केन्द्रीय विद्यालय संगठन, रायपुर संभाग

KENDRIYA VIDYALAYA SANGATHAN RAIPUR REAGION

TWO DAYS WORKSHOP FOR PGTs (CHEMISTRY)

DATE: 26 TO 27-09-2022

VENUE: K.V. RAIGARH

CHIEF PATRON : SHRI VINOD KUMAR
DEPUTY COMMISSIONER KVS RO RAIPUR

PATRON: SHRI A.K. MISHRA
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Mrs. FARHANA KHAN, PGT(CHEM)KV BMY BHILAI.

Two Days Workshop For The PGT(s) Cjemistry
Venue: KV Raigarh(C.G.)
Time Schedule for Two Days Workshop

Date	9.30-10.00AM	10AM-12Noon	12-12.45PM	12.45PM-2.30PM	2.30-2.45PM	2.45-4.00PM
26.09.22	Registration ,Aims and Objectives& work allotment	Presentation by the Participants of their pre Workshop Works	Lunch	Preparation Of Model papers and Competency based questions with hints	Tea Break	Preparation of VSA,SA,LA,Objectice type questions with hints
27.09.22	Stock taking by the Course Co ordinatorof day I work	Editing and finalizing Chapter wise Gist	Lunch	Editing and finalising CBQ in terms of numbers and quality	Tea Break	Editing and finalising VSA,SA,LA,Objectice type questions in terms of numbers and quality

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LIST OF PARTICIPANTS

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SOLUTIONS

KEY CONCEPTS

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

EXPRESSING CONCENTRATIONS OF SOLUTIONS

- Mass percentage: Mass of solute per 100g of solution. Mass%= (mass of solute/total mass solution) x 100
- Volume percentage: volume of solute per 100 mL of solutions.
- Parts per million: parts of a component per million (10^6) parts of the solution.
- Mole fraction(x): It is the ratio of no. of moles of one component to the total no. of moles of all the components present in the solution.
- Molarity: No. of moles of solute dissolved in one litre of solution.
- Molality(m): No. of moles of solute per kg of the solvent.
- Molality is independent of temp. whereas molarity is a function of temp. because vol. depends on temp. and mass does not.

HENRY'S LAW

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

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

$$P=K_H X$$

K_H is Henry's law constant.

APPLICATION OF HENRY'S LAW

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

RAOULT'S LAW:- It states that:

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

$$P_A = P^0_A X_A; \quad P_B = P^0_B X_B$$

The total pressure is equal to sum of partial pressure.

$$P_{total}=P_A+P_B$$

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

$P_A \alpha X_A \quad P_A = P^0_A X_A$

IDEAL SOLUTION

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

CONDITIONS

I. $P_A = P^0_A X_A \quad P_B = P^0_B X_B$ II $\Delta Hmix = 0$ III $\Delta Vmix = 0$

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

NON IDEAL SOLUTION

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

CONDITIONS

I. $P_A \neq P^0_A X_A \quad P_B \neq P^0_B X_B$ II $\Delta Hmix \neq 0$ III $\Delta Vmix \neq 0$

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

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

Ex: mixture of ethanol and acetone.

$P_A > P^0_A X_A \; ; \; P_B > P^0_B X_B$

$\Delta Hmix =$ Positive, $\Delta Vmix =$ Positive

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

Ex: mixture of chloroform and acetone.

$P_A < P^0_A X_A \quad P_B < P^0_B X_B$

$\Delta Hmix =$ negative, $\Delta Vmix =$ negative

AZEOTROPE

Mixture of liquid having the same composition in liquid and vapour phase and boil at constant temp. Azeotrope are of two types:-

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

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

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

1. RELATIVE LOWERING OF VAPOUR PRESSURE

$(P^O_A - Ps)/P^O_A = X_B, \quad X_B = n_B / n_A + n_B$

For dilute solution, $n_B << n_A$, hence n_B is neglected in the denominator. $(P^O_A - Ps)/P^O_A = n_B / n_A$ $(P^O_A - Ps)/P^O_A$

$= W_B \times M_A / M_B \times W_A$

2. ELEVATION OF BOILING POINT

$\Delta T_b = k_b m$ Where $\Delta T_b = T_b - T^O_b$

k_b= molal elevation constant/ Ebullioscopic constant m=molality

$M_B = k_b \times 1000 \times W_B / \Delta T_b \times W_A$

3. DEPRESSION IN FREEZING POINT

$\Delta T_f = k_f m$ Where $\Delta T_f = T^O_f - T_f$

K f= molal depression constant/ Cryoscopic constant m=molality

$M_B = k_f \times 1000 \times W_B / \Delta T_f \times W_A$

4. OSMOTIC PRESSURE

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

$\pi = CRT$

$\pi = n_B/VRT$(n_B =no.of moles of solute; V= volume of solution(L)R= 0.0821Latmmol-^{1}; T= temperature in kelvin

ISOTONIC SOLUTION

Two solutions having same osmotic pressure and same concentration.

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

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

VAN'T HOFF FACTOR (i)

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

i = normal molecular mass/ observed molecular mass

= observed colligative properties/ calculated value of colligative properties i<l

(for association) i>l (for dissociation)

MODIFIED FORMS OF COLLIGATIVE PROPERTIES

1) $(P^O_A - Ps)/P^O_A = i \times X_B$ 2) $\Delta_{Tb} = i \times k_b m$ 3) $\Delta T_f = i \times k_f m$ 4) $\pi = i \times CRT$

Expressing concentration of a solution

Mass % (W/W)
= mass of one component / total mass x 100

Mass by Volume % (w/V)
= volume of the solute / 100ml solution x 100

Volume % (V/V)
= volume of one component / total volume x 100

Mole fraction (X)
X = no. of moles of component / total no. of moles

$X_A = n_A / (n_A + n_B)$ $X_B = n_B / (n_A + n_B)$

ppm
used when solute present in traces

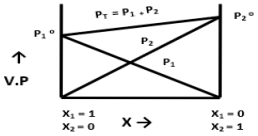
ppm = no. of parts of component / total no. of parts of all components of the solution x 100

molarity (M)
= no. of moles of solute / vol. of the solution in l.
temperature dependant
V changes with temperature

molality (m)
= no.of moles of the solute / mass of the solvent in Kg.
Temperature independent

Solutions

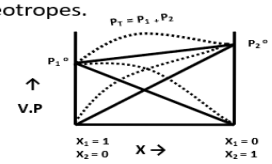
Ideal Solutions
Obey Raoults Law over a range of concentrations
$\Delta H_{min} = 0$, $\Delta V_{min} = 0$
A-A, B-B force of attraction = A-B force of attraction.



Non ideal Solutions
Do not obey Raoults Law
$\Delta H_{min} \neq 0$, $\Delta V_{min} \neq 0$
A-A, B-B force of attraction ≠ A-B force of attraction.

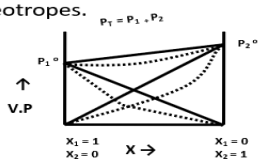
+ve deviation
ΔH_{min} = +ve, ΔV_{min} = +ve
A-A, B-B force of attraction stronger than A-B force of attraction.
eg:- a. Ethanol, Acetone
↓
H-bonded weakened after mixing
b. CS_2 and acetone
c. Ethanol water.

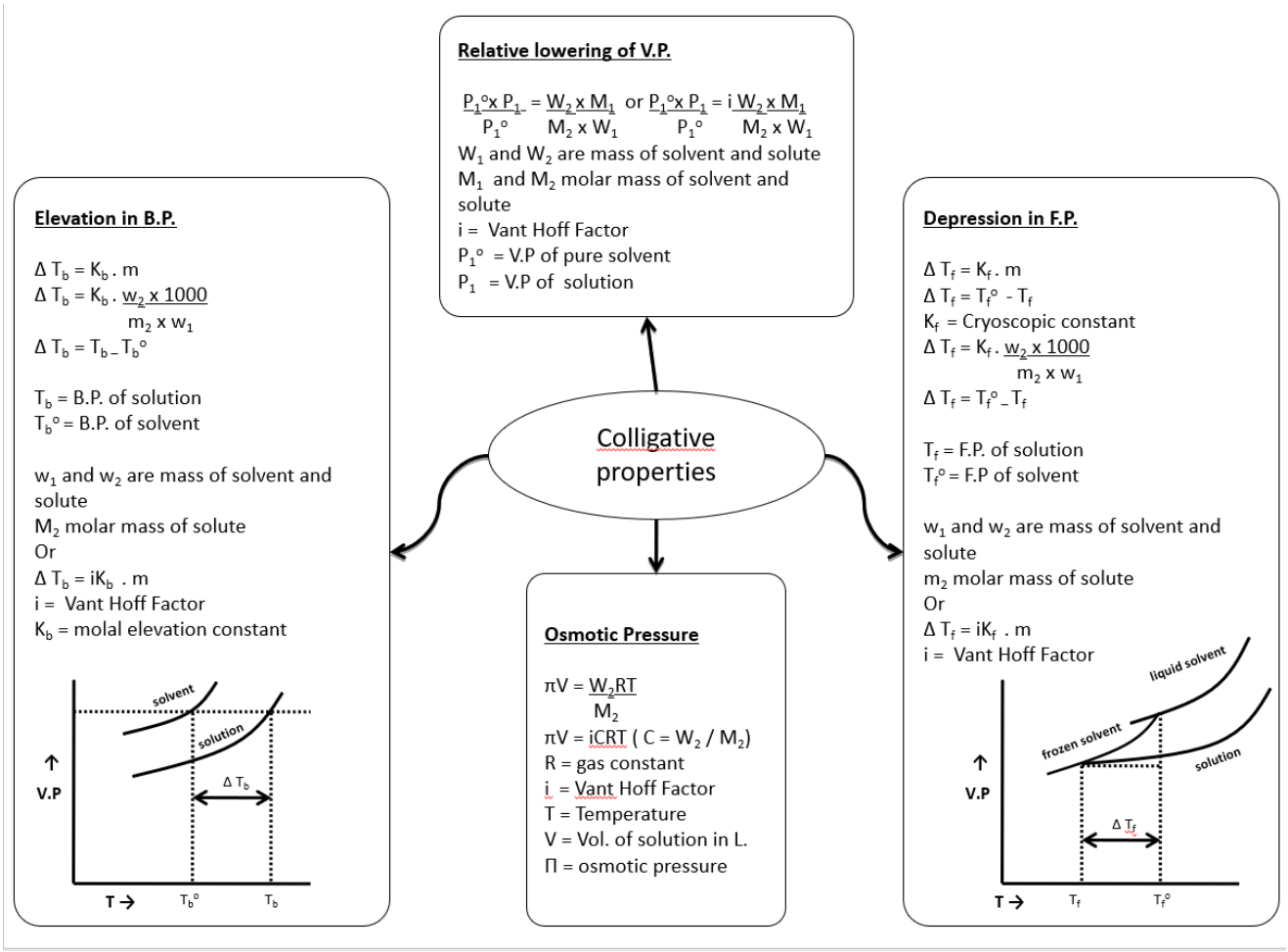
They are minimum boiling azeotropes.



-ve deviation
ΔH_{min} = -ve, ΔV_{min} = -ve
A-A, B-B force of attraction weaker than A-B force of attraction.
eg:- a. Phenol and aniline
↓
H-bonded stronger after mixing
b. $CHCl_3$ and acetone
c. HNO_3 and H_2O

They are maximum boiling azeotropes.





Multiple Choice Questions

1. 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
2. 3 moles of P and 2 moles of Q are mixed, what will be their total vapour pressure in the solution if their partial vapour pressures in pure state are 80 and 60 torr respectively?
   (a) 80 torr (b) 140 torr (c) 72 torr (d) 70 torr
3. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?
   (a) Phenol and aniline (b) Chloroform and acetone
   (c) Nitric acid and water (d) Methanol and acetone
4. Colligative properties depend on
   (a) the nature of the solute (b) the number of solute particles in solution
   (c) the physical properties of solute (d) the nature of the solvent
5. Which of the following aqueous solutions should have the highest boiling point?
   (a) 1.0 M Glucose (b) 1.0 M Na_2SO_4 (c) 1.0 M KCl (d) 1.0 M Urea
6. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M $MgSO_4$ solution is
   (a) the same (b) about twice (c) about three times (d) about six times
7. An unripe mango placed in a concentrated salt solution to prepare pickles shrinks because

(a) it gains water due to osmosis (b) it loses water due to reverse osmosis
(c) it gains water due to reverse osmosis (d) it loses water due to osmosis

8. K_H value for Ar(g), CO_2 (g), HCHO (g) and CH_4 (g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.
(a) HCHO < CH_4 < CO_2 < Ar (b) HCHO < CO_2 < CH_4 < Ar
(c) Ar < CO_2 < CH_4 < HCHO (d) Ar < CH_4 < CO_2 < HCHO

9. Sprinkling of salt helps in clearing the snow covered roads in hills. The phenomenon involved in the process is
(a) lowering in vapour pressure of snow
(b) depression in freezing point of snow
(c) melting of ice due to increase in temperature by putting salt
(d) increase in freezing point of snow

10 . What will be the degree of dissociation of 0.1 M $Mg(NO_3)_2$ solution if van't Hoff factor is 2.74?
(a) 75% (b) 87% (c) 100% (d) 92%

ASSERTION& REASON TYPE QUESTIONS

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

i. **Assertion and reason both are correct statements and reason is correct explanation for assertion.**
ii. **Assertion and reason both are correct statements but reason is not correct explanation for assertion.**
iii. **Assertion is correct statement but reason is wrong statement.**
iv. **Assertion and reason both are incorrect statements.**

1. **Assertion (A) :** 0.1 M solution of KCl has greater osmotic pressure than 0.1 M solution of glucose at same temperature.
Reason (R) : In solution, KCl dissociates to produce more number of particles.
2. **Assertion:** If on mixing the two liquids, the solution becomes hot, it implies that it shows negative deviation from Roult's law.
Reason(R): Solution which shows negative deviation from Roult's law are accompanied by decrease in volume.
3. **Assertion (A) :** An ideal solution obeys Henry's law.
Reason (R) : In an ideal solution, solute-solute as well as solvent solvent interactions are different from solute-solvent interaction.
4. **Assertion(A):** When a solution is separated from the pure solvent by a semi-permeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.
Reason(R): Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.
5. **Assertion(A):** Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than or less than both the components.
Reason(R): The composition of the vapour phase is same as that of liquid phase of the azeotropic mixture.

2 - MARK QUESTIONS

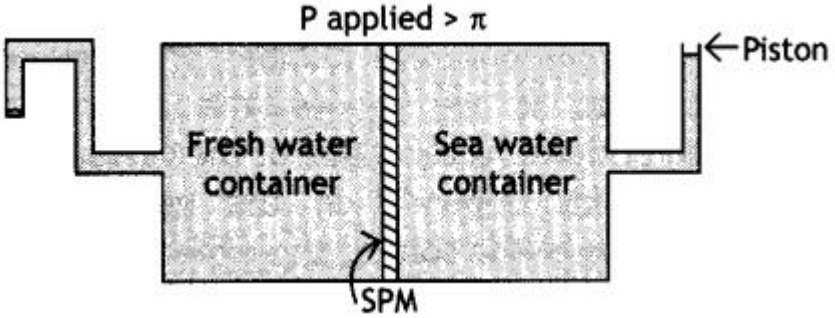
1. Vapour pressure of two liquid A & B are 120 and 180mm Hg at a given temp. If 2 mole of A and 3 mol of B are mixed to form an ideal solution, calculate the vapour pressure of solution at same temperature.
2. 18 g of glucose, $C_6H_{12}O_6$ (Molar mass = 180 g mol^{-1}) is dissolved in 1 Kg of water in a sauce pan. At what temperature will this solution boil?
3. (a) Why is the freezing point depression of 0.1M NaCl solution nearly twice that of 0.1M glucose solution?
   (b) What is the effect of temperature on Henry's law constant (K_H) and on solubility of a gas on liquid?
4. How is that measurement of osmotic pressure is more widely used for determining molar masses of macromolecules than the elevation in boiling point or depression in freezing point of their solutions?
5. (a) Why is an increase in temperature observed on mixing chloroform and acetone?

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

3 - MARKS QUESTIONS

1. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).
   (Given: Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1})
2. A solution is made by dissolving 30 g of non-volatile solute in 90 g of water. It has a vapour pressure of 2.8 kPa at 298 K. At 298 K, vapour pressure of pure water is 3.64 kPa. Calculate the molar mass of the solute.
3. Answer the following questions:
   (a) Why is 1 molar aqueous solution more conc. than a 1 molal solution?
   (b) Which out of molarity and molality will change with temperature and why?
   (c) Will the molarity of a solution at 50^0C be same, less or more than molarity at 25^0C ?
4. On dissolving 3.24 g of sulphur in 40 g of benzene, boiling point of solution was higher than that of benzene by 0.81 K. Kb value for benzene is 2.53 K Kg mol-1. What is the molecular formula of sulphue? (Atomic mass of sulphur = 32 g/mol)
5. Answer
   (a) What happen to vapour pressure of water if a table spoon of salt is added to it?
   (b) Why does the use of pressure cooker reduce the cooking time?
   (c) Two liquid A & B are mixed and the resulting solution is found to be cooler. What do you conclude about deviation of solution from ideal behavior?

6. Given below is the sketch of a plant for carrying out a process.



(a) Name the process occurring in the above plant.
(b) To which container does the net flow of solvent take place?
(c) Give one practical use of the plant.

5 - MARKS QUESTIONS

1. (a) Define the term osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property.

Explain.
(b) Calculate the boiling point of a solution prepared by adding 15 g of NaCl to 250 g of water. (Kb for water = 0.512 K Kg mol-1 and molar mass of NaCl = 58.5 g/mol).

2. (a) State the following:
(i) Henry's Law about partial pressure of a gas in a solution.
(ii) Raoult's Law in its general form in reference to solutions.

(b) 0.004 M soln of Na_2SO_4 is isotonic with 0.01 M soln of glucose at the temp. What is the apparent degree of dissociation of Na_2SO_4 ?

CASE BASED QUESTIONS

Q1. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into its cells through osmosis. When placed in water containing less than 0.9% (mass/ volume) salt, blood cells swell due to flow of water in them by osmosis.

(a) People taking a lot of salt or salty food suffer from puffiness or edema. What is the reason behind this?

(b) The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. How?

(c) Why the direction of osmosis gets reversed if a pressure larger than the osmotic pressure is applied to the solution side? Write its one application.

OR

(c) What care is generally taken during intravenous injections and why?

Q2. In order to overcome the scarcity of drinking water in a remote village in Gujarat, Arnav and Aariv two young entrepreneurs still in their high school, have developed a unique water purifier that is capable of converting sea water into drinking water. It works on the principle of concentration difference between two solutions. Based on your understanding of solutions answer the following questions about the product made by Arnav & Aariv:
(a)Name the phenomenon/ process based on which this product is made?
(b)How difference in concentration of solutions help in converting sea water into drinking water?
(c)What arrangement they must have created in their product to covert sea water into drinking water?

OR

(c)Equimolar solutions of NaCl and glucose are not isotonic. Why?

Q3. Aariv Sharma is very fond of a special drink made by his grandmother using different fruits available in their hometown. It has an outstanding taste and also provide great health benefits of natural fruits. He thought of utilizing his grandmother recipe to create a new product in the beverage market that provide health benefits and also contain fizziness of various soft drinks available in the market. Based on your understanding of solutions chapter, help Aariv Sharma to accomplish his idea by answering following:

(a) How he can add fizz to the special drink made by his grandmother?
(b) What is the law stated in the chapter that can help Aariv to make his drink fizzy?
(c) What precautions he should take while bottling so that his product does not lose fizz during storage and handling across long distances? OR

(c)The mole fraction of helium in a saturated solution at 20°C is 1.2 x 10-6. Find the pressure of helium above the solution. Given Henry's constant at 20°C is 144.97 kbar.

ANSWERS

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

ASSERTION REASON: 1(i); 2(ii); 3(iv); 4(iii); 5(ii)

2-MARKS

1. Total moles = 2 + 3 = 5

P solution = $P_A^{\circ} x_A + P_B^{\circ} x_B$

$= \frac{2}{5} \times 120 + \frac{3}{5} \times 180$ = 48 + 108 = 156mm.

2. w_1 = weight for solvent (H_2O) = 1 Kg

w_2 = weight of solute glucose = 18 g

M_2 = molar mass of solute, glucose = 180 g mol^{-1}

K_b = 0.52 K Kg mol^{-1}

$$T_b^0 = 373.15K$$

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_2} = 0.052 \text{ K}$$

$$\Delta T_b = T_b - T_b^0 \Rightarrow 0.052 = T_b - 373.15 \Rightarrow T_b = 373.202\ K$$

3. (a) NaCl is an electrolyte and dissociates completely whereas glucose being a non-electrolyte does not dissociate.Hence, the number of particles in 0.1M NaCl solution is nearly double than that in 0.1M glucose solution.Depression in freezing point being a colligative property is nearly twice for NaCl solution than for glucose solution of same molarity.

(b) Solubility of a gas in liquid decreases with increase in temperature. K_H value increases with the increase in temperature.

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

(i) Osmotic pressure is measured at the room temperature and the molarity of solution is used instead of molality.

(ii) Compared to other colligative properties, its magnitude is large even for very dilute solutions.

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

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

3-MARKS QUESTIONS

1. $\Delta T_f = i\ K_f \times m$

   $= i \times K_f \times W_2 \times 1000 / M_2 \times W_1$

   W_2 = 3.9 g, W_1 = 49 g, ΔT_f = 1.62 K,

   M_2 = 122 g mol^{-1}

   K_f = 4.9 K kg mol^{-1}

   1.62 = i×4.9×3.9×1000122×49

   or i = 1.62×122×494.9×3.9×1000 = 0.506

   Since i is less than 1, the solute is associated.

2. $(P_0 - P_s)/P_0 = \frac{WB/MB}{\frac{WB}{MB} + \frac{WB}{MA}}$

M_B = 20 g /mol

3. (a)A molar solution contains one mole of solute in one litre of solution while a one molal solution contains one mole of solute in 1000 g of solvent. If density of water is 1, then one mole of solute is present in 1000 ml of water in one molar solution while on mole of solute is present in less than 1000 ml of water in one molar solutions. Thus, one molar solution is more concentrated.
   (b)Molarity changes with rise in temperature. Volume of a solution increases with rise in temperature and this causes change in molarity because it is related as moles of solute in a given volume of solution.
   (c) Molarity at 50^0C of a solution will be less than that of 25^0C because morality decreases with temperature. This is because volume of the solution increases with increase in temperature but number of moles of solute remains the same.
4. $M_B = \frac{Kbx\ WBx1000}{\Delta Tbx\ WA}$
   $= \frac{2.53x\ 3.24x\ 1000}{0.81\ x\ 40}$
   = 253g/mol
   No. of atoms in one molecule of sulphur = 253/32 = 7.8 = 8
   So molecular formula of sulphur is S_8.
5. (a) Addition of non volatile solute lower the vapour pressure of solvent(water)
   (b)At higher pressure over the liquid, the liquid boils at high temperature. Therefore, cooking occur fast.
   (c)Positive deviation.
6. (a) Reverse osmosis
   (b) To fresh water container
   (c) This can be used as a desalination plant to meet potable water requirements.

5 - MARKS QUESTIONS

1. (a) Net flow of solvent molecules from the pure solvent to the solution through semi permeable membrane is called osmosis.
The extra pressure that applied from solution side to prevent the flow of solvent through SPM is called osmotic pressure.
Osmotic pressure is a colligative property because it depends upon no. of moles of solute.
(b) $\Delta Tb = \frac{i\ x\ Kb\ x\ WB\ x\ 1000}{MB\ x\ WA}$

$= \frac{2\ x\ 0.512\ x\ 15\ x\ 1000}{58.5\ x\ 250}$

= 1.052 K
Boiling point of the solution = 373 + 1.052 = 374.052 K

2.(a) (i) The partial pressure of a gas, p in vapour phase is proportional to the mole fraction of the gas in solution.

(ii) In a solution, the partial pressure of each volatile component is directly proportional to its mole fraction in the solution.
(b) For isotonic solutions,
π (Na_2SO_4) = π (glucose)
π (Na_2SO_4) = i x C x R x T = i x 0.004 x RT
π (glucose) = i x C x R x T = 1 x 0.01 x RT
i x 0.004 x RT = 1 x 0.01 x RT
i = 2.5
α = i – 1/n – 1 = 2.5 – 1/ 3 – 1= 0.75
Degree of dissociation is 75%.

CASE BASED QUESTIONS

1. (a) People experience water retention in tissue cells and intercellular spaces due to osmosis.
(b) Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.
(c) The pure solvent flows out of the solution through the semi permeable membrane due to reverse osmosis. It is used in desalination of sea water.

OR

(c) During intravenous injection, the concentration of the solution should be same as that of blood so that they are isotonic. Because if the solution concentration is hypertonic than blood cell will shrink and if it is hypotonic than blood cell will swells / burst.

2. a) The product is based on the phenomenon of Reverse Osmosis between solutions of two different concentration.
b) When solutions of two different concentration are separated by a semipermeable membrane and excess pressure is applied on the solution of higher concentration, solvent flow from higher concentration to lower concentration. This is called Reverse Osmosis and same can be used to treat seawater and convert into drinking water.
c) Following arrangement must have been made:
i) Use of a semipermeable membrane.
ii) Separate Compartment having seawater and Drinking Water separated by semipermeable membrane.
iii) Excess pressure applied in compartment having sea water.

OR

(c) NaCl is an electrolyte and gets dissociated to two ions (Na^+ and Cl^-) and exerts almost double osmotic pressure than glucose which is a non-electrolyte and does not dissociate.

3. (a) Carbondioxide is a gas which provide fizz and tangy flavour. He can dissolve Carbondioxide gas in the drink.
(b) Henry's law which states that solubility of a gas in liquid is directly proportional to partial pressure of the gas.
(c) Bottles should be sealed under high pressure of CO_2 and capping should be done perfectly to avoid leakage of CO_2 as any loss of partial pressure will result into decrease in solubility.

OR

(c) $p_{He} = K_H \times X_{He}$
$= (144.97 \times 10^{3} bar)(1.2 \times 10^{-6}$
$= 0.174$ bar

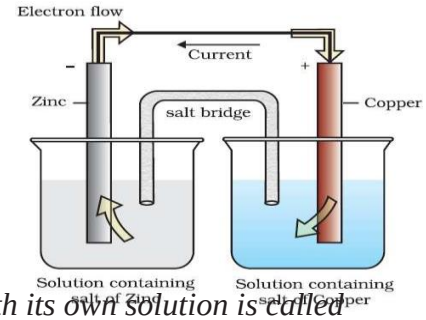
ELECTROCHEMISTRY

It is a branch of chemistry that deals with the relationship between chemical energy and electricalenergy and their inter conversions.

ELECTROCHEMICAL CELLS

These are devices that convert chemical energy of some redox reactions to electrical energy. Theyare also called Galvanic cells or Voltaic cells. An example for Galvanic cell is Daniel cell.

It is constructed by dipping a Zn rod in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by asalt bridge.



A salt bridge is a U-tube containing an inert electrolyte like $NaNO_3$or KNO_3 in a gelly like substance. The functions of a salt bridge are:

1. *To complete the electrical circute*
2. *To maintain the electrical neutrality in the two half cells.*

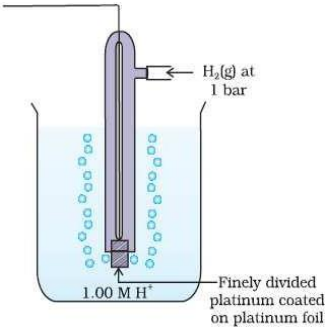
Electrode Potential

The tendency of a metal to lose or gain electron when it is in contact with its own solution is called ***electrode potential***. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, *standard reduction potential is taken as the standard electrode potential*.

The ***cell potential*** *is the difference between the electrode potentials (reduction potentials) of the cathode and anode.*

The cell ***electromotive force (emf)*** *of the cell is the potential difference between the two electrodes,when no current is flow through the cell.*

i.e. $E_{cell} = E_{right} - E_{left}$ **Or** $E_{cell} = E_R - E_L$.



Measurement of Electrode Potential

The potential of individual half-cell cannot be measured.
We can measure only the difference between thetwo half-cell potentials that gives the emf of the cell.
For this purpose a half-cell called **Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE)** is used.

Electrochemical series

It is a series in which various electrodes are arranged in the decreasing order of their reduction potential. In this table, fluorine is at the top indicating that fluorine gas (F_2) has the maximum tendency toget reduced to fluoride ions (F^-). Therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent.

Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent whilelithium metal is the most powerful reducing agent in an aqueous solution.

Nernst Equation

Nernst proposed an equation to relate the electrode potential of an electrode (or, emf of a cell) withthe

electrolytic concentration.
He showed that for the electrode reaction:

$$E_{Cell} = E^0_{cell.} + \frac{2.303RT}{nF} \log [M^{n+}]$$

Where E constant (8.314 $JK^{-1} mol^{-1}$), *F* is Faradayconstant (96500 C mol^{-1}), *T* is temperature in Kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+}.

For a general electrochemical reaction of the type:
aA + bB — ne^- —→ cC + dD

Nernst equation can be written as:

$$E_{cell} = E^0_{cell} + \frac{0.0591}{n} \log \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Equilibrium Constant from Nernst Equation

For a Daniel cell, the emf of the cell at 298K is given by:

$$E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

When the cell reaction attains equilibrium, $E_{cell} = 0$

$$E^0_{cell} = \frac{0.0591}{n} \log Kc \text{ at 298 K}$$

Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed.
Also the reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, if the emf of the cell is *E* and *nF* is the amount of charge passed,
then the Gibbs energy of the reaction, $\Delta G = -nFE_{cell}$
If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$. So, $\Delta G^0 = -nFE^0_{cell}$
Thus, from the measurement of E^0_{cell}, we can calculate the standard Gibbs energy of the reaction.

Conductance of Electrolytic Solutions

Resistance (R): The electrical resistance is the hindrance to the flow of electrons. Its unit is ohm (Ω). The resistance of a conductor is directly proportional to the length of the conductor (l) and inversely proportional to the area of cross-section (A) of the conductor.
i.e. R α l /A
or, R = a constant x l/A
or, R = ρ x l/A, where ρ (rho) is a constant called resistivity. Its unit is ohm-metre (Ω m) or ohm-centimetre (Ω cm).
1 Ω m = 100 Ω cm, 1 Ω cm = 10^{-2} Ω m
Resistivity is defined as the resistance offered by a conductor having unit length and unit area of cross- section.

Conductance (G): It is the inverse of resistance.
i.e. G = 1/R.
Its unit is ohm^{-1} or mho or Siemens (S)
Or, $G = \frac{1}{P} \times \frac{A}{l}$
Or, G = k x A/l
Where, ***k*** is called ***conductivity***. It is defined as the conductance of a conductor having unit length and unit area of cross-section.
Its unit is $ohm^{-1} m^{-1}$ or mho m^{-1} or S m^{-1} .
1 S cm^{-1} = 100 S m^{-1} 1 S m^{-1} = 10^{-2} S cm^{-1}
There are of two types of Conductance - electronic or metallic conductance and electrolytic or ionic

conductance.

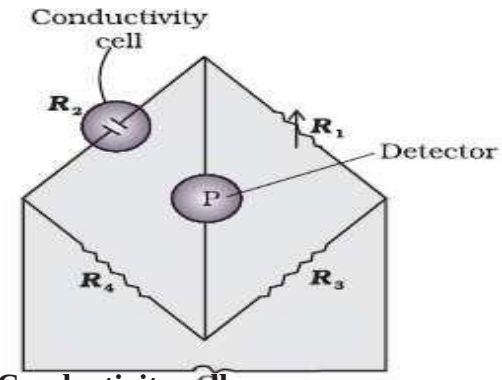
Measurement of the conductivity of ionic solutions

We know that, conductivity G = k x A/ l So conductivity, k = G x l/A

The quantity l/A is called ***cell constant*** (G*). It depends on the distance between the electrodes and their area of cross-section. Its unit is m^{-1}.

i.e. conductivity = conductance x cell constant

So in order to determine the conductivity of an electrolytic solution, first determine the resistance by usinga Wheatstone bridge. It consists of two resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. It is connected to an AC source (an oscillator, O) and a suitable detector (a headphone or other electronic device, P). Direct current (DC) cannot be used since it causes thedecomposition of the solution.



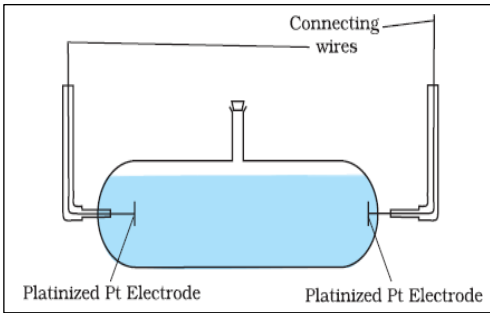
The bridge is balanced, when no current passes through the detector. Under this condition,

$R_1/R_2 = R_3/R_4$

Therefore, the unknown resistance, $R_2 = \frac{R_1 R_4}{R_3}$

By knowing the resistance, we get the value of conductance and conductivity.

Conductivity cell



It consists of two platinum electrodes coated with platinum black. The electrodes are separated by adistance l and their area of cross-section is A.

The cell constant of a conductivity cell is usually determined by measuring the resistance of the cellcontaining a solution whose conductivity is already known (e.g. KCl solution).

Molar conductivity (λm)

It is the conductivity of 1 mole of an electrolytic solution kept between two electrodes with unit area of cross section and at a distance of unit length. It is related to conductivity of the solution by the equation,

λm= k/C (where C is the concentration of the solution)Or, λm = 1000 fi/M (where M is the molarity)

The unit of molar conductivity is $\Omega^{-1} cm^2 mol^{-1}$ or $S\ cm^2 mol^{-1}$.

$1 S\ m^2 mol^{-1} = 10^4 S\ cm^2 mol^{-1}$ $1 S\ cm^2 mol^{-1} = 10^{-4} S\ m^2 mol^{-1}$

Variation of conductivity and Molar conductivity with concentration (dilution)

Both conductivity and molar conductivity change with the concentration of the electrolyte.. *For both strong and weak electrolytes, conductivity always decreases with dilution*. This is because conductivity is the conductance of unit volumeof electrolytic solution. *As dilution increases, the number of ions per unit volume decreases and hence the conductivity decreases*.

For both strong and weak electrolytes, the molar conductivity increase with dilution (or decreasewith increase in concentration), but due to different reasons.

For strong electrolytes, as dilution increases, the force of attraction between the ions decreases andhence the

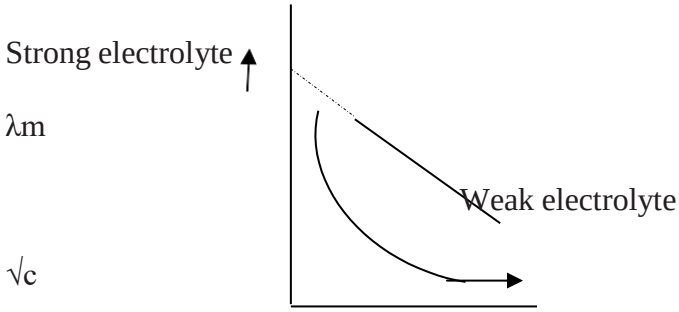
ionic mobility increases. So, molar conductivity increases. When dilution reaches maximum or concentration approaches zero, the molar conductivity becomes maximum and it is called the limiting molar conductivity (λ^0m).

For strong electrolytes, the relation between λm and concentration can be given as: $\lambda m = \lambda^0 m - A\sqrt{c}$

Where 'c' is the concentration and A is a constant depends on temperature, the nature of the electrolyteand the nature of the solvent. All electrolytes of a particular type have the same value for 'A'.

For weak electrolytes, as dilution increases, the degree of dissociation increases. So the number ofions and hence the molar conductivity increases.

The variation of λm for strong and weak electrolytes is shown in the following graphs:



For strong electrolytes, the value of λ^0m can be determined by the extrapolation of the graph. But for weak electrolytes, it is not possible since the graph is not a straight line. So their λ^0m values are calculated by applying Kohlrausch's law of independent migration of ions.

Kohlrausch's law of independent migration of ions

The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and the cation of the electrolyte.

Thus if an electrolyte on dissociation gives $n_{(+)}$ cations and $n_{(-)}$ anions, its limiting molar conductivity is given as:

$\lambda^0m = n_{(+)}\lambda^0_{(+)} + n_{(-)}\lambda^0_{(-)}$ For NaCl, $\lambda^0m_{(NaCl)} = \lambda^0_{(Na+)} + \lambda^0_{(Cl-)}$ For $CaCl_2$, $\lambda^0m_{(CaCl2)} = \lambda^0_{(Ca^{2+})} + 2 \times \lambda^0_{(Cl-)}$

Applications of Kohlrausch's law

1) ***Determination of λ^0m of weak electrolytes***

By knowing the λ^0m values of strong electrolytes, we can calculate λ^0m of weak electrolytes. For e.g.we can determine the λ^0m of acetic acid (CH_3COOH) by knowing the λ^0m of CH_3COONa, NaCl and HCl as follows

$\lambda^0m\ (CH_3COONa) = \lambda^0 CH_3COO^- + \lambda^0 Na^+$ (1)

$\lambda^0m\ (HCl) = \lambda^0 H+ + \lambda^0\ Cl$ (2)

$\lambda^0m\ (NaCl) = \lambda^0 Na+ + \lambda^0 Cl$ .....(3)

$\lambda^0m\ (CH_3COONa) + \lambda^0m\ (HCl) - \lambda^0m\ (NaCl) = \lambda^0 CH_3COO^- + \lambda^0 Na^+ + \lambda^0 H^+ + \lambda^0 Cl^- - \lambda^0 Na^+ - \lambda^0 Cl^-$
$= \lambda^0 CH_3COOH$

Determination of degree of dissociation of weak electrolytes

By knowing the molar conductivity at a particular concentration ($\lambda^c m$) and limiting molar conductivity

$$Ka = \frac{c\,\alpha^2}{1-\alpha}$$

(λ^0m), we can calculate the degree of dissociation (α) as, $\alpha = \frac{\lambda^c m}{\lambda^0 m}$

Electrolytic Cells and Electrolysis

In an electrolytic cell, the electrical energy is converted to chemical energy. The dissociation of an electrolyte by the passage of electricity is called electrolysis.

For e.g. when $CuSO_4$ solution is electrolysed by Cu electrodes, Cu is deposited at the cathode and Cu^{2+} ions are liberated from the anode.

Quantitative Aspects of electrolysis – Faraday's laws

1) **Faraday's first law**

It states that the amount of substance deposited or liberated at the electrodes (m) is directly proportional to the quantity of electricity (Q) flowing through the electrolyte.

Mathematically, $m \alpha Q$

Or, $m = zQ$

Where z is a constant called electrochemical equivalent (ECE). Z = equivalent weight/96500

But quantity of electricity is the product of current in ampere (I) and time in second (t).

i.e. Q = It

Therefore, ***m= zIt***

1 Faraday is the charge of 1 mole of electron or it is the amount of electricity required to deposit one gram equivalent of any substance. Its value is 96500 C/mol.

For the deposition of 1 mole of Na, the amount of charge required = 1 F (Since $Na^+ + e^- \rightarrow Na$)

For Ca, Q = 2F (since $Ca^{2+} + 2e^- \rightarrow Ca$)

2) **Faraday's second law**

It states that *when same quantity of electricity is passed through solutions of different substances,the amount of substance deposited or liberated is directly proportional to their chemical equivalence.*

For e.g. when same quantity of electricity is passed through solutions of two electrolytes A and B, then

Mass of A deposited = Equivalent mass of AMass of B deposited Equivalent mass of B

Products of electrolysis

The products of electrolysis depend on the following factors:

i) *The nature of the electrolyte*: The electrolyte may be in molten state or in aqueous solution state. For e.g. if molten NaCl is electrolysed, Na is deposited at the cathode and chlorine is liberated at the anode.

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

At cathode: $Na^+ + e^- \rightarrow Na$ At anode: $Cl^- \rightarrow ½ Cl_2 + e^-$

If NaCl solution is electrolysed, we get H_2 gas at the cathode and Cl_2 gas at the anode. NaCl solution contains 4 ions – Na^+, Cl^-, H^+ and OH^-

Cathode reaction: $H^+ + e^- \rightarrow ½ H_2$ Anode reaction: $Cl^- \rightarrow ½ Cl_2 + e^-$

NaOH is formed in the solution. Products of electrolysis

The products of electrolysis depend on the following factors:

ii) *The nature of the electrolyte*: The electrolyte may be in molten state or in aqueous solution state. For e.g. if molten NaCl is electrolysed, Na is deposited at the cathode and chlorine is liberated at theanode.

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Cathode reaction: $H^+ + e^- \rightarrow ½ H_2$Anode reaction: $Cl^- \rightarrow ½ Cl_2 + e^-$

iii) *The type of electrodes used*: If the electrode is inert (e.g. Pt, gold, graphite etc.), it does not participate in the electrode reaction. While if the electrode is reactive, it also participate in the electrode reaction.

iv) *The different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.* Some of the electrochemical processes are very slow and they do not take place at lower voltages**. So some extra potential (called *overpotential*) has to be applied, which makes such process more difficult to occur.**

For e.g. during the electrolysis of NaCl solution, the possible reactions at anode are: Cl^- (aq) → ½ Cl_2 (g) + e^-; E^0_{cell} = 1.36 V

$2H_2O$ (l)→ O_2 (g) + $4H^+$(aq) + $4e^-$; E^0_{cell} = 1.23 V

At anode, the reaction with lower value of E^0_{cell} is preferred and so water should get oxidised in preference to Cl^- (aq). However, on account of overpotential of oxygen, the first reaction is preferred andhence Cl_2 is formed at anode.

Batteries

A battery is basically a galvanic cell in which the chemical energy of a redox reaction is converted to electrical energy. They are of mainly 2 types – primary batteries and secondary batteries.

a) Primary cells:

These are cells which cannot be recharged or reused. Here the reaction occurs only once and after useover a period of time, they become dead E.g. Dry cell, mercury button cell etc.

1. Dry Cell

It is a compact form of Leclanche cell. It consists of a zinc container as anode and a carbon (graphite)rod surrounded by powdered manganese dioxide (MnO_2) and carbon as cathode. The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The electrode reactions are:

Anode: Zn(s) → Zn^{2+} + $2e^-$

Cathode: MnO_2+ NH_4^++ e^-→ MnO(OH) + NH_3

Ammonia produced in this reaction forms a complex with Zn^{2+} and thus corrodes the cell. The cell has a potential of nearly 1.5 V.

2. Mercury cell

Here the anode is zinc – mercury amalgam and cathode is a paste of HgO and carbon. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:

Anode reaction: Zn(Hg) + $2OH^-$ → ZnO(s) + H_2O + $2e^-$Cathode reaction: HgO + H_2O + $2e^-$ → Hg(l) + $2OH^-$

The overall reaction is : Zn(Hg) + HgO(s) → ZnO(s) + Hg(l)

The cell has a constant potential of 1.35 V, since the overall reaction does not involve any ion in solution.

b) Secondary cells

A secondary cell can be recharged and reused again and again. Here the cell reaction can be reversedby passing current through it in the opposite direction. The most important secondary cell is lead storage cell, which is used in automobiles and invertors.

It consists of lead as anode and a grid of lead packed with lead dioxide (PbO_2) as the cathode. The electrolyte is 38% H_2SO_4 solution.

