Ans. For a first order reaction, log $[R]_1/[R]_2 = k(t_2-t_1)$ / 2.303
k = 2.303/(t_2-t_1) x log $[R]_1$ / $[R]_2$
= 2.303 / (60−0) x log (1.24 × 10^{-2} / 0.20 × 10^{-2}) = 2.303/60 x log (6.2) min^{-1}

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

43. Match the statement in column I and column II

Column I		Column II	
a	Catalyst alter the rate of reaction	p	Cannot be fraction or zero
b	molecularity	q	Proper orientation is not there always
c	2nd half-life of first order reaction	r	By lowering the E_a energy
d	$e^{-Ea/RT}$	s	Is same as the first
e	Energetically favorable reactions are sometimes slow	t	Total probability is one
f	Area under Maxwell Boltzmann curve is constant	u	Fraction of molecules with energy equal or greater than E_a

Ans. (a—r), (b—P), (c—s), (d—u), (e—q), (f—t)

CASE BASED STUDY QUESTIONS (CBQ) - 4MARKS

44. Chemical kinetics deals with rate of chemical reactions; how fast reactants get used up or how fast products are formed in the reaction. Differed chemical reactions have different speed. Rate of reaction depends upon concentration of reactants, temperature, pressure especially in gaseous reactions and presence of catalyst. Chemical reaction takes place as a result of collision between reacting molecules. The rate of reaction does not depend upon total number of collisions rather it depends upon number of effective collisions. In a redox reaction, if E°cell is +ve, ΔG° will be –ve and 'K' equilibrium constant will be high i.e. products formed will be more than the reactants.

(a) k (The rate constant), (Activation Energy) E_a and 'A' (Arrhenius constant) are $3 \times 10^{-4}\ s^{-1}$, $104.4\ kJ\ mol^{-1}$ and $6.0 \times 1014\ s^{-1}$ respectively. What is value of 'k' when $T \rightarrow \infty$?

Ans. Arrhenius constant $k = Ae^{-Ea/RT} \Rightarrow k = Ae^{-Ea/\infty} = Ae^{\circ} = A = 6.0 \times 10^{14}\ s^{-1}$

(b) What is meant by activation energy?

Ans. The extra energy which must be supplied to reactants in order to undergo effective collision to form products.

(c) What does $e^{-Ea/RT}$ represent?

Ans. It represents fraction of molecules possessing activation energy (Ea) or more than Ea.
(d)What type of molecules undergoes effective collisions?
Ans. Those molecules which possess activation energy and collide in proper orientation undergo effective collisions.

45. The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.
Answer the following questions:
(i) What is average rate of reaction?
Ans. Change in conc. Of reactant or product per unit time.

(ii) Write two factors that affect the rate of reaction.
Ans. (a)Concentration (b) Temperature.

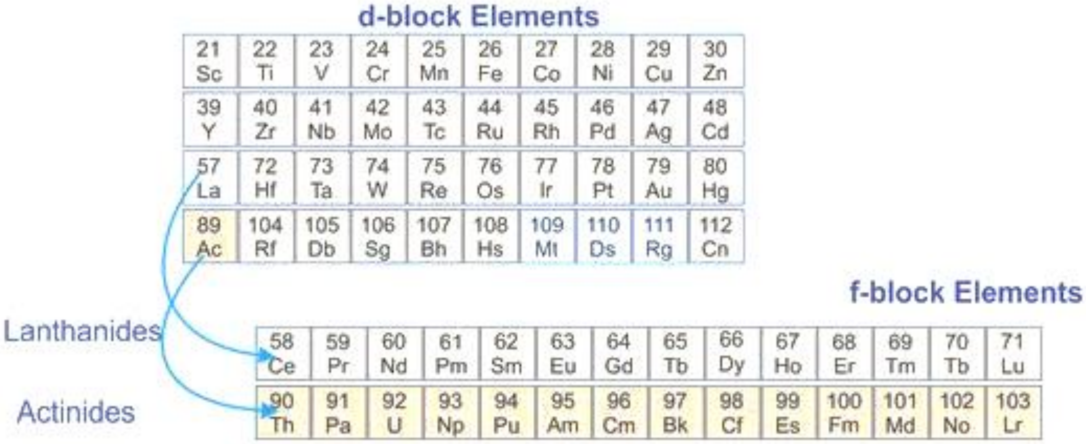
(iii) (a) What happens to rate of reaction for zero order reaction?
(b) What is the unit of k for zero order reaction?
Ans (a) Rate is independent of conc. of reactants

(b) mol L^{-1} s^{-1}

OR

(iii) (a) For a reaction P + 2Q --→ Products Rate = $k[P]^{1/2}[Q]^1$. What is the order of the reaction?
(b) Define pseudo first order reaction with example.
Ans. (a) 3/2 or 1.5
(b) A reaction appears to be of higher order but follows first order.
Example – hydrolysis of ester.

UNIT-8 The d- and f- block Elements



- **Position in periodic table:** * Between s block & p- block elements in Gr. 3 to Gr. 12 (total 10 groups)
- **General Electronic configurations** of d- block elements: $(n-1)d^{1-10}\ ns^{1-2}$.
  - Exceptions in 1st Transition series: Chromium (Cr: at. no. 24) [Ar] $3d^5\ 4s^1$
  - Copper (Cu: at. no. 29) [Ar] $3d^{10}\ 4s^1$.
  - Group 11 elements are called coinage metals. (Copper, silver, gold)

- Transition elements are defined as one which have incompletely filled d-orbitals in their ground states or any of its oxidation states.
- Zinc, Copper & mercury of group 12 elements are not regarded as transition elements as these have fully filled d^{10} configuration in ground state & common oxidation states.

Table Outer electron configuration of the transition elements ground state

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	7	7	9	10	10

- **General Properties of the Transition Elements (d- block elements):**

Physical Properties:

Metallic properties: All the elements show metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre except Zn, Cd and Hg.

The trend in melting points of transition metals belonging to 3d, 4d and 5d series is shown by the following graph:

In general, greater the number of valence electrons, stronger is the resultant metallic bonding.

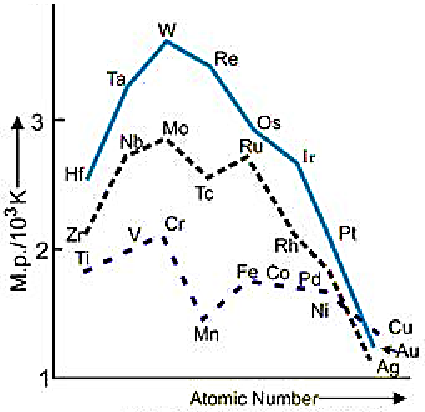


Fig. Trends in melting points of transition elements

Enthalpy of atomization: Transition metals have high enthalpy of atomization due to strong metallic bond & high density.

Also, the metals of the second and third series have greater enthalpies of atomization than the elements belonging to the first series.

Atomic and ionic sizes: The atomic radii of the elements of 3d-series (1st transition series elements) decreases as the atomic number increases.

The atomic radii increase from 3d to 4d. The atomic radii of the 4d and 5d transition series are very close due to lanthanoid contraction.

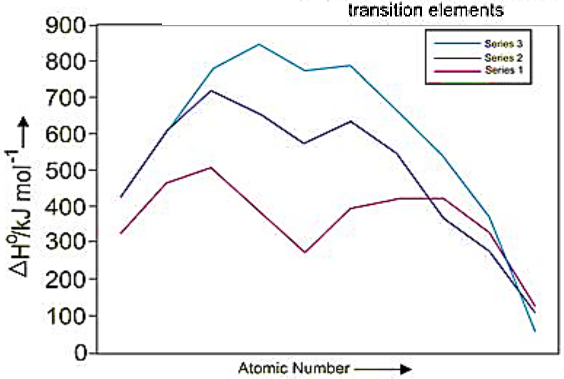


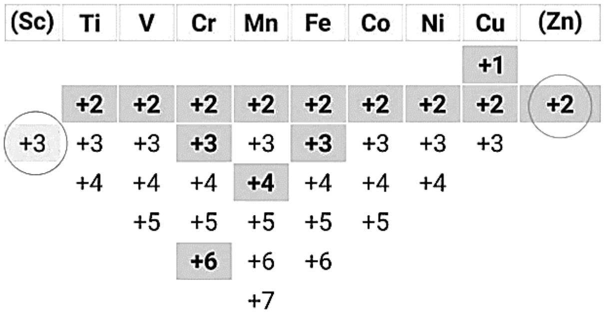
Fig. Trends in enthalpies of atomisation of transition elements

Ionisation enthalpy: There is a slight and irregular variation in ionization energies of transition metals due to irregular variation of atomic size. The ionization enthalpy of 5d transition series is higher than 3d and 4d transition series because of lanthanoid contraction.

Oxidation state: Transition metals show variable oxidation states due to the tendency of (n-1)d as well as ns electrons to take part in bond formation.

Mn exhibits a large no. of oxidation states due to the presence of electronic configuration $3d_54s_2$ from +2 to +7.

Here, the common oxidation states of the first-row transition elements are provided below:



(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
								+1	
	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3	+3	+3	**+3**	+3	**+3**	+3	+3	+3	
	+4	+4	+4	**+4**	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

(a) Oxidation state of a metal zero in a compound is Ni in $[Ni(CO)_4]$.

(b) Maximum oxidation state of a metal is +8 for Os (osmium) in compound OsO_4.

Magnetic Properties: Most of transition metals are paramagnetic in nature due to the presence of unpaired electrons. It increases from Sc to Mn due to the increased number of unpaired electrons and then starts decreasing as the number of unpaired electrons decreases.

$Sc^{3+}(3d^0)$, Cu^+ $(3d^{10})$, Zn^{2+} $(3d^{10})$ are diamagnetic.

Formation of coloured Ions: They form coloured ions due to the presence of incompletely filled d-orbitals $(n-1)d^{1-9}$. They can undergo d-d transition by absorbing colour from visible region and radiating complementary colour. [$(n-1)d^0$ & d^{10} are colourless or white]

Formation of complex compounds: The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation. For example: $[Fe(CN)_6]^{3-}$, $[Ni(CO)_4]$ etc

Catalytic properties: Most of transition metals are used as catalyst because of

(i) presence of incomplete or empty d-orbitals,

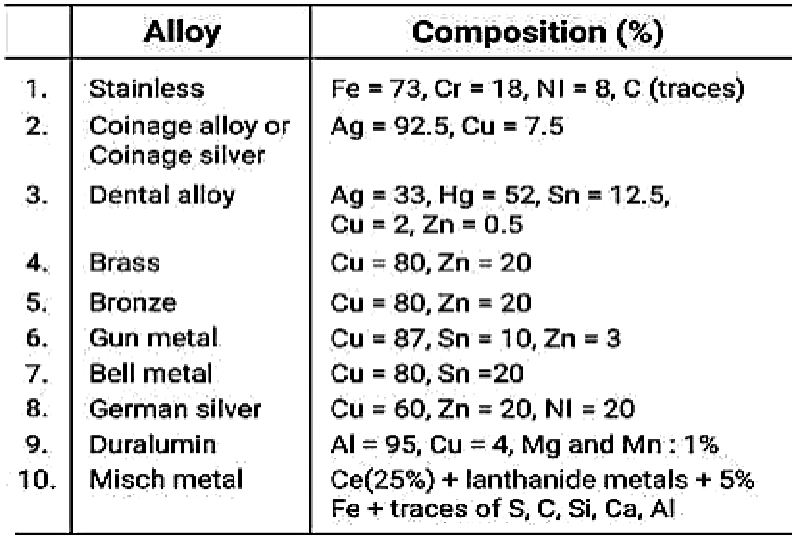
(ii) large surface area,

(iii) variable oxidation state,

(iv) ability to form complexes, e.g., Fe, Ni, V_2O_5, Pt, Mo, Co are used as catalyst.

Formation of Interstitial Compounds: Transition metals have voids or interstitials in which C, H, N, B etc. can fit in, resulting in the formation of interstitial compounds. They are non-stoichiometric, i.e., their composition is not fixed, e.g.,steel. They are harder and less malleable and ductile.

Alloy formation: Alloy is a homogeneous mixture of two or more metals. Due to the comparable size of transition metals, one metal can displace other metal in the crystal lattice and this results in the alloy formation. The alloys so formed are hard and have high melting points.



	Alloy	Composition (%)
1.	Stainless	Fe = 73, Cr = 18, NI = 8, C (traces)
2.	Coinage alloy or Coinage silver	Ag = 92.5, Cu = 7.5
3.	Dental alloy	Ag = 33, Hg = 52, Sn = 12.5, Cu = 2, Zn = 0.5
4.	Brass	Cu = 80, Zn = 20
5.	Bronze	Cu = 80, Zn = 20
6.	Gun metal	Cu = 87, Sn = 10, Zn = 3
7.	Bell metal	Cu = 80, Sn =20
8.	German silver	Cu = 60, Zn = 20, NI = 20
9.	Duralumin	Al = 95, Cu = 4, Mg and Mn : 1%
10.	Misch metal	Ce(25%) + lanthanide metals + 5% Fe + traces of S, C, Si, Ca, Al

Remember: (1) In 1st Transition series, the positive standard reduction potential is for Cu as $E^o_{Cu2+/Cu}$ = +0.34 V, this is due to high Δ_aH (enthalpy of atomization) & low $\Delta_{hydr}H$ (hydration enthalpy).

(2) Acidic nature of metal oxides increases with increase in oxidation state.

(3) Basic nature of metal oxides decreases with increase in oxidation state. e.g. MnO (Mn^{2+}) is basic but Mn_2O_7 (Mn^{7+}) is basic. $MnO + H_2O \rightarrow Mn(OH)_2$ (a base) & $Mn_2O_7 + H_2O \rightarrow 2HMnO_4$ (an acid)

(g) Mn exhibits a large no. of oxidation states due to its electronic configuration $3d^54s^2$ from +2 to +7.

Some Important Compounds of Transition Elements

Potassium dichromate, $K_2Cr_2O_7$ (Ore: Chromite ore→ $FeCr_2O_4$)

It used in leather industry and as an oxidant for preparation of many azo compounds.

Manufacture: Ore is fused with sodium or potassium carbonate in air.

(i) $FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.2H_2O$ can be crystallised.

(ii) $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

Here, $Na_2Cr_2O_7$is highly hygroscopic. So, $K_2Cr_2O_7$ is formed by heating the solution of sodium dichromate with potassium chloride, orange crystals of potassium dichromate crystallise out.

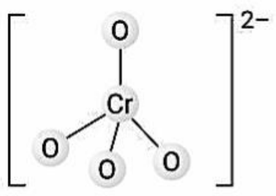
(iii) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Effect of pH on chromium salt: The chromates ((yellow solution) and dichromates (orange solution) are interconvertible in aqueous solution depending upon pH of the solution.

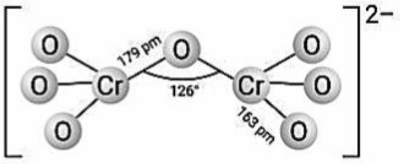
2 CrO_4^{2-} (yellow) + $2H^+$ (acidic, pH decreases) → $Cr_2O_7^{2-}$ (orange) + H_2O

$Cr_2O_7^{2-}$ (orange) + $2OH^-$ → $2CrO_4^{2-}$ (yellow) + H_2O

The structure of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are given:



Chromate ion



Dichromate ion

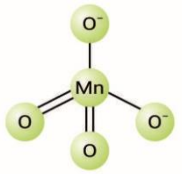
Sodium and potassium dichromates are strong oxidising agents.
In acidic solution, its oxidising action can be represented as follows:
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Potassium permanganate, $KMnO_4$ (Ore: Pyrolusite MnO_2)
Manufacture: When finely powdered MnO_2 is fused with KOH oxidised with air, K_2MnO_4 is obtained, followed by electrolytic oxidation of manganate (VI) ion.

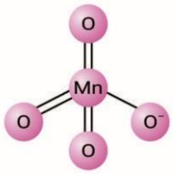
$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_4^{2-} \xrightarrow{\text{Electrolytic oxidation in alkaline solution}} MnO_4^-$$

Physical properties: $KMnO_4$ as dark purple crystals, comparatively less water soluble.
(i) When $KMnO_4$ is heated or in sun light, it decomposes to K_2MnO_4. $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
(ii) $KMnO_4$ is an oxidizing agent in acidic medium. Its oxidation state changes from +7 in MnO_4^- to +2 (Mn^{2+}) state. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (iii) Structures of manganate & permanganate ions ➔



Tetrahedral manganate (green) ion



Tetrahedral permanganate (purple) ion

(iv) $KMnO_4$ is reacted in alkaline solution of iodine.
$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$

The inner transition elements: (f- block elements)
General electronic configuration of f- block elements: (n-2) f^{0-14} (n-1) $d^{0,1}$ ns^2. It has two series.
(a) Lanthanoids: ($4f^{0-14}$ $5d^{0-1}$ $6s^2$) The 14 elements immediately following lanthanum, i.e. Cerium (Ce=58) to Lutetium (Lu=71) are called lanthanoids. They belong to first inner transition series. Lanthanum (57) has similar properties.

(b) Actinoids: ($5f^{1-14}$ $6d^{0-1}$ $7s^2$) The 14 elements immediately following actinium (Ac = 89), with atomic numbers Thorium (Th = 90) to Lawrencium (Lr = 103) are called actinoids. They belong to second inner transition series. Actinium (89) has similar properties. All elements are radioactive. Elements after uranium (U-92) are called transuranic elements or synthetic elements.

Atomic and Ionic Sizes: In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f-orbitals. Due to lanthanoid contraction:

(i) Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.
(ii) Separation of lanthanoid elements are difficult.
(iii) The atomic size of Zr (at. no. = 40 & Zr (at. no. 72) are nearly same.

Oxidation states: Lanthanoids → +3, (+2 & +4) Actinoids → +3 (+4 to +7).
Uses: (i) Ziegler Natta catalyst is $TiCl_3 + Al(CH_3)_3$, used to manufacture polyethene.
(ii) AgBr is used in photography

Simple questions of different types with possible answers:
Assertion reason questions: (1 mark each)
Directions: These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

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

Q.1) Assertion: Cuprous ion (Cu^+) has unpaired electrons while cupric ion (Cu^{+2}) does not.
Reason: Cuprous ion (Cu^+) is colourless whereas cupric ion (Cu^{+2}) is blue in the aqueous solution.

Q.2) Assertion: Transition metals show variable valency.
Reason: Transition metals have a large energy difference between the ns^2 and (n – 1) d electrons.

Q.3) Assertion: Transition metals are good catalysts.
Reason: V_2O_5 or Pt is used in the preparation of H_2SO_4 by contact process

Q.4) Assertion: The transitions of first row transition metal ions are mostly colourless.
Reason: The transition metal ions having $3d^1$ to $3d^9$ have one or more unpaired electrons.

Q.5) Assertion: The standard electrode potential value of Cu^{2+}/Cu is positive (+0.34V).
Reason: It has high standard enthalpy of atomization & low standard hydration enthalpy.