The cell reactions are:

Anode: Pb(s) + SO_4^{2-} (aq) → $PbSO_4$(s) + 2e-

Cathode: PbO_2(s) + SO_4^{2-}(aq) + $4H^+$(aq) + 2e- → $PbSO_4$(s) + $2H_2O$ (l)

The overall cell reaction is: Pb(s)+PbO_2(s)+$2H_2SO_4$(aq) → $2PbSO_4$(s) + $2H_2O$(l)

On charging the battery, the reaction is reversed and $PbSO_4$(s) on anode and cathode is converted into Pb and PbO_2, respectively.

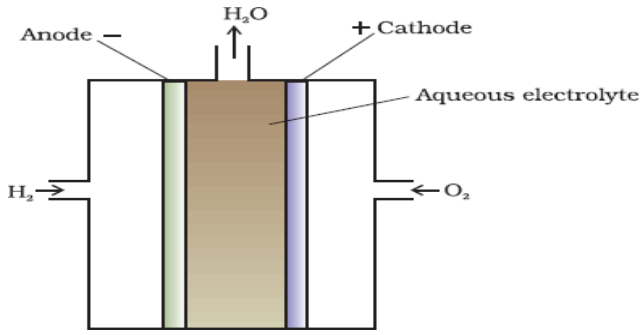
Another example for a secondary cell is nickel – cadmium cell. Here the overall cell reaction is

Cd (s)+$2Ni(OH)_3$ (s) → CdO (s) +$2Ni(OH)_2$ (s) +H_2O(l)

Fuel cells

These are galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy.

One example for fuel cell is ***Hydrogen – Oxygen fuel cell***, which is used in the Apollo space programme. Here hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. To increase the rate of electrode reactions, catalysts like finely dividedplatinum or palladium metal are filled into the electrodes.



The electrode reactions are:

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

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

Overall reaction is: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Advantages of Fuel cells

1. The cell works continuously as long as the reactants are supplied.
2. It has higher efficiency as compared to other conventional cells.
3. It is eco-friendly (i.e. pollution free) since water is the only product formed.
4. Water obtained from $H_2 – O_2$ fuel cell can be used for drinking.

Corrosion

It is the process of formation of oxide or other compounds of a metal on its surface by the action ofair, water-vapour, CO_2 etc. Some common examples are: The rusting of iron, tarnishing of silver, formation of green coating on copper and bronze (verdigris) etc.

Most familiar example for corrosion is rusting of iron. It occurs in presence of water and air. It is a redox reaction. At a particular spot of the metal, oxidation takes place and that spot behaves as anode. Here Fe is oxidized to Fe^{2+}.

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

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+. This spot behaves as cathode. The reaction taking place at this spot is:

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

The overall reaction is: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2\,H_2O\,(l)$

The ferrous ions (Fe^{2+}) are further oxidised to ferric ions (Fe^{3+}) and finally to hydrated ferric oxide ($Fe_2O_3.\,x\,H_2O$), which is called rust.

Methods to prevent corrosion

1. By coating the metal surface with paint, varnish etc.
2. By coating the metal surface with another electropositive metal like zinc, magnesium etc. The coating of metal with zinc is called galvanisation and the resulting iron is called galvanized iron.
3. By coating with anti-rust solution.
4. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object (sacrificial protection).

Mind map

Types of Cells

Electrochemical cell:- The electrodes are fitted in same electrolyte or different electrolytes joined by a salt

Electrolytic cell :- Device in which conversion of electrical energy into chemical energy is done.

Galvanic cell:- It involves a redox reation for the conversion of chemical energy into electrical energy

Daniell cell:-
Cathod :- copper metal
Anode :- Zinc metal
Electrolyte :- Aquous salt solution of the metal involved
Cell reaction
Reduction :- $Cu^{2+} + 2\,e^- \rightarrow Cu(s)$ (cathode)
Oxidation:- $Zn(s) \rightarrow Zn^{2+} + 2\,e^-$ (anode)
Cell representation
Zn| Zn2+ (1M)|| Cu2+(1M)| Cu
Anode salt bridge cathode

Componen

Half Cell celll → Two portions of

Electrolyte :- A compound that dissociate into ionsand conducts electric

Electrode
Cathode - Reduction
Anode - Oxidation

Salt Bridge :- U- shape inverted tube connecting two electrolytic solution

Electrod e

Standard electrode potential- Electrode potential when concentration of all species in half cell is unity at 298 K.

Potential difference between electrode

Positive E^0 – weaker reducing agent than H+/H2

Negative E^0 – strong reducing agent than H+/H2

Standard Hydrogen electrode
Electrode :- Pt coated with Pt black
Electrolyte :- acidic solution, pressure 1 bar
Pt(s) | H2(g)| H^+(aq)

Electrochemical series:- A series of half cells arranged in increasing order of standard electrode potential.

Nernst Equation

$Mn^{+}(aq) + ne^{-} \longrightarrow M(s)$

$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]}$

$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$

At equilibrium

, $E^0_{cell} = \frac{2.303RT}{nF} \log Kc$

or,

$E^0_{cell} = \frac{0.0591}{n} \log Kc$ at 298 K

Relation between cell potential and Gibb's energy

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

Relation between Equillibriumconstant and Gibb's energy

$\Delta G^0 = -\frac{2.303RT}{} \log Kc$

Electrical Resistance:- $R = \frac{1}{P} \times \frac{A}{l}$

Unit : ohm ; P= resistivity unit: Ohm-metre

Measured by conductivity cell

Conductance (G) : Inverse of resistance

$G = \frac{1}{R}$ unit : Simenes

Increasing on dilution of solution

Molar conductivity (Λm): $\Lambda m = \frac{k}{C}$ k is in Sm^{-1} C $=molm^{-3}$

$\Lambda m = Sm^2mol^{-1}$ or Scm^2mol^{-1}

$\Lambda m = \frac{k}{M \times 1000}$

Limiting molar conductivity (Λ^0_m)

If molar conductivity reaches a limiting value when $c \rightarrow 0$, $\Lambda m = \Lambda^0_m$

Strong electrolyte

$\Lambda m = \Lambda^0_m - Ac^{1/2}$

Weak electrolyte

$\alpha = \Lambda m / \Lambda^0_m$

Kohlrausch´s law of independent migration of ions:

Limiting molar conductivityof an electrolytecan be represented as sum of individual contribution of anions and cations of electrolyte.

$\Lambda^0m\ (CH_3COONa) = \lambda^0CH_3COO^- + \lambda^0Na^+$ $\Lambda^0m\ (NaCl) = \lambda^0Cl^- + \lambda^0Na^+$ $\Lambda^0m\ (MgCl_2) = \lambda^0Cl^- + \lambda^0Mg^{2+}$

Application :- (i) To calculate Λ^0_m for any electrolyte from λ^0 of individual ion.

(ii) To determine value of degree of dissociation and dissociation constant for weak electrolytes.

(iii) To calculate Λ^0_m for weak electrolyte using Λ^0_m of strong electrolyte

$\lambda^0CH_3COOH = \lambda^0m\ (CH_3COONa) + \lambda^0m\ (HCl) - \lambda^0m\ (NaCl)$

$= \lambda^0CH_3COO^- + \lambda^0Na^+ + \lambda^0H^+ + \lambda^0Cl^- - \lambda^0Na^+ - \lambda^0Cl^-$

Faraday's Law of

First law m = Zit Where Z is electrochemical equivalent

Second law : $\frac{m1}{m2} = \frac{E1}{E2}$

Where E = $\frac{\text{atomic mass}}{\text{Valency}}$

Products of electrolysis

(i) Nature of material being electrolysed
(ii) Type of electrodes
(iii) Concentration of electrolyte

Corrosion

Electrochemical phenomenon in which metal oxide of metal forms coating on the metal surface.
Rusting of Iron , Tarnishing of silver

Methods of prevention of Rusting

1. Barrier Protection : Painting, oiling and greasing
2. Sacrificial protection : Galvanization process
3. Electrical or Cathodic protection for underground pipes
4. Using Anti-rust solutions : Alkaline Phosphate or alkaline chromate solutions.

Batteries

Primary Batteries reaction occurs only once and cannot be reused. Mercury cell. Leclanche cell or dry cell

Secondary batteries can be recharged by passing current in opposite direction and can be reused. Lead storage Battery, Nickel- cadmium cell.

MCQ (1x10)

1. Standard solution of KNO_3 is used to make a salt bridge because
   (a) Velocity of K^+ is greater than that of NO^{-3} .
   (b) Velocity of NO^{-3} is greater than that of K^+.
   (c) Velocity of both K^+ and NO^{-3} are nearly same
   (d) KNO_3 is highly soluble in water.
2. Galvanised iron sheets are coated with
   (a) Carbon
   (b) Copper
   (c) Zinc
   (d) Nickel
3. How many coulombs are required for the oxidation of 1 mole of H_2O to O_2?
   (a) 1.93×10^5 C
   (b) 9.65×10^4 C
   (c) 3.86×10^5 C
   (d) 4.825×10^5 C
4. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 and 0.153 respectively. The standard electrode potential of Cu^+/Cu half cell is
   (a) 0.184 V
   (b) 0.827 V
   (c) 0.521V
   (d) 0.490 V
5. 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
6. For a spontaneous reaction,? ΔG, equilibrium constant K and E^0cell will be respectively.
   (a) – ve > 1, + ve
   (b) + ve > 1 – ve
   (c) -ve, < 1, -ve
   (d) -ve, > 1, -ve
7. The amount of electricity required to deposit 1 mol of aluminium from a solution of $AlCl_3$ will be
   (a) 0.33 F
   (b) 1 F
   (c) 3 F
   (d) 1 ampere
8. Standard electrode potentials are Fe^{2+}/Fe, E° = – 0.44; Fe^{3+}/Fe^{2+}, E° = 0.77 V. Fe^{2+}, Fe^{3+} and Fe blocks are kept together then
   (a) Fe^{3+} increases
   (b) Fe^{3+} decreases
   (c) Fe^{2+}/Fe^{3+} remains unchanged
   (d) Fe^{2+} decreases?

9. The E^0M^{3+}/M^{2+} values for Cr, Mn, Fe and Co are -0.41, + 1.57, + 0.77 and +1.97 V respectively. For which one of the metals, the change in oxidation state from +2 to +3 is easiest?
   (a) Cr
   (b) Mn
   (c) Fe
   (d) Co
10. The highest electrical conductivity of the following aqueous solutions is of?

(a) 0.1 M acetic acid
(b) 0.1 M chloro acetic acid
(c) 0.1 M fluoroacetic acid
(d) 0.1 M difluoro acetic acid

2-mark Questions

1. Electrolysis of KBr(aq) gives Br_2 at anode but does not give F_2 . Give a reason.
2. For the standard cell, Cu(s) |Cu^{2+} (aq) || (aq Ag^+ |Ag(s) , $E^0_{Cu2+/cu}$ = + 0.34V $E^0_{Ag+/Ag}$ = 0.80 V,

(i) Identify the cathode and the anode as the current is drawn from the cell.
(ii)Write the reaction taking place at the electrodes.
(iii) Calculate the standard cell potential

3. The cell reaction as written is spontaneous if the overall EMF of the cell is positive. Comment on this statement.
4. Write any three differences between potential difference and e.m.f.
5. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decreases with dilution?

3-Mark Questions

1. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

2. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

3. Calculate Equilibrium constant K for the reaction at

$298K\ Zn(s)+Cu^{2+}(aq)\rightleftharpoons Zn^{2+}/aq)+Cu\ E^0{}_{Zn}{}^{2+}1Zn = -0.076v;\ E^0Cu^2+/Cu =$ +0.34v.

4. What is the cell potential for the cell at $25^0C\ Cr/Cr^{3+}10.1\ m]//Fe^{2+}(0.01m)/Fe$ $E^0{}_{cr+/cr} = -0.74V$; $E^0Fe^{2+}/Fe = -0.44V$.

5-Mark Questions

1. (a) The conductivity of 0.20 mol L^{-1} solution of KC1 is 2.48 X 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation
(a). Given λ,°(k^+) = 73.5 S cm^2 mol^{-1} and λ °(cl) = 76.5 S cm^2 mol^{-1}.
(b) What type of battery is mercury cell? Why is it more advantageous than dry cell?

2. (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu?
(b) Calculate emf of the following cell at 298 K:
Mg(s) | Mg^{2+}(0.1 M) 11 Cu2+ (0.01) | Cu(s) [Given $E°_{cell}$, = + 2.71 V, 1 F = 96500 C mol^{-1}]

Assertion and Reason Type Questions

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the following choices:

(a) Both Assertion and Reason are true and the Reason is the correct explanation for Assertion.

(b) Both Assertion and Reason are true and the Reason is not correct explanation for Assertion

(c) Assertion is true but the Reason is false.

(d) Both Assertion and Reason are false.

(e) Assertion is false but Reason is true.

1. Assertion (A): Cu is less reactive than hydrogen.
   Reason (R): $E°Cu^{2+}/Cu$ is negative.
2. Assertion (A): E cell should have a positive value for the cell to function.

Reason (R). $E_{cadlode} - E_{anode}$

3. Assertion (A): Conductivity of all electrolytes decreases on dilution.
   Reason (R): On dilution number of ions per unit volume decreases.
4. Assertion (A): Mercury cell does not give steady potential.
   Reason (R): In the cell reaction, ions are not involved in solution.
5. Assertion (A): Electrolysis of NaCl solution gives chlorine at anode instead of 02.
   Reason (R): Formation of oxygen at anode requires overvoltage.

<u>Case based question</u>

1. **Read the passage given below and answer the following questions:**

Standard electrode potentials are used for various processes:

(i) It is used to measure relative strengths of various oxidants and reductants.

(ii) It is used to calculate standard cell potential.

(iii) It is used to predict possible reactions.

A set of half-reactions (in acidic medium) along with their standard reduction potential, E^o (in volt) values are given below

$I_2 + 2e^- \longrightarrow 2I^-$; $E° = 0.54$ V

$Cl_2 + 2e^- \rightarrow 2Cl^-$; $E° = 1.36$ V

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$; $E° = 1.50$ V

$Fe^{3+} + e^- \longrightarrow Fe2+$; $E° = 0.77$ V

$O_2 + 4H^+ + 4e^- \longrightarrow 2H2O$; $E° = 1.23$ V

The following questions are multiple choice questions. Choose the most appropriate answer**:**

(i) Which of the following statements is correct?

(a) CI^- is oxidised by O_2 (b) Fe^{2+} is oxidised by iodine

(c) I^- is oxidised by chlorine. (d) Mn^{2+} is oxidised by chlorine

(ii) Mn^{3+} is not stable in acidic medium, while $Fe^{3+}$is stable because

(a) O_2 oxidises Mn^{2+} to Mn^{3+}

(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}

(c) Fe^{3-}oxidises H_2O to O_2

(d) Mn^{3+} oxidises H_2O to O_2

(iii) The strongest reducing agent in the aqueous solution is

(a) I^- (b) Cl (c)Mn^{2+} (d) Fe^{2+}

(iv) The emf for the following reaction is

$I_2 + KCl \rightleftharpoons 2KI + Cl_2$

(a) -0.82 V (b) + 0.82V (c)-0.73V (d) +0.73

2. Read the passage given below and answer the following questions:

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is $M_{(s)} \mid M^+$(aq.; 0.05 molar) || M^+(aq; 1 molar) $\mid M_{(s)}$.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) For the above cell,

(a) Ecell <0;ΔG>0 (b) Ecell >0;ΔG<0

(c) Ecell <0;ΔG^0>0 (d) Ecell >0;ΔG^0<0

(ii) The value of equilibrium constant for a feasible cell reaction is

(a) < 1 (b) = 1 (c) > 1 (d) zero

(iii) What is the emf ofthe cell when the cell reaction attains equilibrium?

(a) 1 (b) 0 (c) > 1 (d) < 1

(iv) The potential of an electrode change with change in

(a) concentration of ions in solution (b) position of electrodes

(c) voltage of the cell (d) all of these

MCQ (1x10)

1. Answer: (c) Velocity of both K^+ and NO^{-3} are nearly same
2. Answer: (c) Zinc
3. Answer: (a) 1.93×10^5 C
4. Answer: (c) 0.521V
5. Answer: (a) Y > Z > X
6. Answer: (a) – ve > 1, + ve
7. Answer: (c) 3 F
8. Answer: (b) Fe^{3+} decreases
9. Answer: (a) Cr
10. Answer: (d) 0.1 M difluoro acetic acid

2 <u>Mark Questions</u>

1. Ans: Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br^- , H_2O ,F^- are in the following order. Br^- H_2O F^- . Therefore in aq Solution of KBr. Br– ions are oxidized to Br2 in preference to H_2O . On the other hand, in aqueous solution of KF, H2O is oxidized in preference to F^- . Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.
2. Ans: (i) From the cell representation, Ag / Ag+ electrode is cathode and Cu / Cu^{2+} an electrode is anode.

   ii. Ans: At anode: Cu(s) → Cu^{2+} (aq) +2e- , At cathode Ag^+ (aq) +2e →Ag(s)

   iii. E^0cell= E^0 cathode- E^0 anode , E^0cell= $E^0_{Ag+|Ag}$ - $E^0_{Cu2+|Cu}$,

E^0cell = 0.80V – (+0.34V) = 0.46V

3. Ans :- If the e.m.f of a cell is positive, then the Gibbs free energy of the overall reaction is less than zero.

$$\Delta G = -nFEcell$$

Therefore, if Ecell is positive, then the cell reaction is spontaneous.

4. Ans.

E.M.F	POTENTIAL DIFFERENCE
1. It is the difference between the electrode potential of two electrodes when no current is flowing through the circuit.	1. It is the difference of potential between the electrodes in a closed circuit.
2. It is the maximum voltage obtained from a cell.	2. It is less than the maximum voltage obtained from a cell.

3. It is responsible for the steady flow of current.	3. It is not responsible for the steady flow of current.

5. Ans: The limiting molar conductivity of an electrolyte is the sum of limiting ionic conductivity of the cations and anion each multiplied with the number of ions present in one formula unit of the electrolyte.

On dilution the number of ions per unit volume decreases. Hence the conductivity decreases.

3-Mark Questions

1.

Ans .I = 0.5 A

t = 2 hours = $2 \times 60 \times 60$ s = 7200 s

Thus, $Q = It$

= $0.5\ A \times 7200\ s$ = 3600 C

We know that $96487\ C = 6.023 \times 10^{23}$ number of electrons.

Then, $3600\ C = \frac{6.023 \times 10^{23} \times 3600}{96487}$ number of electrons

$= 2.25 \times 10^{22}$ number of electrons

Hence, 2.25×10^{22} number of electrons will flow through the wire.

2. Ans.A lead storage battery consists of a lead anode, a grid of lead packed with lead oxide (PbO_2) as the cathode, and a 38% solution of sulphuric acid (H_2SO_4) as an electrolyte.
When the battery is in use, the following cell reactions take place:
At anode: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$
At cathode: $PbSO_{4(s)} + SO_4^{2-}{}_{(aq)} + 4H^-{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$
The overall cell reaction is given by,
$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$
When a battery is charged, the reverse of all these reactions takes place.
Hence, on charging, $PbSO_{4(s)}$ present at the anode and cathode is converted into $Pb_{(s)}$ and $PbO_{2(s)}$ respectively.

3. **Ans** .From the reaction, n =2
$E^0{}_{cell} = E^0 cu^2 + / cu - E^0 Zn^2 + / Zn$
= + 0.34v – (-0.76v) = 1.10V

$E^0{}_{cell} = \frac{2.303RT}{nF} \log k_c$

At 298k **,** $E^0{}_{cell} \times \frac{n}{0.059} \log k_c$

Log k_c = $E^0{}_{cell} \times \frac{n}{0.059}$

= $1.10 \times \frac{2}{0.059} = 37.29$

$K_c = Antilog\ 37.29$

$= 1.95 \times 10^{37}$

4. **Ans.**The cell reaction is
$2Cr + 3Fe^{2+}\ 6e^- \rightarrow 2Cr^{3+} + 3Fe$
Nernst Equation –

$$E_{cell} = \left(E^0_{Fe^{2+}/Fe} - E^0_{Cr^{3+}/Cr} \right) - \frac{0.059}{6} \log \frac{\left[Cr^{3+}\right]^2}{\left[Fe^{2+}\right]^3}$$

$$=(-0.44v - (-0.74v) - \frac{0.059}{6} \log \frac{(0.10)^2}{(0.01)^3}$$

$$= 0.3V - \frac{0.059}{6} \log 10^4$$

= 0.3V – 0.0394V

= +0.2606 V

5-Mark Questions

a. answer

(a) $M = 0.20 \text{ mol L}^{-1}$, $\kappa = 2.48 \times 10^{-2} \text{ S cm}^{-1}$, $\Lambda_m = ?$, $\alpha = ?$

$\lambda^\circ_{(K+)} = 73.5 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda^\circ_{(Cl^-)} = 76.5 \text{ S cm}^2 \text{ mol}^{-1}$

$\Lambda^\circ_{(KCl)} = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-} = 73.5 + 76.5 = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$

Now, $\Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000 \times 2.48 \times 10^{-2}}{0.20}$

$\Rightarrow \quad \Lambda_m = \frac{248}{2} = 124 \text{ S cm}^2 \text{ mol}^{-1}$

$\therefore \quad \alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{124}{150.0} = 8.26 \times 10^{-1}$

$\Rightarrow \quad \alpha = 8.26 \times 10^{-1} \times 10^2 = 82.6\%$

(b) Mercury cell is primary cell because it is not rechargeable.
Its effeciency is higher than dry cell. Its voltage remains constant over long period of time.

b. answer

(a) It states that the mass of the substance deposited is directly proportional to charge passed through electrolyte.

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

2Faraday of charge is required to deposite 1 mole of copper, i.e. 63.5 g of Cu.

(b)

$$Mg(s) \longrightarrow Mg^{2+} + 2e^-$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+} + Cu(s) \qquad n = 2$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]} = 2.71 \text{ V} - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$\Rightarrow \quad E_{cell} = 2.71 \text{ V} - \frac{0.0591}{9} \log 10 = 2.71 \text{ V} - 0.0295 = 2.68 \text{ V}.$$

Assertion and Reason Type Questions

1. Solution: (c) Cu is less reactive than hydrogen because E°Cu^{2+} Cu is positive.
2. Solution: (c) Ecell = Ecathode – Eanode. To have positive value of Ecell, Ecathode > Eanode.
3. Solution: (a) Conductivity depends on number of ions per unit volume which decreases on dilution of electrolytes.
4. Solution: (e) Mercury cell gives a steady potential because in the cell reaction ions are not involved in the solution.
5. Solution: (a) Formation of oxygen has lower value of E° than formation of chlorine even then it is not formed because it requires overvoltage.

Case based question

Answer 1:

i. Ans **(c) :** The half cell having the higher reduction potential will undergo reduction process.
ii. Ans- (d) : Electrode potential of Mn^{3+} is higher than O_2.
iii. Ans; - (a) I^- Due to least electrode potential value

iv. Ans: (a) -0.82V

Answer 2:

i. Ans- (b)
ii. Ans- (c)
iii. Ans- b
iv. Ans (a)

CHEMICAL KINETICS
Weightage – 7 marks (2022-23)

GIST of the topics –

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

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

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

Unit of rate of reaction:- 1. **$MolL^{-1}s^{-1}$** **2. atm s^{-1}**

2. Unifying rate of reaction

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

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

Similarly, for the reaction

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

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

3. Differential rate law (Rate law)

a A + b B→ c C + d D

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

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

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

This is differential rate equation.

4) Order of reaction:-

For the reaction a A + b B→ c C + d D

Rate = $K[A]^x [B]^y$ x + y = order of reaction

(where x & y may or may not be equal to stoichiometric coefficient)

Note:

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

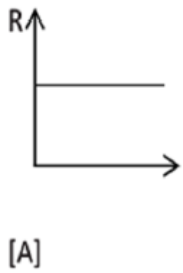
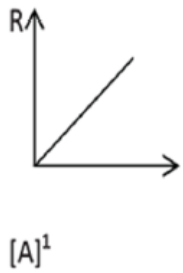
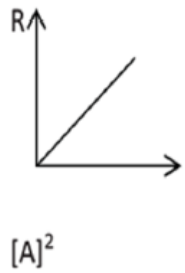
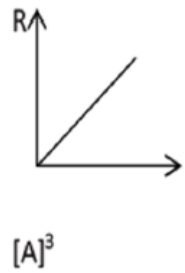
ii. if x + y = 2, reaction is called **II order reaction**.

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

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

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

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

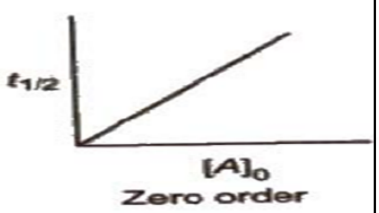
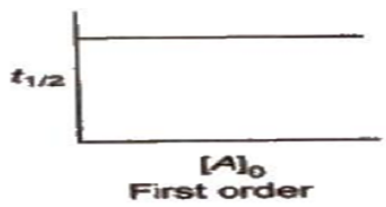
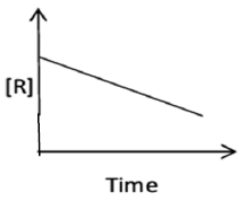
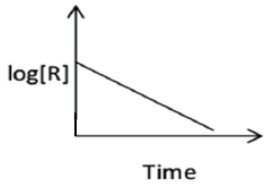
Order of reaction	zero	first	second	third
Unit of rate constt.	$MolL^{-1}s^{-1}$	s^{-1}	$Mol^{-1}L^{+1}s^{-1}$	$Mol^{-2}L^{+2}s^{-1}$
Relation b/w rate & conc of Reactant	$R \alpha [A]^0$	$R \alpha [A]^1$	$R \alpha [A]^2$	$R \alpha [A]^3$
Graph b/w rate & conc of Reactant				

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

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

2. For I order reaction $t_{1/2}$ is independent of conc. of reactant.

3. $t_{1/2}$ α $[conc]^{1-n}$ where n = order of reaction.

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

7. Arrhenius equation

log K = log A – E_a/2.303RT

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

- **<u>IMPORTANT DEFINITIONS-</u>**

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

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

molecularity of reaction is two and order of reaction is one.

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

Types of reaction based on molecularity

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

NOTE:

i. It is theoretical value.

ii. It cannot be zero or a non-integer.

iii. molecularity greater than three is not observed.

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

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

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

NOTE:-

Rate = $K[A]^x [B]^y$

x + y = order of reaction.

i. Order of a reaction is an experimental quantity

ii. It can be zero and even a fraction

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

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

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

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

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

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

8. Examples- Zero order reaction: $H_2 + Cl_2 \rightarrow 2HCl$

I order reaction : All natural and artificial radioactive reactions.

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

Order

Zero order

$K = (R_0 - R) / t$
R_0 = Initial concentration
R = concentration at time t.
rate = $-d[R]/dt = K[R]^0$
$t1/2 = R_0 / 2K$
K = rate constant
t1/2 = half life

Unit of K = mol/l/sec
eg:- $2NH_3 \rightarrow N_2 + 3H_2$

Pseudo First order

Concentration of one component do not affect order
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

rate K = $[CHCOOC_2H_5]$

First order

$K = (2.303/t) \log (R_0/R)$
R_0 = Initial concentration
R = concentration at time t.

rate = $-d[R]/dt = K[R]^1$
K = rate constant

Unit of K = sec^{-1}
eg:- $C_2H_4 + H_2 \rightarrow C_2H_6$

Elementary Reaction
Reaction takes place in one step
$H_2 + O_2 \rightarrow 2H_2O$

Second order
rate = $-d[R]/dt = K[R]^2$
unit of K = $mol^{-1}\ l\ sec^{-1}$

Third order
rate = $-d[R]/dt = K[R]^3$
unit of K = $S^{-1}mol^{-2}\ l^2$

Theories of Chemical Reactions

Activated Complex Theory

According to Arrhenius reactants collide to form intermediate called activated complex. The energy required to form activated complexes is called activation energy (E_a)
$K = A\ e^{-Ea/RT}$
A = Arrhenius factor or frequency factor
R = gas constant
K = rate constant of chemical reaction
Energy released when complex decompose to form products.
Increase in temperature increases molecular collisions and reaction rate too.
Every 10° rise in temp. K doubles.

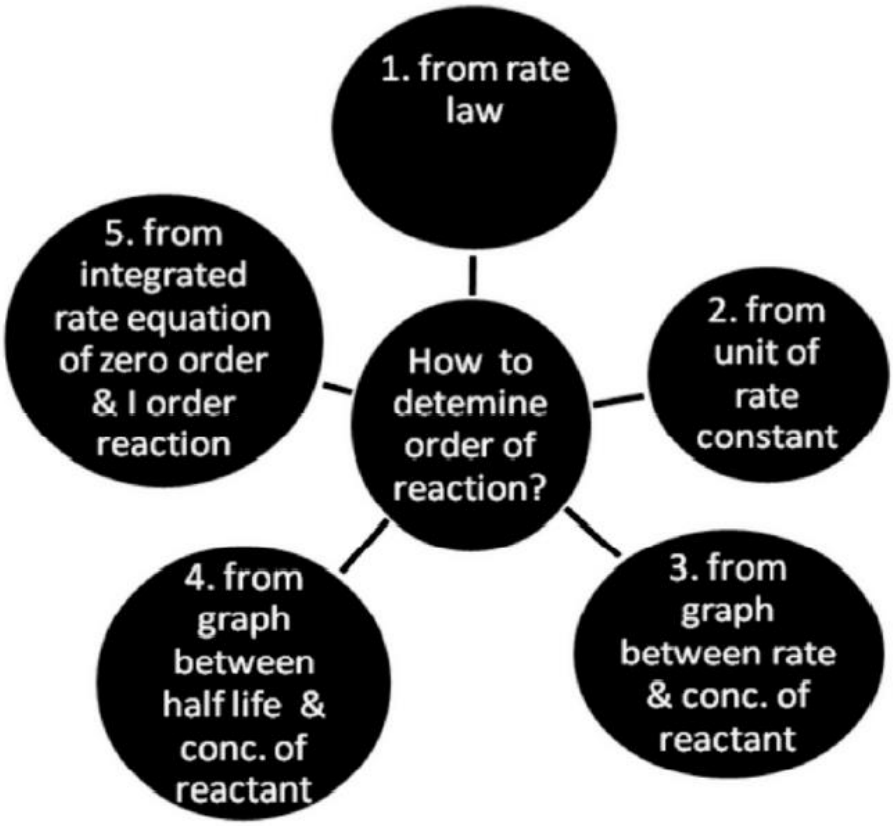
$\log \frac{K_2}{K_1} = [E_a/2.303R]\ [(T_2 - T_1) / T_1T_2]$

If we plot ln K vs 1/T slope = -Ea/R

Collission Theory

Reactants are hard spheres and products formed when they collide effectively with each other. The number of collisions per second per unit volume of reaction mixture is called collision frequency (Z)
rate = $Z_{AB}\ e^{-Ea/RT}$

molecules with sufficient K.E. and proper orientation facilitates breaking of bonds between reactants and formation of bond between products.
rate = $PZ_{AB}\ e^{-Ea/RT}$
P = probability or sterric factor account for the orientation of molecules.



Multiple Choice Questions –

1. The slope in Arrhenius plot, is equal to:

(a) $-\frac{E_a}{2.303R}$	(b) $\frac{E_a}{R}$	(c) $-\frac{R}{2.303E_a}$	(d) None of these

2. The term – dx/dt in a rate equation refers to :
(a) the conc. of a reactant (b) the decrease in conc. of the reactant with time
(c) the velocity constant of reaction (d) None of these

3. Instantaneous rate of a chemical reaction is
(a) rate of reaction in the beginning (b) rate of reaction at the end
(c) rate of reaction at a given instant (d) rate of reaction between two specific time intervals

4. Order of reaction is decided by
(a) temperature (b) mechanism of reaction as well as relative concentration of reactants
(c) molecularity (d) pressure

5. A zero order reaction is one whose rate is independent of

(a) the concentration of the reactants (b) the temperature of reaction
(c) the concentration of the product
(d) the material of the vessel in which reaction is carried out

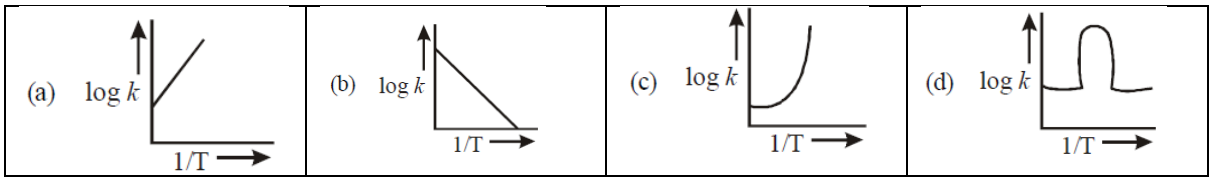
6. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A]\,[B]^2$ then the order of the reaction is
(a) 3 (b) 6 (c) 5 (d) 7

7. Which of the following influences the reaction rate performed in a solution?
(a) Temperature (b) Activation energy (c) Catalyst (d) All of the above

8. A catalyst increases the reaction rate by:
(a) decreasing enthalpy (b) increasing internal energy
(c) decreasing activation enthalpy (d) increasing activation enthalpy

9. In a reaction, the threshold energy is equal to
(a) activation energy + normal energy of reactants
(b) activation energy - normal energy of reactants
(c) normal energy of reactants - activation energy
(d) average kinetic energy of molecules of reactants

10. A graph plotted between log k vs 1/T for calculating activation energy is shown by



Assertion Reason Questions –

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:
(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Assertion is false but reason is true.

1. Assertion : Order of a reaction with respect to any reactant or product can be zero, positive, negative and fractional.
Reason : Rate of a reaction cannot decrease with increase in concentration of a reactant or product. (Ans - c)

2. Assertion : The rate of a reaction sometimes does not depend on concentration.
Reason : Lower the activation energy faster is the reaction. (Ans - b)

3. Assertion – Order and molecularity of a reaction is always same.
Reason – Order is determined experimentally whereas molecularity by a balanced elementary reaction.

4. Assertion – In a first order reaction, if the concentration of the reactant is doubled, its half-life is also doubled.
Reason – Half-life of a reaction does not depend upon initial concentration of the reactant in a first order reaction.

5. Assertion – Average rate and instantaneous rate of a reaction has the same unit. Reason – Average rate becomes instantaneous rate when time interval is too small.

Two Marks Questions –

1. (a) How does catalyst alter rate of a reaction?
   (b) A reaction is 50% complete in 2 hours and 75% completes in 4 hours. What is the order of the reaction?

2. (a)What is the unit of rate constant for a Pseudo first order reaction?
 (b) What is the overall order of reaction which has the rate expression r= k $[A]^2[B]^0$?

3. What is the effect of adding a catalyst on :
(a) Activation energy (Ea) and (b) Gibbs energy (ΔG) of a reaction.

4. A first order reaction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.

Given : [log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7]

5. The decomposition of NH_3 on Pt surface is a zero order reaction. What are the rate of formations of N_2& H_2 if k= 2.5 x 10^{-4} mol $L^{-1}s^{-1}$.

Three Marks Questions –

1. A reaction is first order in A and second order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of B three times?
(iii) How is the rate affected when the concentrations of both A and B are doubled?
2. A 1st order reaction is 40% complete in 50 minutes. Calculate the value of rate constant. At what time will the reaction be 80% completed?
3. In the given reaction $A + 3B \rightarrow 2C$,the rate of formation of C is 2.5 x 10^{-4} mol$L^{-1}s^{-1}$.

Calculate the i) rate of reaction ii) rate of disappearance of B

4. Give three important differences between rate of reaction and rate constant of reaction.5. Give four important differences between order of reaction molecularity of reaction.

Five Marks Questions –

1. (i) For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	20	40
$[CH_3COOCH_3]$/mol L^{-1}	0.40	0.20	0.10

a) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

b) Calculate the average rate of reaction between the time interval 20 to 40 seconds.

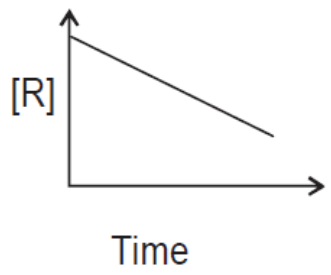
(ii) Why does the rate constant is nearly doubled for every 10° C rise in temperature?

(iii) Write the equation of temperature dependence rate of a chemical reaction.

2. (i) The rate constant of a first order reaction increases from 4×10^{-2} to 24×10^{-2} when the temperature changes from 300 K to 350 K. Calculate the energy of activation.

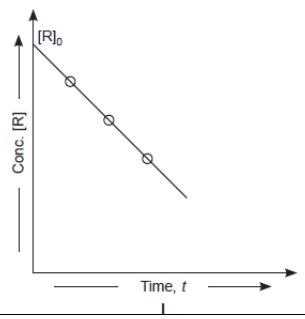
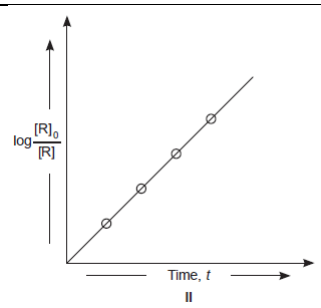
(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021, log 6 = 0.7782)

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

	a) Predict the order of reaction b)What does the slope of the above line indicate?

Passage/Case based questions –

1. Observe the following graphs and answer the questions based on these graphs.

(*a*) What is order of reaction shown in graph I?

(*b*) What is slope in graph II?

(*c*) How does $t_{1/2}$ varies with initial concentration in zero order reaction?

OR

If $t_{1/2}$of first order reaction is 40 minute, what will be $t_{99.9\%}$for first order reaction?

2. Read given passage and answer the questions that follow:

Chemical kinetics deals with rate of chemical reactions, how fast reactants get used up or how fast products are formed in the reaction. Different 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 results 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, $\Delta G°$ will be –ve and 'K' equilibrium constant will be high i.e. products formed will be more than the reactants.

(*a*) What is meant by activation energy?

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

(*c*) If $Fe^{3+} + 2I^- \rightarrow Fe^{2+} + I_2$ has E° = 0.24V, what is the value of log K? What does value of 'K' indicate?

OR

What type of molecules undergo effective collisions?

LAST THREE YEARS BOARD QUESTIONS

1. In a reaction $2N_2O_5$ (g) $\rightarrow 4NO_2(g) + O_2(g)$, the concentration of N_2O_5 decreases from 0.5 mol/L to 0.4 mol/L in 10 minutes. Calculate the average rate of this reaction and rate of production of NO_2 during this period.

2. A first order reaction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.

Given : [log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7]

3. a) Draw the plot of *ln* k vs 1/T for a chemical reaction. What does the intercept represent? What is the relationship between slope and Ea?

b) A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$.[log 2 = 0.3010]

4. In the given reaction, A + 3B → 2C, the rate of formation of C is 2.5×10^{-4} $molL^{-1}s^{-1}$.

Calculate the i) rate of reaction ii) rate of disappearance of B.

5. A first order reaction is 40% complete in 80 minutes. Calculate the value of rate constant (k). In what time will the reaction be 90% completed.

6. The rate of a reaction quadruples when the temperature changes from293 K to 313 K. Calculate the energy of activation of the reaction assumingthat it does not change with temperature.

7. For the reaction : $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

The rate of formation of $NO_2(g)$ is 2.8×10^{-3} M s^{-1}. Calculate the rate of disappearance of $N_2O_5(g)$.

8. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.

(Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK^{-1} mol^{-1})

----------x----------

ANSWERS -

Multiple Choice Questions –

1. (a) 2. (b) 3. (c) 4. (b) 5. (a) 6. (a) 7. (d)

8. (c) 9. (a) 10. (b)

Assertion Reason Questions – 1. (c) 2. (b) 3. (d) 4. (d) 5. (b)

Two Marks Questions –

Ans.1. (a) It increases rate of reaction by providing a new path having low activation energy.
(b) Since half-life remains constant so it is a first order reaction.

Ans. 2 (a) s^{-1} (b) 2

Ans –3 (a) Ea decreases (b) Gibbs energy doesn't change.

Ans. 4. 15 minutes

Ans. 5. – rate of formation of N_2 = 2.5 x 10^{-4} mol $L^{-1}s^{-1}$&

rate of formation of H_2 = 7.5 x 10^{-4} mol $L^{-1}s^{-1}$

Three Marks Questions –

Ans. 1. (i) Rate = $K[A]^1 [B]^2$
(ii) Rate = $K[A]^1 [3B]^2 = 9K[A]^1 [B]^2$ hence, it becomes 9 times.
(iii)Rate = $K[2A]^1 2[B]^2 = 8K[A]^1 [B]^2$ hence, it becomes 8 times.
Ans. 2 – find k by taking values a = 100 & a-x = 60 i.e. = 0.01028 min^{-1} and then using

this value of k, find the time when the reaction will complete 80%, i.e. =156.52 min.

Ans. 3. (i) 2.5 x 10^{-4} $molL^{-1}s^{-1}$ ii) 7.5 x $molL^{-1}s^{-1}$

Ans. 4.

S.No.	Rate of reaction	Rate constant of reaction
1	It is the change in concentration of reactant or product in a unit interval of time.	It is the rate of reaction when molar conc. of each of the reactants is unity.
2	Its unit is $molL^{-1}s^{-1}$	Its unit depends upon the order of reaction.

3	The rate of reaction at any instant of time depends upon the molar conc. of the reactants at that time.	The rate constant does not depend upon the molar conc. of the reactants.

Ans. 5.

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

Five Marks Questions –

Ans.1.(i) (a)Value of rate constant (k) remains constant at time 20 and 40 sec

(b) 0.005 mol $L^{-1}s^{-1}$

(ii) An increase in temperature will raise the average kinetic energy of the reactant molecules. Therefore, a greater proportion of molecules will have the minimum energy necessary for an effective collision.

(iii) Arrhenius equation, $k = A\ e^{-Ea/RT}$

Ans. 2. (i) By using the formula, $\log k_2/k_1 = Ea/2.303\ R\ [T_2-T_1]/T_1.T_2$

Ea = 24125 J

(ii) a) Zero order reaction b) Concentration of the reactant decreases with time.

Passage/Case based questions –

Ans. 1. (a) Zero order reaction.

Ans. (b) k/2 303 where '*k*' is rate constant.

Ans. (c) $t_{1/2}$ is directly proportional to initial concentration.

OR

Ans. $t_{99.9\%} = 10\ t_{1/2} = 10 \times 40 = 400$ minutes

2. Ans. (a) The extra energy which must be supplied to reactants in order to undergo effective

collision to form products.

Ans. (b) It represents fraction of molecules possessing activation energy (Ea) or more than Ea.

Ans. (c) $\log K = nE°/0.0591 = 2 \times 0.24/0.0591V = 8.122$

The value indicates that products are formed 10^8, times than reactants.

OR

Ans: Those molecules which possess activation energy and collide in proper orientation undergo effective collisions.

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d and f Block Elements
Weightage – 7 marks (2022-23)

KEY POINTS-

Elements from 3rd group to 12th group in the Modern Periodic table are called d-block elements. In these elements their last electron enters in the penultimate d- sub shell. They are placed in between s-block and p-block elements. They show a regular transition from the highly electropositive metals of s-block elements to the less electropositive p-block elements. So, they are called **transition elements.**

Transition elements can be defined as elements which contain partially filled d-orbitals in their atomic state or in any of their oxidation state. This definition does not include Zn, Cd and Hg. So, they are not regarded as transition elements. Or, they are called **pseudo transition elements**.

Electronic Configuration

General outer electronic configuration of d-block elements is (n-1) d^{1-10} ns^{1-2}. There is only a small difference in energy between (n-1) d orbital and ns orbital. So, in some cases ns electrons are also transferred to (n-1) d level.
The electronic configurations of Cr and Cu in the 3d series show some exceptions.
$_{24}Cr$ – [Ar] $3d^5$ $4s^1$ $_{29}Cu$ – [Ar] $3d^{10}$ $4s^1$
This is due to the extra stability of half-filled and completely-filled electronic configurations. (d^5 or d^{10}) The electronic configurations of Zn, Cd and Hg are represented by the general formula (n-1) d^{10} ns^2. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. So, they are not regarded as transition elements.

General characteristics of transition elements

1. Atomic and ionic radii

In a given transition series, the atomic and ionic radii first decrease, then become constant and increases towards the end of the series. This is because in transition elements the new electron enters in a d orbital. Initially since there is a few numbers of d electrons, the shielding effect is very poor. As the atomic number increases,

2. Melting and boiling points

In a given transition series the melting and boiling points 1st increases up to the middle and then decreases. This can be explained in terms of metallic bond strength which depends on the number of unpaired electrons. As the number of unpaired electron increases, the metallic bond strength increases. Hence the melting point also increases.

3. Ionisation enthalpy

The ionisation enthalpy of transition elements generally increases from left to right. This is Another factor which affects the m.p is heat of atomization. Mn and Tc have low melting point even though they have d^5 due to increase in nuclear charge. But the increase is not regular. This can be explained as follows.

After the removal of one electron, the relative energies of 4s and 3d orbitals get changed. Hence the remaining electron in the 4S level is transferred to 3d level. So, the unipositive ions have d^n configuration with no 4s electrons. During this re-organisation of electrons, some energy is released and it is known as exchange energy. So the net energy required to remove the 1st electrons is equal to the sum of ionisation enthalpy and exchange energy.

The first ionisation enthalpies of Cr and Cu are low. This is because the removal of one electron does not

change their d configuration. Similarly, first ionisation enthalpy of Zn is high because after the removal of one electron there is no change in the d configuration.

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

$3d^{10}4s^{2}$ $3d^{10}4s^{1}$

The 2nd I.E of Cr and Cu are very high. This is because the removal of one more e^{-} from these metals disrupted their stable configuration (d^5 or d^{10})

The 2nd I.Es of Mn and Zn are low, this is because after the removal of one more electron, they attain the stable half-filled or completely filled electronic configuration.

4. Oxidation State -Transition metals show variable oxidation states. This is because in these elements d and s electrons have comparable energies. So in chemical reaction along with s-electrons, d-electrons also participate. In a given transition series, the

maximum oxidation state increases up to the middle and then decreases. This is due to the half-filled or noble gas configuration. The common oxidation state of 1st row transition elements is +2. The maximum oxidation state increases from top to bottom in a group. In lower oxidation state, the transition element mainly forms ionic compounds.

Sc generally shows +3 oxidation state because after the removal of 3 electrons, it gets a stable noble gas configuration. The oxidation state of Zn is +2 because of the completely filled configuration of Zn^{2+}.

5. Electrode Potential -

The electrode potential values of first row transition series generally increases from left to right with some exceptions. The $E^0(Cu^{2+}/Cu)$ is positive (+0.34V), while the E^0 values of all the other first row transition elements are –ve. This is because the high energy to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. So, Cu does not easily react with acid and liberate H_2. Only oxidizing acids [HNO_3 and hot Conc. H_2SO_4] react with Cu and the acid get reduced.

Along the series the E^0 values become less –ve due to the increase in the sum of 1st and 2nd ionisation enthalpies. The E^0 values of Mn^{2+} and Zn^{2+} are more –ve, this is because of the half-filled configuration of Mn^{2+} (d^5) and completely filled configuration of Zn^{2+} (d^{10}). $E^0(M^{3+/}M^{2+})$ value of Sc is very low and that for Zn is very high. This is because of their stable electronic configuration.

E^0 (Mn^{3+}/Mn^{2+}) is high because of the stable half-filled configuration of Mn^{2+}. Similarly E^0 (Fe^{2+}/Fe^{3+}) is low, this is because after the removal of one electron from Fe^{2+}, it gets a stable electronic configuration.

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

$3d^6$ $3d^5$

Q. Explain why Cu^{+} is not stable in aqueous solution?

This is due to the much more –ve hydration enthalpy of Cu^{2+} (aq) than Cu^{+}. In the case of Cu^{2+}, the hydration enthalpy is more compensated by ionisation enthalpy than in Cu^{+}.

6. Magnetic Properties

Transition metals show mainly two types of magnetic properties- paramagnetism and diamagnetism. Some transition metals also show ferromagnetism which is an extreme case of paramagnetism.

Paramagnetism arises from the presence of unpaired electrons. Each unpaired e- is associated with a spin magnetic moment and an orbital magnetic moment. For the compounds of 1st row transition elements, the contribution of orbital magnetic moment is effectively cancelled and so only spin magnetic moment is considered. It is determined by the no. of unpaired e^{-}s and is calculated by the spin only formula:

$\mu_s = \sqrt{n(n+2)}$ where n is the no. of unpaired electrons and μ_s is the spin only magnetic moment in the unit of Bohr Magneton (B.M).

The magnetic moment increases with increase in no. of unpaired e^-s. Thus, the observed magnetic moment gives an idea about the no. of unpaired e^-s present in the atom or ion.

7. Formation of coloured ions or compounds

Most of the Transition metals ions or compounds are coloured. This is because of the presence of partially filled d orbitals. When an electron from a lower energy d orbital is exited to higher d level, it absorbs energy and this is equal to the energy of certain colours in visible region. So, the colour observed is the complementary colour of the light absorbed.

In aqueous solution most of the Transition metal ions are coloured since water molecules act as the ligands.

Among Ti^{2+} and Ti^{4+}, Ti^{2+} is coloured while Ti^{4+} is colourless. This is because Ti^{4+} has no partially filled d orbitals.

Ti^{2+} - [Ar] $3d^2$ Ti^{4+} - [Ar] $3d^0$

Similarly, among Cu^+ and Cu^{2+}, Cu^{2+} is coloured while Cu^+ is colourless. This is due to the lack (absence) of partially filled d orbitals in Cu^+.

8. Formation of Complexes

Transition metals form a large no. of complexes. This is due to:

1. Comparatively smaller size
2. High ionic charge
3. Presence of partially filled d orbitals
4. 4. Ability to show variable oxidation state
5. Eg: $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Ni(CO)_4]$ etc.

9. Catalytic Property

Transition metals act as catalysts in a large no. of chemical reactions. This is due to –

a) their large surface area and
b) their ability to show variable oxidation state.

10. Interstitial Compound Formation

These are formed when smaller atoms like H, N, C, B etc. are trapped inside the crystal lattice of the metal. They are usually non-stoichiometric and neither typically ionic nor covalent. E.g.: Fe_3H, Mn_4N, TiC, $VH_{0.56}$, $TiH_{1.7}$ etc.

Some the properties of these compounds are:

1) They have high melting point. 2) They are very hard.
3) They retain metallic conductivity. 4) They are chemically inert.

11. Alloy Formation- Alloys are homogeneous solid solutions of elements in which at least one element is a metal. They are formed by atoms with metallic radii within about 15% of each other. Because of similar radii and other characteristics of Transition metals, they readily form alloys. The alloys formed are hard and have high m.p. e.g.: Bronze (Cu, Zn), Stainless steel (Fe, C, Ni, Mn and Cr).

Some Important Compounds of Transition Elements

1. <u>Potassium dichromate ($K_2Cr_2O_7$)</u>

Potassium dichromate is generally prepared from chromite ore ($FeCr_2O_4$). The preparation involves three steps.

1. Conversion of chromite ore to sodium chromate

Chromite ore is first fused with sodium carbonate in presence of air to form sodium chromate. $4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$

2. Acidification of sodium chromate to sodium dichromate

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to orange sodium dichromate.
$2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$

3. Conversion of sodium dichromate to potassium dichromate

The solution of sodium dichromate is treated with potassium chloride so that orange crystals of potassium dichromate crystallise out. $Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$

Properties

The chromate and dichromate are inter convertible in aqueous solution depending upon pH of the solution. Chromate on acidification gives dichromate and the dichromate on treating with alkali gives chromate.

$2\ CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

$Cr_2O_7^{2-} + 2OH^- \rightarrow 2\ CrO_4^{2-} + H_2O$

The oxidation state of chromium in chromate and dichromate is +6.

Sodium and potassium dichromats are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis.

Oxidising Property $K_2Cr_2O_7$ is a good oxidising agent in acidic medium. Its oxidising action can be represented as follows:

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

Thus, acidified potassium dichromate will oxidise.

1) Iodides to iodine-

$6\ I^- \rightarrow 3I_2 + 6\ e^-$

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

$6I^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$

2) Iron(II) (ferrous) to iron(III) (ferric)

$6\ Fe^{2+} \rightarrow 6Fe^{3+} + 6\ e^-$

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

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

Thus, acidified potassium dichromate will oxidise

The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

2. Potassium permanganate ($KMnO_4$)

Potassium permanganate is commercially prepared from Pyrolusite (MnO2). The preparation involves two steps. In the first step MnO2 is fused with KOH to form potassium manganate (K2MnO4).

Then K2MnO4 is electrolytically oxidised to potassium permanganate.

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

$3MnO4^{2-} + 4H+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

Properties -

Potassium permanganate forms dark purple crystals which are iso-structural with those of $KClO_4$.

When heated it decomposes and liberate O_2.

$2KMnO_4 \rightarrow K2MnO_4 + MnO_2 + O_2$

$KMnO_4$ is a good oxidizing agent in acidic, basic and neutral media. The oxidizing action in acidic medium is due to the reaction:

$MnO_4^- + 8H^+ + 5e- \rightarrow Mn^{2+} + 4H_2O$

Acidified permanganate solution oxidises:

1) Oxalates to carbon dioxide:

$5\ x\ (C_2O_4^{2-} \rightarrow 2\ CO_2 + 2e^-)$

$2 \times (MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$

$5\ C_2O_4^{2-} + 2\ MnO_4^- + 16H^+ \rightarrow 10\ CO_2 + 2Mn^{2+} + 8H_2O$

In alkaline or neutral medium,

permanganate ion is reduced to MnO_2

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

In alkaline medium it oxidises

1) Iodide to iodate

$(MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-) \times 2$

$I^- + 6OH^- \rightarrow IO^{3-} + 3\ H_2O + 6\ e^-$

$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO^{3-}$

Uses: It is used as an oxidising agent in acidic, basic and neutral medium. It is used as a primary standard in volumetric analysis. It is used for the bleaching of wool, cotton, silk and other textile fibres and also for the decolourisation of oils.

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last electron enters in the anti-penultimate f-subshell are called f-block elements. They include lanthanides of the 6th period and actinides of the 7th period. They are also called inner transition elements. Since lanthanum ($_{57}La$) closely resembles lanthanides, it is also included along with them. Similarly, actinium ($_{89}Ac$) is included along with actinoids because of its close resemblance with them.

The Lanthanoids or lanthanides

The 14 elements after lanthanum of the 6th period are called lanthanides or lanthanoids or lanthanons or rare earths. They include elements from $_{58}Ce$ to $_{71}Lu$. They are generally represented as Ln.

Atomic and ionic radii - Lanthanide Contraction

In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanide series (though very slightly) is called lanthanide contraction.

Reason: In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and as a result the radii decreases.

Consequences:

- Due to Lanthanide Contraction the 2nd and 3rd row transition series elements have similar radii. E.g. Zr – 160pm and Hf -159pm
- Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.
- The basic character of their hydroxides decreases from lanthanum to lutetium. i.e, $La(OH)_3$ is more basic than $Lu(OH)_3$.

Oxidation number

In lanthanoids, the most common oxidation state is +3. However, +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filled or filled f subshells. Cerium shows the oxidation state +4 due to its noble gas configuration. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu and Yb shows +2 oxidation state because of the stable f^7 or f^{14} configuration. Sm shows +2 oxidation state also.

General properties of Lanthanoides

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. Their hardness increases with increasing atomic number. They have typical metallic structure and are good conductors of heat and electricity.

Most of the lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions is due to the presence of f electrons. But La^{3+} or Lu^{3+} ion are colourless. The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

<u>Uses of Lanthanides -</u>

The main use of the lanthanoids is for the production of alloy steels. An important alloy is mischmetall which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A great deal of mischmetall is used in Magnesium based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

The Actinoids or Actinones

The 14 elements after actinium in the 7th period of modern periodic table are called actinides or actinoids or actinones. They include elements from $_{90}Th$ to $_{103}Lr$. Most of them are artificially prepared and are short lived. They are radioactive. The elements after Uranium are artificially prepared and so they are called **trans-uranium elements or trans-uranic elements**.

Atomic and ionic radii

In actinoid series the atomic and ionic radii decreases regularly from left to right. This is known as Actinoid contraction. **Oxidation state**

Common oxidation state of actinoids is +3. The elements in the first half of the series show higher oxidation states. The maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.

Comparison between lanthanoids and acinoids

1.Most of the actinoids are artificially prepared and are radioactive.

2.The first ionisation enthalpy of early actinoids is lower than those of lanthanoids.

3.Actinoid contraction is greater from elements to elements than lanthanoid contraction. This is due to greater shielding effect of 5f electrons.

Multiple Choice Questions-

Q.1- The ability of d- block elements to form complexes is due to -

(A) small and highly charged ions

(B) Vacant low energy orbital to accept lone pair of electrons from ligands

(C) Both A & B are correct

(D) None is correct

Q.2- Mohr's salt is a -

(A) Normal salt (B) Acid salt

(C) Basic salt (D) Double salt

Q3- In alkaline solution MnO_4^- changes to–

(A) MnO_4^{2-} (B) MnO_2

(C) Mn_2O_3 (D) MnO

Q.4- Which of the following is not a characteristic property of transition metal -

(A) High enthalpy of atomisation

(B) Formation of interstitial compounds

(C) Diamagnetism

(D) Variable oxidation state

Q.5- Which of the following is not a transition metal ?

(A) Sc

(B) Mn

(C) Zn

(D) Co

Q.6- catalysts used in contact process of manufacture of sulphuric acid are –

(A) NO (B) V2O5

(C) Mo (D) Platinised asbestos

Q.7- If a transition-metal compound absorbs violet radiation in the visible region, its colour would be

(A) Yellow green (B) Yellow
(C) Orange (D) Blue

Q.8- Which of the following will give a pair of enantiomorphs ?
(A) $[Cr(NH_3)_6][Co(CN)_6]$ (B) $[Co(en)_2Cl_2]Cl$
(C) $[Pt(NH_3)_4][PtCl_6]$ (D) $[Co(NH_3)_4Cl_2]NO_2$

Q.9- The pair in which both the elements generally shows only one oxidation state is -
(A) Sc and Zn (B) Zn and Cu
(C) Cu and Ag (D) Zn and Au

Q.10- Transition elements show variable oxidation states because they lose electrons from the following orbitals -

(A) ns and np (B) (n – 1) d and ns
(C) (n – 1) d (D) ns

Assertion Reason Questions –

The following questions given below consist of an "Assertion" (A) and "Reason" (R) Type questions. Use the following Key to choose the appropriate answer.

(A) If both (A) and (R) are true, and (R) is the correct explanation of (A).
(B) If both (A) and (R) are true but (R) is not the correct explanation of (A).
(C) If (A) is true but (R) is false.
(D) If (A) is false but (R) is true.
(E) If Assertion & Reason are false.

Q.11- **Assertion :** Tungsten has a very high melting point.
Reason : Tungsten is a covalent compound.

Q.12- **Assertion :** $TiCl_4$ is colourless compounds.
Reason : Ti_4^+ has no unpaired electron.

Q.13- **Assertion :** Mn atom losses ns electrons first during ionisation as compared to (n – 1)d electrons.
Reason : The effective nuclear charge experienced by (n – 1) d electrons is greater than that by ns electrons.

Q.14- **Assertion :** KMnO4 is oxidising agent in neutral, acidic and basic medium.
Reason : Equivalent mass of KMnO4 in acidic medium is 31.6.

Q.15- **Assertion :** All the members of actinide series are radioactive in nature.
Reason : The electrons are gradually accommodated in 5f-energy subshell.

Q.16- **Assertion :** Ionisation of transition metals involve loss of ns electrons before (n – 1) d electrons.
Reason : Filling of ns orbitals take place before the filling of (n – 1)d orbitals–

Short Answer Type Questions (2)

Q.17- Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have *d*4 configuration.
Q.18- Give two uses of potassium permanganate.
Q.19- Transition metal form coloured compounds. why?
Q.20-Explain why Cu^+ ion is not stable in aqueous solutions?
Q.21- What are transition elements?

Short Answer Type Questions (3)

Q22- With the help of ionic equations describe what happens when-
(a) pH of a solution of dichromate ions is raised.
(b) Potassium manganate is electrochemically oxidised.

Q23- Suggest reasons for the following features of the transition metals-

(a) A transition metal exhibits higher oxidation states in oxide and fluorides.

(b) The highest oxidation state is exhibited in oxoanions in metal.

(c) Write the different oxides of chromium and mention basic and acidic oxides.

Q.24 **How will you obtain the following?**

(a) Cuprous chloride from copper sulphate.

(b) Silver from silver nitrate.

(c) Ferrous sulphate from ferrous ammonium sulphate.

Q.25- Give reasons for the following:

(a) Transition metals have high enthalpy of atomisation.

(b) Among the lanthanoids, Ce (III) is easily oxidised to Ce (IV).

(c) Fe^{3+} / Fe^{2+} redox couple has less positive electrode potential than Mn^{3+}/Mn^{2+} couple.

Q.26-(a) Write the steps involved in the preparation of : $K_2Cr_2O_7$ from Na_2CrO_4 .

(b) What is meant by lanthanoid contraction ? What effect does it have on the chemistry of the elements which follow lanthanoids ?

Case Study Based Questions

Q.27- Read the given passage and answer the questions that follow:

The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is $(n-1)\ d^{1-10}\ ns^{1-2}$The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e. 3d, 4d and5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation stables, complex formation, formation of coloured ions, alloys, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point.

(a) Why are Zn, Cd and Hg non-transition elements?

(b) Which transition metal of 3d series does not show variable oxidation state?

(c) Why do transition metals and their compounds show catalytic activity?

(d) Why are melting points of transition metals high?

(e) Why is Cu^{2+} ion coloured while Zn^{2+} ion is colourless in aqueous solution?

Q.28- Read the following passage and answer the questions that follow:

$KMnO_4$ and $K_2Cr_2O_7$ are most important chemicals which are used as oxidising agents and disinfectants.

K_2MnO_4 is prepared by fusing MnO_2 with KOH in presence of O_2. K_2MnO_4 is electrolysed to get purple coloured $KMnO_4$. Na_2CrO_4 is prepared by heating chromite ore with Na_2CO_3 in presence of O2. Na_2CrO_4 is converted into $Na_2Cr_2O_7$ by reacting with concentrated H_2SO_4. $Na_2Cr_2O_7$ is reacted with KCl to get $K_2Cr_2O_7$, orange coloured solid, soluble in water, changes to yellow coloured CrO_4^{2-} in basic medium, $KMnO_4$ acts as oxidising agent in acidic, neutral as well basic medium. In acidic medium, it converts Fe^{2+} to Fe^{3+}, Sn^{2+} to Sn^{4+}, COO^- to CO_2. In basic medium it converts $I^-$to IO^{3-}. $K_2Cr_2O_7$ acts as oxidising agent only in acidic medium, converts H_2S to S, SO_2 to $SO4^{2-}$, I^- to I_2. Lanthanoids and actinoids belong to f-block elements with general electronic configuration $(n-2)\ f^{1\ to\ 14}\ (n-1)\ d^{0-2}\ ns^2$. All actinoids are radioactive. Both show contraction in atomic and ionic radii but actinoid contraction is more than lanthanoid contraction. Lanthanoid show +3 oxidation state, few elements show +2 and+4 oxidation states also. Actinoids show +3, +4, +5, +6, +7 oxidation states.

(a) Which lanthanoid shows +4 oxidation state and why?

(b) Give two similarities between lanthanoids and actinoids.

(c) Complete the equation and balance: $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow$?

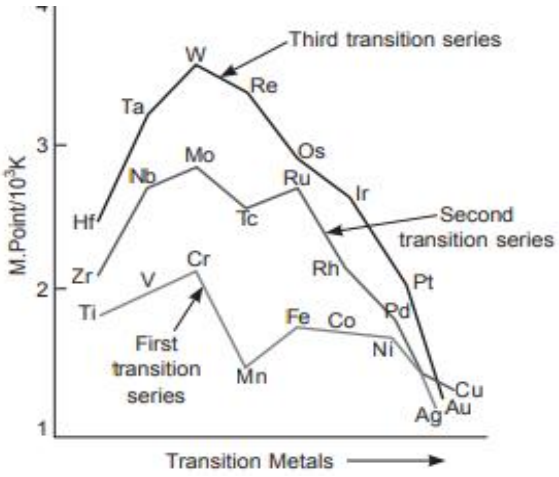
(d) Convert sodium chromate to sodium dichromate. Give chemical equation.

$2Na_2CrO_4 + H_2SO_4$ (conc.) $\rightarrow$?

(e) Complete the following:

$MnO_4^{2-} + H^+ \rightarrow ?$

Q.29-Observe the graph of transition metal and their melting points and answer the questions based on the graph and related concepts.



(a) Why does W (tungsten) has highest melting point?

(b) Which element in 3d series has lowest enthalpy of atomisation and why?

(c) Why is mercury liquid?

(d) Why are transition metals less electropositive than 's'-block elements?

(e) How does density vary from left to right in 3d series and why?

Q.30 (a)- Write the steps involved in the preparation of $K_2Cr_2O_7$ from chromite ore.

(b) Name one alloy of lanthanoid metal. Write any one use.

Q.31 - Give reasons for the following features of the transition metals-

(i) Out of the Cu+ and Cr+ which would not be the coloured ion ?

(ii) The common oxidation state of lanthanoids is +3. Why?.

(iii) Basic character of hydroxides decreases from La to Lu. Why?.

(iv) Cadmium is used to extinguish nuclear fire.

(v) Blue colour of $CuSO_4$ solution is discharged slowly when an iron rod is dipped into it.

ANSWERS

Multiple Choice Questions

Ans.1- C

Ans.2- D

Ans.3- B

Ans.4- C

Ans.5- C

Ans.6- B

Ans.7- A

Ans.8- B

Ans.9- A

Ans.10- B

Assertion Reason -

Ans.11- C

Ans.12- A
Ans.13- A
Ans.14- B
Ans.15- B
Ans.16- B

Short Answer Type Question (2 Marks) -

Ans.17- Cr^{2+} changes from d^4 to d^3(stable half filled t_2g).On the other hand, the change from Mn^{2+} to Mn^{3+} results in the half-filled (d^5)

Ans.18- (a) It is used as volumetric reagent for the estimation of ferrous salt, oxalate etc.

$MnO_4^- + 8H^+ + 5Fe^{++} \longrightarrow Mn^{2+} + 5Fe^{++} + 4H^2O$

(b) When 1% alkaline KMnO4 solution (Baeyer's reagent) is added to an organic compound having C = C or C ≡ C (dipole or triple bond) its pink colour is decolourised and presence of double bond or triple bond is detected.

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$ The E^0 is favourable for this

Ans.19- Due to incompletely filled d-orbital there is d-d electron transition.

Ans. 20- Cu^+ in aqueous solution undergoes disproportionation to form Cu & Cu^{2+}.

Ans.21- d- block elements which have incompletely filled d subshell in ground state as well as normal oxidation state are called as transition elements.

Short Answer Type Question (3 Marks) -

Ans.22- a) The reactions are described with the help of the following ionic equations :

$Cr_2O_7^{2-}$ + $2OH^-$ ----------> $3CrO_4^-$ + H_2O

Orange high PH yellow

When pH is increased, i.e. solution is more basic, orange coloured dichromate ion changes to yellow coloured chromate ion.

(b) MnO_4^{2-} ----------electrolysis ------> MnO_4^- + e^-

green Purple

Ans.23- (a) Because oxygen and fluorine are most electronegative elements so the transition metals are oxidised to their higher oxidation states with oxygen and fluorine.

(b) Because the highest oxidation state of metal in oxoanions is stabilised by O_2^- ion, therefore, the metal shows highest oxidation state in oxoanions. Example: $Cr_2O_7^{2-}$ (dichromate) and MnO4 – (permanganate) have the highest oxidation states of metal i.e., Cr (VI) and Mn(VII) respectively.

(c) Oxides of Cr : CrO, Cr_2O_3, CrO_2 and CrO_3 Oxidation state of Cr : + 2 + 3 + 4 + 6 respectively. Nature of the oxide: Basic, Amphoteric & Acidic respectively.

Ans. 24 (a) **Ans. 24 (a)**-$2CuSO_4 + 2NaCl + SO_2 + 2H_2O \rightarrow Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$

Cuprous Chloride

b) $2\ AgNO_3 + Zn \rightarrow 2\ Ag + Zn\ (NO_3)_2$

(c) $FeSO_4.\ (NH_4)_2SO_4\ .\ 6\ H_2O + 4NaOH \rightarrow Fe(OH)_2 + 2NH_3 + 2Na_2SO_4 + 8\ H_2O$

ppt.

$Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O$

Ferrous sulphate

Ans.25 (a)- Transition elements have large number of unpaired electrons in their atoms. Because of which they have stronger interatomic interaction. Thus, stronger bonding between the atoms resulting in higher enthalpies of atomisation.

Ans.25 (b)-Ce (III) has 4f1 5d0 6s0 configuration. It can have extra stability due to empty f-orbitals by changing into Ce (IV). Due to this reason Ce (III) is easily oxidised to Ce (IV).

Ans.(c)- Mn^{2+} is more stable than Mn^{3+} due to extra stability of Mn^{2+} (d^5 i.e., half-filled d-orbitals) while Fe^{3+} (d^5) has extra stability than Fe^{2+}. The less positive value of E° of Fe^{3+}/Fe^{2+} than E° Mn^{3+}/Mn^{2+} indicates that the tendency to change Fe^{2+} into Fe^{3+} is more than that of Mn^{2+} into Mn^{3+}.

Ans.26-(a) Steps involved in the preparation of $K_2Cr_2O_7$ are :

(i) $2Na_2CrO_4 + H2SO4 \longrightarrow Na2Cr2O7 + Na2SO4 + H2O$

(ii) $Na2Cr2O7 + 2KCl \longrightarrow K2Cr2O7 + 2NaCl$

Ans.26-(b) The decrease in atomic and ionic size with the increase in atomic number in lanthanoids is called lanthanoid contraction. It has the following effects :

(i) The ionisation energy in 5d series is more than that in 3d and 4d series.

(ii) Atomic & ionic size of 4d ad 5d elements becomes almost identical.

(iii) There is resemblance between properties of elements 4d and 5d transition series.

Case Study Based Questions

Ans.27-- a) It is because neither they nor their ions have incompletely filled d-orbitals.

b) Scandium (Sc) and Zinc (Zn).

c) It is because they show variable oxidation state, can form intermediate complexes and have large surface area for adsorption of gases.

d) It is due to strong interatomic forces of attraction due to presence of unpaired electrons.

e) It is because Cu^{2+} has one unpaired electron and undergoes d-d transition by absorbing light from visible region and radiate blue colour, whereas Zn^{2+} is colourless due to absence of unpaired electron.

Ans.28- a) 'Ce' shows +4 oxidation state because it has stable noble gas electronic configuration.

b) (i) Both show contraction, lanthanoid and actinoid contraction.

(ii) Both form-coloured ions and undergo f-f transition.

c) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

d) $2Na_2CrO_4 + H_2SO_4$ (conc.) $\rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

e) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

Ans.29 (a). It is due to presence of most number of unpaired electrons and there is more frequent metal-metal bonding in 5d series than 3d and 4d series.

Ans. (b) Zinc has lowest enthalpy of atomisation due to weak metallic bond which is due to absence of unpaired electrons.

Ans (c). It is due to larger size, absence of unpaired electron and weak interatomic attraction and weaker metallic bond.

Ans (d). It is due to smaller atomic size and higher ionisation enthalpies.

Ans (e). Density goes on increasing from Sc to Cu because atomic mass increase more than atomic volume.

Long Answer Type Questions (5 Marks) –

Ans. 30- (a) Steps involved in the preparation of $K_2Cr_2O_7$ are :

(i) 4FeCr2O4 + 8Na2CO3 + 7O2 --------->. 8Na2CrO4 + 2Fe2O3 + 8CO2

(ii) $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr2O7 + Na2SO4 + H2O$

iii) $Na2Cr2O7 + 2KCl \longrightarrow K2Cr2O7 + 2NaCl$

(b) The name of alloy of lanthanoid is Mischmetall. It is used in bullet shells & lighter flint.

Ans 31-(i) Cu+, because there is no unpaired electron in d-orbitals.

Ans-(ii) It is due to lanthanoid contraction.

Ans-(iii It is due to lanthanoid contraction.

Ans.(iv) Cadmium absorbs neutrons, stops nuclear fission reaction and extinguishes nuclear fire.

Ans. (v) Because Cu^{2+} is reduced to Cu in presence of iron rod

$CuSO_4 + Fe \rightarrow Cu + FeSO_4$

Blue green

CONCEPT MAP

THE d-AND f-BLOCK ELEMENTS

The purple solution so obtained is concentrated and dark purple, needle-like crystals of $KMnO_4$ having metallic lustre are obtained.

* **Potassium dichromate:** Potassium dichromate is obtained from chromite ($FeCr_2O_4$). The ore is mixed with soda ash and lime and roasted to obtain sodium chromate.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8CO_2(g) + 8Na_2CrO_4$$

sodium chromate

Sodium chromate so obtained is reacted with sulphuric acid to obtain sodium dichromate.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

sodium chromate → sodium dichromate

Sodium sulphate crystals are removed first and then the solution is cooled to obtain crystals of sodium dichromate dihydrate.

Hot concentrated solution of sodium dichromate is mixed with potassium chloride to obtain crystals of potassium dichromate.

$$Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

potassium dichromate

* **Chromyl chloride test:** This is a confirmatory test for chlorides. When a solid chloride salt is heated with potassium dichromate and conc. H_2SO_4, orange coloured vapour of chromyl chloride is obtained.

$$K_2Cr_2O_7 + 4\,NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4\,NaHSO_4 + 2CrO_2Cl_2 + 3\,H_2O$$

chromyl chloride (orange-red vapour)

Chromyl chloride vapour when passed through water give yellow-coloured solution containing chromic acid.

* **The f-block elements (inner- transition elements) :** The elements which in their elemental or ionic form have partly filled f-orbitals are called f-block elements. There are two series of inner-transition elements, each having 14 elements. The elements in which 4f orbitals are progressively filled are called lanthanoids. The elements in which 5f orbitals are progressively filled are termed actinoids.

Lanthanoids: The fourteen elements after lanthanum (atomic no. 58-71) are called lanthanoids or lanthanons. The general electronic configuration of lanthanoids is $4f^{1-14}\,5d^{0-1}\,6s^2$.

Oxidation states :.Lanthanoids in aqueous solution and in the solid state exhibit oxidation states of + 2, + 3 and +4. The trivalent state (+ 3) being more stable.

Magnetic properties : Trivalent ions of lanthanoids (except La^{3+} and Lu^{3+}) are paramagnetic.

* **Lanthanoid contraction :** The steady cumulative decrease in the atomic and ionic sizes in going from Ce to Lu is called lanthanoid contraction. It arises due to the increased nuclear charge and poor shielding effect of the 4f electrons.Direct consequences of the lanthanoid contraction are (a) Almost equal size of Hf^{4+} and Zr^{4+}. (b) Decrease in the basic character of lanthanoid hydroxides with increase in the atomic number. $La(OH)_3$ is the most basic, while $Lu(OH)_3$ is least basic.

* **Actinoids :** The fourteen elements (atomic number 90-103) after actinium are called actinoids. These are also called second series of inner-transition elements. The general eletronic configuration of actinoids is $5f^{0-14}\,6d^{0-1}\,7s^2$.

Oxidation states : Actinoids show variable oxidation states. The oxidation state of 3 + is the most common.

Coloured ions/salts: Most M^{3+}, M^{4+} ions of actinoids are coloured. Ions having 0, 1 and 7 electrons in f-subshells are colourless. The ions having 2, 3, 4, 5 and 6 electrons f-orbitals are coloured.

* **Misch metal :** The alloy containing 94-95% a rare earth element, iron up to 5% and traces of sulphur, carbon, calcium and aluminium is called misch metal.

* **Pyrophoric alloys :** A typical composition of a pyrophoric alloy is cerium 40.5%, lanthanum + neodymium 44%, iron 4.5%, aluminium 0.5% and the remainder calcium, silicon and carbon. The pyrophoric alloys containing rare-earth metals are used in the preparation of ignition devices, e.g., tracer bullets and shells and flints for lighters.

COORDINATION COMPOUNDS

Key Points

A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. These ions or molecules are bonded to the metal atom or ion by a coordinate bond.
Example: **$K_4[Fe(CN)_6]$**
They do not dissociate into simple ions when dissolved in water.

- **Double salt**

When two salts in stoichiometric ratio are crystallised together from their saturated solution they are called double salts.
Example: $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt)
They dissociate into simple ions when dissolved in water.

- **Coordination entity:**

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.
Example: In $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ represents coordination entity.

- **Central atom or ion:**

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it is called the central atom or ion.
Example: In $K_4[Fe(CN)_6]$, $Fe^{2+}$is the central metal ion.

- **Ligands:**

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

- **Counter ions:**

The ions present outside the coordination sphere are called counter ions.
Example: In the complex $K_4[Fe(CN)_6]$, K^+ is the counter ion.

- **Coordination polyhedron:**

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ ion defines a coordination polyhedron about the central atom.
Examples: $[PtCl_4]^{2-}$ is square planar, $[Ni(CO)_4]$ is tetrahedral while $[Co(NH_3)_6]^{3+}$ is octahedral.

- **Denticity:**

The number of ligating (linking) atoms present in a ligand is called denticity.

- **Unidentate ligands or Monodentate ligands:**

The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands.
Examples: H_2O, NH_3, CO, CN^- etc.

- **Didentate ligand or Bidentate ligand:**

The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.
Examples: Ethylenediamine ($H_2NCH_2CH_2NH_2$) has two nitrogen atoms, oxalate ion ($C_2O_4^{2-}$) has two oxygen atoms which can bind with the metal atom.

- **Polydentate ligand:**

When several donor atoms are present in a single ligand, the ligand is called polydentate ligand.
Examples: In $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate and Ethylenediaminetetraacetate ion **$EDTA^{4-}$** 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 ethylenediamine and cupric ion, $[Cu(en)_2]^{2+}$.

- **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.

- **Werner's coordination theory:**

Werner was able to explain the nature of bonding in complexes.
The postulates of Werner's theory are:
Metal shows two different kinds of valencies: primary valence and secondary valence.

- **Primary Valence**

1. This valence is normally ionisable.
2. It is equal to positive charge on central metal atom.
3. These valences are satisfied by negatively charged ions.
4. It is equal to oxidation state of central metal ion.

- **Secondary Valence**

1. This valence is non – ionisable.
2. The secondary valence equals the number of ligand atoms coordinated to the metal. It is also called coordination number of the metal.
3. It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.

- **Oxidation number of central atom:**

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

- **Homoleptic complexes:** Those complexes in which central metal atom/ion is coordinate bonded to only one kind of donor atoms. For example: $[Co(NH_3)_6]^{3+}$

- **Heteroleptic complexes:** Those complexes in which central metal atom/ion is coordinate bonded to more than one kind of donor atoms.

Isomers: Two or more compounds which have same chemical formula but different arrangement are called isomers.

- **Types of isomerism:**

(a) Structural Isomerism -

- **Linkage isomerism:**

1. It arises in a coordination compound containing ambidentate ligand.
2. In the isomerism, a ligand can form linkage with metal through different atoms.
3. Example: $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$. .

- **Ionisation isomerism:**

1. It arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion**.**
2. Example: $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

- **Solvate isomerism:**

1. It is isomerism in which solvent is involved as ligand.
2. If solvent is water it is called hydrate isomerism, e.g. $[Cr(H_2O)_6]Cl_3$.

Coordination isomerism:

1. This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.
2. Example: $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(CN)_6][Cr(NH_3)_6]$.

- **Stereoisomerism:** This type of isomerism arises because of different spatial arrangement.
- **Geometrical isomerism:** It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.
- **Optical isomerism:** Optical isomers are mirror images that cannot be superimposed on one another.

- **Magnetic properties of Coordination Compounds:**

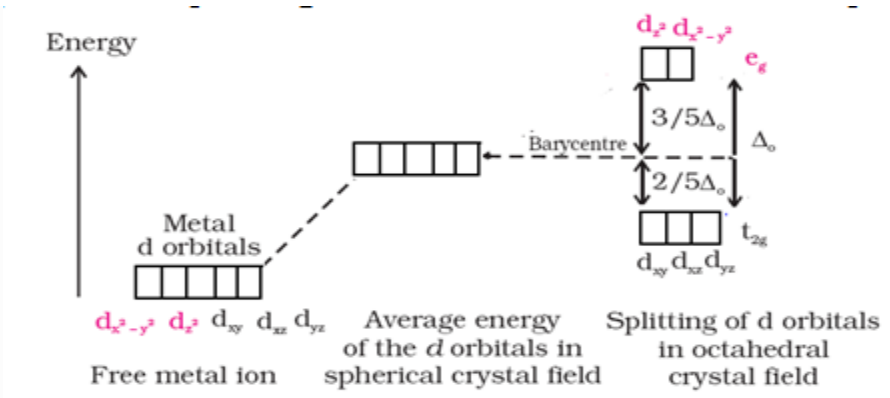
A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if allthe electrons in the coordination compound are paired.

Magnetic moment : $\mu = \sqrt{n(n+2)}$ where n is number of unpaired electrons.

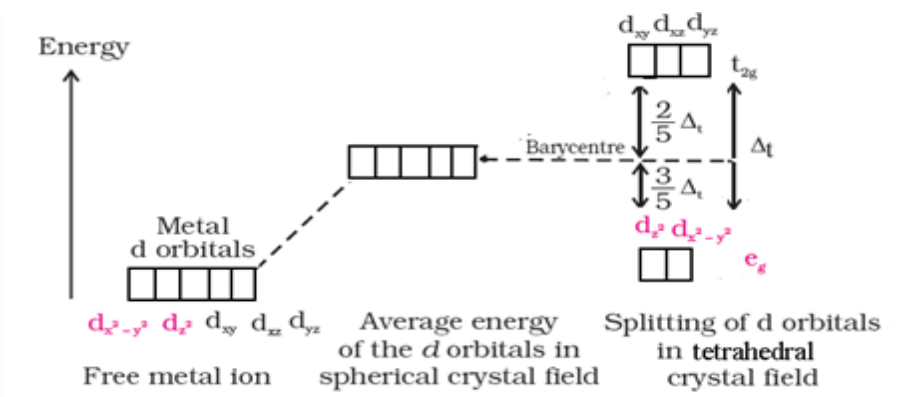
- **Crystal Field Theory:**

1. It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion.
2. It is theoretical assumption.

- **Crystal field splitting in Octahedral coordination complexes:**



- **Crystal field splitting in Tetrahedral coordination complexes:**



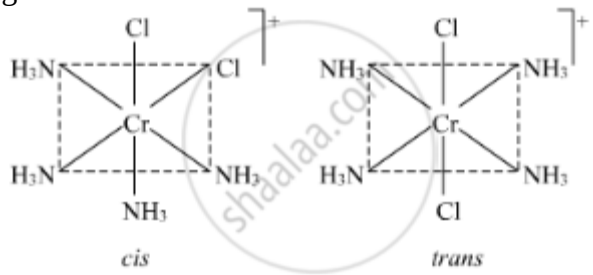
- For the same metal, the same ligands and metal-ligand distances,

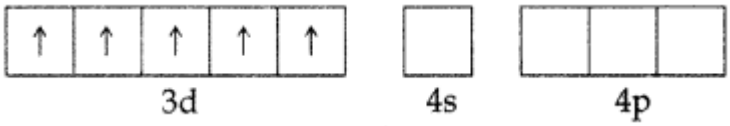
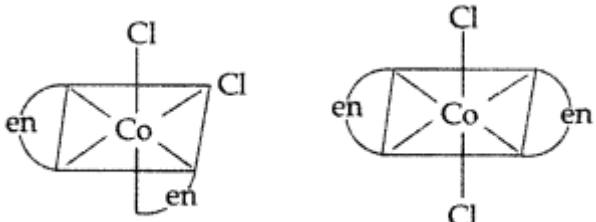
$\Delta_t = 4/9\ \Delta_o$

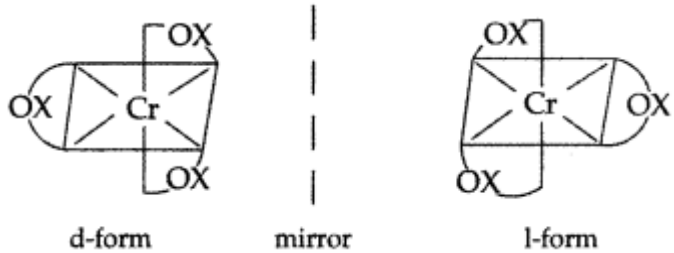
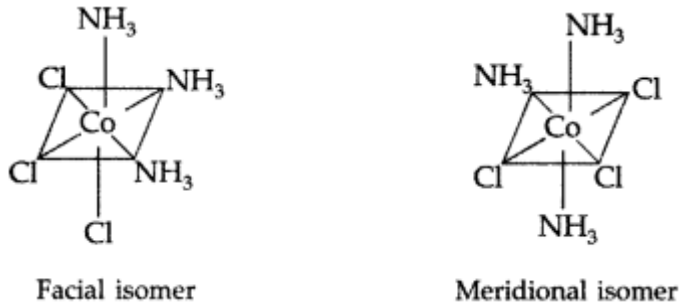
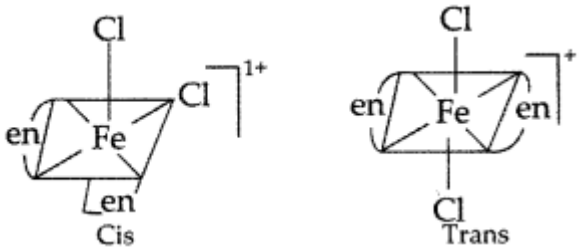
	MCQ Type Questions:
1.	IUPAC name of $[Pt(NH_3)_3Br(NO_2)Cl]$ Cl is (a) triamminechlorodibromidoplatinum (IV) chloride (b) triamminechloridobromidonitrochloride- platinum (IV) chloride (c) triamminebromidochloridonitroplatinum (IV) chloride (d) triamminenitrochlorobromoplatinum (IV) chloride
2	Primary and secondary valence of Pt in $[Pt(en)_2Cl_2]$ are (a) 4, 4 (b) 4, 6 (c) 6, 4 (d) 2, 6
3	The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ are called (a) Ionization isomers (b) Linkage isomers (c) Co-ordination isomers (d) Geometrical isomers
4	The oxidation state of nickel in $[Ni(CO_4)]$ is (a) 0 (b) 1 (c) 2 (d) 3
5	According to Werner's theory of coordination compounds (a) Primary valence is ionisable (b) Secondary valence is ionisable (c) Primary and secondary valencies are lonisable (d) Neither primary nor secondary valence is ionisable
6	Which of the following has square planar structure? (a) $[NiCl_4]^{2-}$ (b) $[Ni(CO)_4]$ (c) $[Ni(CN)_4]^{2-}$ (d) None of these
7	The ligand $(NH_2CH_2CH_2NH_2)$ is (a) bidentate (b) tridentate (c) tetradentate (d) pentadentate
8	Which of the following is a hexadentate ligand? (a) $EDTA^{4-}$ (b) $(COO)_2^{2--}$ (c) en (d) NH_3
9	Mohr's salt is (a) $Fe_2(SO_4)_3.(NH_4)_2SO_4.6H_2O$ (b) $FeSO_4.(NH_4)_2.SO_4.6H_2O$ (c) $MgSO_4.7H_2O$ (d) $FeSO_4.7H_2O$
10	Which of the following is not a neutral ligand? (a) H_2O (b) NH_3 (c) ONO^{--} (d) en
	<u>Assertion Rseason Type questions</u> **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) 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
11.	**Assertion :** NF_3 is a weaker ligand than $N(CH_3)_3$. **Reason :** NF_3 ionizes to give F^- ions in aqueous solution
12.	**Assertion :** $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic. **Reason :** $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.
13.	**Assertion :** $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. **Reason :** d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$.
14.	**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.
15.	**Assertion**: $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons. **Reason**: Because it has d^2sp^3 type hybridization.
	<u>2 Marks type questions</u>:
16.	Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex.
17.	Using IUPAC norms write the formulae for the following : (a)Pentaamminenitrito-O-cobalt(III) ion (b)Potassium tetracyanidonickelate(II)
18.	Write the hybridization and geometry of $[Ni(CN)_4]^{2-}$ [Atomic number , Ni = 28].
19.	Give the formulae of the following compounds : (a) Potassium tetrahydroxidozincate(II) (b) Hexaammineplatinum(IV) chloride
20.	Which complex ion is formed when undecomposed AgBr is washed with hypo solution in photography?
	<u>3 Mark questions:</u>
21.	Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory: $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$
22.	$CoSO_4CI.5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions. (i) Identify 'A'and 'B' and write their structural formulas. (ii) Name the type of isomerism involved. (iii)Give the IUPAC name of 'A' and 'B'.