Q.6) Assertion: Acidified $KMnO_4$ solution acts as a good reducing agent.
Reason: In this reaction Mn^{+7} reduces to Mn^{2+}.

Answers: Assertion – reason questions:

Qu. No.	**1**	**2**	**3**	**4**	**5**	**6**
Answer	**(d)**	**(c)**	**(b)**	**(d)**	**(a)**	**(d)**

Multiple Choice questions (MCQs): (1 mark each)

Qu.1) Zinc and mercury do not show variable valency like other d-block elements because

(a) they are soft & silvery. (b) their d-shells are complete
(c) they have only two electrons in the outermost subshell. (d) their d-shells are incomplete.

Solution: (b) These elements have electronic configuration (n-1) d^{10} ns^2.

Qu.2) Generally, transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compound will be coloured in solid state?
(a) Ag_2SO_4 (b) CuF_2 (c) ZnF_2 (d) Cu_2Cl_2

Solution: (b) Cu^{2+} has 1 unpaired electron in CuF_2, hence, it is coloured in solid state.

Qu.3) Which of the following oxidation state is common for all lanthanoids?
(a) +2 (b) +1 (c) +4 (d) +3.

Solution: (d) +3 oxidation state is most common for all lanthanoids.

Qu.4) When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because
(a) CO_2 is formed as the product (b) Reaction is exothermic
(c) MnO_4^- catalyzes the reaction (d) Mn^{2+} acts as auto-catalyst

Solution: (d) When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because Mn^{2+} acts as an auto-catalyst.

Qu.5) Which of the following is amphoteric oxide? Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4
(a) V_2O_5, Cr_2O_3 (b)Mn_2O_7, CrO_3 (c) CrO, V_2O_5 (d) V_2O_5, V_2O_4

Solution: (a) V_2O_5 and Cr_2O_3 are amphoteric oxides because both react with alkalies as well as acids.

Remember: In lower oxides, the basic character is predominant while in higher oxides, the acidic character is predominant.

Qu.6) Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?
(a) They have high melting points in comparison to pure metals. (b) They are very hard
(c) They retain metallic conductivity. (d) They are chemically very reactive.

Solution: (d) Interstitial compounds are chemically inert.

Qu.7) $KMnO_4$ acts as an oxidizing agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidized to (a) I_2 (b) IO^- (c) IO_3^- (d) IO_4^-

Solution: (c) $2KMnO_4 + KI + H_2O \rightarrow 2KOH + 2MnO_2 + KIO_3$

Qu.8) Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7 (Mn_2O_7) because
(a) fluorine is more electronegative than oxygen
(b) fluorine does not possess d-orbitals
(c) fluorine stabilizes lower oxidation state

(d) in covalent compounds fluorine can form single bond only while oxygen forms double bond

Solution: (d) The highest oxidation state of manganese in fluoride is +4 (MnF_4) but in oxides it is +7 (Mn_2O_7) because in covalent compounds fluorine can form single bond only while oxygen forms double bond.

Qu.9) Although zirconium belongs to 4d transition series and hafnium to 5d transition series even then they show similar physical and chemical properties because

(a) both belong to d-block (b) both have same number of electrons

(c) both have similar atomic radius (d) both belong to the same group of the periodic table

Solution: (c). Zirconium and hafnium have similar atomic radius hence they show similar physical and chemical properties due to lanthanoid contraction.

Qu.10) Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium?

(a) Both HCl and $KMnO_4$ act as oxidizing agents.

(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidizing agent.

(c) $KMnO_4$ is a weaker oxidizing agent than HCl.

(d) $KMnO_4$ acts as a reducing agent in the presence of HCl.

Solution: (b) HCl is not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium. The reason is that if HCl is used, the oxygen produced from $KMnO_4$ + HCl is partly utilized in oxidizing HCl to Cl_2, which itself acts as an oxidizing agent and partly oxidises the reducing agent.

Very Short questions: (1 mark each)

Qu.1) Name the ore from which potassium dichromate crystals are manufactured?

Ans: Chromite ore ($FeCr_2O_4$)

Qu.2) Write the general electronic configuration of d block elements.

Ans. $(n-1)\ d^{1-10}\ ns^{1-2}$.

Qu.3) **Zn, Cd & Hg are not regarded as transition elements. Why?**

Ans. These elements have general electronic configuration $(n-1)d^{10}\ ns^2$ in there elemental state. Also these elements have fully filled d orbitals in their ground state & their common oxidation state (of +2). These elements have low melting points, generally form white compounds, etc.

Qu.4) Cr, Mo, W are hard & highly metallic. Why?

Ans. These metals have maximum number of unpaired electrons in their (n-1) d orbitals.

Qu,5) Transition elements have high enthalpy of atomization. Why?

Ans. This is due to the presence of one or more unpaired electrons in d orbitals forming strong metallic bond. The enthalpy of atomisation is more for 4d & 5d transition series than 3d transition series due to more nuclear charge & high (charge /(radius) ratio.

Qu.6) Name the oxo metal anions in the first transition series in which the metal exhibits oxidation state equal to its group number.

Ans. From Sc to Mn the oxidation state leading to the maximum stability corresponding values of sum of 4s & 3d electrons. the element. Example: In group 3, Sc forms $[Sc(III)O_2]^-$ or in group 4, Ti forms $[Ti(IV)O_3]^{2-}$ etc.

Qu,7) Ni (II) compounds are more stable than Pt(II) compounds but Ni (IV) compounds are less stable than Pt (IV) compounds. Why?

Ans. We know that an element having low Δ_iH is less stable & its ion is more stable.

It is experimentally observed that sum of first & second ionization enthalpies of Ni is less than that of Pt so, Ni (II) compounds are more stable than Pt (II) compounds.

It is further observed that sum of the first four ionization enthalpies of Ni is much higher than that of Pt. Hence Ni (IV) compounds are less stable than Pt (IV) compounds.

Qu.8) Most of the transition metal compounds are coloured in solid & aqueous states. Why?

Ans. This is due to the presence of unpaired electrons in (n-1)d orbitals i.e. d^1 to d^9. In presence of ligands, the degeneracy of d orbitals is lost & it splits up into two sets of orbitals t_{2g} & e_g (according to C.F. theory). When electrons of lower energy state of d orbitals absorb some energy of white light & jump to higher d orbitals, the remaining energy emitted is the colour of the compound. Example: If an ion of transition metal absorbs light of wavelength 4500Aº (blue), the complementary colour emitted is yellow. [d^1 & d^{10} are colourless or white].

Qu.9) Why is $KMnO_4$ solution stored in coloured bottles?

Ans. $KMnO_4$ decomposes in sun light. $2KMnO_4 \xrightarrow{\text{Sun light}} K_2MnO_4 + MnO_2 + O_2$

Qu.10) Acidified potassium dichromate solution is an oxidizing agent. Explain.

Ans. $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$.

Here, Cr(VI) reduces to Cr(III), so, acidified potassium dichromate solution is an oxidizing agent.

Qu.11) Which of the 3d series of transition elements exhibits the largest number of oxidation states & why?

Ans. Mn $[3d^5\ 4s^2]$ shows the oxidation states of +2 to +7.

Qu.12) Why copper (I) compounds are unstable in aqueous solution?

Ans. Copper (I) compounds undergo disproportionation reaction in aqueus solution & forms more stable copper (II) compounds. $2\ Cu^+ \rightarrow Cu^{2+} + Cu$.

Q.13) Account for the increasing oxidising power of in the series: $VO^{2+} < Cr_2O_7^{2-} < MnO_4^-$?

Ans. A strong oxidising agent forms a stable species of lower oxidation state in which it is reduced. In MnO_4^-, Mn (+7) is reduced to Mn^{2+} least reduced state Mn(2+)

Qu.14) Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

Ans. This is because oxygen & fluorine are more electronegative elements.

Qu.15) Why Hf & Zr of group 4 elements have equal atomic radii?

Ans. This is due to lanthanoid contraction.

Short answer questions: (2 marks each)

Qu.1) Many transitions elements & their compounds act as catalysts in chemical reactions. Why?

Ans. This is due to (i) Transition elements provide a large surface area with free valencies or active sites for the 'activity' for activity for reactants to be adsorbed & increase the reactant concentration, on the surface to increase the rate of the reaction.

(ii)Transition elements have variable oxidation states to form unstable intermediate compound with the reactant following lower activation energy path to form the products & catalyst is regenerated.

Example: $SO_2 + ½O_2 \xrightarrow{V2O5} SO_3$

Steps (a) $SO_2 + V_2O_5 \overset{\Delta}{\rightarrow} SO_3 + V_2O_4$ (b) $V_2O_4 + ½O_2 \rightarrow V_2O_5$.

Qu.2) What is the effect of change in pH to the chromium salt?

Ans. (a) $Cr_2O_7^{2-} + OH^- \xrightarrow{\text{increasing pH (alkali added)}} 2CrO_4^{2-} + H_2O$

(orange dichromate) (yellow chromate)

(b) $2CrO_4^{2-} + 2H^+ \xrightarrow{\text{decreasing pH (acid added)}} Cr_2O_7^{2-} + H_2O$

(yellow chromate) (orange dichromate)

Qu.3) What is misch metal? What is its use?

Ans. It is an alloy of lanthanoid metals (≈ 95%) & iron (≈ 5%) & traces of S, C, Ca, Al etc.
It is used in Mg based alloy to produce bullets, shell & lighter flint.

Qu.4) Give reasons: (a) **Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. Why?**

Ans: Zr, a member of 4d series and Hf, a member of 5d series, belong to same group. They are chemically so similar that their separation is difficult. This is due to the fact that both have same size due to lanthanide contraction. The radii of these elements are 160 pm (Zr) and 159 pm (Hf).

(b) Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?

Ans: The electronic configuration of Ce is $4f^1 5d^1 6s^2$. Usually 5d' and $6s^2$ electrons are lost by the lanthanoids in their reactions i.e., they exhibit +3 oxidation states. But Ce exhibit +4 oxidation state also because it gains extra stability by losing $4f^1$ electron because it will give rise to completely filled orbitals.

Qu.5) Give reasons: (a) **Why first ionization enthalpy of Cr is lower than that of Zn?**

Ans: The electronic configuration of chromium and zinc are respectively:

Cr (24) = [Ar] $3d^5 4s^1$ Zn (30) = [Ar] $3d^{10} 4s^2$

It is easy to remove electron from $4s^1$ orbital (unpaired) of Cr rather than from $4s^2$ orbital (paired) of Zn.

(b) Transition elements show high melting points. Why?
Ans: The high melting points of transition metals are due to strong metallic bonds between the atoms of these elements. This is because of involvements of greater number of electrons in the interatomic metallic bonding from (n – 1) d orbitals in addition to ns electrons.

Short answer questions: (3 marks each)

Qu.1) Write the reactions involved in the preparation of potassium dichromate from chromite ore.
Ans. (i) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
(ii) $2Na_2CrO_4$ +(conc.) $H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
(iii) $Na_2Cr_2O_4 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Qu.2) Write the reactions involved in the manufacture of $KMnO_4$ from pyrolusite ore.
Ans. The formula of pyrolusite ore is MnO_2. The manufacture of KMnO4 involves the following reactions.
(i) $2MnO_2 + 4KOH + O_2 \overset{\Delta}{\rightarrow} K_2MnO_4 + 2H_2O$
(ii) $K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

Qu. 3) Compare the properties of lanthanoids & actinoids.
Ans.

Properties	Lanthanoids	Actinoids
Electronic configuration	[Xe] $4f^{1-14}\,5d^{0-1}\,6s^2$	[Rn] $5f^{1-14}\,6d^{0-1}\,7s^2$
Oxidation states	+3 & (+2, +4)	+3 & (+4 to +7)
Basic character	Lanthanoid compounds are less basic	Actinoid compounds are more basic
Tendency to form oxo ions	They do not form oxo ions.	They form oxo ions like UO_2^{+}, PuO_2^{2+} etc

Qu.4) When a brown compound of manganese
(A) is treated with HCl, it gives a gas
(B) The gas taken in excess, reacts with NH_3 to give an explosive compound
(C) Identify compounds A, B and C.
Ans: The compounds A, B and C are as follows: A = MnO_2, B = Cl_2 C = NCl_3.
The reactions are explained as: MnO_2 (A) + 4 HCl → $MnCl_2 + 2H_2O + Cl_2$ (B)
$3 Cl_2 + NH_3 \rightarrow NCl_3$ (C) + 3 HCl

UNIT 9
COORDINATION COMPOUNDS

1. Coordination compounds contain a central atom (or cation) which is coordinated to a suitable number of anions or neutral molecules and usually retain their identity in solution as well as in solid state. These may be a positively charged, negatively charged or a neutral species, $[Co(NH_3)_6]^{3+}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$ etc.
2. In 1893, Werner proposed a theory to explain the structure and bonding in coordination

compounds:
(a) In coordination compounds, metals show two types of valences: Primary valency and secondary valency.
(b) Primary valencies are ionisable.
(c) Secondary valencies are not ionisable.
(d) This theory was successful to very limited extent and could not explain many aspects of coordination compounds.

3. In modern formulations, such spatial, arrangements are called coordination polyhedra.
The species within the square bracket are coordination entities or complexes and the ions outside the square brackets are called counter ions.

LIGAND: A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand.
It may be neutral, positively, or negatively charged.
Examples: H_2O, CN^-, NO^+ etc.
Donor atom: An atom of the ligand attached directly to the metal is called the donor atom.
Example: In the complex, $K_4[Fe(CN)_6]$, CN^- is a donor atom.

Coordination number: The coordination number (CN) of a metal ion in a complex can be defined as the number of donor centre to which the metal is directly bonded.
Example: In the complex , $K_4[Fe(CN)_6]$, the coordination number of Fe is 6.

Denticity: The number of ligating (linking) atoms present in ligand is called denticity.
(i) Unidentate ligands: The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands. Examples: H_2O, NH_3, SO_4^{2-}

(ii) Didentate ligands:
The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.
Examples: Ethylene diamine (en) $H_2NCH_2CH_2NH_2$ has two nitrogen atoms, oxalate ion has two oxygen atoms which can bind with the metal atom.

(iii) Polydentate ligand: When several donor atoms are present in a single ligand, the ligand is called polydentate ligand.
Examples: In $(EDTA)^{4-}$, the ligand is said to be polydentate and Ethylenediaminetetraacetate ion is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

Chelate:An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points.
An example is the complex ion formed between ethylene diamine and cupric ion, $[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$.

Ambidentate ligand: Ligands which can ligate (link) through two different atoms present in it are called ambidentate ligand.
Example: $NO_2^-$and SCN^-. Here, NO_2^- can link through N as well as O while SCN^- can link through S as well as N atom.

5. The types of isomerism shown by coordination compounds are :

(a) Geometrical (or cis-trans) isomerism: Two coordination compounds are said to be **geometrical isomers**, when they differ in the arrangement of their ligands in space. When two identical ligands occupy adjacent position, the isomer is called ‘cis-form’ and when they arranged opposite to one another, the isomer is called ‘trans-form’.

(b) Optical isomerism shown by the chiral molecule, i.e., the molecules which do not have plane of symmetry e.g., $[Cr(ox)_3]^{3-}$.

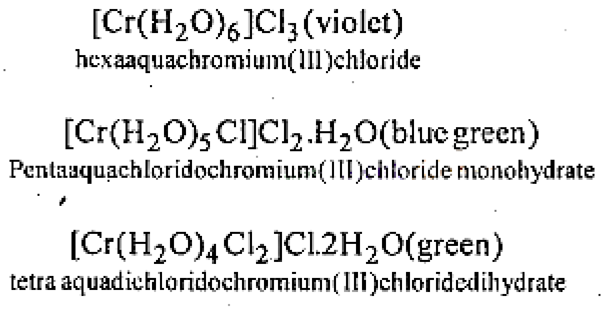
(c) Linkage isomerism occurs in complexes when an ambidentate ligand is present in the coordination sphere, e.g., $[CO(NH_3)_5N0_2]^{2+}$ and $[Co(NH_3)_5(-ONO)]^{2+}$.

(d) Coordination isomerism occurs in those complexes which are made of cationic and anionic coordination entities due to the interchange of ligands between the cation and anion entities, e.g., $[CO(NH_3)_6]$ $[Cr(CN)_6]$ and $[Co(CN)_6]$ $[Cr(NH_3)_6]$.

(e) Ionisation isomerism, is due to the exchange of ions in coordination sphere of metal ion and the ions outside the coordination sphere. These two isomers give different ions in aqueous solution, e.g,

$[Co(NH_3)_5Br]^{2+}$ SO_4^{2-} and $[Co(NH_3)_5(SO_4)]^+$ Br^-

(f) Solvate or hydrate isomerism occurs when water is a part of coordination entity or is outside it, e.g., $CrCl_3$-$6H_2O$ has three isomers.



$[Cr(H_2O)_6]Cl_3$(violet)

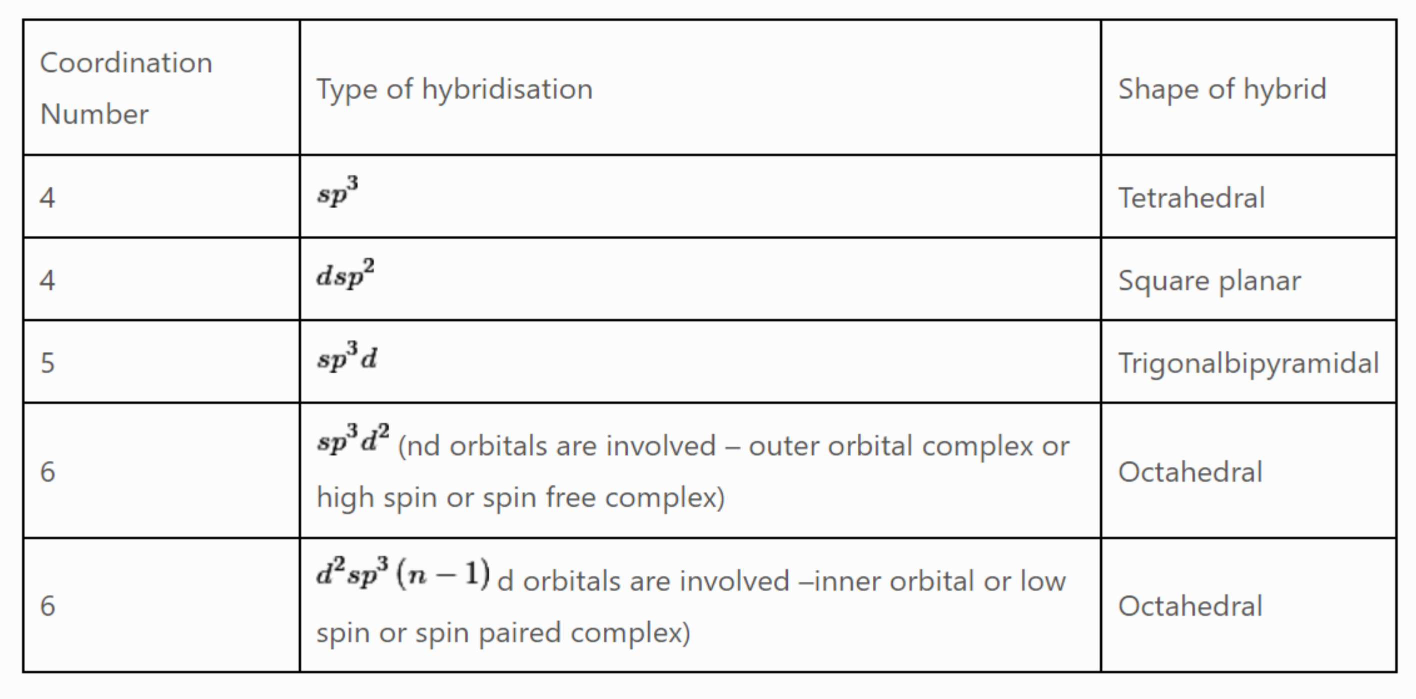
hexaaquachromium(III)chloride

$[Cr(H_2O)_5Cl]Cl_2.H_2O$(blue green)

Pentaaquachloridochromium(III)chloride monohydrate

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$(green)

tetra aquadichloridochromium(III)chloridedihydrate



Coordination Number	Type of hybridisation	Shape of hybrid
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonalbipyramidal
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

6. Magnetic properties:

(i) Inner orbital (low spin) complexes are those complexes in which hybrid orbitals of metal are formed by hybridisation of (n-1) d, ns and np-orbitals, e.g., $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$, $[(Mn(CN)_6]^{3-}$, etc.

(ii) Outer orbital (high spin) complexes are those comp lexes in which the hybrid orbitals of metal are formed by hybridisation ns, np and nd-vacant orbitals, e.g., $[MnF_6]^{3-}$, $[FeF_6]^{3-}$, $[Ni(NH_3)_6]^{2+}$ $[Ni(H_2O)_6]^{2+}$, etc.

11. Importance and applications of coordination compounds:
(a) In many quantitative and qualitative chemical analysis.
(b) In extraction processes of metals, like silver and gold.
(c) Purification of metals like Ni can be achieved by Mond's process through formation and subsequent decomposition of their coordination compounds.
(d) In biological systems the pigment responsible for photosynthesis is chlorophyll, is a coordination compound of magnesium. Haemoglobin, coordination compound, of Fe, acts as an oxygen carrier.
(e) Case of chelate therapy in medicinal chemistry.

In the following questions (Q. No. 1 - 5) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices:
(a) Assertion and reason both are correct statements, and reason is the correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not the correct explanation for assertion.
(c) Assertion is the correct statement but reason is the wrong statement.
(d) Assertion is the wrong statement but reason is the correct statement.

Q.1. Assertion: Oxalate ion is a bidentate ligand.
Reason: Oxalate iron has two donor atoms.

Q.2. Assertion: Linkage isomerism arises in coordination compounds containing ambidentate ligand.
Reason: Ambidentate ligand like NO_2 has two different donor atoms i.e., N and O.

Q.3. Assertion: Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.
Reason: geometrical isomerism is not shown by complexes of coordination number 6.

Q.4. Assertion: The complex $[Cr(H_2O)_3Cl_3]$ does not give precipitate with AgNO3 solution.
Reason: The complex $[Cr(H_2O)_3Cl_3]$ is non-ionizable.

Q.5. Assertion: $[Ni(CO)_4]$ as square planar geometry while $[Ni(CN)_4]^{-2}$ has tetrahedral geometry.
Reason: Geometry of any complex depends upon the nature of ligands attached.

ANSWERS – 1 a, 2 a, 3 c, 4 a, 5 d

VERY SHORT ANSWER TYPE (15 QUESTIONS OF 1 MARK EACH)
1. A coordination compound with the molecular formula $CrCl_3.4H_2O$ precipitates AgCl with $AgNO_3$ solution. It's molar conductivity is found to be equivalent to two ions. What is the structural formula and name of the compound?

Ans. $[CrCl(H_2O)_4]Cl_2$, Tetraaquachloridochromium(III) chloride.

2. Arrange the following complexes in 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. $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_6]Cl_3$

3. Which of the following is more stable complex and why? $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$
Ans. $[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$ as $[Co(en)_3]^{3+}$ is a metal chelate due to presence of bidentate ligand ethylene diamine ligand.

4. Why is CO a stronger ligand than Cl^-?
Ans. It is because CO can form σ (sigma) as well as π-bond, therefore it is stronger ligand than Cl^-.

5. Square planar complexes with coordination number of 4 exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?
Ans. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the ligands to the central metal atom are same with respect to each other.

6. How many isomers are there for octahedral complex $[CoCl_2(en)(NH_3)_2]^+$?
Ans. 4

7. A complex $[M(AA)_2X_2]^{n+}$ of the time is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex.
Ans.cis-octahedral structure.

8. Give IUPAC name of linkage isomer of $[Co(NH_3)_5(NO_2)]^{2+}$.
Ans. Pentaaminenitrito −O− cobalt (III) ion

9. What type of isomerism is shown by the following complex: $[Co(NH_3)_6]$ $[Cr(CN)_6]$
ANS- Co-ordination isomer.

10.Write IUPAC name of coordination isomer of $[Co(NH_3)_6]$ $[Cr(CN)_6]$.
Ans. Hexacyanochromium (III) hexaammine cobalt (III)

11. What type of isomerism is exhibited by the following complex: $[Co(NH_3)_5SO_4]Cl$
Ans. Ionisation isomerism

12. What is spectrochemical series?
Ans. A spectrochemical series is **the arrangement of common ligands in the increasing order of their crystal-field** splitting energy.

13. Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (i) strong field ligand and (ii) weak field ligand. (Atomic no. of Fe=26)
Ans- Atomic no. of Fe=26
Electronic configuration of Fe=[Ar] $3d^6\,4s^2$
Electronic configuration of Fe^{+3}=[Ar] $3d^5$
In case of strong field ligand: $Fe^{+3} = t_{2g}^5\, e_g^0$
In case of weak ligand: $Fe^{+3} = t_{2g}^3\, e_g^2$

14. Why are low spin tetrahedral complexes not formed?
Ans. Low spin tetrahedral complexes are not formed because for tetrahedral complexes, the crystal field stabilization energy is lower than pairing energy

15. Do we call metal carbonyls as organometallics? Why?

Ans- yes, metal carbonyls are called organometallics because C atom of CO is linked to the metal atom. In fact, the metal-carbon bonds have both σ and π character.

MCQs [10 QUESTIONS OF 1 MARK EACH]

1. Predict the number of ions produced per formula unit in an aqueous solution of $[Co(en)_3]Cl_3$

a) 3 b) 4 c) 5 d) 6

2. Which of the following has highest molar conductivity?

a) potassiumhexacyanoferrate(II) b) hexaaquachromium(III)chloride

c) tetraamminedichloridocobalt(III)chloride d) diaminechloridoplatinum(II)

3. Ambidentate ligands like NO^{2-} and SCN^- minus are:

a) unidentate b) didentate c) polydentate d) has variable denticity

4. Which of the following species is not expected to be a ligand?

a) NO b) NH_4^+ c) $NH_2CH_2CH_2NH_2$ d) CO

5. A cheating agent has two or more than two donor atoms to bond to a single metal ion. Which of the following is not a chelating agent?

A. Thiosulphato B. Glycinato C. Oxalato D. Ethane −1,2- diamine

6. $EDTA^{4-}$ is a-

a) monodentate ligand b) bidentate ligand c) ambidentate ligand d) hexadentate ligand.

7. Which of the following is π-acid ligand?

a) NH_3 b) CO c) F^- d) ethylenediammine

8. Total number of unpaired electrons present in Co^{3+} (Atomic number= 27) is

a) 2 b) 7 c) 3 d) 4

9. The geometry of $Ni(CO)_4$ and $[Ni(PPh_3)_2Cl_2]$ are

a) both square planar b) tetrahedral and square planar, respectively

c) both tetrahedral d) square planar and tetrahedral, respectively

10. The CFSE for octahedral $[CoCl_6]^{-4}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{-2}$ will be

a) 18,000/cm b) 16,000/cm c) 8,000/cm d) 20,000/cm.

MCQs ANSWERS: 1 b, 2a, 3a, 4b, 5 a, 6 d, 7 b, 8 d, 9 d, 10 c.

SHORT ANSWER TYPE [5 QUESTIONS OF 2 MARKS EACH]

1. Why do compounds having similar geometry have different magnetic moment?

Ans- It is due to the presence of weak and strong ligands in complexes, if CFSE is high, the complex will show low value of magnetic moment and vice versa.

2. Write the state of hybridization, shape and IUPAC name of the complex $[CoF_6]^{-3}$.

Ans.Hybridization is sp^3d^2 and shape is octahedral.

3. The π-complexes are known for transition metals only. Why?

Ans. Since transition metal atoms have either half-filled or vacant d-orbitals, they can accept ligands with electron density resulting in pπ−dπ bonding.

4. On the basis of crystal field theory explain why Co(III) forms paramagnetic octahedral complex with weak field ligands where as it forms diamagnetic octahedral complex with strong field ligands.

Ans. With weak field ligands, $\Delta_0 < P$, the electronic configuration of Co(III) will be $t_{2g}^4\ e_g^2$ and it has 4 unpaired electrons and is paramagnetic. With strong field ligands, $\Delta_0 > P$, the electronic configuration will be $t_{2t}^6\ e_g^0$. It has no unpaired electrons and therefore is diamagnetic.

5. What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?

Ans. When white light falls on the complex, some part of it absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

LONG ANSWER TYPE QUESTIONS [2 QUESTIONS OF THREE MARKS EACH]

1. Explain with two examples each of the following:

a) coordination polyhedron b) homoleptic complex c) heteroleptic complex

Ans- Coordination polyhedron:

The spatial arrangement of ligand atoms which are directly attached to the central atom.

For example, $[Co(NH_3)_6]^{3+}$ has octahedral geometry and $Ni(CO)_4$ has tetrahedral geometry.

Homoleptic.

Metal is bound to only one kind of donor groups. For example $[Ni(NH_3)_6]^{2+}$,$[Co(NH_3)_6]^{3+}$.

Heteroleptic.

Metal is bound to more than one kind of donor groups. For example $[CoCl_3(NH_3)_3]$,$[NiCl_2(H_2O)_4]$.

2. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration, and coordination number. Also give stereochemistry and magnetic moment of the complex:

a) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ b) $[Co(NH_3)_5Cl]Cl_2$

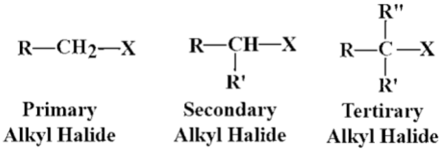
Ans.

IUPAC name	oxidation state	Elect. Confi.	C.N.	Stereochemistry	Magnetic moment
Potassium diaquadioxalatochromate(III) trihydrate	+3	$[Ar]3d^3$	6	cis and trans	3.87
Pentamine chorocobaltate(III) chloride	+3	$[Ar]3d^6$	6	No stereoismerism	4.90

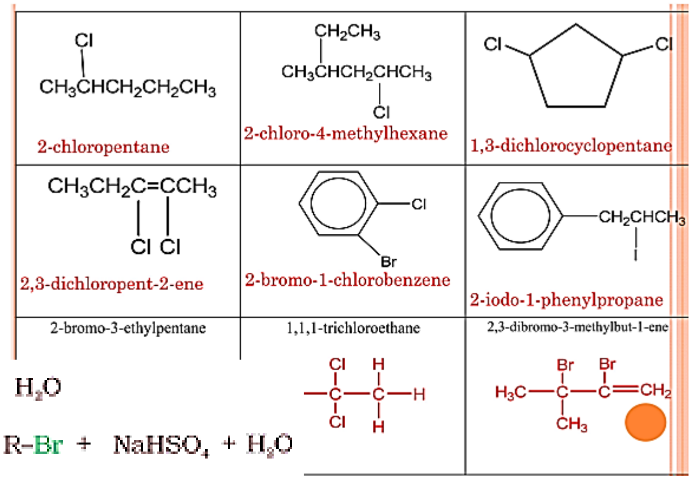
UNIT 10 HALOALKANES AND HALOARENES

1. Haloalkanes are classified as fluoro, chloro, bromo or iodo compounds according to the type of halogen present and as mono-, di- tri-, tetra- haloalkanes, etc., according to the one, two, three, four, etc., halogen atoms respectively present in their molecule.

2. Alkyl halides are further classified as primary (1°), secondary (2°) and tertiary (3°) according to the halogen atom attached to primary, secondary and tertiary carbon atoms, respectively.



3. Due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, while the carbon carries a small positive charge. Consequently, C-X bond is a polar covalent bond.



4. Methods of Preparation of Haloalkanes: Haloalkanes can be prepared from displacement of alcoholic group in alkyl alcohol by halogen acid, PCl_5 or PCl_3. Haloalkanes can also be prepared by addition of halogen acids or halogens on alkene and alkyne. Alkyl halides can also be prepared by free radical halogenation of alkane.

$$R\text{–}OH + HX \xrightarrow{ZnCl_2} R\text{–}X + H_2O$$

$$R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$$

$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$$

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

$$R\text{–}OH \xrightarrow[X_2 = Br_2, I_2]{red\ P/X_2} R\text{–}X$$

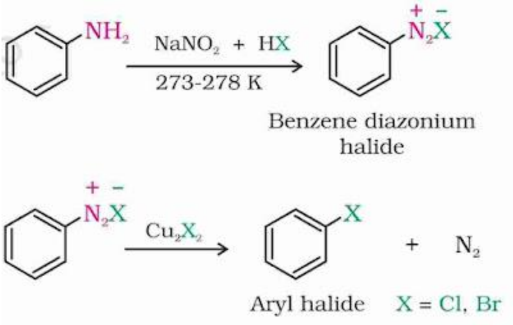
$$R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$$

5. Methods of preparation of Haloarenes. Haloarenes can be prepared by side chain halogenation or nuclear halogenation of aromatic hydrocarbons.

6. From diazonium salts:

(i) By Sandmeyer reaction:

(ii) By Gattermann reaction: Aromatic primary amine is first converted into diazonium salt by treating it with a mixture of $NaNO_2$ and HCl at 0–5°C. The diazonium salt is used to prepare aryl fluoride by first converting it into diazonium fluoroborate and then heating it. Aryl chloride/bromide is obtained by treating diazonium salt with Cu_2Cl_2/Cu_2Br_2 (**Sandmeyer reaction**) or Cu powder and HCl/HBr (**Gatterman reaction**).



7. Chemical reactions of haloalkanes

(a) Nucleophilic substitution reactions:

(i) C-X bond in alkyl halide is more polar due to electron repelling nature of alkyl group and thus readily undergo nucleophilic substitution reaction. These are of two types:

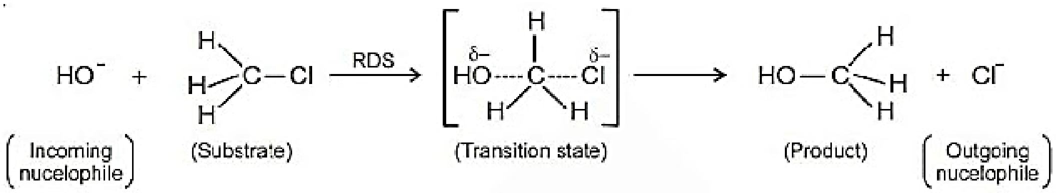
(1) S_N1(Substitution, nucleophilic, unimolecuiar): In such type of reactions, rate = k [RX], i.e., rate, is independent of concentration of nucleophile and occurs in two steps. Such reactions are favoured by polar solvents, forms stable carbocation as reaction intermediate.

(i) $R—X \longrightarrow R^+ + X^-$ (Step 1)

(ii) $R^+ + Nu^- \longrightarrow R—Nu$ (Step 2)

(2) S_N2(Substitution, nucleophilic, bimolecular): In such type of reactions, rate = k [RX] [Nu]⁻, i.e., rate of reaction depends on concentration of nucleophile and take place in one step.

(ii) A S_N2 reaction proceeds with complete stereochemical inversion (100%) while a S_N1 reaction proceeds with racemisation (50% inversion & 50% retention).

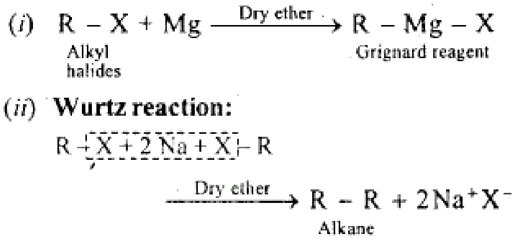


S_N2 reaction: (i) $R\text{-}CH_2\text{-}X > R_2CH\text{-}X > R_3C\text{-}X$ (i) $RCH_2\text{-}I > RCH_2\text{–}Br > RCH_2\text{-}Cl$

S_N1 reaction: (i) $R_3C\text{-}X > R_2CH\text{-}X > RCH_2\text{-}X$ (i) $RCH_2\text{-}I > RCH_2\text{–}Br > RCH_2\text{-}Cl$

(b) Elimination reaction: When a haloalkane with β-halogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from α-carbon and a halogen atom from the a-carbon atom. An alkene is formed as a product, also called β-elimination. $CH_3CH_2 – X + KOH \text{ (alcoholic)} \rightarrow CH_2{=}CH_2 + KX + H_2O$.

(c) Reaction with metals:



(i) $\underset{\text{Alkyl halides}}{R - X} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R - Mg - X}$

(ii) **Wurtz reaction:**

$$R - X + 2\,Na + X - R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R - R} + 2Na^+X^-$$

8. Aryl halides are less reactive towards nucleophilic substitution reaction due to following reasons:

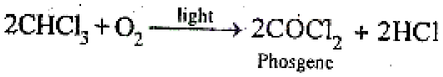
(a) In haloarenes, the lone pair of electrons on the halogen atom are delocalized on the benzene ring due to resonance.

(b) In haloalkanes, the halogen atom is attached to sp^3-hybridized carbon while in haloarenes the halogen atom is attached to sp^2– hybridized carbon.

9. Electrophilic substitution reaction: Haloarenes undergo the usual electrophilic substitution reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel crafts reactions. Halogen atom is slightly deactivating and o, p-directing.

10. Trichloromethane (Chloroform):

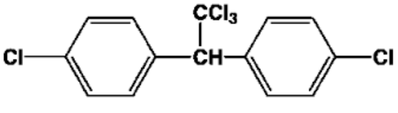
The major use of chloroform today is in the production of the freon refrigerant R-22. Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out Because it is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride (Phosgene).



$$2CHCl_3 + O_2 \xrightarrow{light} \underset{Phosgene}{2COCl_2} + 2HCl$$

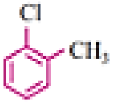
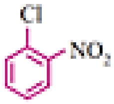
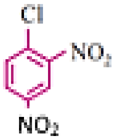
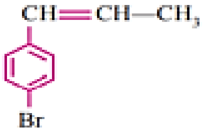
11. Freons are the chlorofluorocarbons compounds of methane and ethane. They are extremely stable, unreactive, non-toxic, noncorrosive, and easily liquefiable gases. Freon-12 (CCl_2F_2) is most common freons in industrial use.