23.	For the complex $[NiCl_4]^{2-}$,Write (i) the IUPAC name. (ii) the hybridisation type. (iii)the geometry of the complex (Atomic no. of Ni = 28)
25.	Name the following coordination entities and draw the structures of their stereoisomers : (i) $[Co(en)_2Cl_2]^+$ (en = ethane-1, 2-diamine) (ii) $[Cr(C_2O_4)_3]^{3-}$ (iii) $[Co(NH_3)_3 Cl_3]$ (Atomic numbers Cr = 24, Co = 27)
	CASE STUDY QUESTIONS
26.	**Read the passage given below and answer the following questions:** Valence bond theory considers the bonding between the metal ion and the ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands.In coordination compounds, the interaction between the ligand and the metal ion causes the five d-orbitals to split-up.This is called crystal field splitting and the energy difference between the two sets of energy level is called crystal field splitting energy.The crystal field splitting energy (Δ_o) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of Δ_o and P (pairing energy). If $\Delta_o < P$, then complex will be high spin. If $\Delta_o > P$, then complex will be low spin. (i)Which of the following ligand has lowest Δ_o value? (a) Cl^- (b) CO (c) F^- (d) NH_3 (ii)How the crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complex is related. (iii) On the basis of crystal field theory, what will be the electronic configuration of d^4 in the given two situations: (a) $\Delta_o > P$ and (b) $\Delta_o < P$ (iv) Using crystal field theory, calculate magnetic moment of central metal ion of $[FeF_6]^{4-}$.
27.	**Read the passage given below and answer the following questions:** To explain bonding in coordination compounds various theories were proposed. One of the important theories was valence bond theory. According to that, the central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands. The appropriate atomic orbitals of the metal hybridise to give a set of equivalent orbitals of definite geometry. The d-orbitals involved in the hybridisation may be either inner d-orbitals i.e., (n - 1) d or outer d-orbitals i.e. nd. For example, Co^{3+} forms both inner orbital and outer orbital complexes, with ammonia it forms $[Co(NH_3)_6]^{3+}$ and with fluorine it forms $[CoF_6]^{3-}$ complex ion. (i) Which of the following is not true for $[CoF_6]^{3-}$? (a) It is paramagnetic. (b) It has coordination number of 6. (c) It is outer orbital complex. (d) It involves d^2sp^3 hybridisation. (ii) Write the structure and magnetic character of $[Co(NH_3)_6]^{3+}$? (iii) Why $[CoF_6]^{3-}$ is paramagnetic ? (iv) Give one example for inner orbital or low spin complex?
	<u>5 Marks questions</u>:
29.	(a) When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$ solution, 3 moles of AgCl are precipitated per mole of the compound.Write: (i) Structural formula of the complex (ii) IUPAC name of the complex (iii) Magnetic and spin behaviour of the complex .

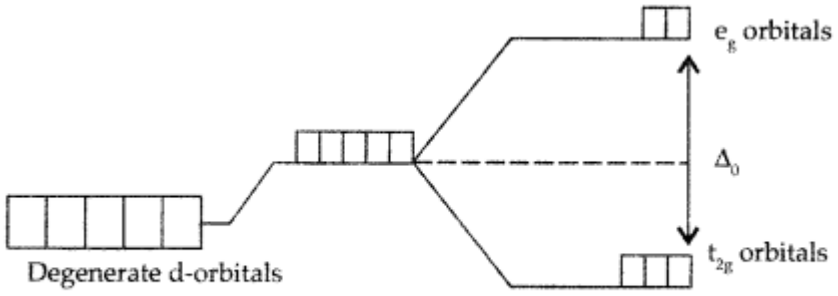
	(b) Giving a suitable example for each, explain the following : (i) Crystal field splitting (ii) Ambidentate ligand
	ANSWER KEY:
	MCQ type questions
1.	(c)
2.	(d)
3.	(b)
4.	(a)
5.	(a)
6.	(c)
7.	(a)
8.	(a)
9.	(b)
10.	(c)
	Assertion Reason type questions
11.	(c)
12.	(b)
13.	(a)
14.	(c)
15.	(d)
	ANSWERS OF 2 Mark type questions:
16.	The IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$ is **Tetraamminedichlorochromium(III) ion**. This complex exhibits geometrical isomerism. 
17.	(i) $[Co(NH_3)_5(ONO)]^{2+}$ (ii) $K_2[Ni(CN)_4]$
18.	The atomic number of Ni is 28 and its valence shell electronic configuration is $3d^8\ 4s^2$. Ni is in +2 oxidation state in the complex $[Ni(CN)_4]^{2-}$. Hence, $[Ni(CN)_4]^{2-}$ is **dsp^2 hybridised** and it is square planar in shape.
19.	(i) $K_2[Zn(OH)_4]$ (ii) $[Pt(NH_3)_6]Cl_4$

20.	Sodium dithiosulphatoargentate (I) complex is formed. $AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$
	<u>ANSWERS OF 3 marks questions</u>
21.	$[CoF_6]^{3-}$, $Co^{3+} \rightarrow (3d^6) \rightarrow t_{2g}^4 e_g^2$ $[Fe(CN)_6]^{4-}$, $Fe^{2+} \rightarrow (3d^6) \rightarrow t_{2g}^6 e_g^0$ $[Cu(NH_3)_6]^{2+}$, $Cu^{2+} \rightarrow (3d^9) \rightarrow t_{2g}^6 e_g^3$
22.	(i) As isomer A reacts with $AgNO_3$ to give a white precipitate, Cl^- must be present in the ionisation sphere. As it does not react with $BaCl_2$, SO_4^{2-} must be present in the coordination sphere. Therefore the formula of A = $[Co(NH_3)_5SO_4]Cl$ (coordination no. of Co = 6) As reactions are reversed for isomer B, formula B = $[Co(NH_3)_5Cl]SO_4$ (ii) The type of isomerism involved is Ionisation isomerism (iii) The IUPAC name of A = Pentaamminesulphatocobalt(III) chloride , B = Pentaamminechloridocobalt(III) sulphate
23.	(i) Tetrachloridonickelate(II) ion (ii) sp^3 (iii) Tetrahedral
24.	In both the cases, Fe is in oxidation state +3. Outer electronic configuration of Fe^{3+} is :  In the presence of CN^-, the 3d electrons pair up leaving only one unpaired electron. The hybridisation involved is d^2sp^3 forming inner orbital complex which is weakly paramagnetic. In the presence of H_2O (a weak ligand), 3d electrons do not pair up. The hybridisation involved is sp^3d^2 forming an outer orbital complex. As it contains five unpaired electrons so it is strongly paramagnetic.
25.	(i)Dichloridobis(ethane-1,2-diamine)cobalt(III) ion  The geometrical isomers of $[CoCl_2(en)_2]^+$ (2 isomers)

	(ii) Trioxalatochromate(III) ion  (iii) Triamminetrichloridocobalt(III) ion The geometrical isomers of $[Co(NH_3)_3Cl_3]$ (2 isomers) : 
	<u>Case Study type</u>
26.	(i) (c) (ii) $\Delta_t = 4/9\ \Delta_o$ (iii) (a) $t_{2g}^4e_g^0$ (b) $t_{2g}^3e_g^1$ (iv) For $[FeF_6]^{4-}$,n = 4, Magnetic moment = 4. 89BM.
27.	(i) (d) It involves d^2sp^3 hybridization. (ii) It is an octahedral, diamagnetic, and inner orbital complex. (iii) Due to presence of 4 unpaired electrons. (iv) $[Co(CN)_6]^{3-}$
	<u>ANSWERS OF 5 marks questions</u>
28.	(i) $[Fe(en)_2Cl_2]Cl$ or x + 0 + 2 (-1) = 1 x + (- 2) = 1 or x = + 3 ∴ Oxidation number of iron, x = + 3 (ii) The complex has two bidentate ligands and two monodentate ligands. Therefore, the coordination number is 6 and hybridization will be d^2sp^3 and shape will be octahedral. (iii) Due to presence of one unpaired electrons in 3d orbitals the complex is paramagnetic. (iv)  The number of geometrical isomers are two. (v) Name of complex: Dichloridobis(ethane-1,2-diamine)iron(III) chloride.
29.	

$$CrCl_3.6H_2O + AgNO_3 \longrightarrow [Cr(H_2O)_6]^{3+} + \underset{\text{3 moles of AgCl}}{3AgCl}$$

(a)(i) $[Cr(H_2O)_6]Cl_3$
(ii) Hexaaquachromium(III) chloride
(iii) Paramagnetic, unpaired electrons = 3
(b)(i) Crystal field splitting: It is the splitting of the degenerate energy levels due to the presence of ligands. When ligand approaches a transition metal ion, the degenerate d-orbitals split into two sets, one with lower energy and the other with higher energy. This is known as crystal field splitting and the difference between the lower energy set and higher energy set is known as crystal field splitting energy (CFSE)



Splitting of d-orbitals in an octahedral complex

(ii) Ambidentate ligand: The unidentate ligands with more than one donor atoms but only one donor atom binds to central metal atom/ion at a time is known as ambidentate ligand. For example, NO_2^- can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms.

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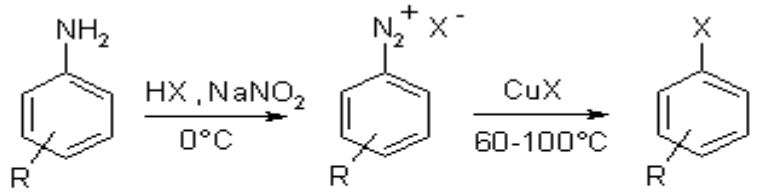
HALOALKANES AND HALOARENES

KEY NOTES

- 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.
- 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. 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.
- **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.
- **Methods of preparation of Haloarenes**

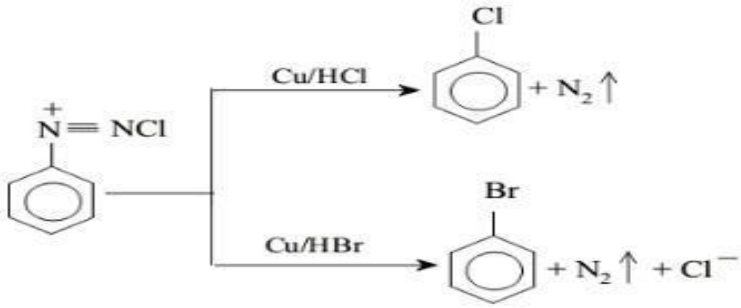
  From diazonium salts:

  (i) By Sandmeyer reaction:



X= CN, Br, Cl, SO_3H

(ii) By Gattermann reaction:



- **Chemical reactions of haloalkanes**

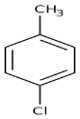
  (a) Nucleophilic Substitution Reactions:

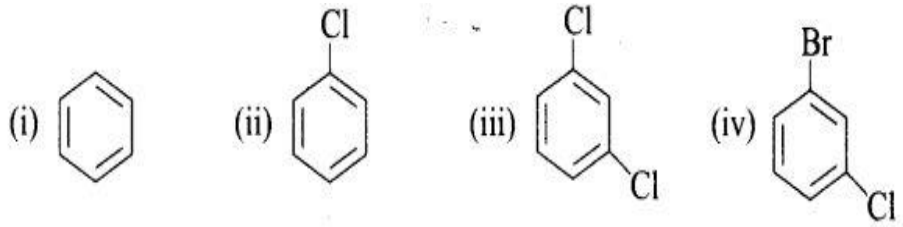
  (i) C-X bond in alkyl halide is more polar due to electron repelling nature of alkyl group and thus readily undergo nucleophilic substitution reaction. These are of two types:

  (1) S_N^1 (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.

  (2) S_N^2 (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.

MULTIPLE CHOICE QUESTIONS

1.	Which of the following is most reactive towards aqueous NaOH? (a) C_6H_5Cl (b) $C_6H_5CH_2Cl$ (c) C_6H_5Br (d) BrC_6H_4Br
2.	Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to (a) formation of a less stable carbonium ion in aryl halides (b) resonance stabilization in aryl halides (c) presence of double bonds in alkyl halides (d) inductive effect in aryl halides
3	The main difference between C – X bond of a haloalkane and a haloarene is (a) C – X bond in haloalkanes is shorter than haloarenes (b) In haloalkanes the C attached to halogen in C – X bond is sp^3 hybridised while in haloarenes it is sp^2 hybridised. (c) C – X bond in haloalkanes acquires a double bond character due to higher electronegativity of X than haloarenes. (d) haloalkanes are less reactive than haloarenes due to difficulty in C – X cleavage in haloalkanes.
4.	Which of the following is a primary halide? (a)Isopropyl iodide (b)Secondary butyl iodide (c)Tertiary butyl iodide (d)Neohexyl chloride
5.	Which is the correct IUPAC name for  (a)Methylchlorobenzene (b)Toluene (c)1-Chloro-4-methylbenzene

	(d)1-Methyl-4-chlorobenzene
6.	Which of the following compounds do not undergo nucleophilic substitution reactions? (a)Vinyl chloride (b)Ethyl bromide (c)Benzyl chloride (d)Isopropyl chloride
7.	Which one is most reactive towards S_N^1 reaction? (a)$C_6H_5CH_2Br$ (b)$C_6H_5CH(C_6H_5)Br$ (c)$C_6H_5CH(CH_3)Br$ (d)$C_6H_5C(CH_3)(C_6H_5)Br$
8.	p-dichlorobenzene has higher melting point than its o- and m- isomers. Why? (a) m- dichlorobenzene is more polar than o-isomer (b) p-isomer has a symmetrical crystalline structure (c) boiling point of o- isomer is more than p-isomers (d) All of these are correct
9.	Chlorobenzene on reaction with NaOH at 300K followed by acidic hydrolysis produces a) Phenol b) Sodium phenoxide c) Benzaldehyde d) Benzoic acid
10.	Arrange the following compounds in the increasing order of their densities  (a) (i) < (ii) < (iii) < (iv) (b) (i) < (iii) < (iv) < (ii) (c) (iv) < (iii) < (ii) < (i) (d) (ii) < (iv) < (iii) < (i)

ASSERTION REASON TYPE QUESTIONS

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

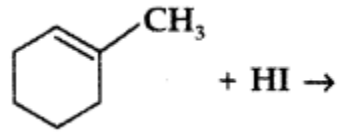
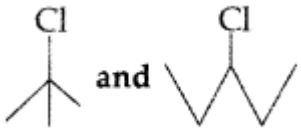
(b) Assertion and reason both are true but Reason is not the correct explanation of assertion.

(c)Assertion is true, Reason is false.

(d) Assertion is false, Reason is true.

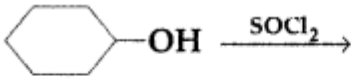
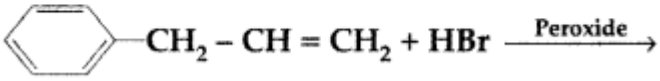
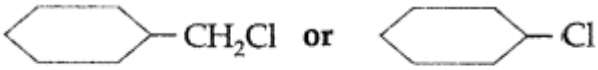
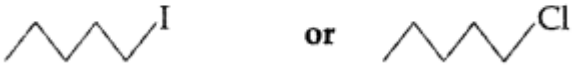
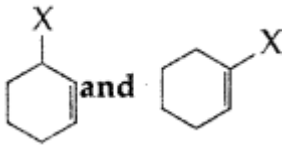
11.	**Assertion:** Primary benzylic halides are more reactive than primary alkyl halides towards S_N^1 reactions. **Reason:** Reactivity depends upon the nature of the nucleophile and the solvent.
12.	**Assertion:** The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides. **Reason:** The intermediate carbanion is stabilised due to the presence of nitro group.
13.	**Assertion:** 4-nitrochlorobenzene undergoes nucleophilic substitution more rapidly than chlorobenzene. **Reason:** Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.
14.	**Assertion:** Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reaction. **Reason:** Nitro group, being an electron withdrawing group decreases the electron density over benzene ring.
15.	**Assertion:** In mono chloroarenes, further electrophilic substitution occurs at ortho & para positions. **Reason:** Halogen atom is a benzene ring deactivator.

SHORT QUESTION ANSWERS (2 MARKS)

16.	Draw the structure of major monohalogen product formed in the following reaction : 
17.	Predict the order of reactivity of the following compounds in S_N^1 reaction : $C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$
18.	In the following pair of compounds, which will react faster by S_N^1 mechanism and why? 

19.	Arrange the following in increasing order of boiling point: (i) $CH_3CH_2CH_2CH_2Br$ (ii) $(CH_3)_3CBr$ (iii) $(CH_3)_2CHCH_2Br$
20.	What happens when ethyl chloride is treated with aqueous KOH?

SHORT QUESTION ANSWERS (3 MARKS)

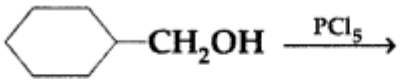
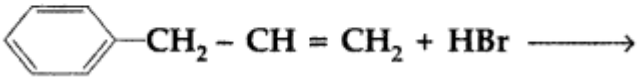
21.	Draw the structure of major product in each of the following reactions : (i)  (ii) 
22.	Which one in the following pairs of substances undergoes S_N^2 substitution reaction faster and why? (i)  (ii) 
23.	How are the following conversions carried out? (i) Benzyl chloride to benzyl alcohol (ii) Methyl magnesium bromide to 2-methyl-propan-2-ol.
24.	Account for the following: (i) The C–Cl bond length in chlorobenzene is shorter than that in CH_3–Cl. (ii) Chloroform is stored in closed dark brown bottles.
25.	Answer the following : (i) Haloalkanes easily dissolve in organic solvents. Why? (ii) What is known as a racemic mixture? Give an example. (iii) Out of  which is an example of allylic halide?

CASE BASED QUESTION

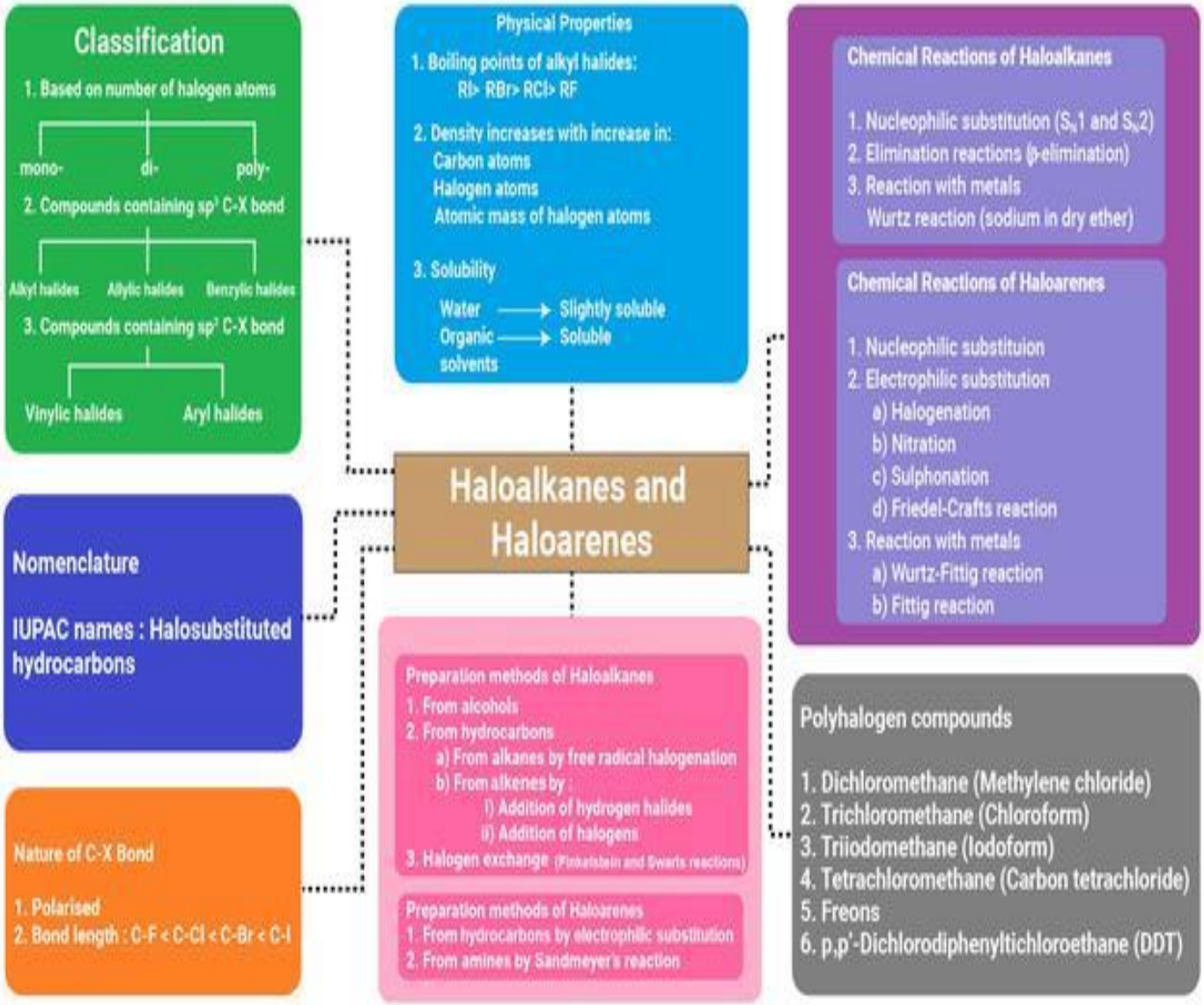
26.	**CASE STUDY - A** The substitution reaction of alkyl halides occurs in S_N^1 and S_N^2 mechanism, whatever mechanism alkyl halide follow for substitution reaction to occur, the polarity of the carbon halogen bond is responsible for the substitution reaction. The rate of S_N^1 reactions are governed by stability of carbocation whereas for S_N^2 reactions steric factor is a deciding

	factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Question 1: Among 1-bromo propane and 2-methyl-2-bromo propane, which will follow S_N^1 mechanism? Question 2:In which of the following inversion of configuration will occur on reaction with aq. alkali : 1-bromopropane or 2-methyl-2-bromo propane? Question 3: What is the role of polar protic solvent in S_N^1 reaction? Question 4: Write example of an alkyl halide having chiral carbon atom.
27.	**CASE STUDY - B** An organic compound X which is manufactured by heating a mixture of chloral and chlorobenzene in the presence of concentrated H_2SO_4 is used as an insecticide. The use of compound X is banned in many countries. The compound is very effective against mosquitoes which spread malaria. Answer the following questions based on the information: Question 1: Name the compound X. Question 2: Give its structural formula. Question 3: Write the IUPAC name of compound X. Question 4: Why is the use of compound X banned in many countries? Should we also advocate the ban of this compound though it is banned in many countries?
28.	**CASE STUDY - C** The substitution reaction of alkyl halides occurs in S_N^1 or S_N^2 mechanism. Whatever mechanism alkyl halide follow for substitution reaction to occur, the polarity of the carbon-halogen bond is responsible for the substitution reaction. The rate of S_N^1 reactions are governed by the stability of carbocation where as for S_N^2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed. Question 1. Predict the stereochemistry of the product formed if optically active alkyl halide undergoes substitution reaction by S_N^1 mechanism. Question 2.Name the instrument used for measuring the angle by which the plane polarised light is rotated. Question 3.Predict the major product formed when 2-bromopentane reacts with alcoholic KOH. Question 4.Write the structure of the products formed when anisole is treated with HI.

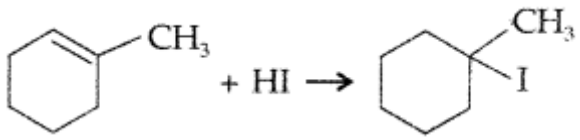
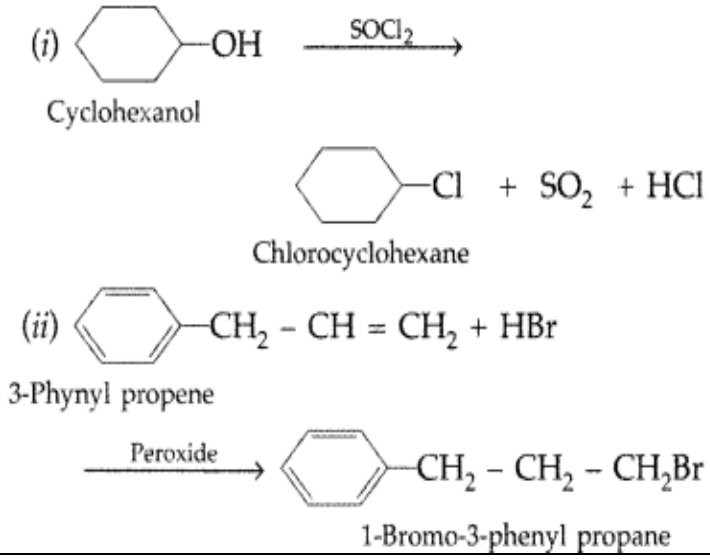
LONG QUESTION ANSWERS (FIVE MARKS)

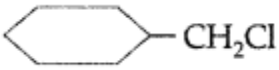
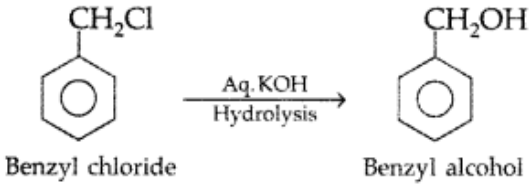
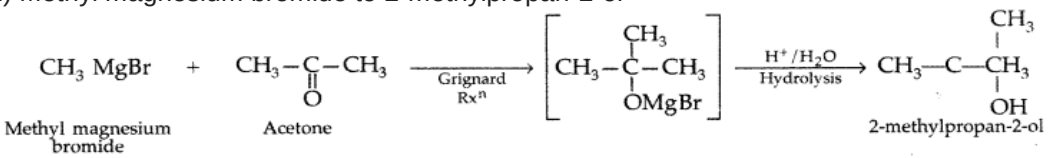
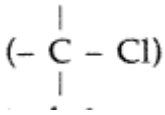
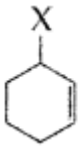
29.	**(a)** Draw the structures of major products in each of the following reactions : (*i*)  (*ii*)  **(b)** Which halogen compound in each of the following pairs will react faster in S_N^2 reaction: (i) CH_3Br or CH_3I (ii) $(CH_3)_3C–Cl$ or $CH_3–Cl$
30.	**(a)** Give reasons : (i) n-Butyl bromide has higher boiling point than t-butyl bromide. (ii) Racemic mixture is optically inactive. **(b)** How can the following conversions be carried out : (i) Aniline to bromobenzene (ii) Chlorobenzene to 2-chloroacetophenone (iii) Chloroethane to butane

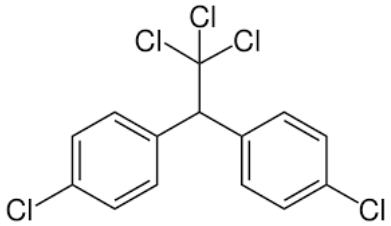
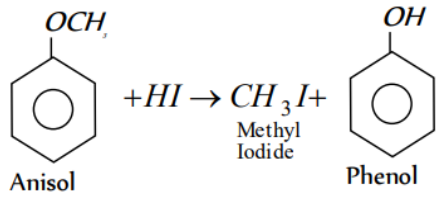
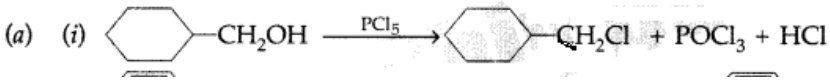
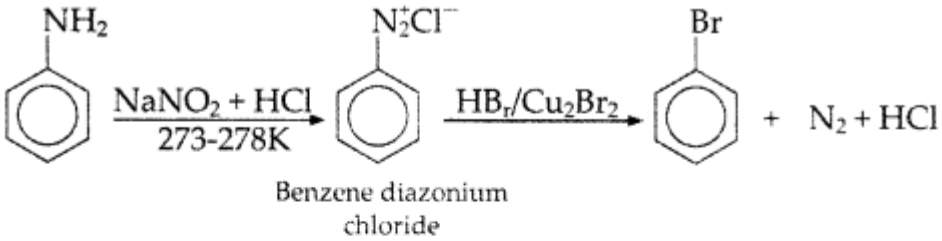
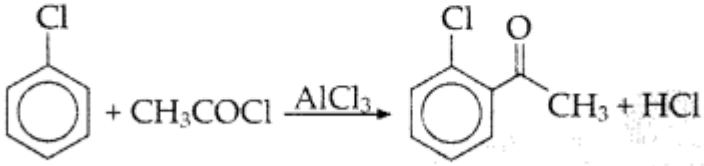
MIND MAP


Classification
1. Based on number of halogen atoms
mono-
di-
poly-
2. Compounds containing sp³ C-X bond
Alkyl halides
Allylic halides
Benzylic halides
3. Compounds containing sp² C-X bond
Vinylic halides
Aryl halides
Physical Properties
1. Boiling points of alkyl halides:
RI> RBr> RCl> RF
2. Density increases with increase in:
Carbon atoms
Halogen atoms
Atomic mass of halogen atoms
3. Solubility
Water → Slightly soluble
Organic solvents → Soluble
Chemical Reactions of Haloalkanes
1. Nucleophilic substitution (Sₙ1 and Sₙ2)
2. Elimination reactions (β-elimination)
3. Reaction with metals
Wurtz reaction (sodium in dry ether)
Chemical Reactions of Haloarenes
1. Nucleophilic substituion
2. Electrophilic substitution
a) Halogenation
b) Nitration
c) Sulphonation
d) Friedel-Crafts reaction
3. Reaction with metals
a) Wurtz-Fittig reaction
b) Fittig reaction
Haloalkanes and Haloarenes
Nomenclature
IUPAC names : Halosubstituted hydrocarbons
Nature of C-X Bond
1. Polarised
2. Bond length : C-F < C-Cl < C-Br < C-I
Preparation methods of Haloalkanes
1. From alcohols
2. From hydrocarbons
a) From alkanes by free radical halogenation
b) From alkenes by :
i) Addition of hydrogen halides
ii) Addition of halogens
3. Halogen exchange (Finkelstein and Swarts reactions)
Preparation methods of Haloarenes
1. From hydrocarbons by electrophilic substitution
2. From amines by Sandmeyer's reaction
Polyhalogen compounds
1. Dichloromethane (Methylene chloride)
2. Trichloromethane (Chloroform)
3. Triiodomethane (Iodoform)
4. Tetrachloromethane (Carbon tetrachloride)
5. Freons
6. p,p'-Dichlorodiphenyltichloroethane (DDT)

Answers

1.	B
2.	B
3.	B
4.	D
5.	C
6.	A
7.	D
8.	B
9.	A
10.	A
11.	B
12.	A
13.	B
14.	A
15.	B
16.	
17.	$C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$
18.	 reacts faster by S_N1 mechanism as it is a tertiary halide and it produces a stable tertiary carbocation.
19.	$(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$
20.	$C_2H_5Cl + aq.\ KOH \xrightarrow{\Delta} C_2H_5OH + KCl$ Chloroethane Ethanol
21.	

22.	(i)  (ii)
23.	(i) Benzyl chloride to benzyl alcohol  (ii) Methyl magnesium bromide to 2-methylpropan-2-ol 
24.	(i)  In haloalkanes, the halogen atom is attached to sp^3-hybridized carbon while in haloarenes it is attached to sp^2 -hybridized carbon whose size is smaller than sp^3 orbital carbon. Therefore C – Cl bond in chloro-benzene is shorter than alkyl chloride. (ii) $CHCl_3$ is stored in dark coloured bottles to cut off light because $CHCl_3$is slowly oxidised by air in presence of light to form an extremely poisonous gas, carbonyl chloride, popularly known as phosgene.
25.	(i) Because the new forces of attraction set up between haloalkanes and solvent molecules are of the same strength as the forces of attraction being broken. (ii) A mixture which contains the equal proportions of two enantiomers of a compound in equal proportions is called racemic mixture Example : (±) butan-2-ol (iii)  is an allylic halide.
26.	Answer 1: 2-methyl-2-bromo propane Answer 2: 1-bromo propane Answer 3: to facilitate breaking of C-X bond Answer 4: any example
27.	Answer 1: DDT Answer 2:

	 Answer 3: IUPAC NAME: 2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane Answer 4: It is banned in many countries as it has harmful effects on microorganisms and vegetation. Yes, we should advocate the ban of DDT
28.	ANSWER 1. Racemic mixture will be formed ANSWER 2. Polarimeter ANSWER 3. Pent-2-ene will be major product. $CH_3—CH(Br)—CH_2—CH_2—CH_3 + KOH(alc) \rightarrow CH3—CH=CH—CH2—CH_3 + KBr + H_2O$ ANSWER 4.  Phenol and CH_3I are formed.
29.(LONG)	 (ii) 3-Phenyl-2-bromopropane (b) (i) CH_3I will react faster in S_N^2 reaction. (ii) $CH_3–Cl$ will react faster in S_N^2 reaction
30.	(a)(i) n-Butyl bromide has higher boiling point than t-butyl bromide because it has larger surface area hence have more Van der Waals' forces. (ii) Rotation due to one enantiomer is cancelled by another enantiomer. (b) **(i) Aniline to bromobenzene**  **(ii) Chlorobenzene to 2-chloroacetophenone**  **(iii) Chloroethane to butane** $2CH_3CH_2Cl + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2—CH_2—CH_3 + 2NaCl$

CHAPTER -11 ALCOHOLS,PHENOLS AND ETHERS

Alcohols and phenols are hydroxy derivative of aliphatic hydrocarbon and benzene respectively

Type of alcohol

Primary	–OH group is attached to primary Carbon
Secondary	–OH group is attached to secondary Carbon
Tertiary	–OH group is attached to teartiary Carbon
Monohydric	1 –OH group
Dihydric	2 –OH groups
Trihydric	3 –OH groups
Polyhydric	More than 3 -OH groups

Ethers are classified on the basis of groups attached to the oxygen atom. Symmetrical ethers have same alkyl group on either side of the ethereal oxygen group

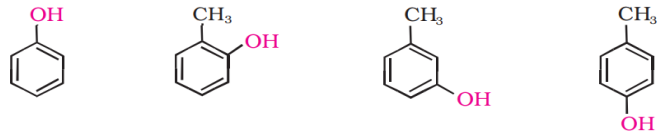
Nomenclature

The name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'. The position of substituents are indicated by numerals

Ethers are named as alkoxy alkane.The larger alkyl group is chosen as the parent hydrocarbon.e.g.

Compound	Common name	IUPAC name
$CH_3–CH_2–CH_2–OH$	n-Propyl alcohol	Propan-1-ol
$CH_3 – CH(OH) – CH_3$	Isopropyl alcohol	Propan-2-ol
CH_3OCH_3	Dimethyl Ether	Methoxymethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane

Phenol involves a benzene ring, in its substituted compounds the terms ortho (1,2- disubstituted), meta (1,3-disubstituted) and para (1,4-disubstituted) are often used in the common names.e.g.



Common name	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

Preparation

Alcohols may be prepared (1) by hydration of alkenes (i) in presence of an acid and (ii) by hydroboration-oxidation reaction (2) from carbonyl compounds by (i) catalytic reduction and (ii) the action of Grignard reagents.

Phenols may beprepared by (1)substitution of (i) halogen atom in haloarenes and (ii) sulphonic acid group in aryl sulphonic acids, by –OH group (2) by hydrolysis of diazonium salts and (3) industrially from cumene.

Alcohols and phenols are acidic in nature. **Electron withdrawing groups** in phenol increase its acidic strength and **electron releasing groups** decrease it. Alcohols undergo Nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidizing agents and carboxylic acids with strong oxidizing agents while secondary alcohols yield ketones. Tertiary alcohols areresistant to oxidation.

The presence of –OH group in phenols activates the aromatic ring towards

Uses of methanol, ethanol, phenol and ether:

Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

- Ethanol is used as a solvent in paint industry and in the preparation of a number of carbon
- compounds. In industry, phenol is used as a starting material to make plastics, explosives such
- as picric acid, and drugs such as aspirin. Phenols are widely used in household products and as intermediates for industrial synthesis.

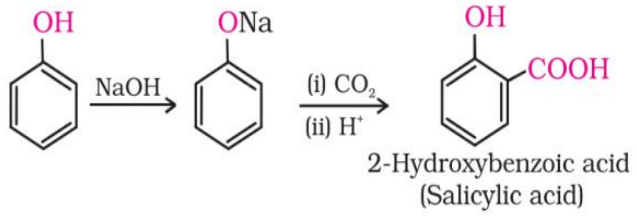
For example, phenol itself is used (in low concentrations) as a disinfectant in household cleaners and in mouthwash. Phenol may have been the first surgical antiseptic.

Vapours of certain ethers are used as insecticides and fumigants for soil.

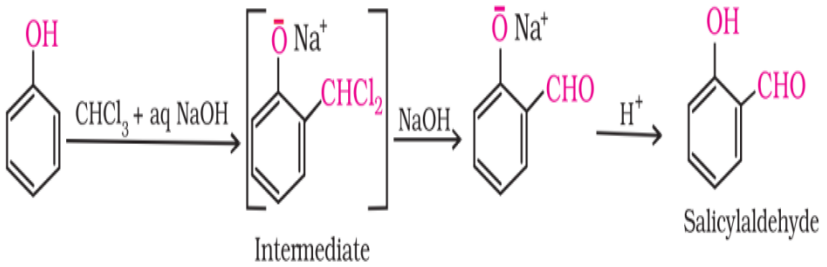
Ethers are also.- important in medicine and pharmacology, especially for use as anesthetics.

Name Reactions

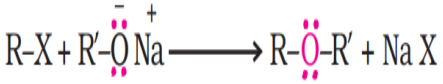
Kolbe's reaction



Reimer-Tiemann reaction



Williamson synthesis



Distinguish test for alcohol and phenols

TEST	Observations	RESULT
1.LUCAS REAGENT TEST- Add $ZnCl_2$ +HCl in the given organic compound	-Turbidity appears immediately -Turbidity appears after 5 min -Turbidity appears on heating	3^oAlcohol 2° Alcohol 1° Alcohol
2. NEUTRAL FERRIC CHLORIDE TEST- Add Neutral ferric Chloride solution in Organic Compound	-Violet colour appears	- Phenol
3.LITMUS TEST- Add few drops of blue litmus solution in organic compound	-Blue litmus turns red	-Phenol

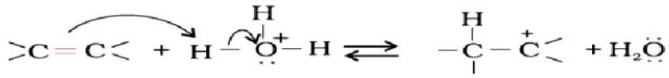
Mechanisms-

Hydration of alkene

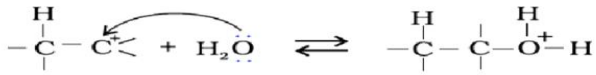
The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

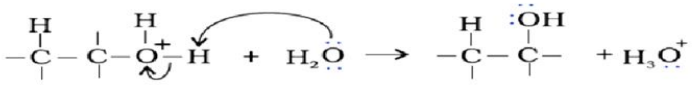
$H_2O + H^+ \rightarrow H_3O^+$



Step 2: Nucleophilic attack of water on carbocation.



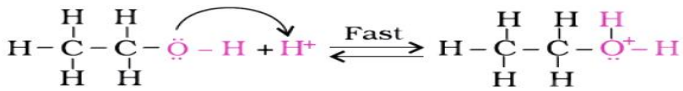
Step 3: Deprotonation to form an alcohol.



Dehydration of alcohol to give alkene

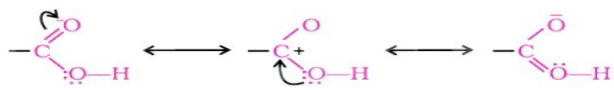
Mechanism

Step 1: Formation of protonated alcohol.

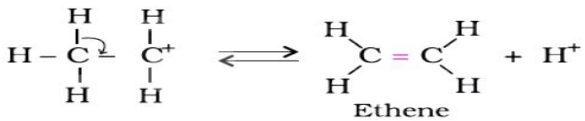


Ethanol — Protonated alcohol (Ethyl oxonium ion)

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



Step 3: Formation of ethene by elimination of a proton.



Dehydration of alcohols to give ether

(i) $CH_3–CH_2–\ddot{O}–H + H^+ \longrightarrow CH_3–CH_2–\overset{+}{\ddot{O}}(H)–H$

(ii) $CH_3CH_2–\ddot{O}(H): + CH_3–CH_2–\overset{+}{O}(H)(H) \rightarrow CH_3CH_2–\overset{+}{O}(H)–CH_2CH_3 + H_2O$

(iii) $CH_3CH_2–\overset{+}{O}(H)–CH_2CH_3 \longrightarrow CH_3CH_2–O–CH_2CH_3 + H^+$

MULTIPLE CHOICE QUESTIONS

Q1.Which of the following has lowest boiling point?

(a) p-Nitrophenol (b) m-Nitrophenol

(c) o-Nitrophenol (d) Phenol

Q2.Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$?