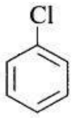
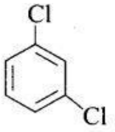
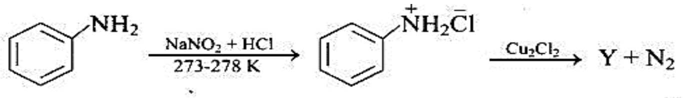
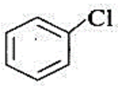
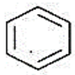
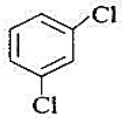
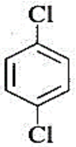
12. DDT: an insecticide used in agriculture



DDT

MULTIPLE CHOICE QUESTIONs (MCQs) with ANSWERS:

1	Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution: (i)  (ii)  (iii)  (a) i < ii < iii (b) i < iii < ii (c) ii < i < iii (d) iii < ii < i	
2	The reaction of $C_6H_5—CH=CH—CH_3$ with HBr produces (a) $C_6H_5—CH_2\,CH_2—CH_2—Br$ (b)  (c)  $C_6H_5—\overset{Br}{CH}—CH_2—CH_3$ (d)  $C_6H_5—CH_2—\overset{Br}{CH_2}—CH_3$	
3	Toluene reacts with halogen in the presence of $FeCl_3$ giving ortho and para compounds. The reactions is: (a) electrophilic elimination reaction (b) electrophilic substitution (c) free radical addition reaction (d) nucleophilic substitution	

4	A solution of (+) 2-chloro-2-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of (a) carbanion (b) carbene (c) free radical (d) carbocation	
5	Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows (a) S_N^1 mechanism (b) S_N^2 mechanism (c) any of the above two depending upon the temperature of reaction (d) Saytzeff rule	
6	Arrange the following compounds in the increasing order of their densities (i)  (ii)  (iii)  (iv)  (a) (i) < (ii) < (iii) < (iv) (b) (i) < (iii) < (iv) < (ii) (c) (iv) < (iii) < (ii) < (i) (d) (ii) < (iv) < (iii) < (i)	
7	Identify the compound Y in the following reaction:  (a)  (b)  (c)  (d) 	
8	The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives ‘X’ and the reaction with Cl_2 in presence of light gives ‘Y’. Thus ‘X’ and ‘Y’ are: (a) ‘X’ = benzyl chloride and ‘Y’ = m-chlorotoluene (b) ‘X’ = benzyl chloride and ‘Y’ = o-chlorotoluene (c) ‘X’ = m-chlorotoluene and ‘Y’ = p-cholorotoluene (d) ‘X’ = p-chlorotoluene and ‘Y’ = benzyl chloride.	
9	Which one is most reactive towards SN1 reaction? (a) C_6H_5-CH_2Br (b) C_6H_5-$CH(C_6H_5)Br$ (c) C_6H_5-$CH(CH_3)Br$ (d) $C_6H_5C(CH_3)(C_6H_5)Br$	
10	Arrange the alkyl halides in the increasing order of their boiling point: R-F, R-Cl, R-Br, R-I (a) R-F< R-Cl< R-Br< R-I (b) R-I< R-Br< R-Cl< R-F (c) R-Cl< R-Br< R-I< R-F (d) R-F< R-Br< R-Cl< R-I	
11	The hybridisation of C-X bond in haloarenes is (a) sp^3 (b) sp^2 (c) sp (d) sp^2d	
12	When considering electrophilic aromatic substitution reaction, electron withdrawing group (nitro) are observed as (a) o- ,p- directing and activating (b) o-,p- directing and deactivating (c) m- directing and activating (d) m- directing and deactivating	
13	The conversion of chlorobenzene to phenol the reagent used is	

	(a) NaOH (b)NaOH / 623K, 300atm (c) NaOH / 323K, 600atm (d) CH_3OH	
14	S_N^2 reaction mechanism leads to: (a) Retention of configuration (b) Racemisation (c) Inversion of configuration (d)None of these	
15	$(CH_3)_2CH\text{-}Cl + NaI \rightarrow (CH_3)_2CH\text{-}I + NaCl$ The above reaction is known as: (a) Finkelstien reaction (b) Kolbe's Reaction (c) Swartz Reaction (d) Wurtz Reaction	
16	Methyl fluoride can be prepared from methyl bromide by the reaction which is known as a) Finkelstien reaction (b) Kolbe's Reaction (c) Swartz Reaction (d) Wurtz Reaction	
17	A Grignard reagent is prepared by reaction of magnesium in dry ether on: (a) C_2H_5OH (b) C_2H_5CN (c) C_2H_6 (d) C_2H_5Cl	
18	The best method for conversion of an alcohol into an alkyl chloride is by treating the alcohol with: (a) PCl_3 (b) PCl_5 (c) $SOCl_2$ in presence of pyridine (d) HCl/ anhydrous $ZnCl_2$	
19	Strongest nucleophile among the following is: (a) OH^- (b) H_2O (c) NH_3 (d) $C_2H_5O^-$	
20	Chlorobenzene reacts with Mg in dry ether to give a compound (A) which further reacts with ethanol to yield (a) phenol (b) benzene (c) ethyl benzene (d) phenyl ether.	

ANS- 1(a) 2(c) 3(b) 4(d) 5(a) 6(a) 7(a) 8(d) 9(d) 10(a) 11(b) 12(d) 13(b) 14(c) 15(a) 16 (c) 17(d) 18(c) 19(d) 20(b)

ASSERTION AND REASONING QUESTIONS: -

Directions: In the following questions, A statement of Assertion (A) is followed by a statement of Reason (R). Mark the correct choice as.

(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) Assertion is false and Reason is True

1	(A): Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution. (R): Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.
2	(A: It is difficult to replace chlorine by -OH in chlorobenzene in comparison to that in chloroethane. (R): Chlorine-carbon (C-Cl) bond in chlorobenzene has a partial double bond character due to resonance.

3	(A): Nucleophilic substitution of iodoethane is easier than chloroethane. (R): Bond energy of C-I is less than that of C-Cl bond.
4	(A): Addition of HBr to alkene in presence of peroxide gives anti-Markownikoff's Product. (R): This addition follows ionic mechanism.
5	(A): In mono-haloarenes, Electrophilic substitution occur at o,p position (R): Halogen atom is ring deactivator

ANSWERS- 1(a) 2(a) 3(a) 4(c) 5(b)

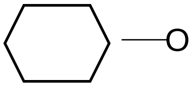
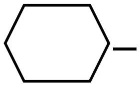
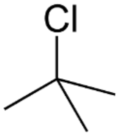
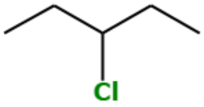
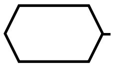
Very Short Answer Type Questions:- (1 MARK Each)

1	Classify the following as primary, secondary or tertiary bromide: (a) $CH_3CH_2CH_2CH(Br)CH_3$ (b) $CH_3CH_2C(CH_3)(Br)CH_2CH_3$
2	Name the compound according to IUPAC system: $(CH_3)_2CHCH_2CH_2Br$
3	Write the structure of 1,4-Dibromobut-2-ene
4	Write the product of the following reaction: $CH_3CH_2CH = CH_2 + HBr + \text{Peroxide} \rightarrow ?$
5	Why is the product formed during SN1 reaction optically inactive?
6	(i) Which reacts faster by SN2 pathway and why? (a) $CH_3CH_2\ CH_2Br$ or, (b) $(CH_3)_3\ C\text{-}Br$ (ii) Draw the structures of the enantiomers of 3-methylpent-1-ene in 3- dimension.
7	Write the equation for the preparation of 1−Iodobutane from 1-Chlorobutane
8	Write IUPAC name of:- tertiary butylbromide.
9	Explain why: Electrophilic reaction in haloarenes occur slowly.
10	Arrange bromomethane, bromoform, chloromethane and dibromomethane in order of increasing boiling point.
11	Arrange CH_3F, CH_3I, CH_3Br, CH_3Cl in the order of increasing S_N^2 reactivity
12	Which of the following molecules are chiral: $CH_3CHBrC_2H_5$ (I), CH_3CH_2OH (II) , CH_3Cl (III)?
13	Predict the type of reaction involved in the preparation of DDT from chlorobenzene.
14	What is an ambident nucleophile? Give an example
15	Benzyl chloride is highly reactive towards S_N1 reaction. Explain.

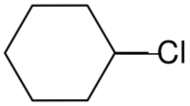
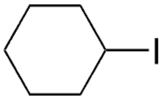
ANSWERS

1	(a) 2^0 (b) 3^0
2	1-Bromo-3-methylbutane
3	$BrCH_2\text{-}CH{=}CHCH_2Br$
4	$CH_3CH_2CH_2CH_2Br$
5	Because the product is a racemic mixture which is formed by attack on the carbocation intermediate from either side with equal probability. Hence the product is a 50:50 mixture of both enantiomers.
6	(i) $CH_3CH_2\ CH_2Br$: Because there is less crowding around the carbon attached to the halogen; hence approaching nucleophile is less hindered. (ii) Correct structures.
7	1-chlorobutane + NaI → 1−iodobutane

8	2-bromo-2-methylpropane
9	Due to resonance, the electron density increases more at *ortho*- and *para*-positions than at *meta*-positions. Further, the halogen atom because of its –I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.
10	Chloromethane< bromomethane< dibromomethane < bromoform
11	The order of S_N2 reactivity is CH_3F< CH_3Cl< CH_3Br< CH_3I due to large size of iodide ion it acts as a good leaving group.
12	$CH_3CHBrC_2H_5$ (I) is chiral because of presence of four different substituents at the C centre.
13	Electrophilic substitution reaction.
14	Nucleophiles which can attack through two different sites are called ambident nucleophiles. Example is cyanide ion (CN^-).
15	Due to resonance benzyl carbocation is stabilized.

1	Write the major products of the following: (a)  OH + $SOCl_2$ → (b)  OCH_3 + HI →
2	Why is sulphuric acid not used during the reaction of alcohols with KI?
3	In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction and why?  and 
4	Identify A and B in the following: -Br + Mg + Ether → A ; A + H_2O → B
5	During conversion of R-OH to R-Cl conversion, $SOCl_2$ is more suitable reagent as compared to HCl, PCl_5, or PCl_3 why?

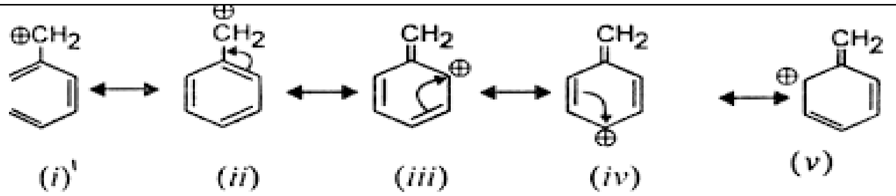
	ANSWERS

1	(a)  (b)  CH_3OH
2	H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding acid, HI which is then oxidised by it to I_2.
3	The reactivity in S_N1 reaction is governed by the stability of the intermediate carbocation. The former alkyl halide forms 3^0 carbonium ion whereas the latter forms 2^0 carbocation on ionisation. Since 3^0 carbocation is more stable than 2^0 carbocation, the former will undergo faster S_N1 reaction.
4	A:  -MgBr B: 
5	$SOCl_2$ is more suitable reagent as compared to HCl, PCl_5, OR PCl_3 because the gaseous by-products (SO_2 and HCl) escape leaving behind chloroalkanes in almost pure state.

	Long Answer Type Questions:-	
1	Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.	
2	a) Which compound in each of the following pairs will react faster in $S_N{}^2$ reaction with OH^-? Explain your answer (i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl b) Will benzyl halide prefer substitution through S_N1 or S_N2 mechanism? Justify your answer	
3	Write the reactions involved in the following: a) Finkelstien reaction (b) Swartz Reaction (c) Wurtz Reaction	
4	a) Explain why phosphoric acid and not sulphuric acid is used with KI during the preparation of alkyl iodides from alcohols. b) Grignard reagents should be prepared under anhydrous conditions. Why?	

ANSWERS

1	KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.
2	a) (i) CH_3I since I is a better leaving group (ii) CH_3Cl since it is a primary halide and so steric hindrance is less. b) S_N1, resonance stabilized benzyl carbocation is formed. resonance structures

	
3	(a) CH_3-X + NaI → CH_3-I + NaX; X= Cl, Br (b) CH_3- Br + AgF → CH_3-F + AgBr (c) $2CH_3$-X + 2Na → CH_3-CH_3 + 2NaX; X= Cl, Br
4	a) KI is expected to give HI on heating with H_2SO_4 and it is HI which is expected to convert alcohols to alkyl iodides. However, H_2SO_4 is a strong oxidising agent it oxidises HI to iodine which cannot react with alcohols. To overcome the problem the non- oxidizing acid H_3PO_4 is used instead of H_2SO_4. b) Grignard reagents are very reactive, so they react with any source of proton to form alkane. R-Mg-X + H-OH → R-H + Mg(OH)X Therefore, it must be prepared in anhydrous conditions.

UNIT- 11 ALCOHOLS, PHENOLS AND ETHERS

1. Alcohols and phenols may be classified as monohydric, dihydric, trihydric or polyhydric according to number of hydroxyl groups they contain one, two, three or many respectively in their molecules.

2. Primary (1°), secondary (2°) and tertiary (3°) alcohols are those in which as the OH group is attached to a primary, secondary and tertiary carbon atoms respectively.

3. Ethers are classified as simple or symmetrical ethers if the alkyl or aryl groups attached to the oxygen atom are same, and mixed or unsymmetrical ethers if the two groups are different.

4. Preparation of Alcohols

(a) From alkenes:

(i) By acid catalyzed hydration: The addition reaction takes place in accordance with Markovnikov's rule.

(ii) By hydroboration-oxidation

(b) From carbonyl compounds

(i) By reduction of aldehydes and ketones: On reduction, aldehydes give 1° alcohols and ketones give 2° alcohols.

(ii) By reduction of carboxylic acids and esters

(iii) From Grignard reagents

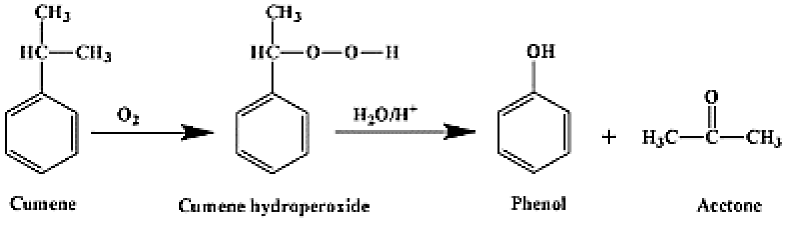
5. Phenols may be prepared by substitution of halogen in

(a) Haloarenes

(b) Sulphonic acid group in benzene sulphonic acid

(c) From hydrolysis of diazonium salts

(d) Industrially from Cumene:



6. Chemical reactions of alcohols and phenols:

(a) Reactions involving the cleavage of the O-H bond:

(*i*) Reaction with alkali metals – acidic nature:

$$2ROH + 2M \longrightarrow 2R-O^{-}M^{+} + H_2$$

(*ii*) Reaction with carboxylic acids:

$$RCO\boxed{-OH + H-}OR' \xrightleftharpoons{conc.H_2SO_4} \underset{Ester}{RCO-OR'} + H_2O$$

(*iii*) Reaction with halogen acids:

$$CH_3CH_2-OH + H-Cl \xrightarrow[\Delta]{Anhy.ZnCl_2} CH_3CH_2-Cl + H_2O$$

(b) Reactions involving the alcohol as dehydration

(*i*) Dehydratic

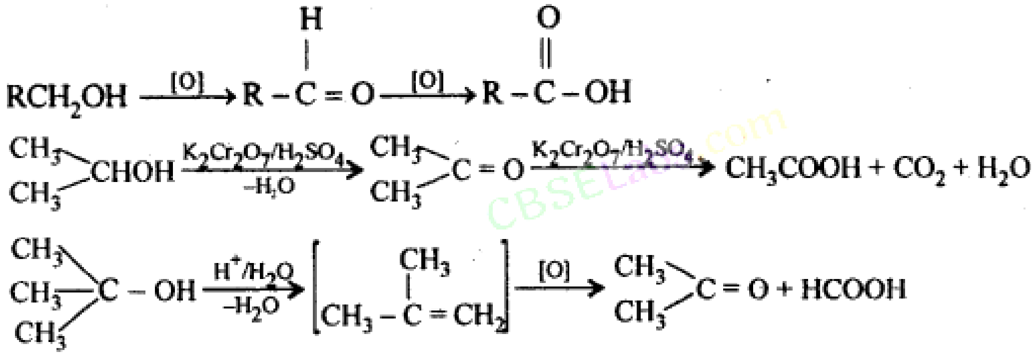
$$CH_3-CH_2$$

$$CH_2=CH_2 + H_2O$$

(*ii*) With heated alumina (Al_2O_3):

$$2CH_3CH_2OH \xrightarrow[513-523K]{Al_2O_3} CH_3CH_2-O-CH_2CH_3 + H_2O$$

(*iii*) Oxidation:



$$RCH_2OH \xrightarrow{[O]} R-\overset{H}{\overset{|}{C}}=O \xrightarrow{[O]} R-\overset{O}{\overset{||}{C}}-OH$$

$$(CH_3)_2CHOH \xrightarrow[-H_2O]{K_2Cr_2O_7/H_2SO_4} (CH_3)_2C=O \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3COOH + CO_2 + H_2O$$

$$(CH_3)_3C-OH \xrightarrow[-H_2O]{H^+/H_2O} \left[CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2\right] \xrightarrow{[O]} (CH_3)_2C=O + HCOOH$$

7. Reactions of phenols:

(a) Electrophilic substitution reaction: The presence of -OH group in phenols activates the aromatic ring towards electrophilic substitution and directs the incoming group to the ortho and para positions due to resonance effect.

(b) Kolbe's reaction: In this reaction sodium phenoxide is treated with $C0_2$ at 400K under 3-7 atm pressure, sodium salicylate is formed which is acidified to get salicylic acid.

(c) Reimer-Tiemann reaction: In this reaction phenol reacts with chloroform in presence of NaOH and produce salicyldehyde.

8. Preparation of Ethers:

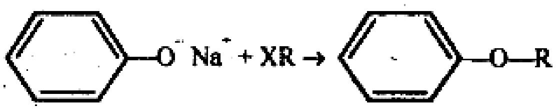
(*a*) **By dehydration of alcohols: (for simple ethers)**

$$2\,CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

(*b*) **Williamson synthesis: (for mixed ethers)**

$$R-X + R'-\ddot{\underset{\cdot\cdot}{O}}Na \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-R' + NaX$$

(*c*) **For aryl ethers, sodium phenoxide reacts with RX**



9. Physical Properties:

(a) Boiling point of ethers are much lower than corresponding alcohols because ethers do not form intermolecular H-bonding.

(b) Slightly soluble in water.

10. Chemical properties:

(a) Cleavage of C-O bond in ethers:

$$R-O-R' + HX \longrightarrow RX + R'-OH \xrightarrow[(excess)]{H-X} R'-X + H_2O$$

(b) Electrophilic substitution: In this, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions.

GROUP A (ASSERTION –REASON TYPE QUESTIONS- 1 MARK EACH)

While answering these questions, you are required to choose any one of the following four responses.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

1. Assertion: Phenols give o- and p-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.
Reason: -OH group in phenol is o and p-directing
Ans: (a) Assertion and reason both are correct statements but the reason is a correct explanation for assertion.

2. Assertion: Ethanol is a weaker acid than phenol.
Reason: Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.
Ans. (c)

3. Assertion: The bond angle in alcohols is slightly less than the tetrahedral angle.
Reason: In alcohols, the oxygen of –OH group is attached to sp^3 hybridized carbon atom.
Ans. (a)

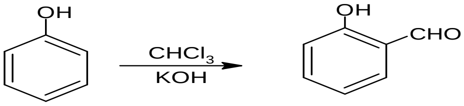
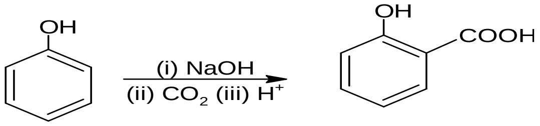
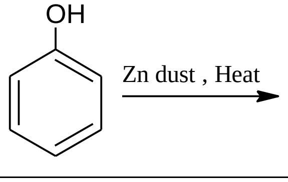
4. Assertion: The water solubility of the alcohols follow the order t-butyl alcohol < s-butyl alcohol < n-butyl alcohol.
Reason: Alcohols do not form H-bonding with water to show soluble nature.
Ans: (c)

5. Assertion: Phenol is less acidic than p-nitrophenol

Reason: Phenolate ion is more stable than P-nitrophenolate ion.

Ans: (c)

GROUP B (VERY SHORT ANSWER TYPE QUESTIONS- 1 MARK EACH)

1	“Alcohols have higher boiling points than alkanes, ethers and alkyl halides of comparable molecular mass” Give reason
Hint	Higher Inter molecular force- more boiling point (intermolecular H-bonding in alcohols)
2	“ROH with three or fewer carbon atoms are water soluble but those with five or more carbon atoms are insoluble”. Give reason
Hint	Formation of H bonding with water
3	Arrange the following in order of their increasing boiling point: n-butane, ethanol, water, propane.
Hint	Propane < n-butane < ethanol < water
4	Give reasons- Molecular mass of ethanol and dimethyl ether is same, however ethanol is a liquid at room temperature but dimethyl ether is a gas.
Hint	Hydrogen bonding in ethanol.
5	What happens when ethyl bromide reacts with sodium ethoxide?
Hint	Diethyl ether formed. Reaction is Williamsons ether synthesis
6	What happens when phenol is treated with chloroform and alc KOH?
Hint	 (Salisalydehyde) (Reimer Tiemann Reaction)
7	Give one chemical test to distinguish between tert. butyl alcohol and n-butyl alcohol
Hint	Lucas Test: t-alcohol gives turbidity quickly
8	Give an example of hydroboration–oxidation reaction
Ans.	$H_3C—CH=CH_2 \xrightarrow[(ii)\ H_2O_2]{(i) B_2H_6} H_3C—CH_2—CH2\text{-}OH$ (Hydroboration oxidation reaction)
9	Give an example of Kolbe’s reaction
Ans.	 (Kolbe’s reaction)
10	Identify the product. 
Ans.	C_6H_6 (Benzene)

GROUP C (MULTIPLE CHOICE QUESTIONS- 1 MARK EACH)

1.Which of the following alcohol is most soluble in water

a) Propanol b) Hexanol c) Pentanol d) Butanol.

Ans:(a)

2.**In the reduction:** R — CHO + H_2 → RCH_2OH the catalyst used is:

(a) Ni (b) Pd (c) Pt (d) Any of these.
Ans: (d) Any one of Ni, Pt or Pd can be used in the reduction of aldehydes.

3.**Alkenes convert into alcohols by**
(a) hydrolysis by dil. H_2SO_4 (b) hydration of alkene by alkaline $KMnO_4$
(c) hydrolysis by water vapours and conc. HNO_3 (d) hydration of alkene by aqueous KOH
Ans: (a)

4. n-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?
(a) PCl_5 (b) Reduction (c) Oxidation with potassium dichromate (d) Ozonolysis
Ans: (c) Primary alcohol on oxidation give aldehyde which on further oxidation give carboxylic acid whereas secondary alcohols give ketone.

5.Catalytic dehydrogenation of a primary alcohol gives a
(a) Ketone (b) Aldehyde (c) Sec. alcohol (d) Ester.
Ans: (b)

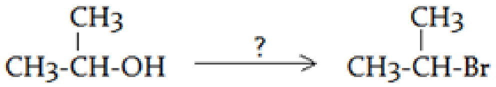
6.Which of the following is more acidic than alcohol?
(a) Phenol (b) Cyclohexanol (c) Methanol (d) Ethanol
Ans: (a)

7. Which one of the following compounds is obtained by the oxidation of primary alcohol with nascent oxygen? (a) Alkanal (b) Alkenone (c) Ether (d) Amine
Ans:a)
Explanation: Oxidation of alcohols to aldehydes is partial oxidation; aldehydes are further oxidized to carboxylic acids. Conditions required for making aldehydes are heat and distillation. In aldehyde formation, the temperature of the reaction should be kept above the boiling point of the aldehyde and below the boiling point of the alcohol.

8. Which one is the correct order of reactivity of different types of alcohol towards hydrogen halide?
a) 1° alcohol > 2° alcohol > 3° alcohol
b) 2° alcohol > 1° alcohol > 3° alcohol
c) 3° alcohol > 1° alcohol > 2° alcohol
d) 3° alcohol > 2° alcohol > 1° alcohol
Ans: d) Explanation: Reaction of HX with alcohol depends on the degree of carbonation generated due to heterocyclic cleavage of HX bond. If alcohol is primary alcohol, then reaction will proceed through S_N2 for tertiary alcohol it will proceed with S_N1. For secondary alcohol it can go through both path (S_N1 or S_N2). S_N1 being ionic in nature takes place very fast while S_N2 is molecular in nature reacts slowly. Hence, we can sum up above, Rate of reaction is 3° alcohol > 2° alcohol > 1° alcohol.

9.The dehydration of alcohols is an example of ________
(a) Bimolecular elimination / E_2 reaction (b) S_N2 reaction
(c) S_N1 reaction (d) Unimolecular elimination/E1 reaction
Ans: (d)
Explanation: Alcohol upon reaction with protic acids tends to lose a molecule of water to form alkenes. These reactions are known as dehydration of alcohols. Dehydration of alcohols is an example of Unimolecular elimination reaction.

10.What is the best reagent to convert isopropyl alcohol to isopropyl bromide?



$CH_3-\overset{CH_3}{CH}-OH \xrightarrow{?} CH_3-\overset{CH_3}{CH}-Br$

(a) HBr (b) $SOBr_2$ (c) Br_2 (d) CH_3MgBr

Ans: (b)

Explanation: Thionyl bromide will react with secondary alcohols and give a reasonable percent yield of the bromide.

11. What is IUPAC name of isopropyl alcohol?

(a) Propan-1-ol (b) Propan-2-ol (c) 2-Methylpropan-1-ol (d) 2-Methylpropan-2-ol

Ans: (b)

12. Glycerol is a -----------------alcohol.

(a) Monohydric (b) Dihydric (c) Trihydric (d) Tetrahydric

Ans: (c) The IUPAC name of Glycerol is Propane-1,2,3-triol signifying that there are three hydroxyl groups attached to three different carbon atoms.

13. A compound X with the molecular formula C_3H_8O can be oxidised to another compound Y whose molecular formulae is $C_3H_6O_2$. The compound X may be

(a) $CH_3CH_2OCH_3$ (b) CH_3CH_2CHO (c) $CH_3CH_2CH_2OH$ (d) $CH_3CHOHCH_3$

Ans: (c) $CH_3CH_2CH_2OH$

14. The decreasing order of boiling point of the following alcohols is

(a) 3-methylbuan-2-ol > 2-methylbutan-2-ol > pentan-1-ol

(b) Pentan-1-ol > 3-methylbutan-2-ol > 2-methylbutan-2-ol

(c) 2-methylbutan-2-ol > 3-methylbutan-2-ol > pentan-1-ol

(d) 2-methylbutan-2-ol > pental-1-ol > 3-methylbutan-2-ol

Ans: (b) Pentan-1-ol > 3-methylbutan-2-ol > 2-methylbutan-2-ol

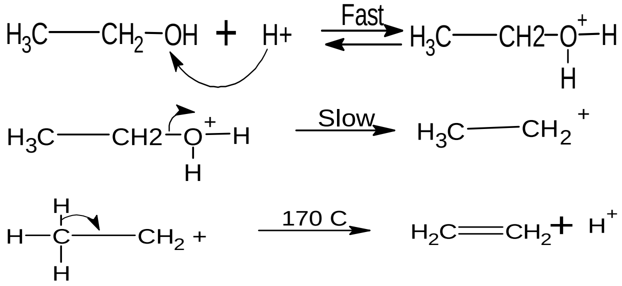
15. An unknown alcohol is treated with "Luca's reagent" to determine whether the alcohol is primary, secondary, or tertiary. Which alcohol reacts fastest and by what mechanism?

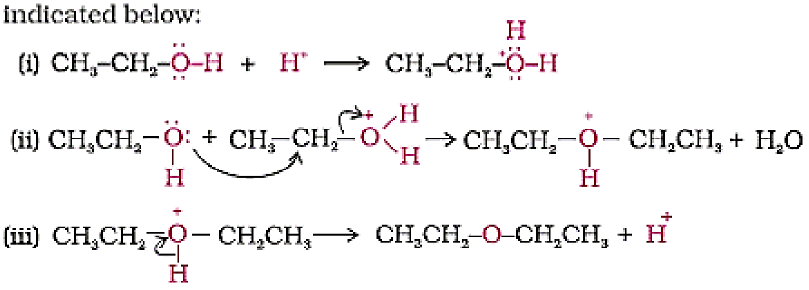
(a) Tertiary alcohol by $S_N{}^2$ (b) Secondary alcohol by $S_N{}^1$

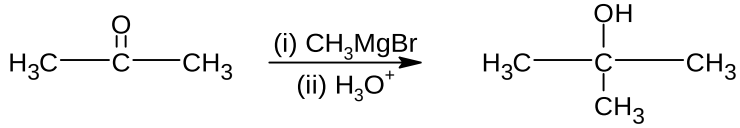
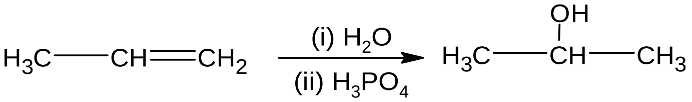
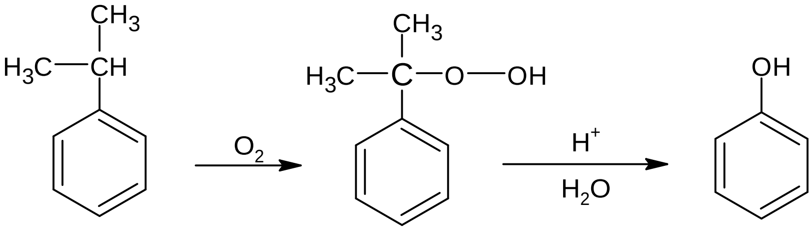
(c) Tertiary alcohol by $S_N{}^1$ (d) Secondary alcohol by $S_N{}^2$

Ans: (c) Tertiary alcohol by $S_N{}^1$

GROUP D (SHORT ANSWER TYPE QUESTIONS 2 MARKS EACH)

1.	Give the mechanism of acid catalysed dehydration of ethyl alcohol if the reaction is carried at 170^0C when ethene is formed.
Ans:	

2.	Give the mechanism of acid catalyzed dehydration of ethyl alcohol if the reaction is carried at 140°C when ether is formed.
Ans.	The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below: 

3	Carry out the following conversions: (i) Propanone to 2-Methylpropan-2-ol. (ii) Propene to propan-2-ol.
Ans.	(i)  (ii)  $H_3C-CH=CH_2 \xrightarrow[\text{(ii) } H_3PO_4]{\text{(i) } H_2O} H_3C-\overset{OH}{CH}-CH_3$
4	Give the equation of reaction for the preparation of phenol from cumene
Ans	
5	What happens when? (a) Sodium metal reacts with absolute alcohol. (b) Vapour of ethyl alcohol is passed through heated aluminium oxide at 360^{0}C.
Ans.	(a) $H_3C-CH2-OH + Na \longrightarrow H_3C-CH2-O-Na + 1/2\ H_2$ (b) $H_3C-CH2-OH \xrightarrow{Al_2O_3} H_2C=CH_2 + H_2O$

GROUP E (LONG ANSWER TYPE QUESTIONS 3 MARKS EACH)

1	(a) Write equation of the following reactions: (i) Bromine in CS_2 with phenol (ii) Treating phenol with chloroform in the presence of aq.NaOH (iii) Anisole reacts with HI
Ans:	i) O-Bromo phenol and P-Bromo phenol ii) O-Hydroxy benzaldehyde iii) Phenol and methyl iodide
2.	(a) What are primary, secondary and tertiary. alcohols? Give one example of each. (b) How do primary, secondary and tertiary alcohols differ in their behaviour towards oxidation?

	(c) Write Williamson reaction
Ans:	(a) primary alcohol:- if α-C is primary – CH_3CH_2OH Sec-alcohol- if α-C is secondary – $(CH_3)_2CHOH$ tert-alcohol- if α-C is tertiary – $(CH_3)_3COH$ b) Primary alcohol oxidises to aldehydes and carboxylic acid, secondary alcohol to ketone and tertiary alcohol cannot be oxidised. c) $C_2H_5ONa + CH_3I \rightarrow C_2H_5OCH_3 + NaI$
3.	Write the equations of preparing ethyl alcohol In one step only from the following compounds: (a) Ethyl iodide, (b) Ethylene, (c) Acetaldehyde.
Hint	Reagent (a) aq. NaOH (b) Conc H_2SO4 170^0C (c) PCC
7.	How does ethyl alcohol react with? (a) PCl_5 (b) Conc. H_2SO_4, (c) Acetyl chloride,
Hint	(a) C_2H_5Cl (b) C_2H_4 (c) Ethyl acetate

UNIT-12 ALDEHYDE KETONE AND CARBOXYLIC ACID (MLL)

Preparataion of Aldehydes

Oxidation of primary alcohol : $RCH_2OH + PCC \dashrightarrow R\text{-}CHO$

Ozonolysis Reaction : $>C=C< \xrightarrow{\text{(i) O3 , (ii) Zn, } H_2O} >C=O + >C=O$

Rosenmund Reduction: $RCOCl + H_2 \xrightarrow{\text{Pd,/ BaSO4}} R\text{-}CHO + HCl$

Stephen Reduction : $R\text{-}CN + SnCl_2 + HCl \longrightarrow R\text{-}CH=NH \xrightarrow{H_3O+} R\text{-}CHO$

Reduction by DIBAL-H : $R\text{–}CN + \text{DIBAL-H} + H_3O^+ \longrightarrow RCHO$

$R\text{–}COOR' + \text{DIBAL-H} + H_3O^+ \longrightarrow RCHO$

Etard Reaction : $C_6H_5CH_3$ (Toluene) $\xrightarrow{\text{(i) } CrO_2Cl_2 \text{ , } CS_2 \text{ (ii) } H_3O+} C_6H_5CHO$

Gatterman Koch Reaction : $C_6H_6 \xrightarrow{\text{CO, HCl, anhyd. } AlCl_3\text{/CuCl}} C_6H_5CHO$

Preparation of Ketone

Hydration of Alkyne : $R\text{-}C \equiv CH \xrightarrow{H_2O\text{, } HgSO_4} R\text{-}COCH_3$

Friedel Craft Acylation : $RCOCl + C_6H_6 + \text{Anhyd. } AlCl_3 \longrightarrow C_6H_5COCH_3$

Physical properties Of Carbonyl Compound:

Solubility: Lower alcohol and aldehydes are water soluble due to intermolecular hydrogen bonding with a water.

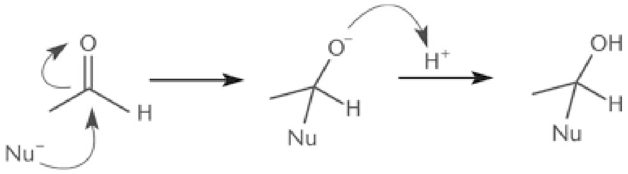
Boiling Point: Alkane < Ether < Aldehyde /Ketone < Amines < Alcohol < Carboxylic Acid

---------------------------------- Boiling Point Increases --------------------->

Alkane < Alkyl Halide < Aldehyde / Ketone < Amines < Alcohol < Carboxylic Acid

--------------------------------------- Boiling Point Increases ----------------------->

Chemical Properties: Aldehyde and ketone undergo nucleophilic addition reaction:



Reactivity of carbonyl Compounds :

Aromatic ketone < Aliphatic Ketone < Aromatic aldehyde < Aliphatic Aldehyde

--------- reactivity increases---------→

Reaction of Aldehydes and ketone (carbonyl compounds)

Addition of NaCN – Cyanohydrin formation

Addition of $NaHSO_3$ – Bisulphite addition product

Addition of Alcohol – Acetal/ Ketal formation

Addition of Ammonia derivatives

Reduction of Aldehyde and Ketone

Reduction of aldehyde to primary alcohol and ketone to secondary alcohol by $NaBH_4$ and $LiAlH_4$.

Reduction to alkane: Clemensen Reduction and Wolf-Kishner reduction

Oxidation of Aldehyde to carboxylic acid by Tollens and Fehlings reagent.

Haloform reaction (Iodoform reaction)

Ketone undergo oxidation only at vigorous condition

Reaction of aldehyde and ketone with base

Cannizaro Reaction and Cross Cannizaro reaction

Aldol Condensation and Cross Aldol Condensation

Carboxylic acid and its derivatives

Preparation of Carboxylic acid :

Oxidation of primary alcohol and aldehyde

Hydrolysis of Ester, Alkane nitrile , Acid anhydride , Amides

Reaction of Grignard reagent with CO_2

Side chain oxidation of aromatic hydrocarbon

Reaction of Carboxylic Acid: (a) Esterification reaction (b) HVZ Reaction (c) Decarboxylation reaction

Acidic Nature of Carboxylic Acid

CF_3COOH > CCl_3COOH > $CHCl_2COOH$ > NO_2CH_2COOH > NC-CH_2COOH > FCH_2COOH > $ClCH_2COOH$ > $BrCH_2COOH$ > HCOOH > $ClCH_2CH_2COOH$ > C_6H_5COOH > $C_6H_5CH_2COOH$ > CH_3COOH > CH_3CH_2COOH

MULTIPLE CHOICE QUESTIONS (MCQs) (1 MARK each)

1. Alcohol vapours when passed over heavy metals like Ag or Cu undergoes dehydrogenation to form aldehyde or ketones. Which of the following alcohol will not give aldehyde or ketone on dehydrogenation.
(a) CH_3CH_2-OH (b) CH_3 CH(OH)CH_3 (c) $(CH_3)_3COH$ (d) $C_6H_5CH_2OH$

2. Which is the suitable oxidising agent to oxidise propanol to propanal ?
(a) acidified $KMnO_4$ (d) $K_2Cr_2O_7$, H_2SO_4 (c) Tollen's reagent (d) PCC

3. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Identify the alkyne that on addition of water will form acetophenone.
(a) C_6H_5 C≡CH (b) C_6H_5 C≡C-CH_3 (c) C_6H_5 C≡C-C_6H_5 (d) CH_3-C≡C-CH_3

4. The aldehyde that cannot be prepared through Rosenmund Reduction is
(a) HCHO (b) CH_3CHO (c) C_6H_5CHO (d) None of the above.