(a) pentan-1-ol (b) 2-methyl butan-1-ol

(c) pentan-2-ol (d) 2-methyl butan-2-ol

Q3. Rate of dehydration of alcohols follows the order:

(a) 2° > 1° > CH_3OH > 3° (b) 3° > 2° > 1° > CH_3OH

(c) 2° > 3° > 1° > CH_3OH (d) CH_3OH > 1° > 2° > 3°

Q4. Phenol on heating with $CHCl_3$ and NaOH gives salicylaldehyde. The reaction is called :

(a) Reimer-Tiemann reaction (b) Gatterman-Koch reaction

(c) Cannizzaro's reaction (d) Hell-Volhard-Zelinsky reaction

Q5.Which of the following ether cannot be prepared by Williamson's synthesis

(a) Ethyl methyl ether (b) Dimethyl ether

(c) Methyl phenyl ether (d) Di-tert.-butyl ether

Q6. Which of the following is used for denaturation of commercial alcohol

(a) Copper sulphate (b) Pyridine

(c) Methyl alcohol (d) All of the above

Q7.The alcohol which is also known as wood spirit is:

(a) Methanol (b) Ethanol

(c) Propanol (d) Butanol

Q8.Find out correct order of acidic strength among the following

(a)Ethanol>Water>Phenol (b)Ethanol<Water<Phenol

(c)Water<Ethanol<Phenol (d)Phenol>ethanol=Water

Q9.Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields.

(a) o-Cresol (b) p-Cresol

(c) 2, 4-Dihydroxytoluene (d) Benzyl alcohol

Q10.The process of converting alkyl halides into alcohols involves.

(a) addition reaction (b) substitution reaction

(c) dehydrohalogenation reaction (d) rearrangement reaction

ASSERTION AND REASON TYPE QUESTIONS

In the following questions 11 to 20, 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 are true and reason is the correct explanation of assertion

(B) Assertion and reason both are true but reason is not correct explanation of the assertion

(C) Assertion is true reason is false

(D) Assertion is false reason is true

Q11.Assertion: Phenols are more acidic than aliphatic alcohols.

Reason: The phenoxide ion is more resonance stabilised than alkoxide ion.

Q12. Assertion: Tertiary alcohols gets converted into an alkene instead of a carbonyl Compounds in the presence of heated metallic copper.

Reason: Tertiary alcohols prefer to undergo dehydrogenation instead of dehydration in the presence of heated copper.

Q13. Assertion: Ethers are non-polar when they are symmetrical.

Reason: Ethers have a bent structure.

Q14. Assertion: n-Butanol has higher boiling point than 2-methyl propan-2-ol.

Reason: Branching increases the strength of van-der-Waal's forces.

Q15. Assertion: It is not possible to prepare anisole from chlorobenzene through Williamson's synthesis.

Reason: The C-Cl bond in chlorobenzene shows partial double bond character due to resonance

Q16. Assertion: Nitro phenol has lower pKa value than phenol.

Reason: The electron withdrawing nature of the nitro group further stabilises the phenoxide ion formed.

Q17. Assertion: Anisole reacts with HI to give phenol and chloromethane.

Reason: The $-OCH_3$ group in anisole enriches the electron density in the ring through Resonance

Q18. Assertion: It is not possible to purify alcohol beyond 95% purity by simple distillation.

Reason: The intermolecular hydrogen bond in alcohol decreases the boiling point of 95% alcohol.

Q19. Assertion: Ethanol can be distinguished from methanol using iodoform test.

Reason: Methanol has a methyl group attached to a carbon containing hydroxyl groups

Q20. .Assertion: Methanol is called wood spirit.

Reason: Methanol can be prepared by the destructive distillation of fresh wood

2 Marks Questions

Q21.Write the mechanism of hydration of ethene to yield ethanol.

Q22.Account for the following:

(i) Propanol has higher boiling point than butane.

(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Q23.Di-phenyl ethers can not be synthesised by williamson's ether synthesis.Explain.

Q24. Phenols do not undergo nucleophilic substitution easily.

Q25.Water is more acidic than alcohol.Give reason.

3 Marks Questions

Q26.Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.

Q27. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to aldehyde.

(ii) Bromination of phenol to p-bromophenol.

(iii) Butan-2-one to butan-2-ol

Q28. Explain the following with an example.

(i) Kolbe's reaction. (ii) Reimer-Tiemann reaction. (iii) Williamson synthesis.

Q29. How do you convert the following?

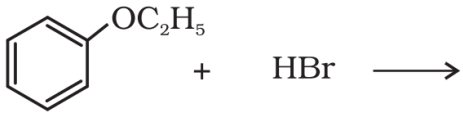
(i) Phenol to anisole

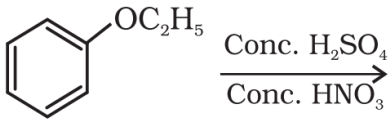
(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol

Q30.Predict the product of the following reactions.

(i) $CH_3-CH_2-CH_2-O-CH_3 + HBr \rightarrow$

(ii) 

(iii) 

CASE BASED QUESTIONS

Q 31. Read the given passage and answer the questions that follow:

Alcohols and phenols are most important compounds used in our daily life. Alcohols are prepared by hydration of alkenes, fermentation of glucose, reduction of aldehydes, ketones, carboxylic acids and esters. Alcohols are soluble in water. Boiling points increase with increase in molar mass and decrease with branching. Alcohols on dehydration gives alkene at 443K, follow carbocation mechanism. Excess of alcohol at 413K on dehydration with conc. H_2SO_4 also follow carbocation mechanism but gives diethyl ether. Alcohols undergo nucleophilic substitution reactions, esterification with carboxylic acids and derivatives like amides, acid halides, acid anhydride. Phenol is prepared from cumene, diazonium salts, anisole, chlorobenzene. Phenol is used to prepare salicylaldehyde, salicylic acid, aspirin, methyl salicylate, p-benzoquinone. Phenol undergoes electrophilic substitution reaction at o & p-position. Ethers are functional isomers of alcohols, have low boiling points. Ethers are used as solvents. Unsymmetrical ethers are prepared by Williamson synthesis. Ethers react with HI and undergo SN^1 or SN^2 mechanism depending upon stability of carbocation formed. Aromatic ethers like anisole undergoes electrophilic substitution at o & p-position.

(a) Out of tert- butyl alcohol and n-butanol, which will undergo dehydration faster and why?

(b) Convert phenol to p-benzoquinone.

(c) Why is C—OH bond length in CH_3OH longer than C—OH bond length in phenol?

(d) Why is ROH bond angle in alcohol less than tetrahedral bond angles?

Q,32. Observe the following table showing boiling points of alcohol, molar mass. Study the table and answer the questions based on table and related studied concept.

Compound	pKa
Ethanol	15.9
Phenol	9.98
o-cresol	10.28
p-cresol	10.14
m-cresol	10.08
o-nitro phenol	7.23
p-nitro phenol	7.15
m-nitro phenol	8.40
2, 4-dinitro phenol	4.0
Picric acid	0.71
m-methoxy phenol	9.65
o-methoxy phenol	9.96
p-methoxy phenol	10.21
m-amino phenol	9.87

(a) Which phenolic compound is most acidic?

(b) What is relationship between pKa and acidic character?

(c) Why are cresols weaker acids than phenol?

(d) Why is o-fluoro phenol weakest acid than p-and m-fluoro phenol?

5 Marks Questions

Q33.(a) Give chemical tests to distinguish between the following pairs of compounds.

(i) Pentan-2-ol and Pentan-3-ol

(ii) Methanol and Phenol

(b) o-nitro phenol is more acidic than o-methoxy phenol. Explain why.

(c) Arrange the following sets of compounds in order of their increasing boiling points:

(i) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(ii) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Q34. (a) How are the following conversions carried out?

(i) Propene → Propan-2-ol.

(ii) Benzyl chloride → Benzyl alcohol.

(iii) Methyl magnesium bromide → 2-Methylpropan-2-ol.

(b) Give reasons for the following :

(i) Boiling point of ethanol is higher in comparison to methoxymethane

(ii) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

Answer Key

Q1-C	Q2-D	Q3-B	Q4-A	Q5-D
Q6-D	Q7-A	Q8-B	Q9-D	Q10-B
Q11-A	Q12-C	Q13-D	Q14-C	Q15-A
Q16-A	Q17-B	Q18-C	Q19-C	Q20-A

Q21-

The mechanism of the reaction involves the following three step:

Step 1: Proptonation of ethene to form carbocation by electrophilic attack of H_3O^+.

Step 2: Nucleophilic attack of water on carbocation.

Step 3: Deprotonation to form an ethanol.

Q22(i) This is due to the presence of intermolecular hydrogen bonding. In propanol

(ii) In ortho nitro phenol, electron withdrawing nitro group is present in ortho position decreases the electron density of Oxygen in –OH.As a result it is easier to lose a proton.

Q23.Aryl halide do not undergo nucleophilic substitution easily due to partial double bond charater in C-X bond of Aryl halide

Q24. The C – O bond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by nucleophile. So, nucleophilic substitution reactions are not very common in phenols and they give many electrophilic substitution reactions

Q25.Because in alkoxide ion accept proton more easily and shift the equilibrium in backward direction

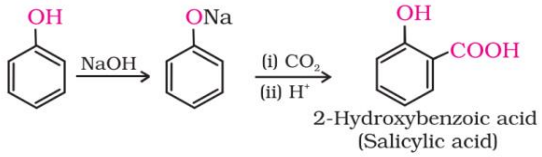
Q26 Ortho nitrophenol is much more volatile in steam due to chelation. Intramolecular hydrogen bonding is present in o-nitrophenol and intermolecular hydrogen bonding in p-nitrophenol.

Q27 (i) CrO_3-H_2SO_4

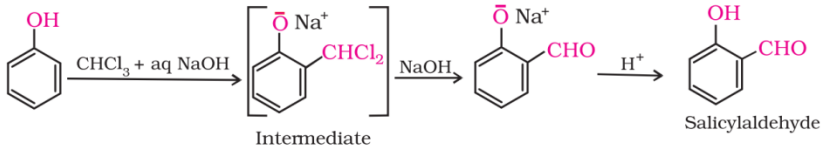
(ii) Br_2 in CS_2

(iii) $NaBH_4$ or Ni/H_2

Q28 (i) Kolbe's Reaction

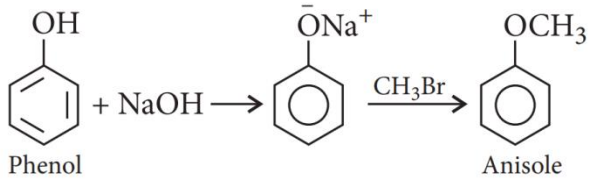


(ii)Reimer-Tiemann reaction

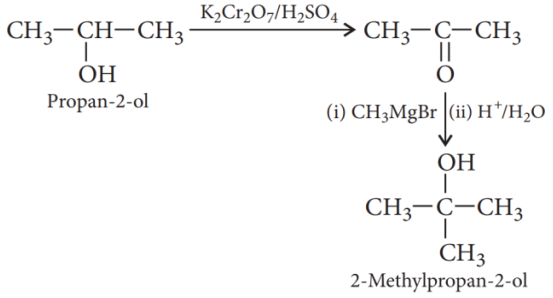


(iii)Williamson synthesis

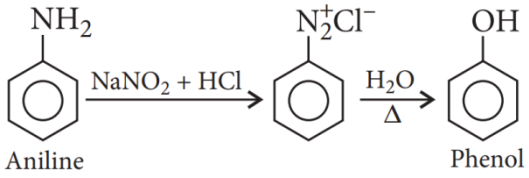
Q.29 (i) Phenol to anisole



(ii) Propan-2-ol to 2-methylpropan-2-ol



(iii)Aniline to phenol



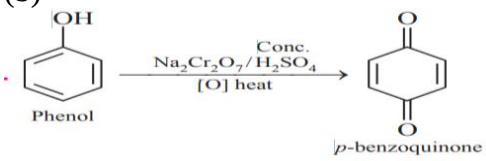
Q.30 (i) $CH_3CH_2CH_3OH$ & CH_3Br

(ii) C_6H_5OH & C_2H_5Br

(iii) p-$NO_2C_6H_4C_2H_5$

Q.31 (a) Tertiary butyl alcohol will undergo dehydration faster because 3° carbocation is more stable

(b)



(c) It is due to resonance in phenol, there is double bond character in C—O bond, therefore shorter than single bond in methanol.

(d) It is due to repulsive interaction between two lone pair of electrons in alcohol.

Q32. (a) Picric acid

(b) Lower the pKa, more will be acidic character.

(c) It is because -CH_3 groups are electron releasing, destabilise phenoxide ion

(d) It is because in o-fluoro phenol, there is strong intramolecular H-bonding

Q33. a (i) By Iodoform test-

Pentan-2-ol gives yellow ppt in iodoform test & pentan-3-ol will not respond this test.

(ii) Phenol with neutral $FeCl_3$ gives violet colour but methanol does not respond to this test.

$$C_6H_5OH + FeCl_3 \rightarrow \underset{\text{Violet colour}}{(C_6H_5O)_3Fe} + 3HCl$$

(b) Due to the electron withdrawing nature of nitro group it form stable nitro phenoxide ion as compare to the methoxy phenoxide ion nitrophenol is more acidic.

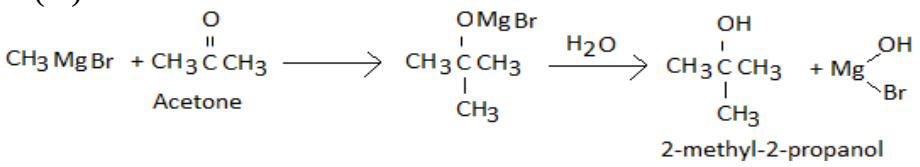
(c) (i) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(ii) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

Q.34. a (i) $CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3CH(Br)CH_3 \xrightarrow{aq.KOH} CH_3CH(OH)CH_3$

(ii) $C_6H_5CH_2Cl \xrightarrow{aq.KOH} C_6H_5CH_2OH$

(iii)



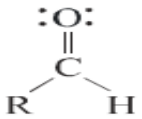
b (i) Due to intermolecular hydrogen bonding in ethanol.

(ii) Due to intermolecular hydrogen bonding between alcohol & water molecules.

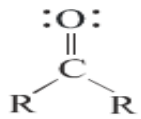
CHAPTER-12 ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Both aldehydes and ketones possess the same general formula $C_nH_{2n}O$ and contain a common carbonyl (>C=O) group. In aldehydes, the carbonyl group is linked to an alkyl group and a hydrogen atom (except formaldehyde, having no alkyl group), while in ketones it is attached with two alkyl (aryl) groups (same or different).

Carbonyl group

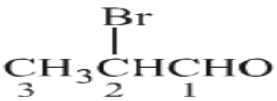


an aldehyde

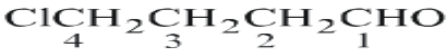


a ketone

I) Nomenclature:- In the IUPAC system of nomenclature, aliphatic aldehydes are named as alkanals. The final -e in the name of the corresponding alkane is substituted by -al. Note that when the -CHO group is attached to a ring, then the compound is called a carbaldehyde. Remember that the carbonyl carbon of the aldehydes is present at the end of the chain and is assigned 1 position. Therefore, it is not necessary to specify its position in the name of the aldehyde.

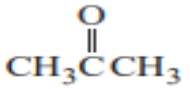


2-Bromopropanal

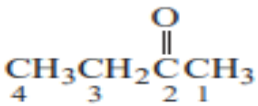


4-Chlorobutanal

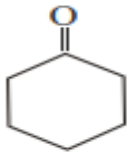
Ketones are named as alkanones in the IUPAC nomenclature. Their names are obtained by replacing final -e in the name of alkane by -one. The carbon chain is numbered in such a way that the carbonyl group gets the lowest number. Carboxylic acids are named by choosing the longest carbon chain containing the –COOH group. The final -e in the name of the alkane is replaced by -oic acid



Propanone (Acetone)

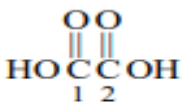


Butan-2-one (Ethyl methyl ketone)

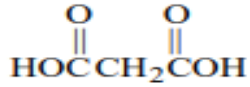


Cyclohexanone

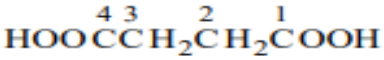
Carboxylic acids containing two carboxyl groups are called dicarboxylic acids. They are named by adding dioic acid as a suffix to the name of the corresponding hydrocarbon. Both the carboxyl carbon atoms are numbered as a part of the main chain. Note that in this case, final- e of the alkane is not dropped



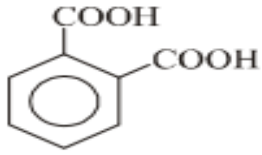
Ethanedioic acid (Oxalic acid)



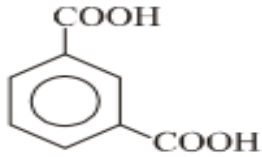
Propanedioic acid (Malonic acid)



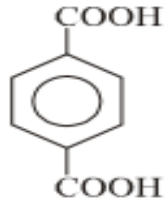
Butane-1,4-dioic acid (Succinic acid)



***o*–Phthalic acid (Phthalic acid)**

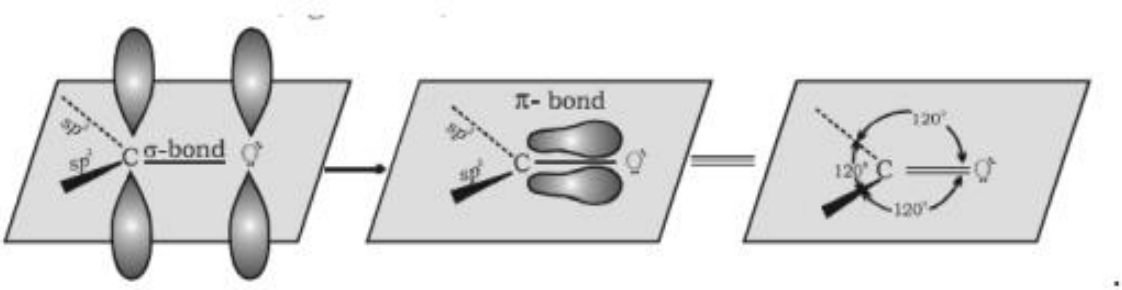


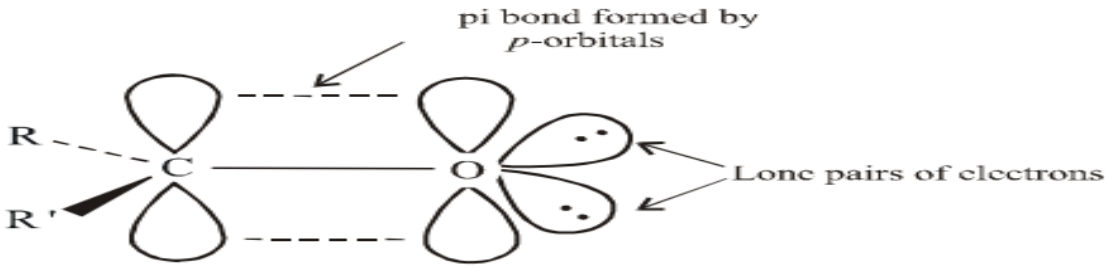
***m*–Phthalic acid (Isophthalic acid)**



***p*–Phthalic acid (Terephthalic acid)**

<u>II)Structure of the Carbonyl Group</u>: The carbonyl carbon atom is sp^2 -hybridized and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a πbond with oxygen by overlap with p-orbital of oxygen. In addition, the oxygen atom also has two nonbonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a Trigonal coplanar structure





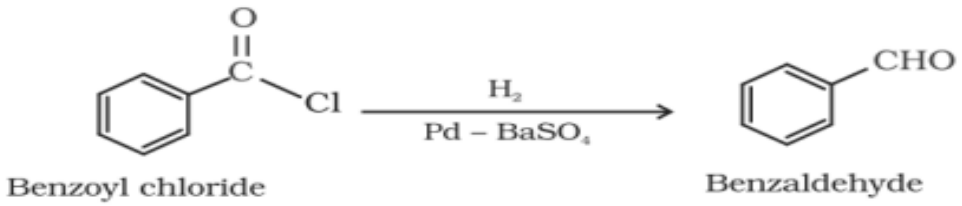
The structure of the carbonyl functional group

The oxygen atom, thus, acquires a partial negative charge (δ^-) whereas the carbon atom gets a partial positive charge (δ^+). This polar nature of the carbonyl group makes the oxygen atom nucleophilic and basic while the carbon atom becomes electrophilic. The physical properties and chemical reactions of aldehydes and ketones are a direct consequence of this polarisation.

<u>III) Methods of preparations for aldehydes and ketones (Carbonyl compounds)</u>

- **From alcohols:** By controlled oxidation of I ° and 2° alcohols with acidified $K_2Cr_20_7$ or $KMn0_4$ or $Mn0_2$ or $Cr0_3$ in CH_3COOH or chromic acid, H_2Cr0_4, in aqueous acetone or pyridinium chlorochromate (PCC) etc.

- **By catalytic dehydrogenation** of 1 ° and 2° alcohols over reduced copper heated to 300°C.
- Ketones can be obtained from 2° alcohols by oxidation with aluminium tert.-butoxide $[(CH_3)_3CO]_3Al$ Unsaturated 2° alcohols can also be oxidised to unsaturated ketones (without affecting the >C=C<) by this reagent.
- **From carboxylic acids**: By dry distillation of calcium "salts of fatty acids, e.g., calcium formate gives formaldehyde and calcium acetate gives acetone. An equimolar mixture of calcium acetate and calcium formate gives acetaldehyde.
- **From gem-dihalides :** By alkaline hydrolysis of terminal gem-dihalides, the aldehydes are formed, while non-terminal one give ketones
- **Hydroboration-oxidation**: Hydroboration (BH_3/ HF) of terminal alkynes followed by oxidation with alk. H_20_2 gives aldehyde, but non-terminal alkynes under similar conditions yield ketone.
- **From Grignard reagents:** On reaction with nitriles, i.e., Grignard reagents give aldehydes with HCN and ketones with RCN.
- **Rosenmund's reduction :** Acid chlorides can be reduced ~to aldehydes with" hydrogen in boiling xylene using Pd or Pt catalyst supported on BaS04. Ketones cannot be prepared by this method. The function of $BaSO_4$ is to poison the catalyst to prevent further reduction of aldehyde to l° alcohol.

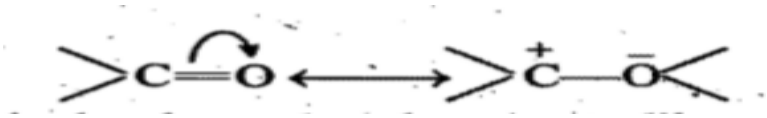


- **Stephen's reduction:** The reduction of alkyl cyanide by $SnCl_2$ and conc. HCl followed by acid hydrolysis to give aldehyde is known as Stephen's reaction

$$RCN + SnCl_2 + HCl \text{ --------> } RCH = NH \text{ ----------> } RCHO$$

<u>IV) Physical properties</u>: Except HCHO (it is a gas), all other aldehydes and ketones are volatile liquids at ordinary temperature. Lower aldehydes have unpleasant odour while, ketones possess pleasant smell. The carbonyl compounds are strongly polar in. nature which results in appreciable· intermolecular attraction. Therefore, their boiling points are higher than those of non-polar substances of comparable molecular weights. However, their boiling points are lower than corresponding alcohols due to the absence of intermolecular hydrogen bonding.

V) Chemical properties: Both aldehydes and ketones contain a >C=O group which is highly polar due to resonance and permanent -I effect of the negative oxygen atom.



The positively charged carbon is readily attacked by the electron rich nucleophiles, while the negatively charged oxygen is attacked by electron deficient electrophiles.

- **Relative reactivity of aldehydes and ketones**

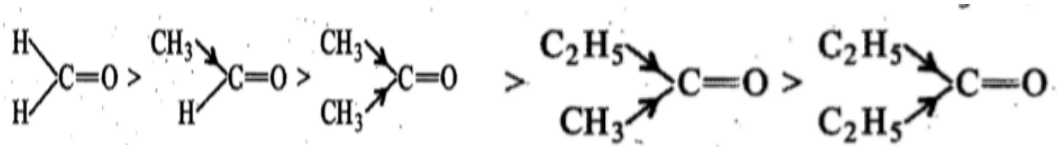
The reactivity of >C=O group for nucleophilic addition depends mainly on

(i) Ability of carbonyl oxygen to carry a negative charge,

(ii) Inductive effect of the groups attached to the carbonyl carbon atom and

(iii) Size of substituent group (steric factor).

The decreasing order of reactivity of >C=O group is as follows:.



Thus, +I effect of alkyl group decreases the reactivity whereas the introduction of negative group (-I effect) , increases the reactivity, e.g. chloral (trichloroacetaldehyde) is more reactive than acetaldehyde as the chlorine atoms increase the positive charge on the carbonyl carbon. The α-H atoms of aldehydes and ketones are reactive (acidic in nature). This is due to the fact that the anion resulting from removal of α-H atom by base gets stabilized by resonance.

- **Reactions common to aldehydes and ketones**

- Substitution reactions: The a-H atom of alkyl group of >C=O compounds can be replaced by halogen atoms (C12 or Br2) even at room temperature. Acetaldehyde on halogenation (chlorination) gives trichloroacetaldehyde (chloral) and acetone yields trichloroacetone. The excess of alkali decomposes the trihalogen compounds to give haloform (CHX_3)

- Acetaldehyde, acetone and methyl ketones ($-COCH_3$) undergo haloform (Iodoform) reaction with X_2 (12) and NaOH.

- **Reactions of carbonyl group**

(i) Addition of hydrogen: Different products are obtained depending on the nature of reducing agents.

- Molecular hydrogen in presence of metallic catalyst (such as Ni, Pt and Pd) reduces aldehydes'and ketones into 1^0 and 2° alcohols respectively.

- With nascent hydrogen produced (such as Zn + CH3COOH, Na +C2H5OH, Na + H20, Zn + alc. NaOH, etc.) gives 1^0 and 2° alcohols (reduction to alcohols).

- With LiAlH4, NaBH4 or LiBH4 (complex metallic , hydrides), aldehydes give 1 ° alcohol while ketones give 2^0 alcohol.

- Unsaturated aldehydes can be reduced to unsaturated alcohols (1°) without affecting C=C in ,presence of reducing agents $LiAlH_4$ in dry ether or $NaBH_4$ in alcohol.

Clemmensen's reduction: Aldehydes and ketones are converted into alkanes, (i.e.,)C=O group is reduced to $>CH_2$ group) when treated with Zn-Hg and conc. HCl. This reaction is known as Clemmensen's reduction.

The same conversion (>C=O into CH_2) can be made by heating aldehydes and ketones with red P and conc HI

Wolff-Kishner reduction: Aldehydes and ketones are conveniently reduced to hydrocarbons in presence of excess ofhydrazine (H 2 N-, NH2) and strong base (NaOH orC2HsONa) on heating

$$>C=O + H_2NNH_2 \xrightarrow{-H_2O} \underset{\text{(Hydrazone)}}{>C=NNH_2} \xrightarrow[\Delta,\ 200^\circ C]{C_2H_5ONa} >CH_2 + N_2$$

(ii) Addition of Grignard reagents: The >C=O group adds onto Grignard reagent and the addition product on hydrolysis decomposes to yield 1°, 2° or 3° alcohol depending on the nature of carbonyl compound. For example, HCHO forms 1^0 alcohol, higher aldehydes (RCHO) give 2^0 alcohols and ketones give 3° alcohol.

(iii)Reaction with thioalcohols: Thioalcohols react more rapidly than alcohols and form thioacetals and thioketals. Replacement of carbonyl oxygen (Condensation reactions)

(iv)Aldol condensation (Reactions involving a-hydrogen): It is a chemical reaction in which two or more molecules of same or different carbonyl compounds containing α -H atoms unite together in the presence of a dilute base such as NaOH, $Ba(OH)_2$ or K_2C0_3 etc., to form a new product which combines the properties of alcohol and aldehyde or ketone, is called aldol condensation

- **Reactions in which aldehydes and ketones differ**

- **Oxidation of aldehydes:** Aldehydes are easily oxidised to corresponding carboxylic acids and thus acts as strong reducing agents. Oxidising agents may be strong (such as acidified $K_2Cr_20_7$ or acidified' $Na_2Cr_20_7$ or acidified $KMn0_4$ or hot conc. $RN0_3$) or mild (such as Tollens' reagent or Fehling's solution or Benedict's solution).

- **Reduction of Tollens' reagent:** It is ammoniacal $AgN0_3$. Aldehydes reduce weak (mild) oxidising agents like ammoniacal $AgN0_3$ (Tollens' reagent) to metallic silver which deposits as mirror (Reducing character of aldehydes). This reaction is known as silver mirror test.

- **Reduction of Fehling's solution**: It is an alkaline solution of cupric ion complexed with sodium potassium tartrate. Aldehydes on heating with Fehling's solution give a reddish brown precipitate of cuprous oxide (Cu_20).

- **Schiff's test of aldehydes:** Schiff's reagent is a dilute solution of p-rosaniline hydrochloride whose pink (red) colour has been discharged by passing $S0_2$ gas. Aldehydes when treated with Schiff's reagent (magenta solution in H_2S0_3) restore its pink colour. Ketones do not give this test.

- **Cannizzaro's reaction:** HCHO, C_6H_5CHO and other aldehydes containing no a-hydrogen atoms on heating with conc. alkali solution undergo oxidation reduction reaction. In this reaction, one molecule of aldehyde is oxidised to carboxylic acid and the other is reduced to 1^0 alcohol (disproportionation). This is known as Cannizzaro's reaction.

CARBOXYLIC ACIDS

Organic compounds containing carboxylic (-COOH) functional group are called carboxylic acids. The -COOH group has its own distinctive properties and has no relation with) C=O and -OH compounds.

I) General methods of preparation

By Oxidation of alcohols, aldehydes and ketones:

Using oxidising agents $K_2Cr_20_7/H_2S0_4$(dil.) or alkaline $KMn0_4$ or air in presence·of catalyst. Aldehyde can be oxidised to corresponding carboxylic acid even with mild oxidising agents such as ammnonical $AgNO_3$ {TolIens' reagent).

By hydrolysis of alkane nitriles: Compounds containing a~ group can be hydrolysed to -C00H group in presence of H^+ (HCI or H_2SO_4) or with alkali.

By carbonation of Grignard reagents: When $C0_2$ (solid ice) is passed through an etheral solution of R-MgX, an addition product is formed which on hydrolysis with a mineral acid yields a carboxylic acid

From alkenes (By carbonylation): A mixture of an alkene, CO and steam is heated under pressure at 350°C in presence of catalyst H_3P0_4, monocarboxylic acid is formed. Ketones react with Mg-Hg over water gives carboxylic acid. This reaction is called **Koch reaction.**

Acidity of carboxylic acids

- The acidic character decreases with the rise of molecular weight. HCOOH is the strongest acid of all fatty acids. Thus, the acidity of carboxylic acid is due to powerful resonance stabilization of the anion.

- Electron attracting group (-I effect) stabilises the anion and therefore increases ionization of the acid. The greater is the -I effect, greater will be the acidic strength,

  i.e., $C1_3CCOOH$> $Cl_2CHCOOH$> $ClCH_2COOH$>CH_3COOH and FCH_2COOH>$CICH_2COOH$> $BrCH_2COOH$> ICH_2COOH (because F > CI > Br > I).

- Electron releasing group (+I effect) destabilises the anion and so decreases the acidity.

  i.e. HCOOH > CH_3COOH>CH_3CH_2COOH> $(CH_3)_2CHCOOH$> $(CH_3)_3C$-COOH

Chemical properties

(1) Reactions due to -C-OH group

(a) Reactions involving proton (removal of H-atom of -OH group):

Salt formation: Monocarboxylic acids react with Na, K, NaOH. $NaHC0_3$ or Na_2CO_3 etc. with the evolution of hydrogen and form corresponding salt.

Reaction with organometallic reagents: R'COOH reacts with RMgX (GR) rapidly to give an alkane (RH) corresponding to the alkyl group of Grignard reagent.

(b) Reactions involving -OH group:

Ester formation: RCOOH reacts with ROH in presence of dehydrating agents like conc. H_2SO_4 or dry HCI gas to form esters.

Formation of acid chlorides: By the action of PCl_5/ PCI_3. $SOCl_2$/pyridine or $C1_2$/Br_2 in presence of red P on carboxylic acids, acid halides are formed.

Formation of acid anhydrides: Dehydration of monocarboxylic acids on heating with P_20_5 gives acid anhydride or when sodium salt of acid is heated with acid chloride, acid anhydrides are formed.

Formation of amides and nitriles: Monocarboxylic acids on treatment with NH_3 form ammonium salts which on heating lose a molecule of water to form corresponding amides

(c) Reactions involving (carbonyl) group:

Reduction· to alcohols: Reduction products depend on the nature of reducing agent. By using $LiAlH_4$ (LAH) in ether solution or ruthenium (Ru) and carbon as catalyst, the -COOH group is reduced to $-CH_20H$ (1^0 alcohol). BH_3/THF or H_2 in presence of copper chromite (CuO $+Cr_20_3$) also reduces -COOH into $-CH_20H$

(d) Reactions involving -COOH group as a whole:

Decarboxylation: On heating anhydrous salt of acid with sodalime forms an alkane with the elimination of CO_2 When sodium formate is heated with sodalime, hydrogen is evolved.

By Kolbe's electrolytic reaction: Electrolysis of Na or K salts (concentrated aqueous solution) of fatty acids yields alkanes.

Reduction to alkanes: On heating with conc. HI and red P at 200°C or catalytic reduction. the -COOH converts into $-CH_3$ to form an alkane.

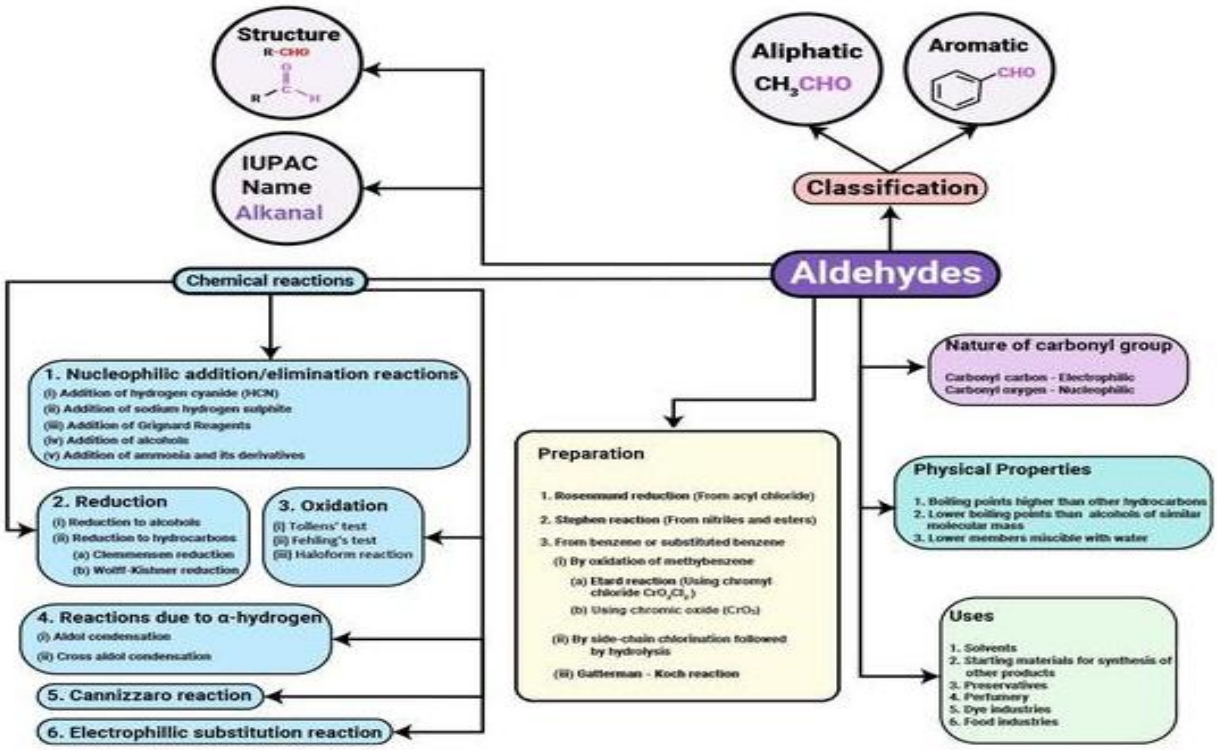
(2) Reactions due to R (alkyl) group

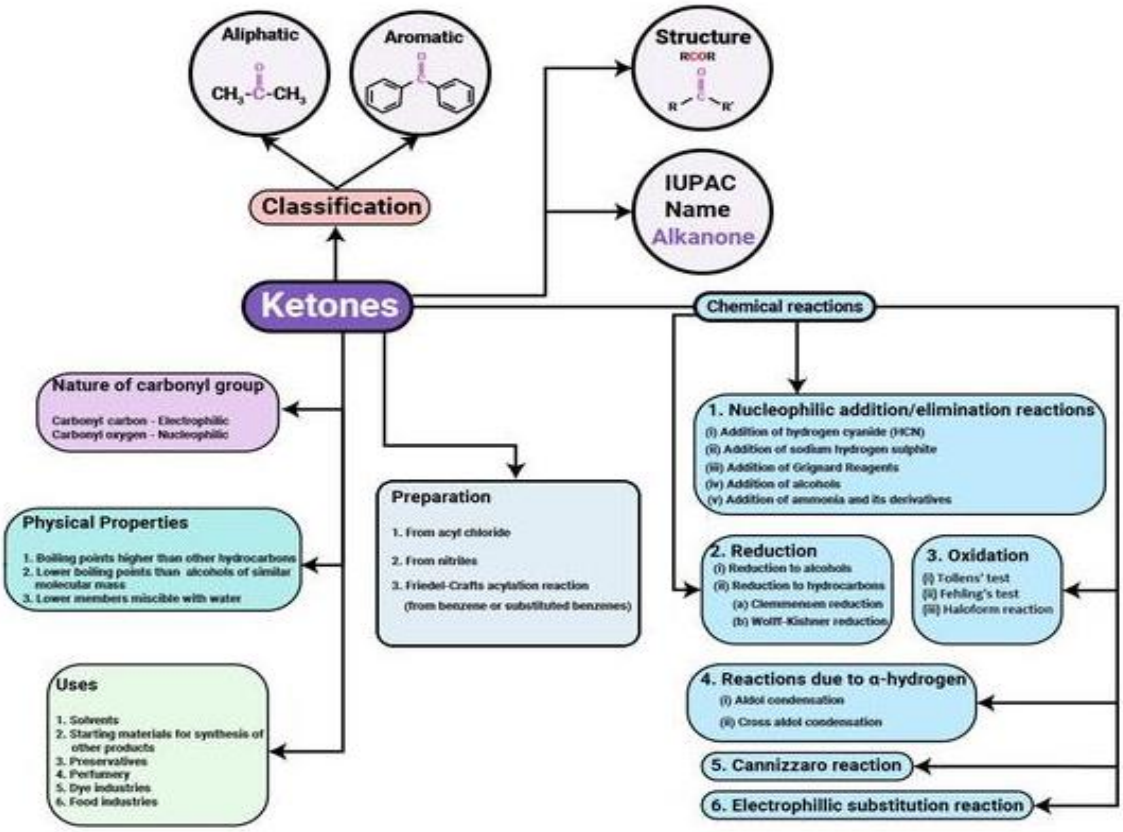
Halogenation: The α-hydrogen atoms are highly reactive due to the presence of electronegative -COOH group. On halogenation ($C1_2$ or Br_2) hi presence of a catalyst (red P or Fe, etc.,), the α -H atoms are replaced by chlorine or bromine atoms. The reaction occurs in presence of sunlight or on boiling. This reaction is known as **Hell-Volhard-Zelinsky (HVZ) reaction.**

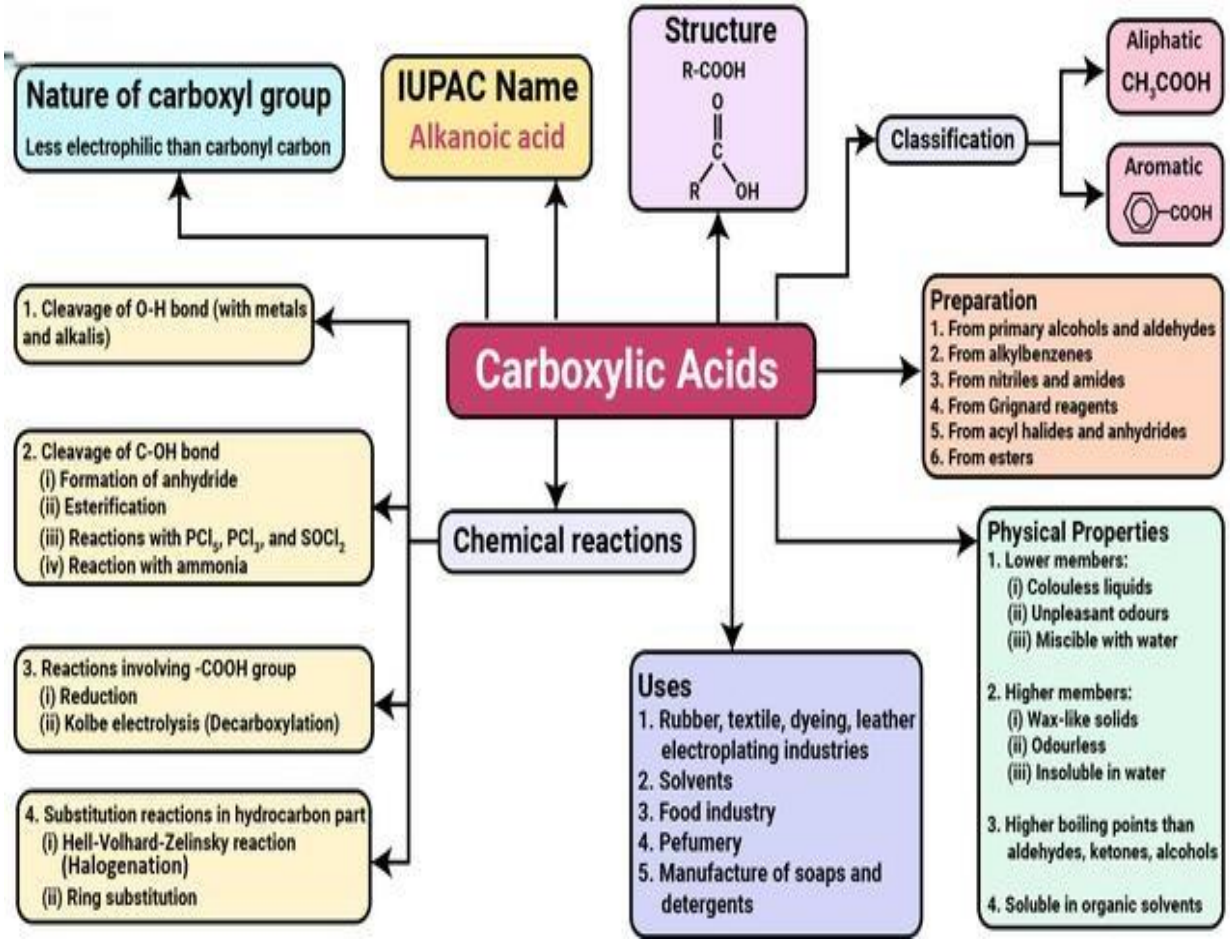
Direct iodination can be done in presence of an oxidising agent like $HI0_3$ or HgO.

Oxidation : Carboxylic acids having at least one β -hydrogen convert into β -hydroxy carboxylic acids on oxidation with H_20_2. Oxidation of a-methylene group takes place by $Se0_2$ to give α -keto acid.