5. One mole alkene on ozonolysis gives two moles of same aldehyde. The alkene is :
(a) Pent-2-ene (b) 2-methyl but-2-ene (c) But-2- ene (d) 2,3 dimethyl but-2-ene.

6. An aromatic hydrocarbon 'A' get oxidised by Chromyl chloride (CrO_2Cl_2) to benzaldehyde. The name of reaction and the compound is :
(a) Benzene, Gatterman Koch reaction (b) Toluene, Etard reaction
(c) Benzyl alcohol , Etard reaction (d) Toluene, Gatterman Koch reaction

7. The reagent to carry out the following conversion is :

$$C_6H_5\text{-}CH_2\text{-}COOC_2H_5 \rightarrow C_6H_5\text{–}CH_2\text{-}CHO$$

(a) $NaBH_4$ (b) $SnCl_2$/HCl (b) Zn / conc. HCl (d) DIBAL-H

8. The most reactive compound towards addition of $NaHSO_3$ to form bisulphite addition product is
(a) CH_3CHO (b) C_6H_5CHO (a) CH_3COCH_3 (d) $C_6H_5COCH_3$

9. Aldehyde and ketones react with HCN to form cyanohydrin.
Which of the following compound will lead to formation of racemic mixture of cyanohydrin?
(a) methanal (b) bezaldehyde (c) acetone (d) benzophenone

10. The compound that will not form silver mirror when heated with Tollen's reagent is
(a) Glucose (b) Ethanal (c) Benzaldehyde (d) Acetone

11. The following carbonyl compounds are treated with I_2 and alkali.
(i) Ethanol (ii) Propanal (iii) Acetophenone (iv) Acetone
The compound that will form yellow precipitate is :
(a) (i) , (ii) and (iii) (b) (i) , (iii), (iv)
(c) (ii) , (iii) and (iv) (d) (i) ,(ii) , (iii), (iv)

12. The reagent that does not reacts both with acetaldehyde and benzaldehyde is
(a) I_2 / NaOH (b) Tollen's Reagent (c) $NaHSO_3$ (d) 2,4-DNP

13. All the carboxylic acids reacts with $NaHCO_3$ to liberate CO_2 with brisk effervescence.

The reagent which can be used to distinguish between methanoic acid and ethanoic acid is
(a) I_2 / NaOH (b) 2,4- DNP (c) Tollens reagent (d) Neutral $FeCl_3$.

14. Following isomeric carbonyl compounds are heated with dilute NaOH.
(i) $CH_3CH_2CH(CH_3)CHO$ (ii) $(CH_3)_3CCHO$ (iii) $(CH_3)_2CHCOCH_3$ (iv) $CH_3CH_2CH_2COCH_3$
The reaction exhibited by above isomeric carbonyl compounds are :
(a) Cannizaro Reaction - (i), (ii) and (iii) ; Aldol reaction- (iv)
(b) Cannizaro Reaction - (ii), Aldol reaction- (i) , (iii) , (iv)
(c) Cannizaro Reaction - (i), (ii) ; Aldol reaction- (iii) , (iv)
(d) Cannizaro Reaction - (ii), (iii) ; Aldol reaction- (i) , (iv)

15. Grignard reagent on reaction with dry ice (CO_2) followed by hydrolysis produce carboxylic acid.
RBr + Mg (in dry ether) -----> RMgBr + CO_2 -------> RCOOMgBr +H_3O^+ ---------> RCOOH
The haloalkane required to prepare $CH_3CH_2CH_2COOH$ is
(a) 1- bromopropane (b) 2- bromopropane (c) 1 bromobutane (b) 2- bromobutane

ANS-1. (c) $(CH_3)_3COH$ 2. (d) PCC 3. (b) $C_6H_5\,C\equiv C\text{-}CH_3$ 4. (a) HCHO 5. (c) But-2- ene
6. (b) Toluene, Etard reaction 7. (d) DIBAL-H 8. (a) CH_3CHO 9. (b) bezaldehyde
10. (d) Acetone 11. (b) (i), (iii), (iv) 12. (a) I_2 / NaOH 13. (c) Tollen's reagent
14. (b) Cannizaro Reaction (ii) ; Aldol reaction- (i) , (iii) , (iv) 15 (a) 1- bromopropane

Assertion Reason Questions (1 MARK)

Directions: In the following questions, A statement of Assertion (A) is followed by a statement of Reason (R). Mark the correct choice as:
(A) Both A and R are true and R is the correct explanation of A.
(B) Both A and R are true but R is NOT the correct explanation of A.
(C) A is true but R is false.
(D) A is false and R is true.

1) Assertion : Carbonyl compound containing α-hydrogen undergo aldol condensation reaction
Reason : α-hydrogen of carbonyl compounds are acidic in nature.

2) Assertion: Benzoic acid has higher pka value than phenol.
Reason: Conjugate base of phenol is less stable than benzoic acid.

3) Assertion: Benzoic acid does not undergo Friedel Craft reaction.
Reason: Caboxylic carbon is less electrophilic than carbonyl carbon.

4) Assertion: Acid catalysed hydrolysis of ester forms carboxylic acid and ketone.
Reason: Both carboxylic acid and ketone contains >C=O group.

5) Assertion : Acetone has higher boiling point than Propane
Reason: Weak dipole –dipole interaction in propane

6) Assertion: Carboxylic acid exists as dimer in gas phase.
Reason: Strong intermolecular hydrogen bonding in carboxylic acid.

7) Assertion: Aldehydes are easily oxidised to carboxylic acid than ketone.
Reason: Aldehydes form silver mirror with Tollen's reagent compared to ketone.

8) Assertion: Benzaldehyde is more reactive towards nucleophilic addition than ethanal.
Reason: Polarity of carbonyl carbon in aromatic aldehyde is reduced due to resonance.

Ans: 1. (A) Both A and R are true and R is the correct explanation of A.

2. (D) A is false and R is true.

3. (B) Both A and R are true but R is NOT the correct explanation of A.

4. (D) A is false and R is true.

5. (A) Both A and R are true and R is the correct explanation of A.

6. (A) Both A and R are true and R is the correct explanation of A..

7. (B) Both A and R are true but R is NOT the correct explanation of A.

8) (D) A is false and R is true.

Very Short Answer Type Question(1Mark)

1. Write the structure of 3-hydroxybutanal.
2. Write the IUPAC nomenclature of $(CH_3)_2C=CH-COOH$.
3. Write the product obtained on heating a mixture of bezaldehyde and formaldehyde with aqueous solution of NaOH.
4. Ethyl Magnesium chloride on reaction with a compound X produces propan-1-ol. Identify the compound X.
5. Write the product of following reaction:

$$CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4}$$

6. Name the reducing agent used to reduce ketone to alkane under acid condition?
7. Arrange the following componds in increasing order of boiling point
   Butanol, Ethoxy-ethane , n-butane , Propanoic acid , Butanal
8. Arrange the compound in increasing order of reactivity towards HCN :
   Acetaldehyde , Acetone , Benzaldehyde, Acetophenone and Benzophenone.
9. Complete the following reaction:
   $C_5H_5CHO + NH_2CONHNH_2$------------------> ?
10. How will you convert ethanoic acid to 2-chloroethanoic acid?

Answers:

1. $CH_3-CH(OH)-CH_2-CHO$
2. 3- Methyl but-2-en-oic acid.
3. $C_6H_5CH_2OH$ (Benzyl alcohol) and $HCOO^-Na^+$ (sodium formate)
4. $CH_3CH_2MgBr + HCHO$ -----------> $CH_3CH_2CH-OMgBr + H_3O^+$ ---------> $CH_3CH_2CH_2OH$
   X --------------> HCHO / Methanal
5. $NaBH_4$ is a mild reducing agent. It can only reduce ketone but not ester.
   $CH_3CH(OH)\ CH_2COOC_2H_5$
6. Zn/Hg + conc, HCl (Clemmensen reduction)

7. n-butane < Ethoxy ethane < butanal < butanol < propanoic acid
8. Benzophenone < Acetophenone < Acetone < Benzaldehyde < Acetaldehyde
9. $C_6H_5CH{=}N\text{-}NH\text{-}CONH_2$
10. CH_3COOH + Red P + Cl_2 ---------> $Cl\text{-}CH_2\text{-}COOH$

Short Answer Type Questions (2 Marks)

1. Give simple chemical test to distinguish the following pair of compounds
(i) Acetophenone and Benzophenone (ii) Ethanal and ethanoic acid.

2. How can you distinguish between following compounds?
(i) Phenol and Ethanoic Acid (ii) Benzyl alcohol and Benzaldehyde

3. How will you convert acetaldehyde to: (i) Butane-1,3-diol (ii) But-2-en-oic acid

4. Write short notes on : (i) Wolff -Kishner Reaction (ii) Fehling solution.

5. Carry out the following conversion:
(i) Propan-2-ol to Ethanoic acid (ii) Benzoic acid to Benzaldehyde.

6. Arrange the following compound in increasing order of reactivity towards nucleophilic addition reaction
(i) Benzaldehyde, Benzophenone, p-tolualdehyde , acetophenone , p-nitrobenzaldehyde.
(ii) Methyl tertiary butyl ketone, Propanone, Propanal , ditertiary butyl ketone.

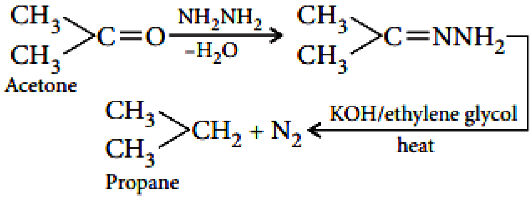
Answers:

1. (i) On reaction with NaOH /I_2 , Acetophenone will form yellow precipitate of CHI_3 and no yellow precipitate with Benzophenone
(ii) On reaction with $NaHCO_3$, brisk effervescence with liberation of CO_2 will take place for ethanoic acid

2. (i) Phenol will form violet colour complex with neutral $FeCl_3$ solution but not with Ethanoic Acid.
(ii) Benzaldehyde will form silver mirror on reaction with Tollen's reagent but not with benzyl Alcohol.

3. (i) CH_3CHO + NaOH ---------> $CH_3\text{-}CH(OH)\text{-}CH_2CHO$ $\xrightarrow{\text{NaBH4}}$ $CH_3CH(OH)\text{-}CH_2CH_2OH$
(ii) CH_3CHO + NaOH ---------> $CH_3\text{-}CH(OH)\text{-}CH_2CHO$ $\xrightarrow{\text{Heat}}$ $CH_3\text{-}CH{=}CH\text{-}CHO$ $\xrightarrow{\text{Tollens reagent}}$
$CH_3\text{-}CH{=}CH\text{-}COOH$

4. (i)



(ii) Fehling solution: Fehling reagent comprises of two solutions - Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). On heating an aldehyde with Fehling's reagent, a reddish-brown precipitate is obtained.

5. (i) $CH_3CH(OH)CH_3 \xrightarrow{PCC} CH_3COCH_3 \xrightarrow{NaOH / I_2 -, H_3O+} CH_3COOH$
   (ii) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{H_2, Pd, BaSO_4} C_6H_5CHO$

6. (i) Benzophenone < acetophenone < p-tolualdehyde < Benzaldehyde < p-nitrobenzaldehyde.
   (ii) ditertiary butyl ketone < Methyl tertiary butyl ketone < Propanone < Propanal.

Long answer type questions:

1. Arrange the following acid in increasing order of the property as indicated: (any three)
(i) Benzoic acid, 4-nitrobenzoic acid, Phenol, 4-methoxybenzoic acid (pKa value)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(iii) $HCOOH$, $F\text{-}CH_2\text{-}COOH$, C_6H_5COOH , $NO_2\text{-}CH_2COOH$, CH_3COOH (Ka value)
(iv) CH_3CH_2OH , CH3COOH, $Cl\text{-}CH_2COOH$, $F\text{-}CH_2COOH$, $C_6H_5CH_2COOH$ (acid strength)

2. Explain Why ? (any three)
(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6 – tri methylcyclohexanone does not.
(ii) There are two – **NH_2** group in semicarbazide however only one is involved in the formation of semi carbazones
(iii) **α** hydrogen of carbonyl carbon is acidic in nature.
(iv) Di-tertiary butyl ketone does not give precipitate with $NaHSO_3$ whereas acetone does.

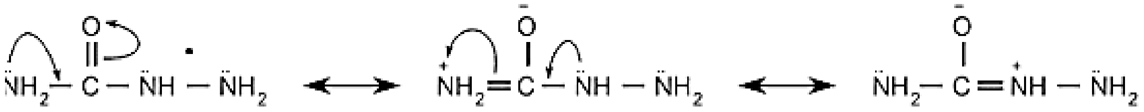
3. Account for the following statement. (any three)
(i) Aromatic aldehydes are less reactive than aliphatic aldehyde towards nucleophilic substitution
(ii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as fast as it is formed.
(iii) The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
(iv) Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones

4. An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

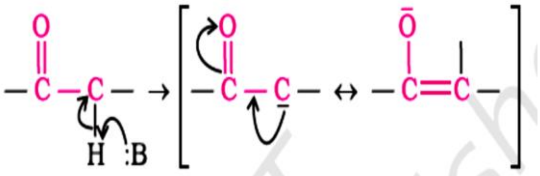
Answers:
1. (i) 4-nitrobenzoic acid < Benzoic acid < 4-methoxybenzoic acid < Phenol (pKa value)
   (ii)$CH_3CH_2CH_2COOH < (CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$
   (iii) $CH_3COOH < C_6H_5COOH < HCOOH < F\text{-}CH_2COOH < O_2NCH_2COOH$
   (iv) $CH_3CH_2OH < CH_3COOH < C_6H_5CH_2COOH < HCOOH < Cl\text{-}CH_2COOH < F\text{-}CH_2COOH$

2. Explain Why ? (any three)
(i) The steric effect of methyl group hinders the attack of CN^- in 2,2,6 – tri methylcyclohexanone

(ii) The lone pair of –NH_2 group adjacent to carbonyl group is involved in resonance.



(iii) The anion formed **after loss of α hydrogen** gets resonance stabilised.



(iv)Two bulky di tertiary butyl group hinders the approach of nucleophile bilsulphite ion.

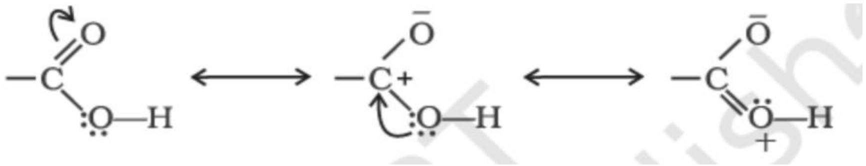
3. Account for the following statement. (any three)

(i) The electrophilicity of the carbonyl compound in aromatic aldehyde decreases due to resonance.

(ii) Formation of ester from carboxylic acid and alcohol is a reversible reaction. Removal of water will shift the equilibrium towards product side.

(iii) Carbonyl compounds have substantial dipole moment and the molecules are associated through strong dipole dipole interaction.

(iv) Carbonyl carbon in carboxylic acid is less electrophilic due to resonance.



4. A – $C_6H_5COCH_3$
   B – CHI_3
   C – C_6H_5COOH

UNIT – 13 AMINES

Definition:	Alkyl or aryl derivatives of NH_3, i.e. R – NH_2 (by replacing H-atom).