MIND MAPS


Structure
R-CHO
IUPAC Name
Alkanal
Aliphatic
CH_3CHO
Aromatic
CHO
Classification
Aldehydes
Chemical reactions
1. Nucleophilic addition/elimination reactions
(i) Addition of hydrogen cyanide (HCN)
(ii) Addition of sodium hydrogen sulphite
(iii) Addition of Grignard Reagents
(iv) Addition of alcohols
(v) Addition of ammonia and its derivatives
2. Reduction
(i) Reduction to alcohols
(ii) Reduction to hydrocarbons
(a) Clemmensen reduction
(b) Wolff-Kishner reduction
3. Oxidation
(i) Tollens' test
(ii) Fehling's test
(iii) Haloform reaction
4. Reactions due to α-hydrogen
(i) Aldol condensation
(ii) Cross aldol condensation
5. Cannizzaro reaction
6. Electrophillic substitution reaction
Preparation
1. Rosenmund reduction (From acyl chloride)
2. Stephen reaction (From nitriles and esters)
3. From benzene or substituted benzene
(i) By oxidation of methybenzene
(a) Etard reaction (Using chromyl chloride CrO_2Cl_2)
(b) Using chromic oxide (CrO_3)
(ii) By side-chain chlorination followed by hydrolysis
(iii) Gatterman - Koch reaction
Nature of carbonyl group
Carbonyl carbon - Electrophilic
Carbonyl oxygen - Nucleophilic
Physical Properties
1. Boiling points higher than other hydrocarbons
2. Lower boiling points than alcohols of similar molecular mass
3. Lower members miscible with water
Uses
1. Solvents
2. Starting materials for synthesis of other products
3. Preservatives
4. Perfumery
5. Dye industries
6. Food industries


Aliphatic
CH_3-C-CH_3
Aromatic
Classification
Structure
RCOR
IUPAC Name
Alkanone
Ketones
Chemical reactions
Nature of carbonyl group
Carbonyl carbon - Electrophilic
Carbonyl oxygen - Nucleophilic
Physical Properties
1. Boiling points higher than other hydrocarbons
2. Lower boiling points than alcohols of similar molecular mass
3. Lower members miscible with water
Uses
1. Solvents
2. Starting materials for synthesis of other products
3. Preservatives
4. Perfumery
5. Dye industries
6. Food industries
Preparation
1. From acyl chloride
2. From nitriles
3. Friedel-Crafts acylation reaction
(from benzene or substituted benzenes)
1. Nucleophilic addition/elimination reactions
(i) Addition of hydrogen cyanide (HCN)
(ii) Addition of sodium hydrogen sulphite
(iii) Addition of Grignard Reagents
(iv) Addition of alcohols
(v) Addition of ammonia and its derivatives
2. Reduction
(i) Reduction to alcohols
(ii) Reduction to hydrocarbons
(a) Clemmensen reduction
(b) Wolff-Kishner reduction
3. Oxidation
(i) Tollens' test
(ii) Fehling's test
(iii) Haloform reaction
4. Reactions due to α-hydrogen
(i) Aldol condensation
(ii) Cross aldol condensation
5. Cannizzaro reaction
6. Electrophillic substitution reaction



TESTS OF ALDEHYDES AND KETONES (Distinction

Tests	Aldehydes	Ketones
1. With Schiff's reagent	Give pink colour.	No colour.
2. With Fehling's solution	Give red precipitate.	No precipitate is formed.
3. With Tollen's reagent	Black precipitate of silver or silver mirror is formed.	No black precipitate or silver mirror is formed.
4. With saturated sodium bisulphite solution in water	Crystalline compound (colourless) is formed.	Crystalline compound (colourless) is formed.
5. With 2,4-dinitrophenylhydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.
6. With sodium hydroxide	Give brown resinous mass (Formaldehyde does not give this test).	No reaction.
7. With sodium nitroprusside and few drops of sodium hydroxide	A deep red colour (Formaldehyde does not respond to this test).	Red colour which changes to orange.

OBJECTIVE TYPE QUESTIONS(MCQ)

1. When a mixture of calcium acetate and calcium formate is heated. It yields:

(a) acetone (b) acetaldehyde (c) formic acid (d) acetic acid

2. Which of the following compounds, is oxidised to prepare ethyl methyl ketone?

(a) Propan-2-o1 (b) Butan-1-ol (c) Butan-2-o1 (d) Tert. butyl alcohol

3. The reagent with which both acetaldehyde and acetone react easily is

(a) Fehling's solution (b) Grignard reagent (c) Schiff's reagent (d) Tollens' reagent

4. A compound that gives a positive iodoform test is:

(a) pentan-1-ol (b) pentan-2-one (c) pentan-3-one (d) pentanal

5. Schiff's reagent is:

(a) magenta solution decolourlsed with sulphurous acid

(b) magenta solution decolourised with chlorine

(c) ammoniacal cobalt chloride solution

(d) ammoniacal manganese sulphate solution

6. When acetaldehyde is heated with Fehling's solution, it gives a red precipitate of:

(a) Cu (b) CuO (c) $CuS0_4$ (d) Cu_2O

7. Hydrocarbons are formed when aldehydes and ketones are reduced with amalgamated zinc and conc. HCl The reaction is called:

(a) Dow reduction (b) Clemensen's reduction

(c) Cope reduction (d) Wolff-Kishner reduction

8. The formation of cyanohydrin from a ketone is an example of:

(a) Electrophilic addition (b) nucleophilic addition

(c) Nucleophilic substitution (d) electrophilic substitution

9. Acetone is mixed with bleaching powder to give:

(a) Ethanol (b) acetaldehyde (c) chloroform (d) phosgene

10. Ketones react with Mg-Hg over water gives:

(a) alcohols (b) pinacols (c) pinacolones (d) none of these

11. Which of the following is not a fatty acid?

(a) Stearic acid (b) Palmitic acid (c) Propionic acid (d) Phenyl acetic acid

12. Formic acid and formaldehyde can be distinguished by treating with:

(a) Benedict's solution (b) Tollens' reagent

(c) Fehling's solution (d) $NaHC0_3$

13. Methyl magnesium bromide on reaction with SO_2 followed by hydrolysis gives

(a) methyl sulphonic acid (b) methane sulphinic acid (c) dithio acetic acid (d) ethanethiol

14. Oxalic acid on treatment with conc. H_2S0_4 gives:

(a) CO only (b) CO_2 only (c) CO_2 + H20 (d) H_20+CO+C02

15. Propionic acid with Br_2/P yields a dibromo product. Its structure would be:

(a) CH_2BrCH_2COBr (b) $CH_2BrCHBrCOOH$

(c) $CHBr_2CH_2COOH$ (d) CH_3CBr_2COOH

ASSERTION REASON TYPE QUESTIONS: -

Following questions consist of an Assertion (A) and the Reason (R). Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation of (A)

(b) If both (A) and (R) are correct but (R) is not the correct explanation of (A)

(c) If (A) is correct but (R) is incorrect.

(d) If (A) is incorrect but (R) is correct.

1. (A) Carbonyl compounds take part in nucleophilic addition reactions.

(R) These reactions are initiated by nucleophilic attack' at the electron deficient carbon atom.

2. (A) Primary alcohols can be easily oxidized to aldehyde.

(R) Aldehydes are prone to further oxidation to carboxylic acids

3. (A) The addition of ammonia derivatives on carbonyl compounds is carried in weakly acidic medium. (R) In the weakly acidic medium, attacking nucleophile-is also protonated.

4. (A) Fehling's reagent is a test for all aliphatic aldehydes.

(R) Aliphatic aldehydes can be easily oxidised even with mild oxidising agents.

5. (A) 2-Methyl propanal undergoes Canniziaro's reaction.

(R) It has an alpha-hydrogen atom.

6. (A) Formaldehyde is a planar molecule.

(R) Carbon atom in formaldehyde is sp^2 -hybridised.

7. (A) Nitromethane can give aldol condensation.

(R) alpha-hydrogen of nitromethane is acidic.

8. (A) Chloral hydrate is stable.

(R) It is stable due to its high molecular weight.

9. (A) Acetaldehyde does not show aldol condensation.

(R) Compounds having at least one alpha-hydrogen give aldol condensation.

10. (A) Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.

(R) Distinction between aldehydes and ketones can be made by Tollens' reagent

❖ **Short Answer Type Questions (2 and 3 marks)**

1. Acetaldehyde undergoes a reaction to form a product which exhibits properties of aldehyde and alcohols

   (i) Name the reaction and give equation.

   (ii) Write the structural formula of the product formed.

   (iii) What are the reagents other than acetaldehyde required for the reaction to take place?

2. Write the structural formulae and names of the four possible aldol condensation products from propanal and butanal. In each case indicate which aldehyde acts as nucleophile and which as electrophile.

3. How do you account for the following?

   (a) Boiling points of aldehydes lie between parent alkanes and corresponding alcohols.

   (b) Aldehydes and ketones have high dipole moments.

4. Four different bottles containing methyl alcohol, ethyl alcohol, acetic acid and acetone have lost their labels. What chemical tests would be performed to identify them?

5. Four different bottles containing isopropyl iodide, acetone, propionaldehyde and heptane have lost their labels. What chemical tests would be performed to identify them?

6. How would you distinguish between:

   (a) Solutions of acetic acid, formic acid and ethanol?

   (b) Calcium formate and calcium acetate?

   (c) Acetic acid and acetone?

7. Arrange the following in order of increasing acidity:

   (i) Propanoic acid, chloro ethanoic acid, 3-bromopropanoic acid and trichloroacetic acid.

   (ii) 2-Fluorobutanoic acid, 2-iodobutanoic acid, 2-bromobutanoic acid and butanoic acid.

   (iii) Acetic acid, 2-methyl propanoic acid, 2,2-dimethyl propanoic acid.

8. How do you account for the following?

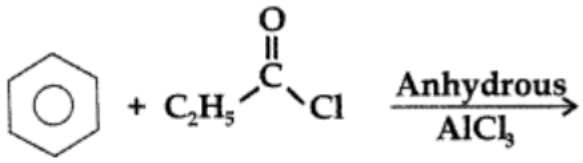
   (a) $NaHS0_3$ is used for the purification of aldehydes and ketones.

   (b) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide

9. Do the following conversions.

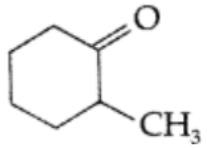
   (a)Methyl chloride to acetone. (b) Propan-1-ol to propanoic acid.

10. (a) Write the structure of the product formed in the following reaction .



(b) Give the structure and IUPAC name of the product formed when propanone is reacted with methylmagnesium bromide followed by hydrolysis.

(c) Write the IUPAC name of the following



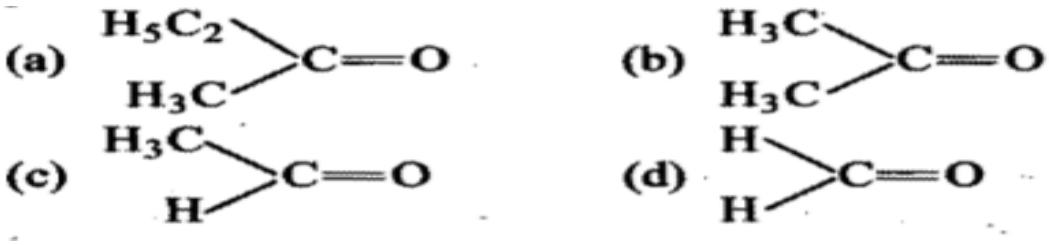
CASE BASED QUESTIONS

Q.I Aldehyde and ketones are specially susceptible to nucleophilic addition reaction because carbonyl is polar. Positive charge on carbon makes it reactive towards. This addition is catalyzed by acid. Reactivity of carbonyl towards nucleophilic addition increases with increase in the electron deficiency at carbonyl carbon. Thus (-I.E.) group increase while (+I.E.) groups decrease the reactivity of carbonyl compounds.

Answer the following question

1.Which is most reactive to give nucleophilic addition - FCH_2CHO and $ClCH_2CHO$?

2. Which among the following carbonyl compounds is most polar



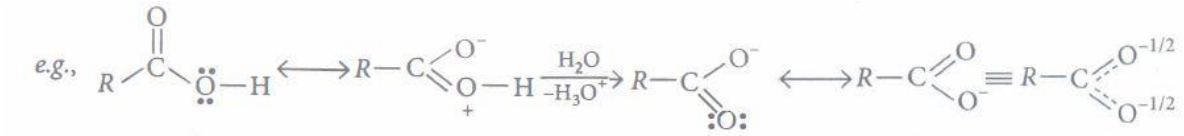
3. Arrange the following in order of their increasing reactivity towards HCN :-

CH_3CHO, CH_3COCH_3 , HCHO, $C_2H_5COCH_3$

4. Mention the criteria for aldehyde to undergo aldol condensation?

Q.II Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion. $RCOOH+H_2O \longrightarrow RCOO^- + H_3O^+$

The acidity of carboxyl group is due to the presence of positive charge on oxygen which liberates proton. The carboxylate ion formed is resonance stabilised.



Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of

carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/ or resonance effects. Electron donating group (EDG) decrease the acidity by destabilising the conjugate base.

Answer the following questions:

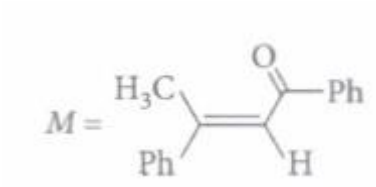
1. Complete the reaction

$$RCOOH + R'OH \xrightleftharpoons{H^+}$$

2.Write one chemical reactions showing the acidic property of carboxylic acid?

3. Arrange the following in decreasing order of their acidic strength and give the reason for your answer. CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$.

4. A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M. The structures of compound J, Kand L, respectively, are-



5 MARKS QUESTIONS

1. How will you differentiate between?

   (i) Acetaldehyde and acetone.

   (ii) Aldehydes and ketones with - (a) Tollens' reagent (b) Fehling's solution.

   (iii) Acetone and diethyl ether.

   (iv) Formaldehyde and acetaldehyde.

   (v) Formaldehyde and ethyl alcohol.

2. What happens when?

   (i) Formic acid is heated with conc. H_2S0_4

   (ii) Dry chlorine is passed through acetic acid in presence of sunlight.

   (iii) Oxalic acid is heated with glycerol.

   (iv) Formic acid is reacted with ammoniacal silver nitrate solution.

   (v) Acetic acid is heated with phosphorus pentoxide.

3. Answer the following:

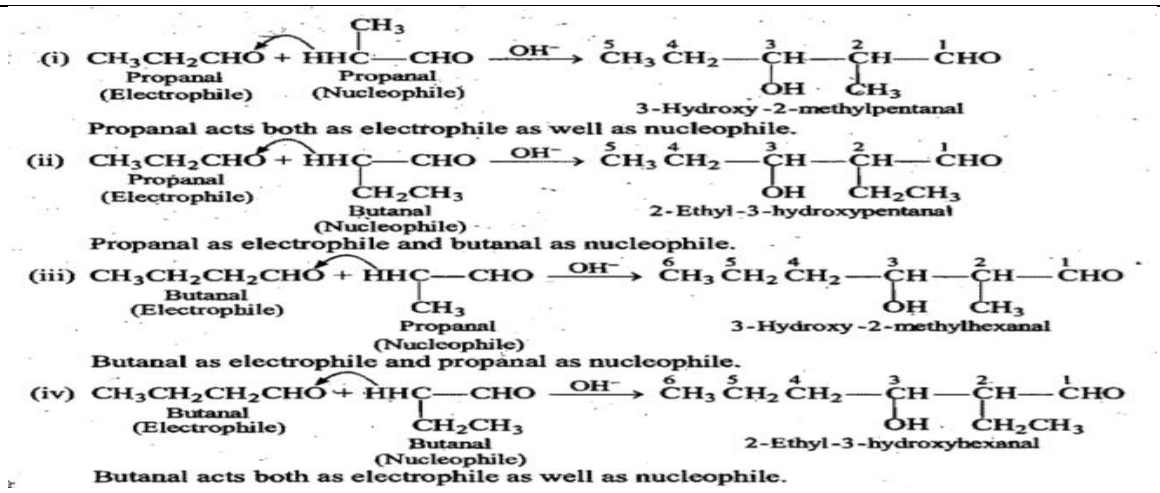
   (i) Why 100% pure acetic acid is named glacial acetic acid?

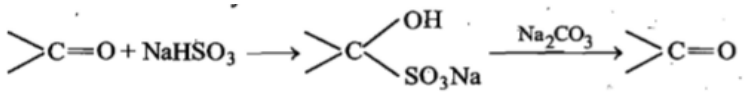
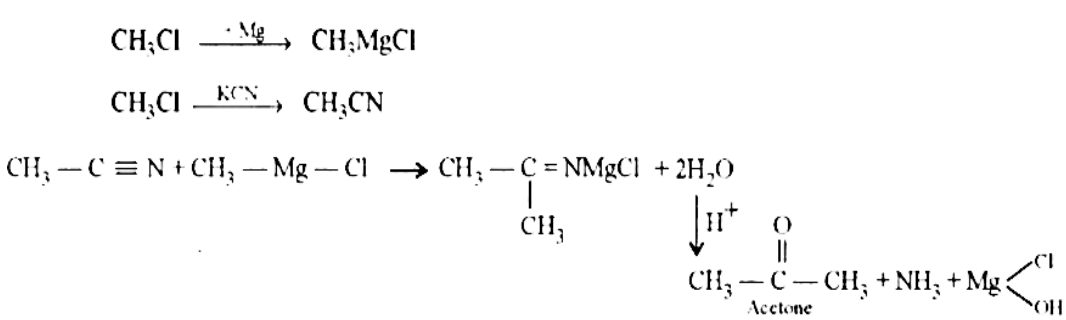
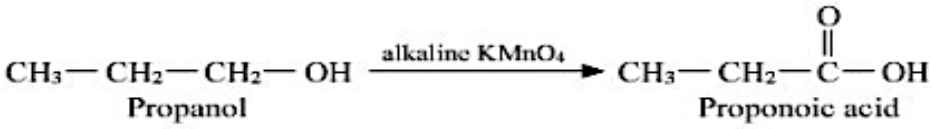
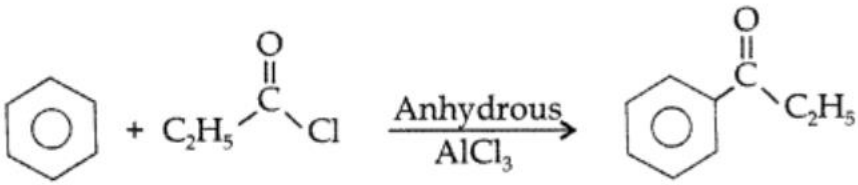
   (ii) Carboxylic acids with five or fewer carbon atoms are water soluble but, higher ones are insoluble

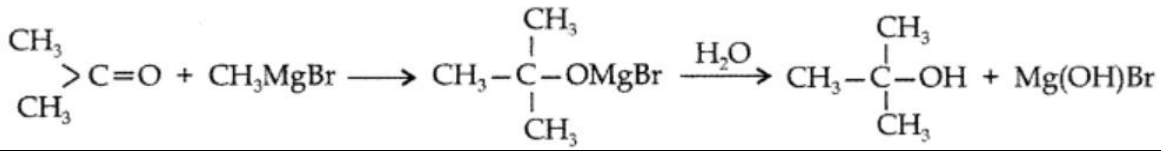
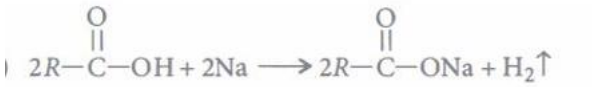
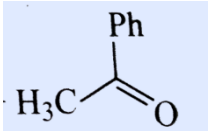
   (iii) Why the bond length of c=o in carboxylic acids is a bit longer than in aldehydes?

   (iv) Highly branched carboxylic acids are less acidic than unbranched acids.

   (v) Acetic acid can be halogenated in presence of phosphorus and chlorine but formic acid cannot be halogenated in the same way.

	MCQ(1 mark each)
	Ans. 1 b 2 c 3 b 4 b 5 a **6 d 7 b 8 b 9 c 10 b 11 d 12 d 13 b 14 d** **15 d**
	ASSERTION REASON TYPE QUESTIONS(1 mark each)
	1. (a) 2. (d) 3. (C) 4.(a) 5. (d) **6.(a) 7. (a) 8.(e) 9.(d) 10. (b)**
	SHORT ANSWER TYPE QUESTIONS(2 MARKS / 3 MARKS)
1	(i) Aldol condensation $CH_3CHO + HCH_2CHO \longrightarrow CH_3CH(OH)CH_2CHO$ (ii) Structure $CH_3-C(H)(OH)-CH_2-CHO$ (iii) Other reagent required is dilute NaOH or mild alkali.
2	
3	**(a) Alkanes have low boiling points as no hydrogen bonding and no dipole-dipole attractive forces are present. Alcohols have high boiling points as intermolecular hydrogen bonding is present. In aldehydes, dipole-dipole forces are present due to polar nature of carbonyl group. Thus, boiling points of aldehydes lie between alkanes and alcohols.** **(b) The large dipole moment is due tothe large contribution" of the polar structure (resonance) to the hybrid.** $>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$
4	**(i) Add $NaHC0_3$ the one which evolves· brisk effervescences contains acetic acid.** **(ii) Add $NaHS0_3$. The one which forms a white crystalline precipitate contains acetone.** **(iii) Perform iodoform test in remaining two bottles. The one which forms a yellow product with I2 and NaOH contains ethyl alcohol**

5	**Isopropyl iodide with alcoholic $AgN0_3$ gives yellow precipitate. Propionaldehyde gives pink colour with Schiff's reagent. Acetone responds to iodoform test.**
6	**(a) Both formic and acetic acid solutions will give effervescences with $NaHC0_3$. Formic acid reduces Fehling's solution and Tollens' reagent while acetic acid do not give these tests. Ethanol neither reacts with $NaHC0_3$ nor with Fehling's solution and Tollen's reagent.**
	(b) Calcium formate on heating forms a gas with pungent smell. Calcium acetate on heating forms vapours of pleasant odour.
	(c) Acetic acid reacts with $NaHC0_3$ to give effervescence, Acetone gives iodoform test and yellow crystalline compound with 2,4-dinitrophenylhydrazine.
7	**(i) $CH_3CH_2COOH < BrCH_2CH_2COOH < ClCH_2COOH < Cl_3CCOOH$**
	(ii) $CH_3CH_2CH_2COOH < CH_3CH_2CHICOOH < CH_3CH_2CHBrCOOH < CH_3CH_2CHFCOOH$
	(iii) $(CH_3)_3CCOOH < (CH_3)_3CHCOOH < CH_3COOH$
8	**(a) Aldehydes and ketones form insoluble crystalline compound with NaHS03 which can be filtered. These on distillation with saturated solution of Na2C03 again give the aldehyde or ketone.**  **(b) The reaction is initiated by the replacement of methyl protons (H+) by 1+.** $CH_3COCH_3 + 3IO^- \longrightarrow CI_3COCH_3 + 3OH^-$
9	a) 
	b) 
10	(a) 

	(b) IUPAC name : 2-methylpropan-2-ol 
	(c) IUPAC name : 2-methylcyclohexanone
	CASE BASED QUESTIONS
QI	**1.** FCH_2CHO **2. (d)** **3.** $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$ **4. A**ldehydes which contain α-hydrogen.
QII	**1.** $RCOOR' + H_2O$  **2.** **3.** $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$ **4.** Reaction of (J) with KOH suggests that it is Cannizzaro reaction. Therefore, (L) is PhCOOK and (J) is (PhCHO). Structure of (M) is given, and it is α−β-unsaturated ketone. It suggests that(M) is obtained by the Aldol condensation of (K) 
1	i) Ans. Acetaldehyde responds to following tests while acetone does not give any of them: (a) Acetaldehyde + Schiff's reagent solution → Pink colour (b) Acetaldehyde + Tollens' reagent → Silver mirror. (c) Acetaldehyde + Fehling's solution → Red precipitate. (d) Acetaldehyde + Sodium hydroxide (conc.) → Brown resinous mass ii) (a) aldehyde + Tollens' reagent → Silver mirror. (b) aldehyde + Fehling's solution → Red precipitate. iii) Ans. Acetone forms yellow coloured iodoform when heated with 12 and NaOH, i.e., it gives iodoform test. Diethyl ether does not give this test. iv) Ans. Acetaldehyde forms yellow precipitate of iodoform with an alkaline solution of iodine, i.e., gives iodoform test. Formaldehyde does not give this test. v) Ans. Formaldehyde responds to following tests while ethyl alcohol does not give any of them (a) HCHO + Schiff's reagent □ Pink colour (b) HCHO + Tollens' reagent □ Silver mirror (c) HCHO + Fehling's solution □ Red precipitate Ethyl alcohol gives iodoform test while HCHO does not.

2.	(i) $HCOOH \xrightarrow{H_2SO_4(conc.)} CO + H_2O$ (ii) $CH_3COOH \xrightarrow[Sunlight]{Cl_2} CH_2ClCOOH$ (iii) At 110°C, formic acid is formed. At 230°C, allyl alcohol is formed. (iv) $HCOOH + Ag(NH_3)_2NO_3 \longrightarrow Ag + 2NH_4NO_3 + CO_2$ (v) $2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$
3.	(i) The melting point of pure anhydrous acetic acid is 17°C. It is solid below this temperature and looks like 'icy' i.e., glacial (ii) The solubility of RCOOH in water is due to hydrogen bonding of -COOH group and water. R-portion being lyophobic resists solubility. As R gets large, this factor prevails over the first factor and thus, higher acids become insoluble. (iii)Due to resonance, there is considerable contribution of the resonance form, there is some single bond character in c=o bond which makes it somewhat longer than in aldehydes. (iv)The –COOH group of the branched acid is shielded from solvent molecules and cannot be stabilized by solvation as effectively as unbranched acid like the acetate anion. (v) This is HVZ reaction. It occurs only in those carboxylic acids which have a-hydrogen atoms. Acetic acid possesses three a-hydrogen atoms but formic acid does not have even a single a-hydrogen atom. Thus, formic acid does not undergo this reaction

AMINES

GIST OF THE CHAPTER

After studying this Unit, you will be able to
• describe amines as derivatives of ammonia having a pyramidal structure;
• classify amines as primary, secondary and tertiary;
• name amines by common names and IUPAC system;
• describe some of the important methods of preparation of amines;
• explain the properties of amines;
• distinguish between primary, secondary and tertiary amines;
• describe the method of preparation of diazonium salts and their importance in the synthesis of a series of aromatic compounds including azo dyes.

Amines are the organic which contain $-NH_2 gp, -NH \quad gp, -N-gp.$ they are called primary

(1°), secondary (2°) and tertiary (3°) amines.

They are considered as derivatives of ammonia obtained by replacement of hydrogen atoms with alkyl or aryl groups.

Amines are usually formed from nitro compounds, halides, amides, imides etc . Aromatic amines are called amines arenes.

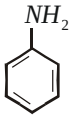
Structure :- Nitrogen is in sp^3 hypridised state and geometry of amines is pyramidal. The three hybridised orbital overlap with other and four one contain unshared pair & electron. Bond angle is 108° in trimethylamine

Nomenclature : Aliphatic Amine is named a prefixing alkyl group to amine. For eg. alkylamine as ethyl amine. In IUPAC system it is termed as Alkanamines for eg. CH_3NH_2 – methanamine

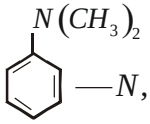
Secondaryamine : $(R_2NH.)$

example - $CH_3NHCH_3 \rightarrow$ dimethylamine – N – Methylmethanamine-

Tertiaryamines :-$(R_3N) \rightarrow$tri alkyl amines , N,N dialkyl alkanamine .

Aromaticamines . 

-Aniline or Benzenamine



—N,N Dimethylaniline = N,NDimethyl benzenamine

If more than one amine group is present at different position in the parent chain, their positions are specified by giving numbers to the carbon atoms bearing $-NH_2\ gp$ and suitable prefix as di, tri, etc is attached to the amines the letter 'e' of the suffix of the hydrocarbon part is retained. For example $H_2N-CH_2-CH_2-NH_2$ (ethane 1-2 diamine)

Preparation of Amines

(I) **<u>Ammonolysis</u>** :- Alkyl halide + $NH_3 \rightarrow$ Primary Amines

(It is N.S.R as X is removed)

$$R-\overset{\curvearrowright}{X}+\ddot{N}H_3 \rightarrow R-\overset{+}{N}H_3\overset{-}{X}$$

eg. $CH_3Cl + NH_3 \rightarrow CH_3NH_2\ HCl$

$$R-\overset{+}{N}H_3X^- + NaOH \rightarrow R-NH_2 + H_2O + \overset{+}{N}aX^-$$

$$CH_3ClNH_2.HCl + NH_3 \rightarrow CH_3NH_2 + NH_4Cl$$

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$$ Quaternary Ammonium Salt

(ii) **<u>Quaternary Ammonium Salts /Chlorides</u>** :-

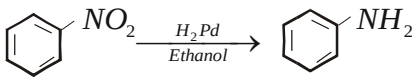
Tertiary Amines + Alkyl halides $\longrightarrow$ Quaternary Ammonium Chloride

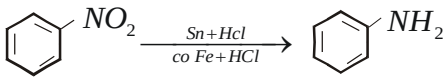
$$(CH_3)_3N + CH_3I \rightarrow \left[(CH_3)_4N\right]^+ 'I^-$$

ORDER OF REACITIVITY OFHALIDE WITH AMINES $RI > RBr > RCl$

(II) **Reduction of Nitro Compounds** :-

Nitro compounds $\xrightarrow[acthat]{H_2/Pd}$ Aniline





III **Reduction of Amides :-**

(a) $CH_3CONH_2 \xrightarrow[H_2O]{LiAlH_4} CH_3-CH_2-NH_2$

(b) $CH_3CONHCH_3 + 4[H] \xrightarrow{Na/C_2H_5OH} CH_3CH_2NHCH_3 + H_2O$

IV **From Cyanides** : Reduction or catalytic hydrogenation produce primary amines. It is used as ascent of seris.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5On]{H_2/Ni} R-CH_2-NH_2$$

V **Hoffmann bromamide degradation Reaction**

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH/KOH \rightarrow CH_3NH_2 + Na_2CO_3/K_2CO_3 + 2NaBr\ or\ 2KBr + 2H_2O$$

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

VI **From isocyanides:-** $CH_3NC + 4H \rightarrow CH_3NHCH_3$

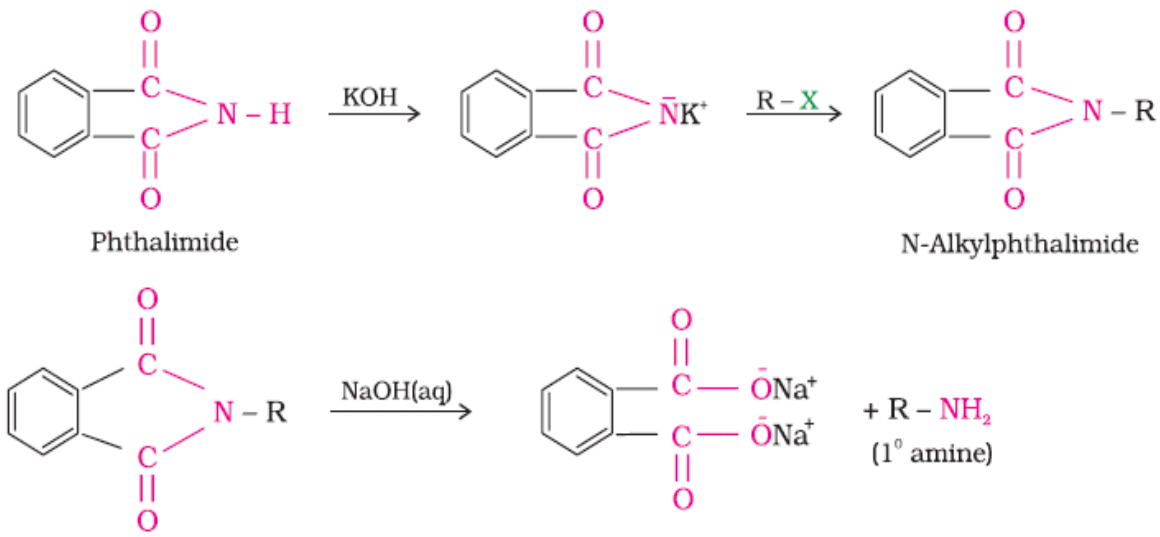
VII From alcohols **:-** $CH_3\ CH_2\ OH + NH_3 \xrightarrow[\Delta/723K]{Al_2O_3} C_2H_5NH_2 + H_2O$

Primary amine + $Alcohol \xrightarrow{Al_2O_3}$ Sec Amine + $Alcohol \xrightarrow{Al_2O_3}$ Tertiaryamies

Tertiary amines+Alochol $\rightarrow$ Quaternary ammonium hydroxide

VIII From Aldehydes :- $CH_3CHO + NH_3 + H_2 \xrightarrow{Ni} CH_3CH_2NH_2 + H_2O$

IX Gabriel Phthalimide Synthesis



Physical Properties :- (1) Lower amines are gases followed by liquids. Higher members are solids .

(ii) Polar in nature & form inter molecular Hydrogen Bonding.

(iii) Lower amines are solids in water but solubility decrease with increase in alkyl group.

(iv) Except methylamines and ethylamine other amines have fishy odour. Aromatic amines are toxic to easy oxidation in air.

(v) Primary Amines have highest boiling point due to more extensive H-bonding. Therefore Primary amines >Secondary Amines>tertiary Amines

(vi) Aniline is steam volatile & obtained by steam distillation.

Chemical Properties :-(Reactions involved)

(i) Basic Character

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

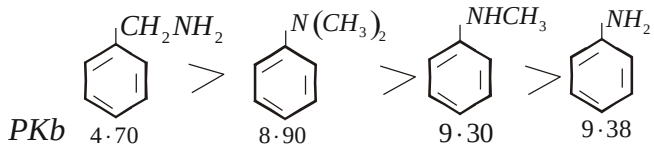
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

Amines are reactive due to difference in electro negativity between nitrogen and hydrogen atoms and presence of unshared pair of electrons over nitrogen . Amines behave as nucleophile .

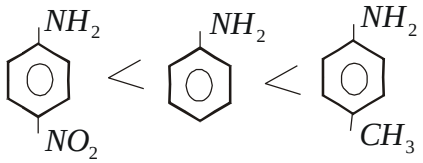
(2) PK_b Values of amines in aqueoues phase and their basic character

$PK_b = -\log K_b -$ Higher value of K_b and lower value of PK_b, stronger will be amine.

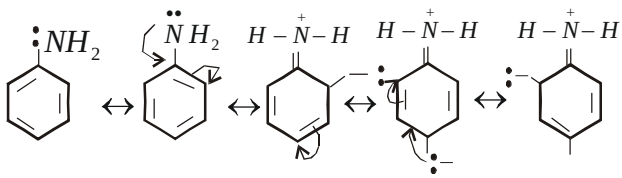
$P-$Toluidine $> m-$Toluidine $>$ Aniline $> O-$Toluidine



The basic strength is also affected by $+I$ or $-I$ effect $>$ solvation effect, steiric hindrance structure etc.



(3) Aniline is less basic then aliphatic amines due it + ve charge on nitrogen in '3' out of five resonating structure.



(4) The electron releasing groups like $-OCH_3, -CH_3$ increases basic strength but electron with drawing groups like $-NO_2, -SO_3, -COOH, -X$ decreases it

(5) **Alkylation :-** $P.$ Amine + Alkylhalide $\rightarrow$ Sec Amine + AlkylHalide

$$Secondary\ Amine + AlkylHalide \rightarrow Tertiarya\ mine \xrightarrow{alkyl\ halide} Quaternery\ salt$$

$$CH_3NH_2 + CH_3I \rightarrow (CH_3)_2NH \xrightarrow{CH_3I} (CH_3)_3N \xrightarrow{(CH_3)I} (CH_3)_4N^+I^-$$

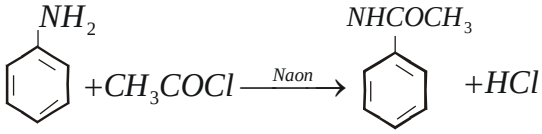
(6) **Acylation:-**

$$C_2H_5NH_3 + CH_3COCl \xrightarrow{Base} C_2H_5\overset{+}{N}H_2CH_3COCl$$

$$\downarrow$$

$$C_2H_5 - \underset{\underset{H}{|}}{N} - \underset{\underset{O}{\|}}{C} - CH_3 + HCl$$

$$C_2H_2 - \overset{\overset{H}{|}}{\underset{\underset{C_2H_5}{|}}{N}} + CH_3COCl \xrightarrow{Base} C_2H_5 - \underset{\underset{C_2H_5}{|}}{\ddot{N}} - \underset{\underset{O}{\|}}{C} - CH_3 + HCl$$



(7) **Bemzoylation**:- $C_6H_5COCl + CH_3NH_2 \rightarrow C_6H_5CONHCH_3 + HCl$

Benzoylchloride Methanamine N-methyl benzaminde

$$C_6H_5NH_2 + C_6H_5COCl \xrightarrow{NaOH} C_6H_5NHCOC_6H_5 + HCl.$$

N-Phenyl Benzamide

(8) **With** HNO_2 :- $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

$$R-NH_2+HNO_2 \xrightarrow[Hcl]{NaNO_2} R-\overset{+}{N}_2-Cl^- \xrightarrow{H_2O} ROH+N_2+HCl$$

$$C_6H_5-NH_2+HNO_2 \xrightarrow[2HCl]{NaNO_2} C_6H_5-\overset{+}{N}_2Cl^- + NaCl + 2H_2O$$

(9) Carbylamine reaction :- (Isocyanide test)

$$R-NH_2+CHCl_3+3KOH \xrightarrow{heat} R-NC+3KCl+3H_2O$$

(Only primary amines give this reaction and not Sec or Tertiary amines)

(10) With Aryl Sulphonyl chloride :- (Hinsberg's test)

Benzene sulphonyl chloride $(C_6H_5SO_2Cl)$ called as Hinsberg's reagent. It is used to distinguish between primary secondary and tertiary amines.

$$C_6H_5SO_2Cl+CH_3NH_2 \xrightarrow{OH^-} C_6H_5SO_2NHCH_3+HCl$$

(N-ethyl benzene sulphonamide)
Soluble in alkali

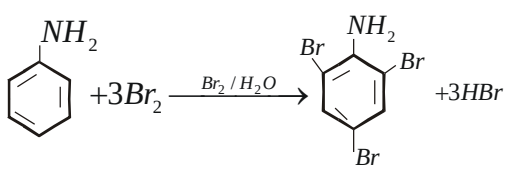
$$C_6H_5SO_2Cl+(CH_3)_2NH \xrightarrow{OH^-} C_6H_5SO_2N(CH_3)_2+HCl$$

(N,Ndimethyl benzene sulphonamide)
Insoluble in alkali

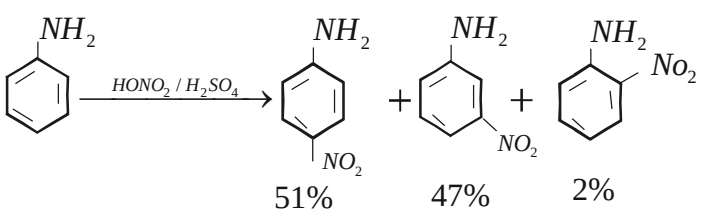
$$(CH_3)_3N+C_6H_5SO_2Cl \rightarrow \text{No Reaction}$$

(11) Bromination, Nitration Sulphonation (as E.S.R. in Amines)

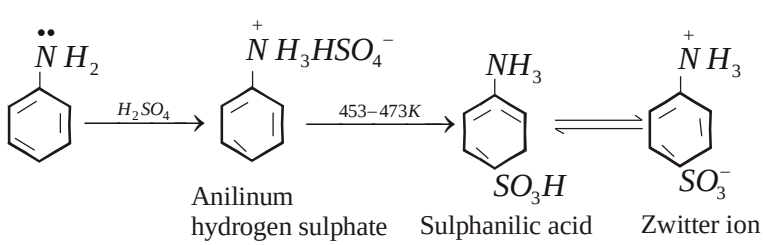
(a)



(b)



(c)



DIAZONIUM SALTS :-

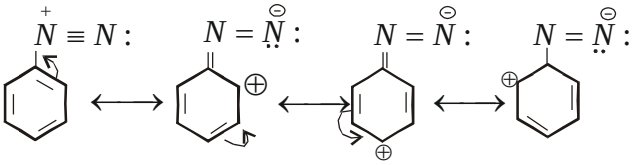
G.Formula $= R-\overset{+}{N} \equiv NX^-$

$R =$ Aryl gp, $X - Cl^-, Br^-, HSO_4^-, BF_4^-$ *etc*

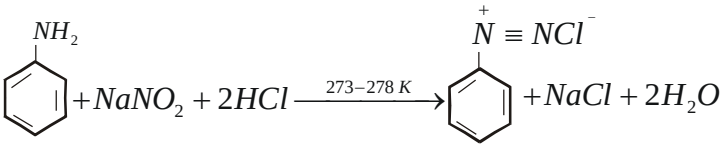
$C_6H_5\overset{+}{N}_2Cl^- \rightarrow$ Benzene diazonium chloride

$C_6H_5N_2^+BF_4^- \rightarrow$ Benzene diazonium tetrafluoroborate

The salts i.e diazonium salts of primary amines are highly unstable . Primary aromatic amines form large no of arene diazonium salts which are stable due to resonance, diazonium ion is stable.

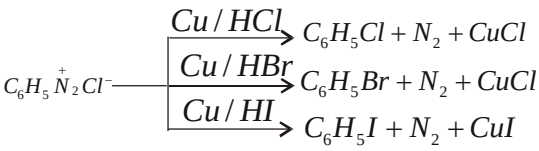


Preparation :-

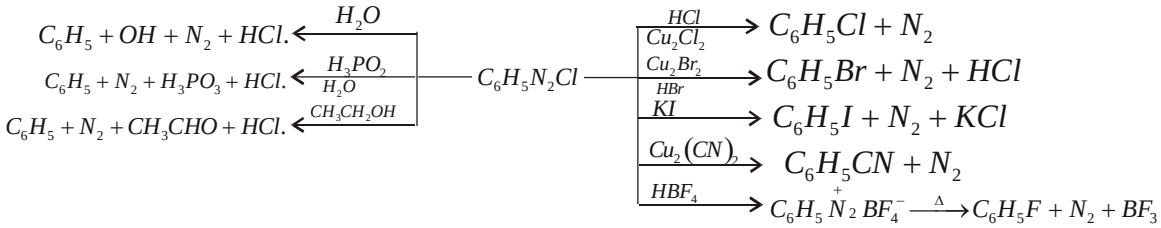


IMPORTANT CHEMICAL REACTIONS

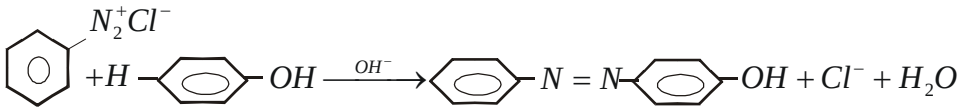
(1) Gattermann reaction :-



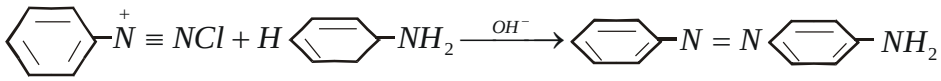
(2) Sandmeyer Reaction :



(3) Coupling Reaction :-



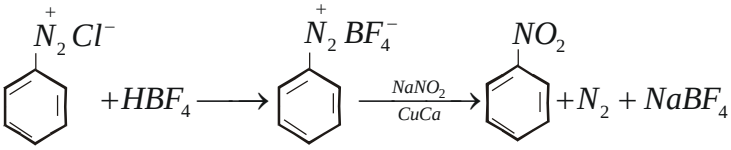
(p-Hydroxyazobenzene)



p-Amminoazobenzene

(Yellowdye)

(4)



Uses :- (1) Used to prepare halobenzene, phenol, nitro bernene
(2) Used in preparation of methyl orange and dyes and also substituted aromatic compound.