Classification & Nomenclature of Amines	S. N.	Type of Amines	Functional group	Common name	IUPAC Name
	Aliphatic Amines	Primary, (1°)	– NH_2	Alkylamine	Alkanamine
		Secondary, (2°)	– NH –	Alkyl alkylamine Or Dialkylamine	N- Alkylalkanamie
		Tertiary, (3°)	– N =	Trialkylamine	N- Alkyl- N-alkylalkanamine
	Aroma-tic Amines	Primary, (1°)	– NH_2	Aniline	Benzenamine or Aniline
		Secondary. (2°)	– NH –	N- Alkylaniline	N- Alkylaniline

	Tertiary, (3^o)	– N =	N- Alkyl- N-alkylaniine	N- Alkyl- N-alkylaniine

Preparation of Amines	(i) By the reduction of Nitro compounds, Nitriles (Cyanides), Isocyanides, Amides: (a) by catalytic reduction, (b) by reduction with active metals (Fe, Sn, Zn) and HCl acid, (c) by using other Reducing agents like, $LiAlH_4$/dry ether. (ii) BY Hoffmann-Bromamide rection: $R – CO - NH_2 + Br_2 + 4\ KOH \rightarrow R – NH_2 + K_2CO_3 + 2KBr + 2H_2O$
Basicity of Aliphatic Amines:	(a) In gaseous States: Ammonia $< 1^o < 2^o < 3^o$ (Due to increasing + I effect of R groups) (b) In aqueous solutions: Ammonia $< 1^o < 3^o < 2^o$ (Due to stearic hindrance, +I effect and solvation effect). Basicity of Aromatic Amines: (a) Aromatic Amines < Ammonia < Aliphatic Amines. **Effect of substituents on basic properties in aromatic amines:** (i) Presence of EDG group: Basic properties increase due to (+ I) effect. (ii) Presence of EWG group: Basic properties decrease due to (- I) effect.
Main Chemical Reactions of Amines:	**(A) Acylation** – Reaction with acid chlorides/acid anhydrides. **(i)** $R'- COCl + H_2N - R \rightarrow R'- CO – NH – R$ (N-alkyl amides) **(ii)** $R'- COCl + HN – R_2 \rightarrow R'- CO – N – R_2$ (N,N-dialkylamides) Note: Tertiary amines do not acylated due to the absence of H-atom at N.
	(B) Carbylamine reactions <u>(or Isocyanide test)</u>: (Distinguished test of Primary amines) **Ar/ R** $– NH_2$ **+** $CHCl_3 + 3KOH$ (alc.) $\rightarrow$ **Ar/R –** $NC + 3KCl + 3H_2O$
	(C) Diazotisation: Conversion of aromatic primary amines into diazonium salts by treating with a cold (273 K) of HNO_2 acid. **Ar** $– NH_2 \xrightarrow{NaNO_2 + HCl}$ **Ar** $– N = N – Cl + 2H_2O$ (Arenediazonium Chloride) But aliphatic primary amines give alcohols with N_2 gas. **R** $– NH_2 \xrightarrow{NaNO2 + HCl}$ **R** $– OH + N_2 + H_2O$
	(D) Electrophilic substitution reaction: Since amino group **($– NH_2$)** is o- & p-directing and strong activating group, aromatic amines undergo electrophilic substitution reactions easily.
Test for amines	1. **Hinsberg's Test** - Hinsberg's Reagent $\rightarrow$ Reagent - $C_6H_5 - SO_2Cl$ (Benzenesulphonyl Chloride) Amines are shaken with the reagent in presence of KOH, Primary amines give clear solution, whereas Secondary amines give precipitate; but tertairy amines do not react.
Reaction of Arene diazonium salts	Deamination: Removal of amino group via diazo group **(- N = N -).** **Ar** $– N = N – Cl + H_3PO_2 + H_2O \rightarrow$ **Ar** $– H + H_3PO_3 + HCl + N_2$
	Replacement of diazo group by Cl, Br, CN group: - By two methods; **(a) Sandmeyer reaction**: (i) **Ar** $– N = N – Cl \xrightarrow{CuCl/HC\ l}$ **Ar** – Cl (ii) **Ar** $– N = N – Cl \xrightarrow{CuBr/HBr}$ **Ar** – Br -, (iii) **Ar** $– N = N – Cl \xrightarrow{CuCN/KCN}$ **Ar** – CN **(b) Gattermann reaction:**

	(i) **Ar** – N = N – Cl $\xrightarrow{Cu/HCl}$ **Ar** – Cl (ii) **Ar** – N = N – Cl $\xrightarrow{Cu/HBr}$ **Ar** – Br (iii) **Ar** – N = N – Cl $\xrightarrow{Cu/KCN}$ **Ar** – CN
	Replacement of diazo group **by – OH :** **Ar** – N = N – Cl + H_2O → **Ar** – OH (Phenol)
	Coupling reaction: **(a)** **Ar** – N = N – Cl + **Ar** – OH --→ **Ar** – N = N – **Ar** – OH **(b)** **Ar** – N = N – Cl + H_2N – **Ar** --→ **Ar** – N = N – NH - **Ar** (Aniline or substituted anilines)

QUESTIONS WITH ANSWERS

Assertion – Reason Type (1 mark)

Given below are two statements labelled as Assertion (A) and Reason (R)

While answering these questions, you are required to choose any one of the following four responses.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

1. Assertion : Aromatic 1°amines can not be prepared by Gabriel phthalimide synthesis.
Reason: Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

Ans. (a)

2. Assertion : Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

Ans. (d)

3. Assertion : Amines are basic in nature.
Reason : Amines have lone pair of electrons on nitrogen atom.

Ans. (a)

4. Assertion : Acetanilide is less basic than aniline.
Reason : Acetylation of aniline results in decrease of electron density on nitrogen.

Ans. (d)

5. Assertion : Nitration of aniline can be conveniently done by protecting the amino group by acetylation.
Reason : Acetylation increases the electron-density in the benzene ring.

Ans.: (c)

Very Short Answer type Questions (1 mark)

1. Arrange the following compounds in decreasing order of basic strengths in their aqueous solutions: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$

Ans. Basicity order: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

2. Arrange the following compounds in an increasing order of their solubility in water : $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

3. Give a chemical test to distinguish between ethylamine and aniline.

Ans. Aniline – gives Azo dye test

4. Write the structure of n-methylethanamine.

Ans : $H_3C—H_2C—NH—CH_3$

5. How may methyl bromide be preferentially converted to methyl isocyanide?

Ans. By carbylamine reaction (or Isocyanide Test).

6. Define 'Diazotization'.

Ans. The conversion of primary aromatic amines into diazonium salts

7. Out of $CH_3—NH_2$ and $(CH_3)_3N$, which one has higher boiling point?

Ans. $CH_3—NH_2$ has higher boiling point than $(CH_3)_3N$.

8. Write IUPAC name of the following compound: $(CH_3CH_2)_2NCH_3$

Ans. N-Ethyl-N-methylethanamine

9. Name the nitrogen containing compound which has the smell of bitter almonds.

Ans. Nitrobenzene.

10. Give one important industrial use of phenyl isocyanide.

Ans. It is used for preparation of N-methylaniline.

11. Why is methylamine stronger base than ammonia?

Ans. Due to presence of electron releasing $–CH_3$ group, having +I effect.

12. What is the product when $C_6H_5CH_2NH_2$ reacts with HNO_2?

Ans. $C_6H_5CH_2OH$ is formed.

13. What is the best reagent to convert nitrile to primary amine?

Ans. $LiAlH_4$ and Sodium/Alcohol

14. What is Hinsberg reagent?

Ans. Benzene sulfonyl chloride ($C_6H_5SO_2Cl$)

15. Why is benzene diazonium chloride not stored and used immediately after its preparation?

Ans. Because of it is an unstable compound in nature. With a slight increase in temperature, it dissociates to give nitrogen gas.

Multiple Choice Questions Type (1 mark)

1. Which of the following does not react with Hinsberg reagent?

(a) Ethylamine (b) $(CH_3)_2NH$ (c) $(CH_3)_3N$ (d) Propan-2-amine

Ans. (c) $(CH_3)_3N$

2. $C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} X \xrightarrow{P/Br_2} Y \xrightarrow[(excess)]{NH_3} Z.$

In above sequence, Z is

(a) Cyanoethane (b) Ethanamide (c) Methanamine (d) Ethanamine

Ans. (d) Ethanamine

3. Oxidation of aniline with $K_2Cr_2O_7/H_2SO_4$ gives

(a) phenylhydroxylamine (b) p-benzoquinone zc) nitrosobenzene (d) nitrobenzene

Ans. (b) p-benzoquinone

4. Which of the following pair of species will yield carbylamine?

(a) CH_3CH_2Br and KCN (b) CH_3CH_2Br and NH_3 (excess)

(c) CH_3CH_2Br and AgCN (d) $CH_3CH_2NH_2$ and HCHO

Ans. (c) CH_3CH_2Br and AgCN

5. The reaction of aniline with benzoyl chloride gives

(a) Benzoin (b) Benzanilide (c) Benzalaniline (d) Benzamide

Ans. (b) Benzanilide

6. Which of the following cannot couple with benzene diazonium chloride?

(a) Aniline (b) Phenol (c) ß-Napthol (d) Benzyl alcohol.

Ans. (d) Benzyl alcohol.

7. The hybrid state of N is R_2NH is

(a) sp^3 (b) sp^2 (c) sp (d) dsp^2

Ans. (a) sp^3

8. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by

(a) $NaBH_4$ (b) H_2-Pd/C (c) $LiAlH_4$ (d) Zn-Hg/HCl

Ans. (c) $LiAlH_4$

9. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2$ NH is

(a) $CH_3 NH_2 < (CH_3)_2 NH < NH_3$ (b) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

(c) $(CH_3)_2 NH< NH_3 < CH_3NH_2$ (d) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

Ans. (d) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

10. Which of the following amines can exhibit enantiomerism?

(a) Benzenamine (b) 2-Butanamine

(c) 2-Propanamine (d) 2-Methyl-propanamine.

Ans. (b) 2-Butanamine

Short Answer type Question (2 marks)

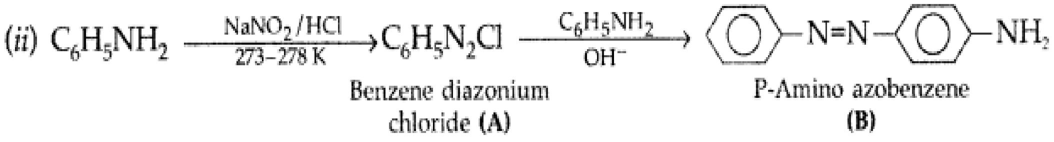
1. Identify A and B in each of the following processes:

$$(i)\ CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{reduction} B \qquad (ii)\ C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$$

Ans.

$$(i)\quad \underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow{NaCN} \underset{\text{Propanenitrile (A)}}{CH_3CH_2\,C \equiv N} + NaCl$$

$$\underset{\text{(A)}}{CH_3CH_2\,C \equiv N} \xrightarrow[Ni/H_2]{reduction} \underset{\text{Propanamine (B)}}{CH_3CH_2CH_2NH_2}$$



2. Describe the following giving the relevant chemical equation in each case :

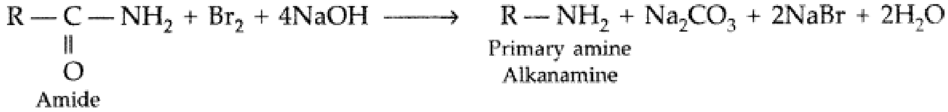
(i) Carbylamine reaction (ii) Hofmann’s bromamide reaction

Ans.

(i) Carbylamine reaction: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic KOH form isocyanides or carbylamines which are foul smelling substances. This reaction is known as carbylamines reaction.

$$\underset{\text{Primary amine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\Delta} \underset{\text{Carbylamine}}{R-NC} + 3KCl + 3H_2O$$

(ii) Hofmann's bromamide reaction: Primary amines can be prepared by treating an amide with Br_2 in an aqueous or alcoholic solution of NaOH.



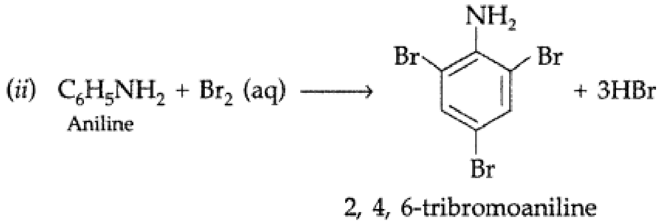
$$\underset{\text{Amide}}{R-\overset{}{\underset{\underset{O}{\|}}{C}}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\substack{\text{Primary amine}\\ \text{Alkanamine}}}{R-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

3. Complete the following reaction equations:

(i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$? (ii) $C_6H_5NH_2 + Br_2$ (aq) → ?

Ans.

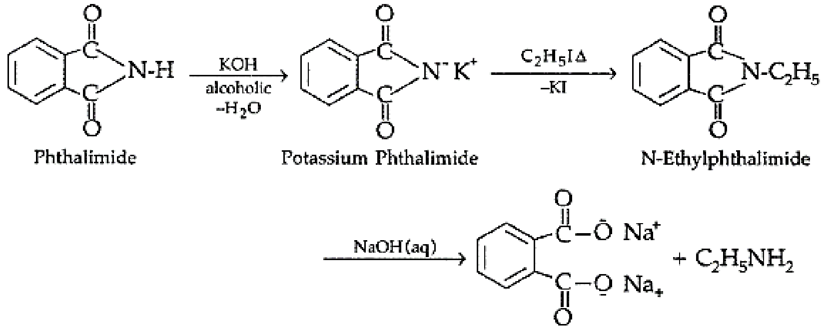
(i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$



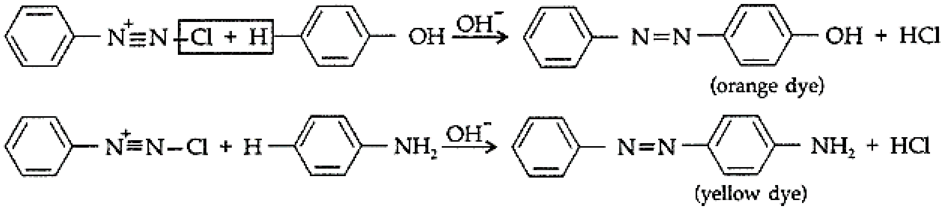
4. Explain the following reactions :

(a) Gabriel Phthalimide reaction (b) Coupling reaction

Ans. (a) Gabriel phthalimide synthesis: It is used to prepare 1° amine (Primary amine). The starting compound is a phthalimide. But aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



(b) Coupling reaction: Arene diazonium salts react with highly reactive aromatic compounds such as phenols and amines to form brightly coloured azo compounds. Ar – N = N – Ar. This reaction is known as coupling reaction.



5. Give reasons :

(i) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(ii) CH_3CONH_2 is weaker base than $CH_3CH_2NH_2$.

Ans. (i) Due to the strong activating effect of the NH_2 group, aromatic amines undergo electrophilic substitution reactions readily than benzene.

(ii) In case of acetamide due to resonance, the lone pair of electrons on the nitrogen atom is delocalized over keto group, which decreases electron density hence less basic while in ethylamine due to +1 effect of ethyl group electron density increases on N-atom and hence basic character increases.

Long Answer type Questions (3 marks)

1. State reasons for the following:

(i) pK_b value for aniline is more than that for methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not soluble in water.

(iii) Primary amines have higher boiling points than tertiary amines.

Ans. (i) Higher the pK_b value, lower will be the basicity therefore aniline is less basic than methylamine because the lone pair of electrons on nitrogen atom gets delocalized over the benzene ring are unavailable for protonation due to resonance in aniline which is absent in case of alkyl amine.

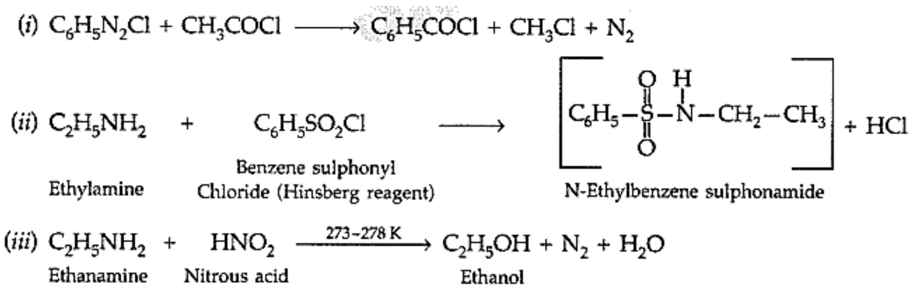
(ii) Ethylamine is soluble in water due to its capability to form H-bonds with water while aniline is insoluble in water due to larger hydrocarbon part, which tends to retard the formation of H-bonds.

(iii) Due to presence of two H-atoms on N-atom of primary amines, they undergo extensive intermolecular H-bonding while tertiary amines due to the absence of a H-atom on the N-atom, do not undergo H- bonding. As a result, primary amines have higher boiling points than 3° amines.

2. Complete the following reaction equations :

(i) $C_6H_5Cl + CH_3COCl \rightarrow ?$ (ii) $C_2H_5NH_2 + C_6H_5SO_2Cl \rightarrow ?$ (iii) $C_2H_5NH_2 + HNO_2 \rightarrow ?$

Ans.



(i) $C_6H_5N_2Cl + CH_3COCl \longrightarrow C_6H_5COCl + CH_3Cl + N_2$

(ii) $\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Benzene sulphonyl Chloride (Hinsberg reagent)}}{C_6H_5SO_2Cl} \longrightarrow \underset{\text{N-Ethylbenzene sulphonamide}}{\left[C_6H_5-\overset{O}{\underset{O}{S}}-\overset{H}{N}-CH_2-CH_3\right]} + HCl$

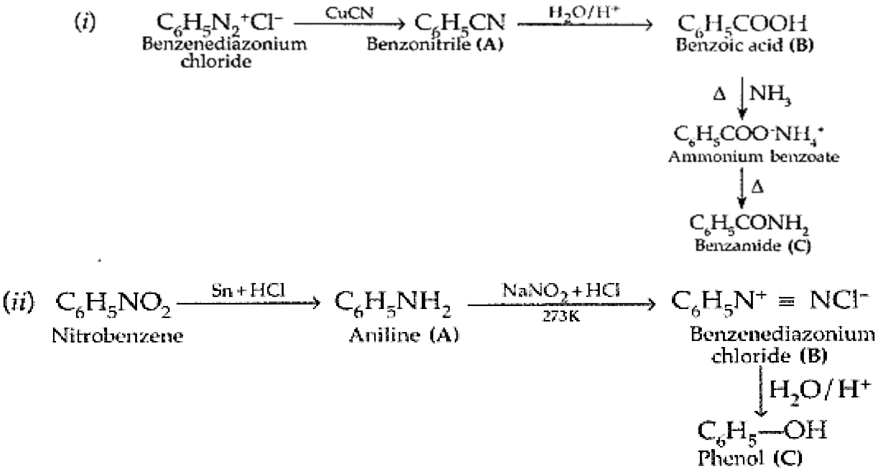
(iii) $\underset{\text{Ethanamine}}{C_2H_5NH_2} + \underset{\text{Nitrous acid}}{HNO_2} \xrightarrow{273-278\,K} \underset{\text{Ethanol}}{C_2H_5OH} + N_2 + H_2O$

3. Give the structure of A, B and C in the following reactions:

(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

Ans.



(i) $\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2^+Cl^-} \xrightarrow{CuCN} \underset{\text{Benzonitrile (A)}}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid (B)}}{C_6H_5COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Ammonium benzoate}}{C_6H_5COO^-NH_4^+} \xrightarrow{\Delta} \underset{\text{Benzamide (C)}}{C_6H_5CONH_2}$

(ii) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Sn+HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273K]{NaNO_2+HCl} \underset{\text{Benzenediazonium chloride (B)}}{C_6H_5N^+ \equiv NCl^-} \xrightarrow{H_2O/H^+} \underset{\text{Phenol (C)}}{C_6H_5-OH}$

UNIT-14 BIOMOLECULES

CARBOHYDRATES:

Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Carbohydrates are also known as saccharides.

CLASSIFICATION OF CARBOHYDRATES:-

Classification of carbohydrates:- On the basis of the molecular size, carbohydrates have been classified into following four types :

(i) Monosacharaides:- The simple carbohydrates that cannot be broken further into smaller units on hydrolysis. e.g :- glucose, fructose, ribose etc

(ii) Oligosaccharides:- These are the carbohydrates which on hydrolysis give 2 to 10 units of monosaccharides. eg:- sucrose, maltose etc.

(iii) Polysaccharides:- These carbohydrates on hydrolysis give large number of monosaccharides units. eg:- cellulose, starch etc.

REDUCING AND NON-REDUCING SUGAR

Those carbohydrates which contain free aldehydic or ketonic group and reduce Fehling's solution and Tollen's reagent are called **reducing sugars**. eg – all monosaccharides, maltose, lactose etc.

Those carbohydrates which do not have free aldehydic or ketonic group and do not reduce Fehling's solution and Tollen's reagent are called **non-reducing sugars**. eg – Sucrose.

PREPRATION OF GLUCOSE

(I) FROM SUCROSE:-

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) FROM STRACH:-

$$\underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+,\ 393K,\ 2-3\ ATM} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

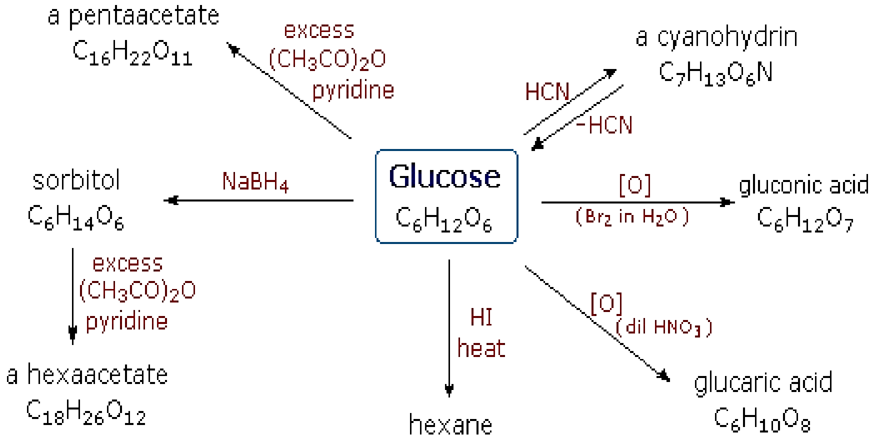
STRUCTURE OF GLUCOSE

How will you prove that glucose has aldehydic group and five alcoholic group?

Following evidences support the open chain structure of glucose

1. It has a molecular formula of $C_6H_{12}O_6$
2. When HI is heated for a long time, n-hexane is formed which indicates that all the six carbon atoms are linked in a straight chain.
3. The oxime is formed when glucose reacts with hydroxylamine and cyanohydrins on the addition of hydrogen cyanide to it. This reaction can confirm the presence of the carbonyl group in glucose.
4. On the reaction of glucose with a mild oxidizing agent like bromine water, the glucose gets oxidized to a carboxylic acid that contains six carbon atoms. This indicates that the carbonyl group is present as an aldehyde group.
5. The presence of -OH group is confirmed after the acetylation of glucose with acetic acid, which gives glucose pent acetate.

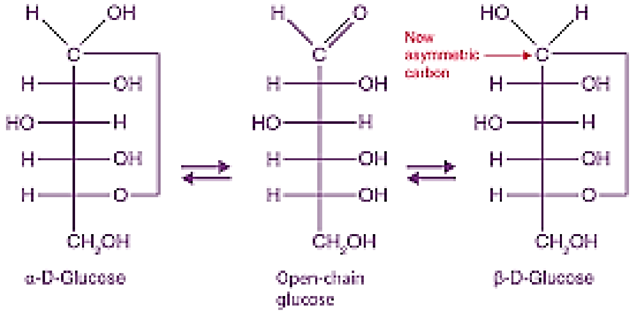
6. Glucose as well as gluconic acid both yields dicarboxylic acid and saccharic acid on oxidation with nitric acid. The presence of primary alcohol is indicated by this.



Other Reactions of Glucose (Presence of ring structure)

Glucose does not give Schiff's test and does not react with sodium bisulphite and NH_3.
Pentaacetyl glucose does not react with hydroxyl amine.
This shows the absence of –CHO group and hence the presence of ring structure.

RING STRUCTURE OF GLUCOSE:



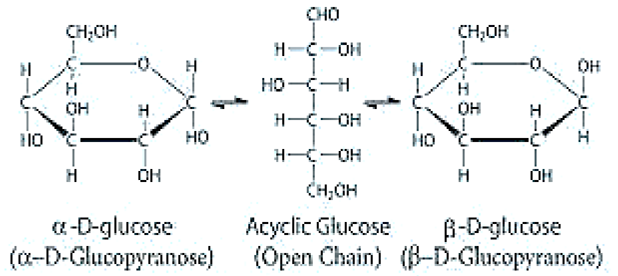
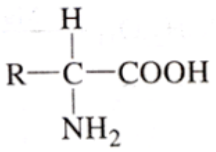


Figure 14.5 Cyclic structures of glucose

Glycosidic linkage: The oxide linkage formed by the loss of a water molecule when two monosaccharides are joined together through oxygen atom is called glycosidic linkage.

AMINO ACIDS

Amino acids contain amino (–NH_2) and carboxyl (–COOH) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as $\alpha, \beta, \gamma, \delta$ and so on. Only α -amino acids are obtained on hydrolysis of proteins.



$$R-\underset{NH_2}{\overset{H}{C}}-COOH$$

Where R is any side chain

Types of amino acids:

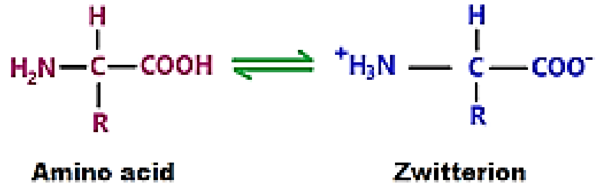
(a) Essential amino acids: The amino acids which cannot be synthesized in the body and must be obtained through diet, are known as essential amino acids. These are 10 in number.
Examples: Valine, Leucine etc.

(b) Non-essential amino acids: The amino acids, which can be synthesized in the body, are known as non-essential amino acids. Examples: Glycine, Alanine etc.

Zwitter ion form of amino acids:

1. Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges.

2. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases



PROTEINS

Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein.

Peptide linkage: Peptide linkage is an amide linkage formed by condensation reaction between –COOH group of one amino acid and $–NH_2$ group of another amino acid (as - CO – NH – bond)

Type Proteins based on molecular shape:-

Fibrous proteins	**Globular proteins**
(i) Polypeptide chains run parallel or anti-parallel and held together by Hydrogen and disulphide bonds.	(i) Chains of Polypeptide coil around to give a spherical shape.
(ii) Generally insoluble in water. e.g. Keratin, collagen, myosin, fibroin.	(ii) Usually soluble in water. e.g., insulin, thyroglobin, albumin, hemoglobin and fibrinogen gets converted into fibrous protein fibroin on clotting of blood.

Denaturation of Proteins: Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, 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 proteins
eg:- coagulation of egg white on boiling, curdling of milk, blood clotting etc.

NUCLIC ACIDS

Nucleic Acids: Nucleic acids are long chain polymers of nucleotides. They are called poly nucleotides. They play an important role in transmission of hereditary characteristics and bio-synthesis of proteins.
Types of nucleic acids: There are two types of nucleic acids. These are DNA and RNA.

Constituents of nucleic acids :- (i) Pentose sugar (ii) Phosphoric Acid iii) Nitrogenous base
Sugar are (i) D–ribose & (ii) D–2-deoxyribose
Nitrogenous bases are Adenine(A), Guanine (G), Thymine(T), Cutosine (C) & Uracil (U)

Deoxyribonucleic acid (DNA)	**Ribonucleic acid (RNA)**
1. It has a double stranded -helix structure in which two strands are coiled spirally in opposite directions. 2. Sugar present is –D–2-deoxyribose 3. Bases: i) Purine bases: Adenine (A) and Guanine (G) ii) Pyrimidine bases: Thymine (T) and cytosine (C) 4. It occurs mainly in the nucleus of the cell. 5. It is responsible for transmission for heredity character.	1. It has a single stranded -helix structure. 2. Sugar present is D–ribose 3. Bases: i) Purine bases: Adenine (A) and Guanine (G) ii) Pyrimidine bases: Uracil (U) and cytosine (C) 4. It occurs mainly in the cytoplasm of the cell. 5. It helps in protein synthesis.

VITAMINS

Vitamins are generally regarded as organic compounds required in the diet in small amount to perform specific biological functions for normal maintenance of optimum growth and health of the organism.
Vitamins are of two types: -
(i) Fat soluble vitamins: example – A, D, E and K.
(ii) Water soluble vitamins: example – B and C

Some important Vitamins, Their sources and their deficiency Diseases

S.N	Vitamins	Sources	Deficiency Diseases
1	A	Fish liver oil, carrot, butter, milk	Night blindness, xeropthalmia
2	C	Citrus fruits, amla, green leafy vegetables	Scurvy
3	D	Fish, egg yolk, exposure to sun light	Rickets, osteomalacia,
4	E	Sunflower oil, wheat, germ oil	Muscular weakness, increased fragility of RBCs
5	K	Green leafy vegetables	Increased blood clotting time
6	B1	Yeast, milk, cereals, green vegetables	Beri-beri,
7	B2	Milk, egg white, liver, kidney	Cheilosis, digestive disorders
8	B6	Yeast, milk, egg yolk, cereals,	convulsions

		grams	
9	B12	fish ,meat, ,egg, curd	Pernicious anaemia

QUESTIONS AND ANSWERS

ASSERTION & REASONING – [Each question is of 1 mark].

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement..

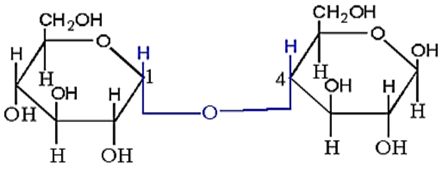
Q1. Assertion (A): Sucrose is a non-reducing sugar.
Reason (R): Sucrose has glycosidic linkage.

02. Assertion (A): Glycine must be taken through diet.
Reason (R): It is a non- essential Amino acid.

03. Assertion(A): β-glycosidic linkage is present in maltose
Reason (R): Maltose is composed of two glucose units in which C–1 of one glucose unit is linked to C–4 of another glucose unit.

04. Assertion : Vitamin D can be stored in our body.
Reason : Vitamin D is fat soluble vitamin.

05. Assertion: β-glycosidic linkage is present in maltose,



Maltose

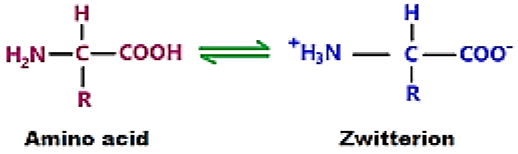
Reason : Maltose is composed of two glucose units in which C–1 of one glucose unit is linked to C–4 of another glucose unit.

Answers: 1a, 2d, 3d, 4a, 5d

VERY SHORT ANSWER TYPE QUESTION – [1 mark each]

1. Why are carbohydrates generally optically active?
Ans. It is due to the presence of Chiral Carbon atoms in their molecules.

2. Write the formula of Zwitter ion for Glycine
Ans:



3. Which of the two components of starch is water soluble?
Ans. Amylose is water soluble.

4. What is the name of the monomer of protein?
Ans. Amino acid is the monomer of protein.

5. Give two examples of nucleic acids.
Ans. DNA and RNA are two examples of nucleic acids.

6. Give some examples of oligosaccharides.
Ans. Sucrose, lactose, and maltose are some examples of oligosaccharides.

7. What happens when Glucose reacts with nitric acid?
Ans. Glucose gets oxidized to Gluconic Acid

$$HO\text{-}CH_2\text{-}(CHOH)_4\text{-}CHO \xrightarrow{HNO_3} HOOC\text{-}(CHOH)_4\text{-}COOH$$

8. Which one of α-helix and β-helix is more stable and why?
Ans. α-helix is right-handed and is more stable due to intermolecular H-bonding between first and fourth amino acid.

9. The sequence of bases in one strand of DNA is TACGGACA. What is the sequence of bases of complementary strand of DNA.
Ans. ATGCCTGT.

10. Name the vitamin whose deficiency causes rickets?
Ans. Vitamin D.

11. Give an example of (a) water soluble vitamin (b) fat soluble vitamin
Ans. (a) Vitamin C (b) Vitamin D.

12. Differentiate Nucleotides and nucleoside.
Ans. Nucleotides: Pentose sugar + N- containing base + Phosphate
Nucleosides: Pentose sugar + N- containing base only.

13.Which functional groups are present in monosaccharides?
Ans. —OH and —CHO or —OH and >CO

14. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain
Ans. In aqueous medium –COOH group loses a proton and amino group accepts to form a zwitter ion.

15. What are the products of hydrolysis of sucrose?
Ans. Glucose and fructose.

MULTIPLE CHOICE QUESTIONS – [1 mark each]

1. Which sugar is present in RNA?
(a) Glucose (b) Fructose (c) β-D- Ribose (d) D-2-Deoxyribose

Ans. (c) β-D- Ribose.

(2) Which sugar is present in DNA?
(a) Glucose (b) Fructose (c) β-D- Ribose (d) D-2-Deoxyribose
Ans. (d) D-2-Deoxyribose.

(3) Which of the following amino acid is neutral?
(a) Aspartic acid (b) Glycine (c) Lysine (d) Arginine
Ans. (b) Glycine

(4) A secondary structure of protein is stabilized by
(a) H-bond (b) peptide bond (c) ionic bond (d) disulphide bond
Ans. (a) H-bond

(5) Scurvy is caused due to deficiency of
(a) Vitamin B1 (b) Vitamin B2 (c) Ascorbic acid (d) Glutamic acid
Ans. (c) Ascorbic acid

(6) Which of the following reagents does not react with glucose?
(a) NH_2OH (b) HCN (c) 2,4–DNP reagent (d) Br_2 water
Ans. (c) 2,4–DNP reagent.

(7) What are the hydrolysis products of lactose?
(a) β–D-galactose and β –D-Glucose (b) α –D-Glucose and α –D-Glucose
(c) α –D-Glucose and β –D-Fructose (d) None of these
Ans. (a) β–D-galactose and β –D-Glucose

(8). Which of the following is incorrect for glucose?
(a) It contains four >CHOH groups (b) It contains one –CH2OH group
(c) It contains one –CHO group (d) It contains one >C=O group
Ans. (d) It contains one >C=O group

(9) Which of the following is/are example(s) of denaturation of protein?
(a) Coagulation of egg white (b) Curding of milk
(c) Clotting of blood (d) Both (a) and (b)
Ans. (d) Both (a) and (b)

(10) Which of the following reactions of glucose can be explained only by its cyclic structure?
(a) Glucose forms Penta aceate.
(b) Glucose reacts with hydroxylamine to form an oxime.
(c) Penta acetate of glucose does not react with hydroxylamine.
(d) Glucose is oxidized by nitric acid to gluconic acid.
Ans. (c) Pentaacetate of glucose does not react with hydroxylamine.

SHORT ANSWER TYPE QUESTIONS – [2 marks each]

1) What is the effect of denaturation on the structure of proteins?
Ans. During denaturation, 2° and 3° structures of proteins are destroyed but 1° structure remains intact. Due to denaturation, the globular proteins (soluble in H_2O) are converted into fibrous proteins (insoluble in H_2O) and their biological activity is lost. For example, boiled egg which contains coagulated proteins cannot be hatched.

2) Define the following as related to proteins
(i) Peptide linkage (ii) Primary structure (iii) Denaturation of protein.

Ans. (i) Peptide linkage- Peptide bond is formed by the condensation of two or more, same or different α-amino acids. -CO -NH- linkage is called peptide linkage.

(ii) Primary structure- Primary structure of proteins give the sequence in which amino acids are linked in one or more polypeptide chains of proteins.

(iii) Denaturation of protein- A process that changes the physical and biological properties without affecting the chemical composition of a protein is called denaturation. The denaturation is caused by certain physical or chemical treatments such as in pH, temperature, presence of some salts or certain chemical agents.

3) Differentiate the following: (i) Globular and fibrous proteins. (ii) Nucleoside and a nucleotide.

Ans. (i) Fibrous proteins: They are long and thread like and tend to lie side by side to form fibers. In some cases, they are held together by hydrogen bonds at many points. These proteins serve as a chief structural material of animal tissues. Examples, keratin, collagen

Globular proteins: The molecules of these proteins are folded into compact units and form spheroid shapes. Intermolecular forces are weak. These proteins are soluble in water or aqueous solution of acids, bases or salts. Globular proteins make up all enzymes, hormones, fibrinogen etc. Examples, hemoglobin, insulin

(ii) The nitrogenous base and a pentose sugar are called as nucleosides. The nitrogenous base, a pentose sugar and a phosphate group are called as nucleotides.

4) What are essential and non-essential amino acids? Give two examples of each type.

Ans. The amino acids which can be made by our bodies and are not required in our diet are called nonessential amino acids. For example, glycine and alanine.

The amino acids which cannot be made by our bodies and must be supplied in our diet are called essential amino acids. For example, valine and leucine.

5) (a) Name the vitamins in each case whose deficiency causes
(i) Night blindness (ii) Rickets
(iii) Poor coagulation of blood (iv) Scurvy
(b)What is isoelectric point?

Ans. (a) (i) Vitamin A (ii) Vitamin D
(iii) Vitamin K (iv) Vitamin C

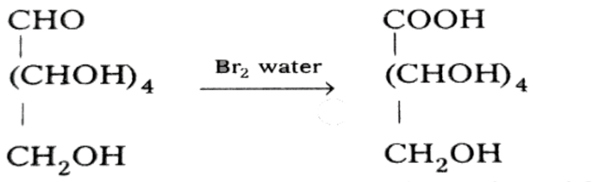
(b)The pH at which no net migration of amino acid takes place under the influence of an applied electric field is called isoelectric point. For example, isoelectric point of glycine is 6.1.

LONG ANSWER TYPE QUESTIONS – [Each question is of 3 mark]

1. What happens when D- Glucose is treated with the following reagents
   (a) Br_2 water (b) PCl_5 (C) HNO_3

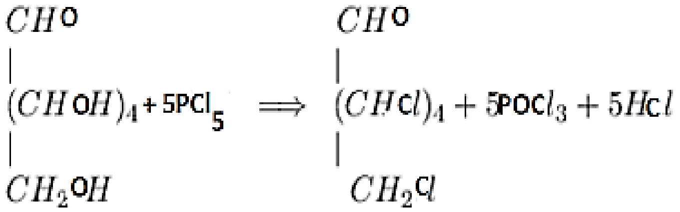
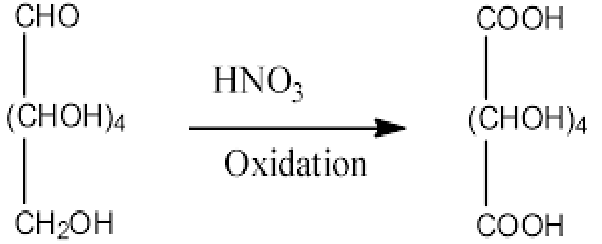
Answer:-

(a) Br_2 water



$$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}\xrightarrow{Br_2\text{ water}}\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{array}$$

gluconic acid

(b) PCl_5	(C) HNO_3
 $$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}+5PCl_5\Rightarrow\begin{array}{c}CHO\\|\\(CHCl)_4\\|\\CH_2Cl\end{array}+5POCl_3+5HCl$$	 $$\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}\xrightarrow[\text{Oxidation}]{HNO_3}\begin{array}{c}COOH\\|\\(CHOH)_4\\|\\COOH\end{array}$$ Saccharic acid

Q. 2. Differentiate between DNA and RNA?

Ans.

DNA (Deoxyribonucleic acid)	RNA (Ribonucleic acid)
1. It occurs mainly in the nucleus of the cell.	1.It occurs in the cytoplasm of the cell
2. It has double stranded α-helix structure in which two strands are coiled spirally in opposite directions.	2.It has single stranded α-helix structure
3. The sugar molecule is 2-deoxyribose.	3. The sugar molecule is ribose.
4. Nitrogenous base uracil is not present.	4. Nitrogenous base thymine is not present.
5. DNA has unique property of replication.	5. RNA usually does not replicate.
6. It is responsible for the transmission for heredity character.	6.Helps in protein biosynthesis