OBJECTIVE TYPE QUESTIONS (MULTIPLE CHOICE)

1. The conversion of benzene diazonium chloride to bromobenzene can be accomplished by
(a) Reimer-Tiemann reaction
(b) Friedel-Crafts reaction
(c) Gattermann reaction
(d) Azo-Coupling reaction

2. The correct IUPAC name for $CH_2 == CHCH_2NHCH_3$ is
(*a*) Allylmethylamine (*b*) 2-amino-4-pentene
(*c*) 4-aminopent-1-ene (*d*) N-methylprop-2-en-1-amine

3. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is _____
(*a*) Sodium amide, $NaNH_2$ (*b*) Sodium azide, NaN_3
(*c*) Potassium cyanide, KCN (*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

4. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is _____.
(*a*) excess H_2 (*b*) Br_2 in aqueous NaOH
(*c*) iodine in the presence of red phosphorus (*d*) $LiAlH_4$ in ether

5. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?
(*a*) H_2 (excess)/Pt (*b*) $LiAlH_4$ in ether (*c*) Fe and HCl (*d*) Sn and HCl

6. Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.
(*a*) 2° R—Br + NH_3
(*b*) 2° R—Br + NaCN followed by H_2/Pt
(*c*) 1° R—NH_2 + RCHO followed by H_2/Pt
(*d*) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat

7. The best reagent for converting, 2-phenylpropanamide into 1-phenylethanamine is _____.
(*a*) excess H_2/Pt (*b*) NaOH/Br_2 (*c*) $NaBH_4$/methanol (*d*) $LiAlH_4$/ether

8.The source of nitrogen in Gabriel synthesis of amines is _____.
(*a*) Sodium azide, NaN_3 (*b*) Sodium nitrite, $NaNO_2$
(*c*) Potassium cyanide, KCN (*d*) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

9. Which of the following statements about primary amines is 'false'?
(*a*) Alkylamines are stronger bases than arylamines.
(*b*) Alkylamines are stronger bases than ammonia.
(*c*) Alkylamines react with nitrous acid to produce alcohols.
(*d*) Arylamines react with nitrous acid to produce phenols

10. Amongst the following, the strongest base in aqueous medium is _____.
(*a*) CH_3NH_2 (*b*) $NCCH_2NH_2$ (*c*) $(CH_3)_2NH$ (*d*) $C_6H_5NHCH_3$

The following questions given below consist of an "Assertion" (A) and "Reason" (R) Type questions. Use the following Key to choose the appropriate answer.

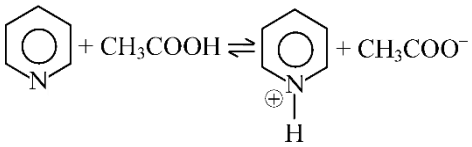
(A) If both (A) and (R) are true, and (R) is the correct explanation of (A).

(B) If both (A) and (R) are true but (R) is not the correct explanation of (A).

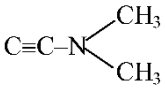
(C) If (A) is true but (R) is false.

(D) If (A) is false but (R) is true.

Q.1 **Assertion :**

this equilibrium favours backward direction. 

Reason : is stronger base than CH_3COO^-

Q.2 **Assertion (A)**.The major product of reaction Ph–  with $H^{\oplus}/H_2O$ will contains amide as only function group .

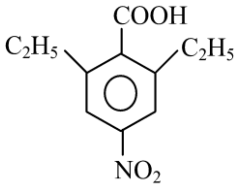
Reason (R) : The major product obtained will be formed due to formation of benzylic carbocation which to stabilised due to + M–effect of benzene ring.

Q.3 **Assertion :** $CH_3CH_2NH_2$, ethylamine, on treatment with CS_2 followed by $HgCl_2$, gives mustard oil smell.

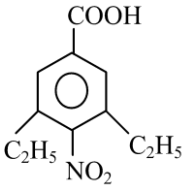
Reason : $CH_3CH_2NH_2$ on treatment with CS_2 produces dithiocarbamic acid

Sol. The mustard oil smell is caused due to alkyl isothiocyanate R–N=C=S.

Q.4 **Assertion :** Acidic character of



(I) is more than



(II)

Reason : In Ist alkyl groups show + R effect while in IInd it shows + I effect.

Q.5 **Assertion :**: Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.

Statement-II : Ammonolysis of alkyl halides yields mainly secondary amines.

Q.6 **Assertion :**: Carbylamine reaction involves chemical reaction between 1° amine and chloroform in basic medium.

Statement-II : In carbylamine reaction, $–NH_2$ group changes into –NC group.

Q.7 **Assertion :**: The main product of reaction of alcoholic silver nitrite and ethyl bromide is nitroethane.

Statement-II : Silver nitrite is predominantly covalent compound.

Q.8 **Assertion :** : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagent

Statement-II : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

Q.9 **Assertion ::** Corbonyl compounds take part in nucleophilic addition reactions.

Statement II: These reactions are initiated by nucleophilic attack at the electron deficient carbon atom.

Q.10 Assertion :: The addition of ammonia derivatives on carbonyl compounds is carried in weakly acidic medium.

Statement II: In weakly acidic medium attacking nucleophile is also protonated.

Q.11 Assertion :: Formic acid reduces mercuric chloride solution.

Statement II : Formic acid has reducing aldehydic group.

Q.12 Assertion :: Acetaldehyde undergoes aldol condensation with dilute NaOH.

Statement II : Aldehyde which do not contain α-hydrogen undergoes aldol condensation.

Q.13 Assertion :: Crossed Cannizzaro reaction between formaldehyde and benzaldehyde give benzyl alcohol and formate ion.

Statement II : Formaldehyde is a better hydride donar than benzaldehyde.

Q.14 . Assertion: Hoffmann's ammonolysis can be used to prepare pure primary amines.
Reason: Ammonolysis of haloalkanes lead to multiple substitution of alkyl groups on nitrogen.

Q. 15. Assertion: Aniline is less basic than ammonia.
Reason: The lone pair on nitrogen in aniline is donated into the ring through resonance.

SUBJECTIVE TYPES QUESTIONS
2 MARKS QUESTIONS

Q. 1. (i) Arrange the following in increasing order of boiling points.
$(CH_3)_3N$, C_2H_5OH, $C_2H_5NH_2$

(ii) Arrange the following in increasing order of base strength in gas phase:
$(C_2H_5)_3N$, $C_2H_5NH_2$, $(C_2H_5)_2NH$

Q. 2. (i) Arrange the following in decreasing order of solubility in water:
$(CH_3)_3N$, $(CH_3)_2NH$,CH_3NH_2

(ii) Arrange the following in decreasing order of the basic character:
$C_6H_5NH_2$, $(CH_3)_3N$, $C_2H_5NH_2$

Q. 3. (i) Arrange the following in increasing order of pKb **values:**
$C_6H_5CH_2NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$

(ii) Arrange the following in decreasing order of solubility in water:
$(C_2H_5)_2NH$, $C_2H_5NH_2$, $C_6H_5NH_2$

Q.4.-(i) Write IUPAC name of the following compound:
$(CH_3CH_2)_2NCH_3$

(ii) Write IUPAC name of the following compound:
$CH_3NHCH(CH_3)_2$

Q. 5. (i) Write IUPAC name of the following compound:
$(CH_3)_2N — CH_2CH_3$

(ii) Complete the following reaction equation:
$C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$ .....

Q. 6- **Account for the following:**
(*i*) Aniline gets coloured on standing in air for a long time.
(*ii*) $MeNH_2$ is stronger base than MeOH..

Q. 7. Account for the following:
(*i*) *pKb* of anili*n*e is more than that of methylamine.
(*ii*) Although trimethylamine and *n*-propylamine have the same molecular weight, but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

Q.8. Give the chemical tests to distinguish between the following pairs of compounds :
(i) Methylamine and dimethylamine
(ii) Aniline and *N*-methylaniline

3 MARKS QUESTIONS

Q. 1. (*i*) Arrange the following compounds in increasing order of dipole moment.

$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH

(*ii*) Give possible explanation for each of the following:

(*a*) The presence of a base is needed in the ammonolysis of alkyl halides.

(*b*) Amides are more acidic than amines.

Q. 2. How are the following conversions carried out:

(*i*) Aniline to fluorobenzene

(*ii*) Benzene diazonium chloride to benzene

(*iii*) Methyl chloride to ethylamine

Q.3.- Give reasons:

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although $–NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m nitroaniline.

Q.4. How will you convert the following:

(i) Nitrobenzene into aniline,

(ii) Ethanoic acid into methanamine,

(iii) Aniline to N-phenylethanamide.

(Write the chemical equations involved.

Q. 5. How are the following conversions carried out:

(*i*) Aniline to fluorobenzene

(*ii*) Benzene diazonium chloride to benzene

(*iii*) Methyl chloride to ethylamine

CASE STUDY BASED QUESTIONS

Q.1- Read the passage given below and answer the following questions:

Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Larger the value of *Kb* or smaller the value of *pKb* stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as —CH_3, —OCH_3, —NH_2, etc., increase the basicity while electron-withdrawing substituents such as —NO_2, —CN, halogens. etc. decrease the basicity of amines. The effect of these substituents is more at *p*- than at *m*-positions.

a. Arrange the following in increasing order of their basic strength:

$C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$

b. Arrange the following compounds in increasing order of their acidic strength:

Methylamine, dimethylamine, aniline, N-methylaniline

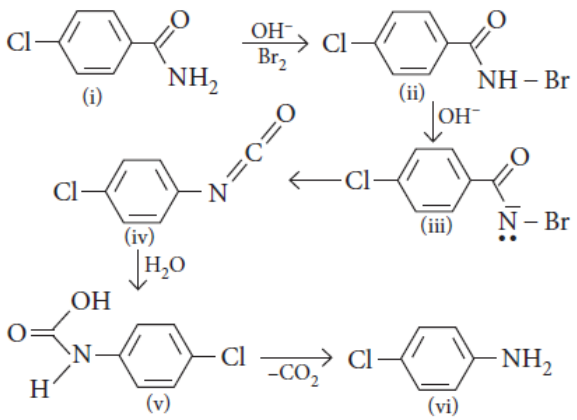
c. Rearrange the following in increasing order of their basic strength:

p-toluidine, N, N-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline

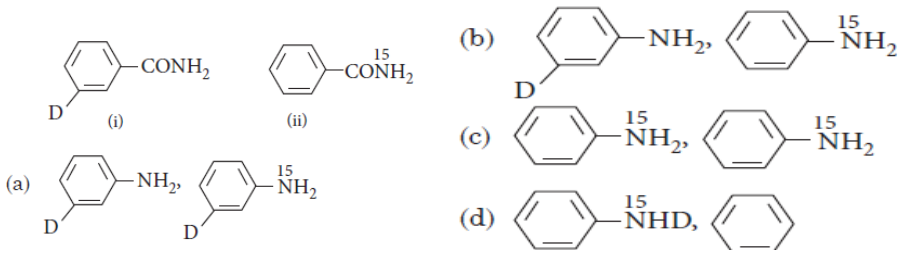
d. Which is more acidic, aniline or ammonia?

Q. 2 **Read the passage given below and answer the following questions: (1×4=4)**.

R$CONH_2$ is converted into *R*NH_2 by means of Hoffmann bromamide degradation. During the reaction amide is treated with Br_2 and alkali to get amine. This reaction is used to descend the series in which carbon atom is removed as carbonate ion (CO_3^{2-}). Hoffmann bromide degradation reaction can be written as :

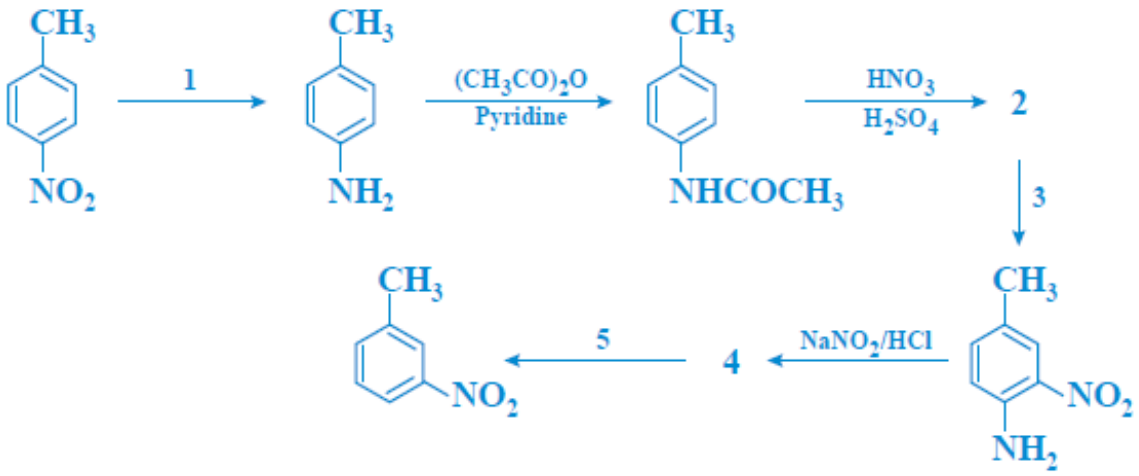


a. Hoffmann bromamide degradation is used for the preparation of
(a) primary amines (b) secondary amines
(c) tertiary amines (d) secondary aromatic amines.
b. Which is the rate determining step in Hoffmann bromamide degradation?
(a) Formation of (i) (b) Formation of (ii)
(c) Formation of (iii) (d) Formation of (iv)
c. Which of the following is used for the conversion of (i) to (ii)?
(a) KBr (b) KBr + CH_3ONa
(c) KBr + KOH (d) Br_2 + KOH
d. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hoffmann bromamide degradation?

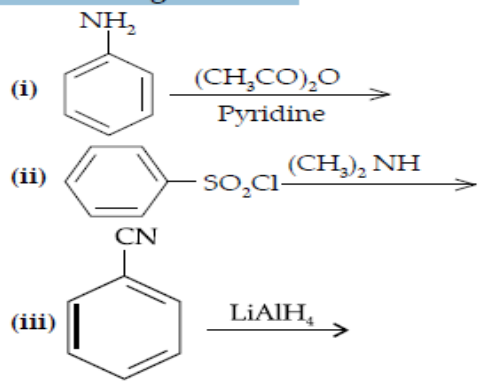


5 MARKS QUESTIONS

Q. 1 Give plausible explanation for each of the following :
(i) Why are amines less acidic than alcohols of comparable molecular masses?
(ii) Why do primary amines have higher boiling point than tertiary amines?
(iii) Why are aliphatic amines stronger bases than aromatic amines?
Q. 2- A hydrocarbon 'A', (C4H8) on reaction with HCl gives a compound 'B', (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C', ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. Identify the compounds 'A' to 'D'. Explain the reactions involved.
Q. 3- Predict the reagents or the products in the following reaction sequence:



Q. 4- (a) Write the structures of the main products of the following reactions:



(b) Give a simple chemical test to distinguish be tween aniline and N,N-dimethylaniline.

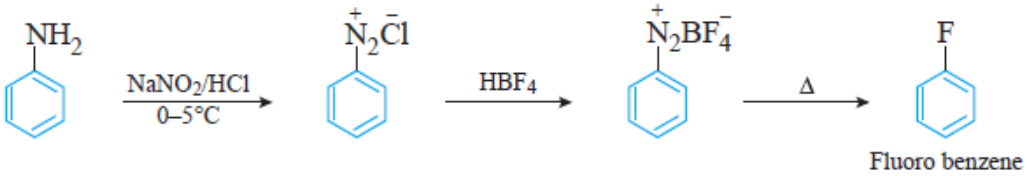
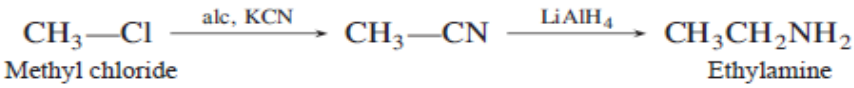
(c) Arrange the following in the increasing order of their pKb values:

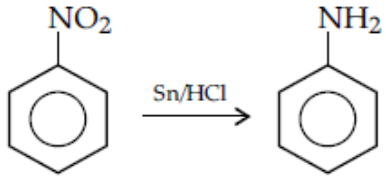
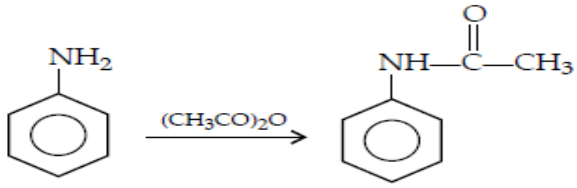
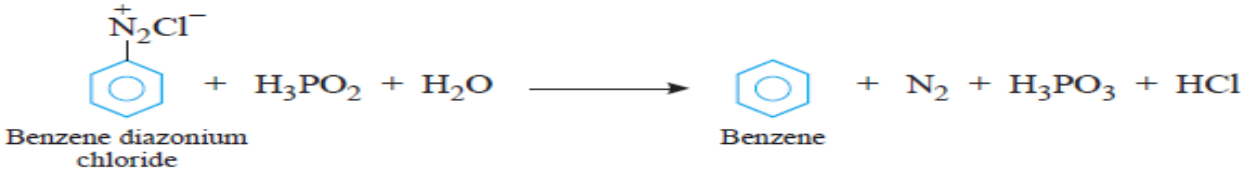
$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$

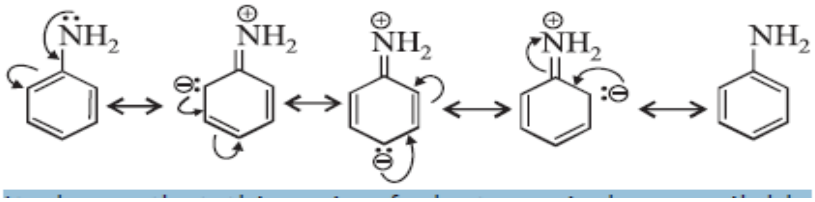
Q. 5- An organic compound A with molecular formula C_7H_7NO reacts with Br_2/aq. KOH to give compound B, which upon reaction with $NaNO_2$ and HCl at 0°C gives C. Compound C on heating with CH_3CH_2OH gives a hydrocarbon D. Compound B on further reaction with Br_2 water gives white precipitate of compound E. Identify the compound A, B, C, D and E; also justify your answer by giving relevant chemical equations.

ANSWERS KEY

	OBJECTIVE TYPE QUESTIONS (MULTIPLE CHOICE) **ANSWERS** 1-c, 2-d , 3- c, 4-d , 5-b , 6-c ,7-b, 8-d, 9-d, 10-c.
	REASON ASSERSION TYPES QUESTIONS **ANSWERS** -1- d, 2- c, 3-b, 4-b, 5-c, 6-a, 7-a, 8-d, 9-a, 10-c, 11-a,12-c,13-a,14-d,15-a
	SUBJECTIVE TYPES QUESTIONS **2 MARKS QUESTIONS**
Ans. 1	**(i) $(CH_3)_3N$ < $C_2H_5NH_2$ < C_2H_5OH** **(ii)** $C_2H_5NH_2$ < $(C_2H_5)_2NH$ < $(C_2H_5)_3N$ Base strength is the ability to donate lone pair. Due to inductive +I effect of C_2H_5 , the negative charge density on nitrogen atom increases. Therefore, lone pair is easily available for donation. $C_2H_5NH_2$ < $(C_2H_5)_2NH$ < $(C_2H_5)_3N$
Ans. 2	**(i)** CH_3NH_2 > $(CH_3)_2NH$ > $(CH_3)_3N$ **(ii)** $(CH_3)_3N$ > $C_2H_5NH_2$ > $C_6H_5NH_2$
Ans. 3	**(i)** $C_6H_5CH_2NH_2$ < $C_6H_5NHCH_3$ < $C_6H_5NH_2$ (ii)$C_2H_5NH_2$ > $(C_2H_5)_2NH$ > $C_6H_5NH_2$
Ans. 4	**(i)** N-Ethyl–N–methylethanamine. **(ii)** N-Methylpropan-2-amine.

Ans. 5	**(i)** N, N-Dimethylethanamine **(ii)** $ArN^{+}{}_{2}Cl^{-} + H_3PO_2 + H_2O \rightarrow ArH + N_2 + H_3PO_3 + HCl$ (where Ar is C_6H_5) Benzene
Ans. 6	(*i*) Due to electron-donating effect (+R-effect) of —NH_2 group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products. (*ii*) Nitrogen is less electronegative than oxygen therefore lone pair of electrons on nitrogen is readily available for donation. Hence, $MeNH_2$ is more basic than MeOH
Ans. 7	(*i*) Refer to Ans. 3(*i*) NCERT Textbook Exercises. (*ii*) *n*-Propylamine has two H-atoms on the N-atom and hence undergoes intermolecular H-bonding, thereby raising its boiling point. Trimethylamine, $(CH_3)_3N$, being a tertiary amine does not have any H-atom on the N-atom. As a result, it does not undergo H-bonding and hence its boiling point is low.
Ans. 8	(i) Methylamine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethylamine does not give this test. (ii) Aniline gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.
	3 MARKS QUESTIONS
Ans. 1	(*i*) $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$ (*ii*) (*a*) To remove HX formed so that the reaction shifts in the forward direction. (iii) Due to +R effect, availability of lone pair of electron on N of —NH2 group decreases. As a result, acid amide is much weaker base than amines. Because of the positive charge on N, as a result of resonance, N can easily lose a proton and behaves, as a weak acid. (*b*)
Ans. 2	(*i*) Aniline to fluorobenzene  (*ii*) Benzene diazonium chloride to benzene (*iii*) Methyl chloride to ethylamine 
Ans. 3	**(i)** Due to the resonance, the electron pair of nitrogen atom gets delocalised towards carbonyl group / resonating structures. **(ii)** Because of +I effect in methylamine electron density at nitrogen increases whereas in aniline resonance takes place and electron density on nitrogen decreases / resonating structures. **(iii)** Due to protonation of aniline / formation of anilinium ion.

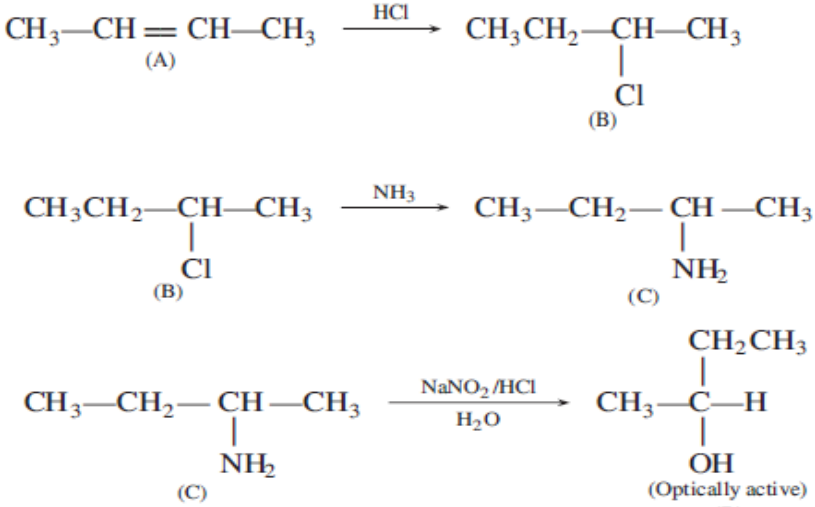
Ans4	(i) Nitrobenzene into aniline  (ii) Ethanoic acid into methanamine $CH_3COOH \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{Br_2} CH_3NH_2$ (iii) Aniline to N-Phenylethanamide 
Ans. 5	(i) Aniline to fluorobenzene (ii) Benzene diazonium chloride to benzene  (iii) Methyl chloride to ethylamine $CH_3—Cl \xrightarrow{alc.\ KCN} CH_3—CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$ Methyl chloride Ethylamine
	CASE STUDY BASED QUESTIONS
Ans. 1 (a)	$C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$
Ans.b	dimethylamine < methylamine < N-methylaniline < aniline.
Ans.c	*p*-nitroaniline < aniline < *p*-toluidine < N, N-dimethyl-*p*-toluidine.
Ans.d	Due to delocalization of the lone pair of electrons of the N-atom of aniline over the benzene ring, aniline is more acidic than ammonia.
Ans 2(a)	A
B	D
C	D
D	B
	5 MARKS QUESTIONS
Ans. 1	(i) In alcohols, the hydrogen atom is attached to more electronegative oxygen atom whereas nitrogen of amines is less electronegative. After the loss of H^+ ion, the negative charge is more easily accommodated on oxygen than in case of nitrogen in amines. Hence, amines have lesser tendency to lose H^+ ions, so they are less acidic than alcohols. (ii) Primary amines ($R – NH_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So primary amines boil at a higher temperature than tertiary amines. (iii) In aromatic amines, the lone-pair of electrons on nitrogenatom is involved in resonance with the benzene ring as shown below for aniline.



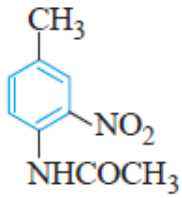
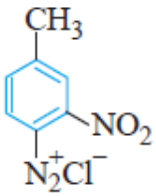
It shows that this pair of electrons is less available for protonation. In case of aliphatic amines electron releasing alkyl groups increase electron density on nitrogen atom. So, aliphatic amines are stronger bases than aromatic amines.

Ans-2

On the basis of structure of 'A', the reactions can be explained as follows:



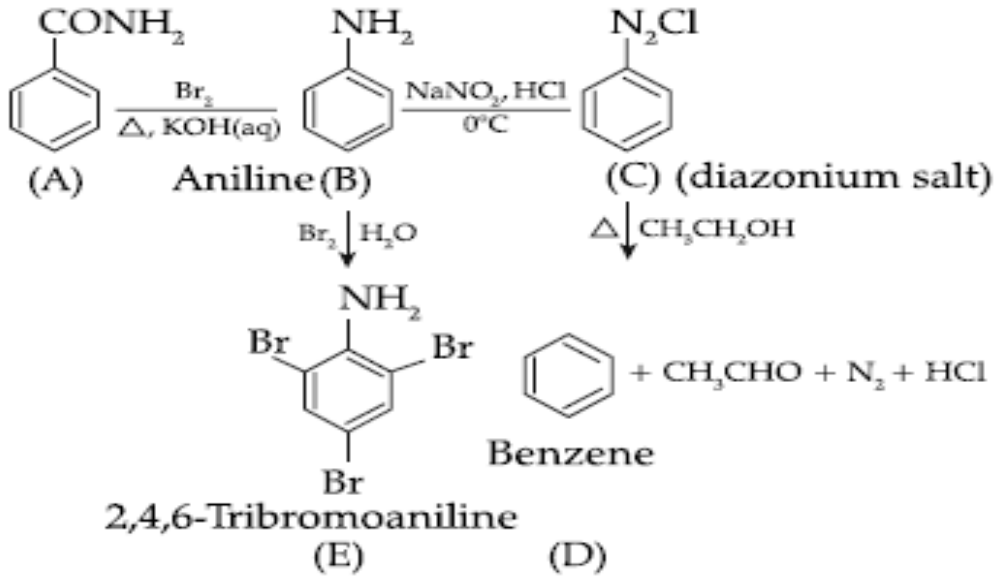
Ans-3

1. Sn–HCl (conc.) 2.  3. H_2O/H^+ 4.  5. H_3PO_2/H_2O

Ans. 4

(a) (i) $C_6H_5NHCOCH_3$
(ii) $C_6H_5SO_2N(CH_3)_2$
(iii) $C_6H_5CH_2NH_2$
(b) Add chloroform in the presence of KOH and heat, then, aniline gives a offensive smell while N, N dimethylaniline does not. (or any other correct test)
(c) $C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

Ans. 5

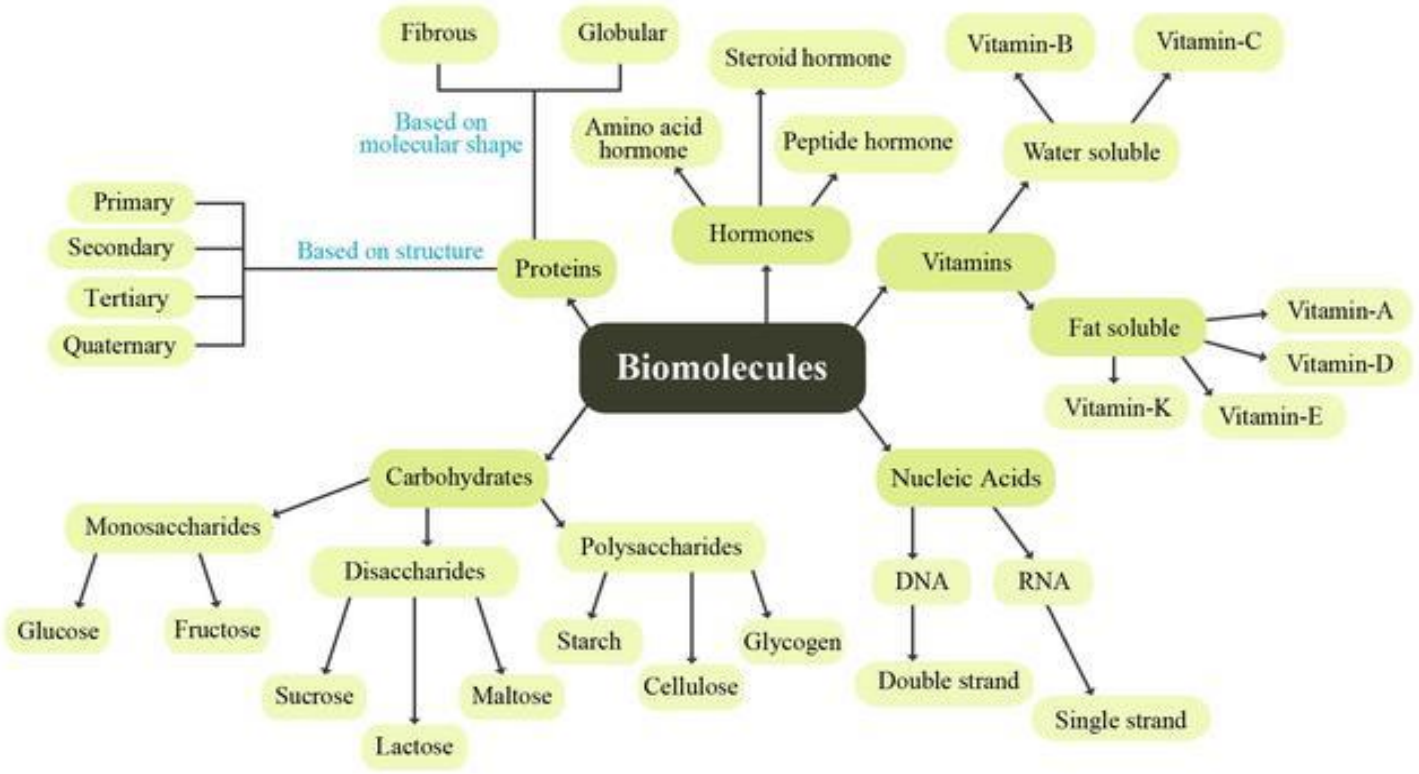


BIOMLOECULES

KEY POINTS	EXPLANATIONS
Monosaccharides	Cannot be hydrolyzed further .eg- glucose, fructose, ribose
Disaccharides	Sucrose (α-D- glucose + β-D-fructose), Maltose(α-D- glucose + α-D- glucose) Lactose(β-D-galactose + β-D-glucose)
Polysaccharides	*Starch* (two components—Amylose and Amylopectin) polymer of α-D- glucose
Amylose	Water soluble , 15-20% of starch.,unbranched chain , C1– C4 glycosidiclinkage.
Amylopectin	Water insoluble , 80-85% of starch.,branched chain polymer, C1–C4 & C1–C6 glycosidic linkage
Cellulose	Straight chain polysaccharide of β -D-glucose units/ joined by C1-C4glycosidic linkage (β-link), not digestible by human / constituent of cell wall of plant cells
Glycogen	Highly branched polymer of α-D- glucose .found in liver, muscles and brain.
reducing sugars	Aldehydic/ ketonic groups free so reduce Fehling's/ Tollens solution and. Eg- maltose and lactose
Non reducing sugars	Aldehydic/ ketonic groups are bonded so can not reduce Fehling's solution and Tollens' reagent. Eg- Sucrose
Anomers.	The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon Such isomers, i.e., α –form and β - form, are called anomers.
Invert sugar	Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.
Glycosidic linkage	Linkage between two monosaccharide through oxygen atom.
Importance of Carbohydrates	Major portion of our food. used as storage molecules as starch in plants and glycogen in animals. Cell wall of bacteria and plants is made up of cellulose. Wood and cloth are cellulose.Provide raw materials for many important industries like textiles, paper, lacquers and breweries.
Essential amino acids	which cannot be synthesised in the body and must be obtained through diet, eg- Valine, Leucine
Nonessential amino acids	which can be synthesised in the body, eg - Glycine, Alanine
zwitter ion.	In aqueous solution, amino acids exist as a dipolar ion known as zwitter ion.
peptide linkage	peptide linkage is an amide linkage formed between –COOH group and –NH2 group of two successive amino acids in peptide chain.
1^0- str. of proteins:	sequence of amino acids in protein.
2^0- str. of proteins:	secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two types of structures viz. α -helix and β - pleated sheet structure.
Tertiary structure of proteins:	Further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular.
Fibrous proteins	Polypeptide chains run parallel, held together by hydrogen and disulphide bonds, fibre– like structure. Water insoluble .Eg- are keratin(in hair, wool, silk) and myosin (present in muscles).
Globular proteins	Chains of polypeptides coil around to give a spherical shape. Water soluble. Eg- Insulin and albumins

Stab.forces2°& 3°	hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
Denaturation of Proteins	When a protein is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. (During denaturation 2° and 3° structures are destroyed but 1º structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk
DNA	pentose sugar (D-2-deoxyribose) + phosphoric acid + nitrogenious bases (A , G , C, T)
RNA	pentose sugar (ribose) + phosphoric acid + nitrogenious bases (A , G , C, U)
Nucleoside / tides	Nucleoside sugar + base Nucleotides sugar + base + phosphate
Phosphodiester link	Linkage between two nucleotides in polynucleotides
Functions of Nucleic Acids	DNA reserve genetic information, maintain the identity of different speciese is capable of self duplication during cell division, synthesizes protein in the cell.

MIND-MAP



QUESTION BANK

I- (MCQ)

1. Which of the following polymer is found in the liver of animals?

   (a) Amylose (b) Cellulose (c) Amylopectin (d) Glycogen

2. The secondary structure of Protein is stabilized by :

   (a) Peptide bonds (b) vander Waals forces (c) Hydrogen bonds(d) Dipole-dipole interactions

3. Nucleic acids are the polymers of:

   a)Nucleosides (b)Nucleotides (c)Bases (d) Sugars

4. DNA and RNA contains four bases each. Which of the following bases is not present in RNA?

   (a) Adenine (b) Uracil(c) Thymine (d) Cytosine

5. The presence or absence of hydroxyl group on which carbon atom of sugar differentiate RNA and DNA

   (a) 2nd (b) 4th (c) 3rd (d) 1st

6. Proteins can be classified in to two types on the basis of their molecular shape i.e. fibrous protein and globular proteins. Examples of fibrous proteins is :

   (a) Insulin (b) Keratin (c) Myoglobin (d) Haemoglobin

7. The reagent used for obtaining osazone derivatives of fructose is

   (a) NH_2OH (b)NH_2-NH_2 (c)NH_2-NHC_6H_5 (d)2,4- DNP

8. The disease resulting from the intake of amino acid deficient diet is:

   (a)kwashiorkar (b)pernicious anaemia (c)PEM (d) haemophilia

9. Keratin present in hair is an example of:

   (a)fibrous protein b) globular protein c) conjugated protein (d)derived protein

10. DNA and RNA differ in:-

    (a)Sugar (b)purines (c)pyrimidines (d)both a) and b)

II-ASSERTION-REASON TYPE

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 (A):** D(+)–Glucose is dextrorotatory in nature.
Reason (R): 'D' represents its dextrorotatory nature.
2. **Assertion (A):** Deoxyribose, $C_5H_{10}O_4$ is not a carbohydrate.
Reason (R): Carbohydrates are optically active polyhydroxy aldehyde or polyhydroxy ketone or substances which give aldehyde or ketone on hydrolysis.
3. **Assertion (A):** Glucose reacts with hydroxylamine to form an oxime and also adds a molecule of hydrogen cyanide to give cyanohydrin.
Reason (R): The carbonyl group is present in the open chain structure of glucose.
4. **Assertion (A):** The two strands of DNA are complementary to each other.
Reason (R): The hydrogen bonds are formed between specific pairs of bases.
5. **Assertion (A):** All naturally occurring α amino acids except glycine are optically active.
Reason (R): Most naturally occurring α amino acids have L-configuration.

III-SHORT ANSWER TYPE-I (2-MARKS)

Q1. Describe what do you understand by primary structure and secondary structure of proteins.
Q2.i)Which of the following is a polysaccharide:Starch, maltose, fructose, glucose.
ii)Write the name of the vitamin responsible for the coagulation of blood.
Q3.i) Glucose on reaction with HI gives n-Hexane. What does it suggest about the structure of glucose.
ii) Give one example each for water-soluble vitamins and fat soluble vitamins.
Q4.i)Write one reaction of D-glucose which cannot be explained by its open chain structure.
ii)What type of linkage is present in nucleic acids?
Q5. i) Explain what is meant by pyranose structure of glucose?
ii) Deficiency of which vitamin causes Scurvy?

IV-SHORT ANSWER TYPE-II (3-MARKS)

Q1. Differentiate between the following:
i) Amylose and Amylopectin ii) Globular protein and Fibrous protein iii) Nucleotide and Nucleoside
Q2. Define the following terms: i)Polysaccharides ii) Denatured protein iii) Vitamins
Q3.i) What are the hydrolysis products of DNA ?
ii) What happens when D-glucose is treated with Bromine water?
iii) What is the effect of denaturation on the structure of protein?
Q4. Write the reactions involved when D-glucose is treated with the following reagents:
i) Br_2 water ii) H_2N-OH iii) $(CH_3CO)_2O$
Q5. i) Write the product when D-glucose is treated conc.HNO_3.
ii) Amino acids show amphoteric behaviour. Why?
iii) Write one difference between α -helix and β -pleated sheet structure of proteins.
Q6.Define: i) Anomers ii) Essential Amino acids iii) Oligosaccharides
Q7.Write the main Structural difference between RNA and DNA. Of the four bases, name those which are common to both DNA and RNA.

V-PASSAGE/CASE STUDY/SOURCE BASED QUESTIONS:-

CASE-1- Read the given passage and answer the questions that follow.
Living system are made up of complex molecules called Biomolecules. Carbohydrate, proteins, enzymes, nucleic acids, lipids, hormones ATP, DNA and RNA play an important role in our daily life. Carbohydrates provide us energy. Protein help in growth and maintenance of body. Nucleic acids, RNA helps in protein synthesis, DNA helps in transfer of genetic characteristics. Fat are source of energy and protect our vital organs.
(a) Why are carbohydrates optically active?

(b) Name two acidic amino acids.
(c) Name a protein which has quarternary structure.
(d) What are products of hydrolysis of fats?
(e) What is role of glycerol in shaving creams?

CASE-2 Read the given passage and answer the questions that follow.

Biomolecules are complex molecules which build up living organisms and required for their growth, maintenance and ability to reproduce. Carbohydrates are polyhydroxy aldehydes and ketones which are major sources of energy. Monosachharides are simple sugars which cannot be hydrolysed. Oligosachharide, on hydrolysis give 2 to 10 molecules of monosachharides. Polysachharides like starch and cellulose on hydrolysis give large number of molecules of glucose a-glucose and b-glucose (Anomers). Proteins are complex nitrogeneous polymers of amino acids connected through peptide bonds. The sequence in which amino acids are linked is called Primary structure. Secondary structures are of 2 types a-helix in globular proteins and b-pleated structure in fibrous proteins involving H-bonds. Tertiary structure has H-bonds, disulphide linkage, ionic bonding and van der Waals' forces. Insulin is hormone for metabolism of glucose, has quarternary structure. Denaturation of protein destroys secondary and tertiary structure, loss of biological activity but primary structure remaining the same.Enzymes are highly specific, work at specific pH, moderate temperature and catalyse biochemical reactions. Hormones perform specific functions and secreated by endocrine glands. Vitamins are essential for healthy body. A, D, E, K are fat soluble vitamins. Vitamin C and B1, B2, B6 are water soluble. B12 is neither water, nor fat soluble. Nucleic acids are polymer of nucleotides. RNA consist of m-RNA, t-RNA, r-RNA. RNA has Adenine, Cytosine, Uracil and Guanine. It helps in protein synthesis. It cannot replicate. DNA contains deoxyribose, A, C, G and Thymine. It transfers genetic characteristics. DNA has double helix structure and undergoes replication.

(a) Name a disachharide which on hydrolysis give glucose and galactose.
(b) What tyhpe of protein is albumin?
(c) Name one non-reducing sugar.
(d) Which one is complementary base of cytosine in one strand of DNA to that in other strand of DNA?
(e) Which linkage by which nucleotide are joined together between 5′ and 3′ atoms of pentose sugar?
(f) Which enzyme can dissolve blood clots to prevent heart attack?

CASE-3. Read the given passage and answer the questions that follow

Carbohydrates are optically active polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis. These work as body fuels and act as a source of energy. These are broadly classified as monosaccharides, disaccharides and polysaccharides.The disaccharides and polysaccharides give molecules of mono-saccharides on hydrolysis.These may be reducing or non-reducing. Reducing sugars reduce Fehling solution and Tollen's reagent. Non-reducing sugars such as sucrose donot reduce Fehling solution and Tollen's reagent. Monosaccharides may be aldoses or ketoses. Among these glucose and fructose are very common. Glucose has one aldehydic group, four 2° alcoholic groups and one 1° alcoholic group while fructose has one keto group, three 2° alcoholic groups and two 1° alcoholic groups.Glucose has pyranose structure and fructose has furanose structure. The monosaccharides in polysaccharides and disaccharides are held together by glycosidic linkages.

The following are multiple choice questions. Choose the most appropriate answer:

i) In which of the following pair, both are reducing sugars?
(a) Glycogen, glucose (b) Galactose, maltose (c) Sucrose, lactose (d) Lactose, maltose
ii) D-Galactose and D-glucose have different configuration of H and OH groups at:
(a) C-2 (b) C-3 (c) C-4 (d) C-5
(iii) Maltose on hydrolysis gives;
(a) Glucose and fructose (b) Glucose and galactose
(c) Glucose and amylose (d) Glucose only
(iv) The number of asymmetric C-atoms in cyclic form of D-glucose is:
(a) 5 (b) 3 (c) 4 (d) 1
(v) The carbohydrate stored in liver of human beings is;
(a) Glucose (b) Glycogen (c) Galactose (d) Amylopectin

<u>VI-LONG ANSWER TYPE-III (5-MARKS)</u>

Q1. a) Write the name of component of starch which is water soluble?
b) Why vitamin C cannot be stored in our body?

c)What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?
d) What type of linkage hold together monomers of DNA ?
e) How nucleosides are differ from nucleotides?
Q2.a) What forces are responsible for the stability of α -helix? Why is it named as **3.6_{13} α -helix** ?
b)What is isoelectric point of amino acids?
c) What do you mean by Native state of protein?

ANSWERS BIOMOLECULES

I ANSWERS OF MCQ;

1-d 2-c 3-b 4-c *5-a 6-b* 7- c 8 –a 9- a 10-d

II-ANSWERS OF ASSERTION-REASON;

1. C 2.D 3.A 4.A 5.B

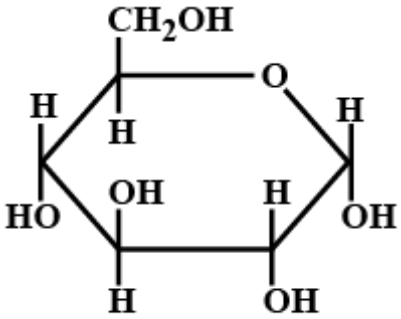
III-ANSWERS OF SHORT ANSWER (TYPE-I)

A1. **Primary structure** : The specific sequence in which the various a-amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein .

Secondary Structure : The conformation which the polypeptide chain assumes as a result of hydrogen bonding is known as secondary structure. The two of secondary structures are α-helix and β-pleated sheet structures.
In α-helix structure, the polypeptide chain forms all the possible hydrogen bonds by twisting into a right-handed screw (helix) with the −NH group of each amino acid residue hydrogen bonded to the >C=O groups of an adjacent turn of the helix. In β-pealed structure. , all peptide chains are stretched out to nearly maximum extension and then laid side by and are held together by hydrogen bonds.
A2. I) Starch ii) Vitamin K
A3. i) Glucose on prolonged heating with HI and red phosphorus gives n-hexane HI (excess)

$$\text{Glucose} \xrightarrow[\Delta]{HI} \underset{(n\text{-Hexane})}{CH_3—CH_2—CH_2—CH_2—CH_2—CH_3}$$

ii) Water soluble vitamin: Vitamin B; Fat soluble vitamin:Vitamin A
A4.i) Despite having aldehydic (-CHO) group. Glucose does not react with NaHSO3 to form addition product
ii) Phosphodiester linkage.
A5.i) The six-membered cyclic structured of glucose is called pyranose structure (a− or b−) in analogy with hetercylic compound pyran.



α-D-(+)-Glucopyranose

ii) Vitamin -C

IVANSWERS OF SHORT ANSWER (TYPE-II)

1.i)

Amylose	Amylopectin
It is a straight-chain polymer of D-glucose units	It is a branched-chain polymer of D-glucose units

Constitutes 20% of starch	Constitutes 80% of starch
It is soluble in water	It is insoluble in water
It contains α-1,4-glycosidic bonds between two glucose units	It contains α-1,4-glycosidic bonds between two glucose unit in the straight chain and α-1,6-glycosidic bonds at the branching

1ii).a: Glycosidic linkage is joint monosaccharide units while peptide linkage is joint amino acid units.
b: Glycosidic linkage is formed by the reaction between aldehyde or ketone group and alcoholic groups while peptide linkage is formed by the reaction between amino acids and carboxyl groups.

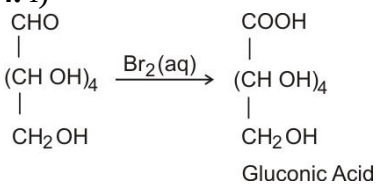
1 iii). a: Fibrous proteins are generally composed of long and narrow strands and have a structural role whereas globular proteins generally have a more compact and rounded shape and have functional roles

b: Fibrous proteins are generally insoluble in water such as keratin, while globular proteins are usually soluble in water such as insulin.
2.i) Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called **polysaccharides.** Some common examples are starch, cellulose, glycogen, gums.
ii) 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 protein**.
iii) organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism are called Vitamins.
3.i)DNA on hydrolysis gives pentose sugar + phosphoric acid + Base(ATGC).
ii) Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.

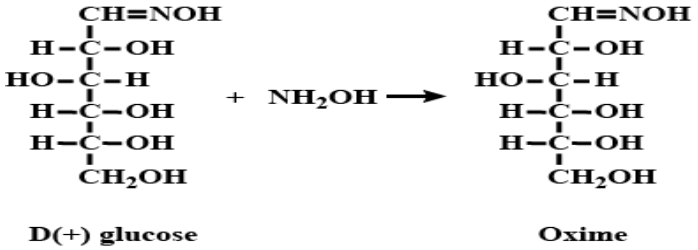
$$\begin{array}{l} CHO \\ (CHOH)_4 \\ CH_2OH \end{array} + (O) \xrightarrow{Br_2,\ water} \begin{array}{l} COOH \\ (CHOH)_4 \\ CH_2OH \end{array}$$

Gluconic acid

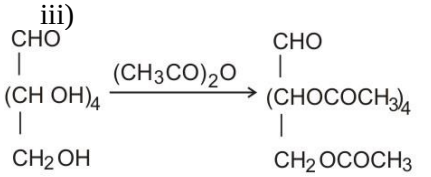
iii) During denaturation 2° and 3° structures are destroyed but 1º structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk.
4. i)



ii)

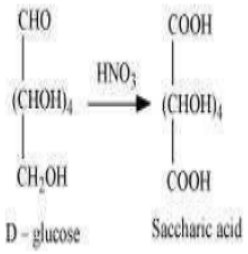


iii)



Glucose penta acetate

5.i)



ii) Amino acids have amino (−NH2) group, basic in nature and accepts a proton and COOH group loses a proton forming a dipolar ion, called the Zwitter ion. In this form, amino acids behave both as acids and bases so they are amphoteric in nature.

iii) In α-helix structure of proteins, the polypeptide chains are stabilized by intramolecular hydrogen bonding whereas β-pealed sheet structure of proteins is stabilized by intermolecular hydrogen bonding.

6.i) The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon Such isomers, i.e., α –form and β -form, are called anomers.

ii) which cannot be synthesised in the body and must be obtained through diet, eg- Valine, Leucine

iii) Oligosaccharides are formed when two or more monosaccharides join together by O-glycosidic bonds. Examples include sucrose, lactose and maltose.

Q7.

DNA	RNA
i)The sugar present in DNA in 2−deoxyribos	i) The sugar present in RNA is D−ribose
ii) DNA has double stranded a-helix structure.	ii) RNA has single a-helix structure
iii)Nitrogenous base **Urasil** is not present.	iii) Nitrogenous base **Thymines** not present.

Common bases present in both DNA and RNA are adenine (A) , guanine (G) and Cytosine (C).

V-ANSWERS OF PASSAGE/CASE STUDY/SOURCE BASED QUESTIONS;

CASE-1. (a) Ans. It is because they contain 'Chiral' carbon atoms.

(b) Ans. Aspartic acid and Glutamic acid.

(c) Ans. Haemoglobin.

(d) Ans. Glycerol and fatty acids.

(e) Ans. Glycerol is hygroscopic in nature, therefore, keep the skin moist.

CASE-2. (a)Ans. Lactose.

(b) Ans. Globular protein.

(c) Ans. Sucrose

(d) Ans. Guanine.

(e) Ans. Phosphodiester linkage.

(f) Ans. Streptokinase

CASE-3: i)d ii) c iii) d iv) b v)c

VI-LONG ANSWER TYPE-III (5-MARKS)

1.a) Amylose b)Vitamin C is water soluble and hence cannot be stored in our body.

c)2-deoxy-D-ribose, thymine and phosphoric acid.

d) Hydrogen bonds

e) The molecule in which one of the nitrogen bases (purines or pyrimidine) is bonded with a sugar molecule is called nucleoside. When the phosphate group is attached to the nucleoside, the compound formed is nucleotide.

2.a)The stability of α -helix structure is due to the hydrogen bonding between -NH- and -CO- Groups of the same polypeptide chains. The α -helix structures is termed as 3.6_{13} because each turn of helix has approximately 3.6 amino acids and a 13 membered ring is formed by hydrogen bonding.

b)The pH at which a particular amino acid does not migrate under the influence of an electric field is called isoelectric point of that amino acid.

c) Native state of protein is the most energetically stable state of a protein. In this state the protein possesses maximum hydrogen bonds and it corresponds to the proteins found in a biological system with a definite configuration and biological activity.

----------x----------x----------x----------x----------

KENDRIYA VIDYALAYA SANGATHAN, RAIPUR REGION

MODEL PAPER 1(2022-23)

CLASS -XII : CHEMISTRY THEORY (043)

MM:70 **Time: 3 hours**

General Instructions:

Read the following instructions carefully.

a) There are 35 questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 short answer questions carrying 3 marks each.

e) SECTION D consists of 2 case- based questions carrying 4 marks each.

f) SECTION E consists of 3 long answer questions carrying 5 marks each.

g) All questions are compulsory.

h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1. Which of the following is most acidic?

a. $(CH_3)_2CHOH$

b. $(CH_3)_3COH$

c. CH_3OH

d. CH_3CH_2OH

2. Which one of the following compounds is more reactive towards SN1 reaction?

a. Methyl chloride

b. Ethyl chloride

c. Isobutyl chloride

d. tert-Butyl chloride

3. $KMnO_4$ is used :

a.as a reducing agent

b. as a corrosion inhibitor

c. as a bleaching agent in textile industry

d. in the preparation of azo compounds

4. The half-life period for zero order reaction is equal to

a. 0.693/k

b. $2k/[R]_0$

c. 2.303/k

d. $[R]_0/2k$

5. Standard electrode potential of three metals X,Y,Z are -1.2 V, +0.5 V and -3.0 V respectively. The reducing power of these metals will be

a. X >Y >Z

b. Y >Z >X

c. Y >X >Z

d. Z >X >Y

6. For the reaction, 2 A +B $\longrightarrow$ Products

Rate=$k[A]^2[B]$. If A is present in large excess, the order of reaction is

a. 3

b. 2

c. 1

d. 0

7. Which of these has highest pKb values?

a. Aniline

b. p-nitroaniline

c. p-toluidine

d. Ammonia

8. The correct IUPAC name of the compound $[Cu(NH_3)_4](NO_3)_2$ is

a. Cuprammonium nitrate

b. Tetraamminecopper(II) dinitrate

c. Tetraamminecopper(II) nitrate

d. Tetraamminecopper(II) dinitrate

9.Which of the following cannot be prepared by Williamson's synthesis?

a. Methoxy benzene

b. tert-butyl methyl ether

c. allyl methyl ether

d. Ditert-butyl ether

10.Carbylamine reaction converts aniline into

a. Nitrobenzene

b. N-methylaniline

c. Benzonitrile

d. Phenyl isocyanide

11. The molar conductivity of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 S cm^2 mol^{-1} respectively. The molar conductivity of CH_3COOH at infinite dilution is:

a. 201.28 S cm^2 mol^{-1}

b. 698.28 S cm^2 mol^{-1}

c. 390.71 S cm^2 mol^{-1}

d. 540.48 S cm^2 mol^{-1}

12. What is the ratio of the rate of decomposition of N_2O_5 to the rate of formation of NO_2 for the given reaction?

$2N_2O_5(g)$ ----------> $4NO_2(g) + O_2(g)$

(a) 1:4 (b) 2:1 (c) 4:1 (d) 1:2

13. Which is not true about a ligand?

a. a ligand can act as Lewis base

b. a ligand can be monodentate or multidentate

c. A monodentate ligand can be a chelating agent

d. A multidentate ligand is a chelating agent

14. Which of the following ketones will not form yellow precipitate of iodoform with $NaOH/I_2$?

a. Pentan-2-one

b. Benzophenone

c. Acetone

d. Acetophenone

Given below are two statements labelled as Assertion (A) and Reason (R) .Select the most appropriate answer from the options given below:

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 but R is true.

15.

Assertion (A): Acetylation with acid chloride is carried out in the presence of base like pyridine.

Reason (R): Base like pyridine neutralises HCl which is formed during the reaction, thereby shifts the equilibrium to the right hand side.

16. **Assertion (A)**: D-(+)-Glucose is dextro rotatory in nature.

Reason (R): 'D' represents its dextrorotatory nature.

Select the most appropriate answer from the options given below:

17.

Assertion(A) : Zirconium and Hafnium have almost similar atomic radii.

Reason(R) : In the group of transition elements, atomic size decreases.

18.

Assertion (A): Aniline does not undergo Friedel Craft's reaction.

Reason (R): $-NH_2$ group on benzene ring shows -R effect.

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

19. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate the activation energy.

20. What happens when D-glucose is treated with the following reagents:

(i) HI (ii) Bromine water ?

OR

Differentiate between the following –

(i) RNA and DNA (ii) Nucleoside and a nucleotide.

21. Explain why

(i) the dipole moment of Chlorobenzene is lower than that of cyclohexyl chloride?

(ii) Alkyl halides, though polar, are immiscible with water?

OR

How the following conversions can be carried out?

i. Propene to Propanol

ii. Toluene to Benzyl alcohol

22. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

23. Write the half-cell reactions taking place in Hydrogen-Oxygen fuel cell.

24.What is the effect of adding a catalyst on-

i. Activation energy, and

ii. Gibb's energy of a reaction?

25. Give one chemical test to distinguish between:

(a) Pentan-2-one and Pentan-3-one (b) Benzaldehyde and Acetophenone.

SECTION-C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

26. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

$C_2H_5ONa + (CH_3)_3 C– Cl \longrightarrow (CH_3)_3 C– OC_2H_5$

(i) Write the IUPAC name of the major product of this reaction?

(ii) Explain giving reason.

(iii) Write a suitable reaction for the preparation of t-butyl ethyl ether.

27. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Explain the hybridisation and geometry of the complex ion?

28. If 1.202 g mL-1 is the density of 20% aqueous KI, determine the following:

(a) Molality of KI (b) Molarity of KI (c) Mole fraction of KI.

29. An aromatic compound 'A'on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

30. Give reasons:

a. n-Butyl bromide has a higher boiling point than t-butyl bromide.
b. Racemic mixture is optically inactive.
c. The presence of nitro group ($-NO_2$) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

OR

Write the main products when
(i) n-butyl chloride is treated with alcoholic KOH.
(ii) 2, 4, 6-trinitrochlorobenzene is subjected to hydrolysis.
(iii) methyl chloride is treated with AgCN.

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31. Proteins are high molecular mass complex biomolecules of amino acid The important proteins required for our body are enzymes, hormones, antibodies, transport proteins, structural proteins, contractile proteins etc. Except for glycine, all o-amino acids have chiral carbon atom and most of them have L-configuration. The amino acids exists as dipolar ion called zwitter ion, in which a proton goes from the carboxyl group to the amino group. A large number of-amino acids are joined by peptide bonds forming polypeptides. The peptides having very large molecular mass (more than 10,000) are called proteins. The structure of proteins is described as primary structure giving sequence of linking of amino acids; secondary structure giving manner in which polypeptide chains are arranged and folded; tertiary structure giving folding, coiling or bonding polypeptide chains producing three dimensional structures and quaternary structure giving arrangement of subunits in an aggregate protein molecule.

(a) Mention the type of linkages responsible for the formation of primary structure of protein.

(b) Amino acids show amphoteric nature. Why?

(c) Name the common types of secondary structure of protein and give one point of difference.

OR

Differentiate between globular protein and fibrous protein.

32. An ideal solution may be defined as the solution which obeys Raoult's law exactly over the entire range of concentration. The solutions for which vapour pressure is either higher or lower than that predicted by Raoult's law are called non-ideal solutions.
Non-ideal solutions can show either positive or negative deviations from Raoult's law depending on whether the A-B interactions in solution are stronger or weaker than A - A and B - B interactions.

Answer the following questions:

(a) Two liquids ‘X’ and ‘Y’ boil at 110°C and 130° C respectively. Which one of the following has higher vapour pressure at 50° C?

(b) When ‘A’ and ‘B’ are mixed the solution becomes warmer and when ‘B’ and ‘C’ are mixed the solution becomes cooler. Which of these solutions will exhibit positive deviation and the negative deviation from Raoult’s law?

(c) Give an example of maximum boiling azeotrope and an example of minimum boiling azeotrope.

OR

The vapour pressure of pure liquids A and B are 450 and 700 mm of Hg respectively,at 350K.Find out the composition of liquid mixture, if total vapour pressure is 600 mm Hg.

SECTION-E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

33. a. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell.

b. Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes.
[Given: Molar mass of Ag = 108 g mol^{-1} 1F = 96,500 C mol^{-1})

OR

a. Why does molar conductivity of an electrolyte solution increase on dilution? Explain.

Calculate e.m.f. of the following cell at 298 K:

$2Cr(s) + 3Fe^{2+}$ (0.1 M) → $2Cr^{3+}$ (0.01 M) + 3 Fe(s)
Given: $E^0(Cr^{3+}|\ Cr) = -0.74$ V $E^0(Fe^{2+}\ |\ Fe) = -0.44$ V

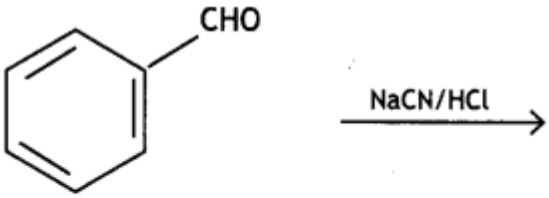
34. a. What is Tollen's reagent? Explain one of it's use.

b. Write chemical equations for the following reactions:
(i) Propanone is treated with dilute $Ba(OH)_2$.
(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl
(iii) Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$.

OR

a. Illustrate the following name reaction giving a suitable example:
(i) Clemmensen reduction
(ii) Aldol condensation

b. Complete the following reactions:

(i) 

(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

(iii) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2/\text{ Red } P_4}$

35.(a)When chromite ore $FeCr_2O_4$ is fused, with NaOH in presence of air, a yellow-coloured compound (A) is obtained, which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms an orange coloured crystalline compound (C).
(i) Write the formulae of the compounds (A), (B), and (C).
(ii) Write one use of the compound (C).
(b) Complete the following chemical equations:
(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O$ →
(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+$ →

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CHEMISTRY MODEL PAPER-1								
S. NO	CHAPTER	MCQ	A/R	VSA1	SA1	CASE BASED	LA	TOTAL WT
		1 MARKS	1 MARKS	2 MARKS	3 MARKS	4 MARKS	5 MARKS	
1	Solution				3(1)	4(1)		7(2)
2	Electrochemistry	2(2)		2(1)			5(1)	9(4)
3	Chemical kinetics	3(3)		4(2)				7(5)
4	d-and f-block Elements	1(1)	1(1)				5(1)	7(3)
5	Coordination compounds	2(2)		2(1)	3(1)			7(4)
6	Haloalkanes and Haloarenes	1(1)		2(1)	3(1)			6(3)
7	Alcohols, phenols and ethers	2(2)	1(1)		3(1)			6(4)
8	Aldehydes, Ketones and Carboxylic Acids	1(1)		2(1)			5(1)	8(3)
9	Amines	2(2)	1(1)		3(1)			6(4)
10	Biomolecules		1(1)	2(1)		4(1)		7(3)
		14(14)	4(4)	14(7)	15(5)	8(2)	15(3)	70(35)

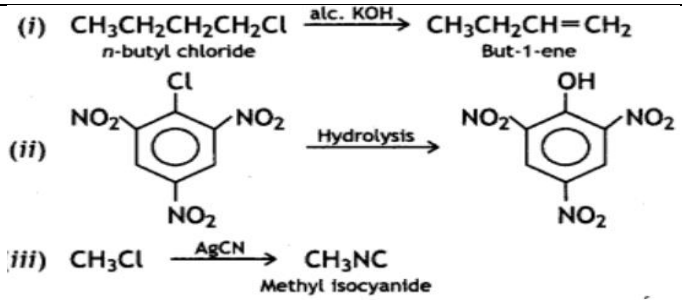
MODEL PAPER (2022-23)

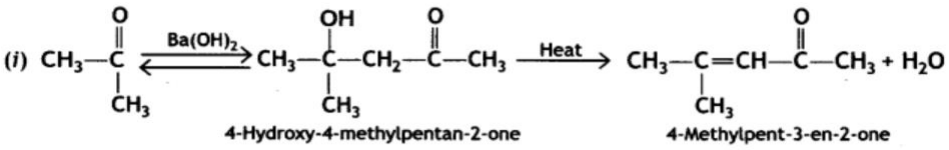
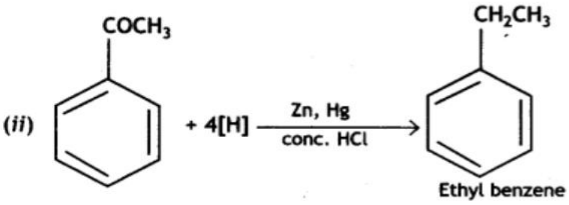
CHEMISTRY THEORY (043)

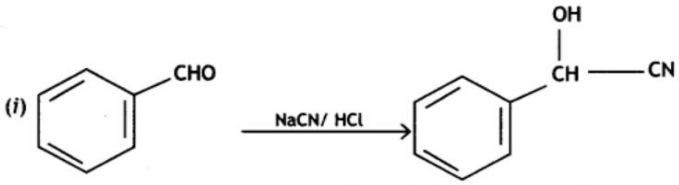
MARKING SCHEME

A.NO	EXPECTED ANSWER	VALUE POINTS
	SECTION-A	
1	c. CH_3OH	1
2	d. tert-Butyl chloride	1
3	c. as a bleaching agent in textile industry	1
4	d. $[R]_0/2k$	1
5	d. Z >X >Y	1
6	c. 1	1
7	b. p-nitroaniline	1
8	c. Tetraamminecopper(II) nitrate	1
9	b. tert-butyl methyl ether	1
10	d. Phenyl isocyanide	1
11	c. 390.71 S cm^2 mol^{-1}	1
12	d. 1:2	1
13	c. A monodentate ligand can be a chelating agent	1
14	b. Benzophenone	1
15	a. Both A and R are true and R is the correct explanation of A	1
16	c. A is true but R is false.	1
17	c. A is true but R is false.	1
18	c. A is true but R is false.	1
	SECTION-B	

19	$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$ We get: $\log \frac{2k}{k} = \frac{E_a}{2.303\times8.314}\left[\frac{308-298}{308\times298}\right]$ $\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{10}{308\times298}\right]$ $\therefore E_a = \frac{\log 2\times2.303\times8.314\times308\times298}{10}$ $= 52897.78\ Jmol^{-1}$ $= 52.9\ kJmol^{-1}$	**2**
20	Reaction to be given for each(i)n-hexane formed (ii) Gluconic acid formed OR Any two differences for each.	**1+1**
21	**(i)** in chloro benzene C-Cl bond is sp^2 hybridised where as in cyclohexyl chloride the C−Cl bond is Sp^3 Hybridised . As sp^2 has more s character and more electronegative than sp^3 Chlorobenzene is less polar than cyclohexyl chloride. **(ii)** Alkyl halides being less polar cannot break the H-bonds present in water.	**1+1**
22	i.By hydroboration-oxidation method OR anti-Makonikov's addition of HBr followed by reaction with KOH(aq) ii.By Chlorination in presence of light, followed by reaction with NaOH(aq)	**1+1**
23	Anode:$2H_2(g) + 4.OH^-(aq) \longrightarrow 4H_2O + 4e^-$ Cathode: $O_2(g) + 2H_2O(l) + 4e- \longrightarrow 4.OH^-(aq)$	**1+1**
24	i. Catalyst lowers the activation energy of the reactants is reduced ii.Catalyst does not change the Gibb's energy of the reaction	**1+1**
25	Any one chemical test for each, giving reaction.	**1+1**
	SECTION-C	
26	Ans. (i) $(CH_3)_3C–O - Na^+ + CH_3CH_2Cl \longrightarrow (CH_3)_2C = CH_2$ (ii)The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus, elimination reaction predominates over substitution. (iii) $(CH_3)_3C–O - Na^+ + CH_3CH_2Cl \longrightarrow (CH_3)_3C – OC_2H_5$	**1+1+1**
27	Oxidation no. Of Mn and its valence confg. Explanation of sp3 hybridisation and reasoning its tetrahedral geometry	**1** **2**
28	(a) 1.506 m (b) 1.45 M (c) 0.0263	**1+1+1**
29	A = C_6H_5COOH, benzoic acid B = $C_6H_5CONH_2$, benzamide C = $C_6H_5NH_2$, aniline (writing reaction is compulsory)	**1** **1** **1**
30	a. n-Butyl bromide has a higher boiling point than f-butyl bromide because it has a larger surface area and hence has more Van der Waals forces. b. Rotation due to one enantiomer is cancelled by another enantiomer. c. The presence of nitro group ($-NO_2$) at ortho and para positions withdraws the electron density from the benzene ring and thus facilitates the attack of nucleophiles. OR	**1** **1** **1**

		
	SECTION-D	
31	(a) Peptide linkage (b) In aqueous solution, the carboxyl group of an amino acid may lose a proton and the amino group can be given a proton to give it a dipolar ion which is referred to as zwitter ion. Thus, in zwitter ionic form, the amino acid can act in both a way as an acid and as a base. (c) 1 example of alpha helix and 1 example of beta pleated to be given	**1+1+2**
32	(a) X has higher vapour pressure (b) Solution of A & B show negative deviation and solution of C & D show positive deviation. (c) 1 example each. OR Use the formula of Raoult's law$$ 600 = (450–700)XA + 700 250XA = 100 $XA = \frac{100}{250} = 0.4$ Use formula XB = 1 − XA Substitute the values we get, XB = 1−0.4 = 0.6 use formula PA = PoA × XA = 450 × 0.4 = 180mm of Hg PB = PoB × XB = 700 × 0.6 = 420mm of Hg	**1+1+2**
	SECTION-E	
33	**a.** Lead storage battery is used in inverters. At Anode:$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ At Cathode:$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$ **b.** Q = I × t …(Charge = Current ∝ Time) . = 2 × 15 × 60 = 1800 C ∵ 96500 C deposit Ag = 108 g ∴ 1800 C deposit Ag = 10896500 × 1800 = 2.0145 g **OR**	**2+3**

	a. Explanation with reason and graph **b** $E_{cell} = ?$ $E^0_{cell} = E^0_{cathode} - E^0_{anode}$ $= (-0.44) - (-0.74)$ $\therefore \quad = -0.44 + 0.74 = +0.30\ V$ Using Nernst equation: $E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$ $= 0.30 - \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.1)^3}$ $= 0.30 - 0.00985 \log \frac{0.0001}{0.001}$ $= 0.30 - 0.00985 \log \left(\frac{1}{10}\right)$ $= 0.30 - 0.00985 (\log 1 - \log 10)$ $= 0.30 - 0.00985 (0 - 1) = 0.30 + 0.00985$ $\therefore \quad E_{cell} = \mathbf{0.3098\ V}$	
34	**a.** Ammonical $AgNO_3$ solution. One use-For distinguishing aldehydes and ketones **b.**   (iii) $C_6H_5COCl + H_2 \xrightarrow[BaSo_4]{Pd} C_6H_5CHO + HCl$ OR a. Each name reaction with example	**2+3**

	b. (i)  Benzaldehyde cyanohydrin (ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow 2CH_3-\underset{\underset{O}{\|}}{C}-CH_2C_6C_5 + CdCl_2$ (iii) $CH_3-\overset{\overset{CH_3}{\|}}{CH}-COOH \xrightarrow[(ii)\ H_2O]{(i)\ Br_2/red\ p_4} CH_3-\overset{\overset{CH_3}{\|}}{\underset{\underset{Br}{\|}}{C}}-COOH$	
35	a.(i) $4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow \underset{\substack{(A)\\ \text{Yellow coloured}}}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$ $2Na_2CrO_4 + H_2SO_4 \rightarrow \underset{(B)}{Na_2Cr_2O_7} + H_2O + Na_2SO_4$ $Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{(C)}{K_2Cr_2O_7} + 2NaCl$ (ii) Potassium dichromate (C) is used as a powerful oxidizing agent in redox titrations in the laboratories. b.(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$ (ii) $Cr_2O_7^{\ 2+} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr3+ + 3Sn^{4+} + 7H_2O$	**3+2**

KENDRIYA VIDYALAYA SANGATHAN, REGIONAL OFFICE, RAIPUR
MODEL PAPER-II 2022-23
CLASS: XII
SUBJECT: Chemistry (043)

TIME: 03 HOURS **MAX.MARKS: 70**

General Instructions:

Read the following instructions carefully.

a) There are 35 questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 short answer questions carrying 3 marks each.

e) SECTION D consists of 2 case- based questions carrying 4 marks each.

f) SECTION E consists of 3 long answer questions carrying 5 marks each.

g) All questions are compulsory.

h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section

1. A hydrocarbon C_5H_{12} gives only one mono-chlorination product on photochemical chlorination. Identify the hydrocarbon.

a. Cyclopentane b. n-Pentane

c. 2, 2 dimethyl Propane d. 2-methyl Butane

2.Phenol reacts with bromine in CS_2 at low temperature to give

a. m-bromophenol b. o-and p-bromophenol

c. p-bromophenol d.2,4,6-tribromophenol

3.When $KMn0_4$ acts as oxidising agent in alkaline medium, the oxidation number of Mn decreases by

a. 1 b. 2 c. 3 d. 5.

4.For a certain redox reaction, E° is positive. This means that

a. ΔG° is positive, K is greater than 1

b. ΔG° is positive, K is less than 1

c. ΔG° is negative, K is greater than 1

d. ΔG° is negative, K is less than 1

5.For a chemical reaction, X + 2Y → Z, if the rate of appearance of Z is 0.50 moles per litre per hour, then the rate of disappearance of Y is

a. 0.5 mol L^{-1} hr^{-1} b. 1.0 mol L^{-1} hr^{-1}

c. 0.25 mol L^{-1} hr^{-1} d. cannot be predicted

6. Which of the following is formed when an alkyl primary amine reacts with nitrous acid?

a. Alkyl nitrite b. Secondary amine

c. Nitroalkane d. Alcohol

7. For the reaction, A +2B → AB_2, the order w.r.t. reactant A is 2 and w.r.t. reactant B is zero. What will be change in rate of reaction if the concentration of A is doubled and B is halved?

a. increases four times b. decreases four times

c. increases two times d. no change

8.According to CFT, how many unpaired electrons are there in a strong ligand field of iron (II) octahedral complex?

a.0 b. 1 c. 2 d.4

9.IUPAC name of m-cresol is _____.

a. 3-methylphenol b. 3-chlorophenol

c. 3-methoxyphenol d. benzene-1,3-diol

10.Hoffmann Bromamide Degradation reaction is shown by _____.

a. $ArNH_2$ b. $ArCONH_2$ c. $ArNO_2$ d. $ArCH_2NH_2$

11.Clemmensen reduction takes place in the presence of

a. Zn-Hg with HCl b. Glycol with KOH

c. H_2 and Pt as catalyst d. $LiAlH_4$

12.The average rate and instantaneous rate of a reaction are equal

a. At the start b. At the end

c. In the middle d. When two rates have a time interval equal to zero

13.When 1 mol $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 mol of AgCl are obtained.

The formula of the complex is :

a. $[CrCl_3(H_2O)_3]\cdot 3H_2O$ b. $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$

c. $[Cr\ Cl(H_2O)_5]Cl_2 \cdot H_2O$ d. $[Cr(H2O)_6]Cl_3$

14.What will happen during the electrolysis of aqueous solution of CuSO4 by using platinum electrodes?

a. Copper will deposit at cathode. b. Copper will deposit at anode

c. Oxygen will be released at cathode. d. Copper will dissolve at anode.

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

Assertion: Bond angle in ethers is slightly less than the tetrahedral angle.

Reason: There is a repulsion between the two bulky (—R) groups.

Select the most appropriate answer from the options given below:

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 but R is true.

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

Assertion : Sucrose is called an invert sugar.

Reason : On hydrolysis, sucrose bring the change in the sign of rotation from dextro (+) to laevo(–).

Select the most appropriate answer from the options given below:

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 but R is true.

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

Assertion: Cu^{2+} iodide is not known.

Reason: Cu^{2+} oxidises I– to iodine.

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 but R is true.

18.Assertion: The product of Hoffmann's bromamide reaction is given by primary amines.

Reason: Primary amines are more basic than secondary amines.

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 but R is true.

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

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

20.What happens when D-glucose is treated with the following reagents?

a. HI b. Acetic anhydride

OR

Give reasons:

a. Vitamin C is not stored in our body?

b. Despite having the aldehyde group, glucose does not give 2, 4-DNP test or Schiff's test.

21. Account for the following:

a. The C-Cl bond length in chlorobenzene is shorter than that in $CH_3 – Cl$

b. Chloroform is stored in dark-coloured bottles

OR

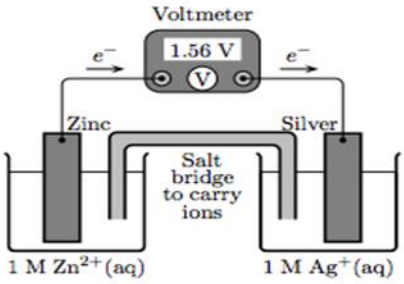
a. Why does p-dichlorobenzene have a higher m.p. than its o- and m-isomer?

b. Why is (±)Butan-2-ol optically inactive?

22. Identify the optically active compounds from the following and draw the structure of two enantiomers?

(a) $[Co(en)_3]^{3+}$ (b) trans-$[Co(en)_2Cl_2]^+$

(c) cis-$[Co(en)_2Cl_2]^+$ (d) $[Cr(NH_3)_5Cl]$



23. Consider Fig. and answer the questions given below

1. How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?
2. What is the role of salt bridge in this cell?

24. For the reaction: $2A + B \rightarrow A_2B$ the rate law is $=k[A][B]^2$ with k = $\mathbf{2.0 \times 10^{-6}\ mol^{-2}\ L^2\ s^{-1}}$.

If the initial concentration of [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1} Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

25.Describe how the following conversions are carried out:

a. Toluene to benzoic acid

b. Bromobenzene to benzoic acid

SECTION C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

26. Write the equations for the following reaction:

a. Phenol is treated with $CHCl_3$ in presence of NaOH

b. Propene is treated with Diborane in presence of Hydrogen peroxide and aqueous NaOH.

c. Acetone is treated with Methyl Magnesium Bromide.

27.Using Valence bond theory, explain the following in relation to the paramagnetic complex

$[Fe(CN)_6]^{3-}$

a. type of hybridization

b. magnetic moment value

c. type of complex – inner, outer orbital complex

28. Answer the following

a. Components of a binary mixture of two liquids A and B were being separated by distillation. After some time, separation of components stopped and composition of vapour phase became same as that of liquid phase. Both the components started coming in the distillate. Explain why does this happen?

b. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C

29.Give reasons for any 3 of the following observations:

a. Aniline is acetylated before nitration reaction.

b. pKb of aniline is lower than the m-nitroaniline.

c. Primary amine on treatment with benzene sulphonyl chloride forms a product which is soluble in NaOH however secondary amine gives product which is insoluble in NaOH.

d. Aniline does not react with methyl chloride in the presence of anhydrous $AlCl_3$ catalyst

30. Predict the major alkene that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol?

a. 1-Bromo-1-methylcyclohexane b. 2-Chloro-2-methylbutane

c. 2,2,3-Trimethyl-3-bromopentane.

OR

Write the equations for the preparation of 1-iodobutane from

a. 1-butanol b. 1-chlorobutane c. but-1-ene.

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow

31.Monosaccharides containing an aldehyde group are called aldoses while those containing a keto group are called ketoses. All monosaccharides containing five and six carbon atoms have cyclic structures, furanose (five-membered) and pyranose (six-membered). During ring formation, C1 aldoses and C2 in ketoses becomes chiral and hence all these monosaccharides exist in two forms called the α-anomer and β-anomer while C1 and C2 are called glycosidic or anomeric carbon atoms. In contrast, stereoisomers, which differ in configuration at any other chiral carbon other than the glycosidic carbon are called epimers. Two molecules of the same or different monosaccharides combine together through glycosidic linkage to form disaccharides

a**.** Which of the following compounds show furanose structures?

i) Glucose ii) Fructose iii) Galactose iv) Maltose

b. In disaccharides, the linkage connecting monosaccharide units is called

i) Glycogen linkage ii) Nucleoside linkage iii) Glycosidic linkage iv) Peptide linkage.

c. Under what conditions glucose is converted to gluconic and saccharic acid? Explain using chemical equation

OR

The two strands in DNA are not identical but are complementary. Explain

32. Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapor pressure and the added solute particles affect the formation of pure

solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high-quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapor pressure lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity.

A.When a non -volatile solid is added to pure water it will:

a. boil above 100°C and freeze above 0°C

b. boil below 100°C and freeze above 0°C

c. boil above 100°C and freeze below 0°C

d. boil below 100°C and freeze below 0°C

B.K_H value for Ar(g), CO2(g), HCHO(g) and CH4(g) are 40.39, 1.67, 1.83 x 10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.

C. H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, Calculate Henry's law constant.

OR

Calculate molality of KI if the density of 20% (mass/mass) aqueous KI is 1.202 gm/ml

Given Molar mass of KI = 39 + 127 = 166 gm/mol

SECTION E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

33. a) Which of the following compounds would undergo Aldol Condensation and why?

i) Methanal ii) Propanone iii) Benzophenone iv) Benzaldehyde

b) Explain :- i) HVZ reaction ii)Wolf-kishner reaction iii) Rosemnund's reaction

34. (a) Answer the following:

i) Which cell is used in hearing aids?

ii) Which cell was used in Apollo Space Programme?

(b) The conductivity of 0.001 M acetic acid solution is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/ mol.

OR

(a) i) How many coulombs are required to reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}

ii) Predict the products of electrolysis of Dilute Sulphuric acid solution using platinum electrodes?

(b) Calculate the EMF of the following cell at 25° C

Ag(s) /Ag^+ (10^{-3} M)// Cu^{2+}(10^{-1} M) /Cu(s) Given E^0 cell = + 0.46V

35. Assign reason for the following

i. The enthalpies of atomization of transition metals are high.

ii. The transition metals and many of their compounds act as catalysts.

iii. From element to element, the actinoid contraction is greater than lanthanoid contraction.

iv. The E^0 value for Mn^{3+} /Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}

v. Scandium (Z = 21) does not exhibit variable oxidation states and yet it is regarded as a transition element.

OR

a) Name an element of lanthanoid series which is well known to shown +4 oxidation state. Is it a strong oxidising agent or reducing agent?

b) Write the chemical equations for the preparation of $KMnO_4$ from MnO_2.

c) Write the ionic equation showing

i) The oxidation of Fe(II) salt by acidified dichromate solution.

ii) The oxidation of Iodides by $KMnO_4$ in alkaline medium

KENDRIYA VIDYALAYA SANGATHAN, RAIPUR REGION

SAMPLE PAPER-II 2022-23

CLASS-XII **BLUE PRINT** **SUB: - Chemistry**

S.NO.e	UNIT	CASE BASED QUESTIONS 1X4=4	Objective Questions 1MARK	SAI 2MARKS	SAII 3MARKS	LA 5MARKS	TOTAL
	SOLUTION	1(4)	0	0	3(1)	0	7
	ELECTROCHEMISTRY	0	1(2)	2(1)	0	5(1)	9
	CHEMICAL KINETICS	0	1(3)	2(2)	0	0	7
	D & F BLOCK ELEMENTS	0	1(2)	0	0	5(1)	7
	COORDINATION CHEMISTRY	0	1(2)	2(1)	3(1)	0	7
	HALOALKANE & HALOARENES	0	1(1)	2(1)	3(1)	0	6
	ALCOHOL, PHENOL & ETHERS	0	1(3)	0	3(1)	0	6
	ALDEHYDES,KETONES & CARBOXYLIC ACID	0	1(1)	2(1)	0	5(1)	8
	AMINES	0	1(3)		3(1)	0	6
	BIOMOLECULES	1(4)	1(1)	2(1)	0	0	7
	TOTAL	2(8)	18(18)	7(14)	5(15)	3(15)	35(70)

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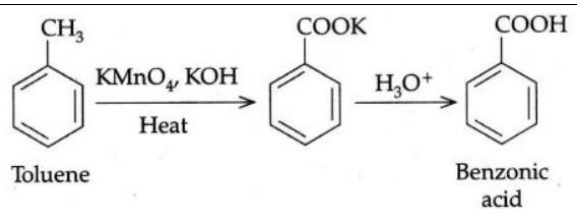
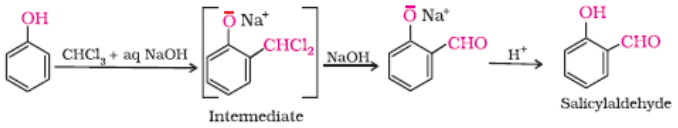
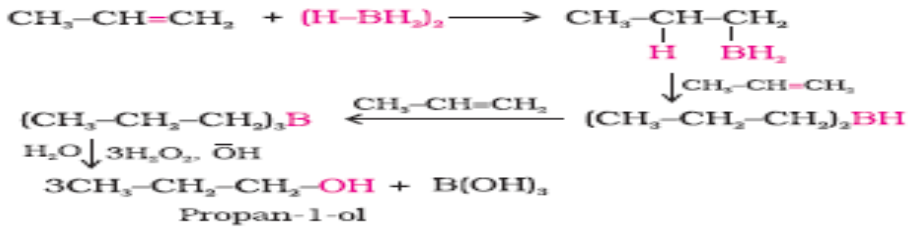
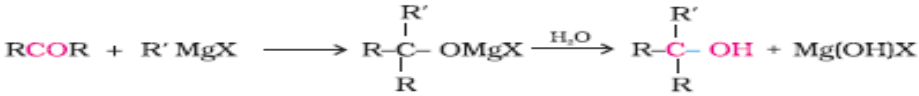
MARKING SCHEME

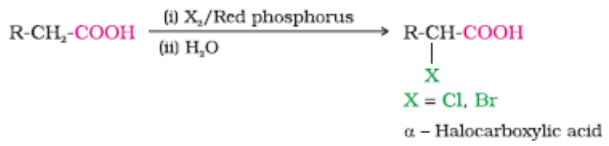
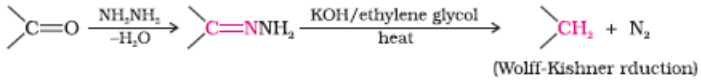
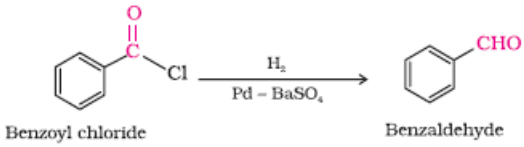
SAMPLE PAPER II

CHEMISTRY CLASS – XII

Q. No.	VALUE POINTS	Marks
	SECTION- A	
1	c. 2, 2 dimethyl Propane	1
2	b. o-and p-bromophenol	1
3	c. 3	1
4	c. ΔG° is negative, K is greater than 1	1
5	b. 1.0 mol L-1 hr-1	1
6	d. Alcohol	1
7	a. increases four times	1
8	a.0	1
9	a. 3-methylphenol	1
10	b. ArCONH2	1
11	a. Zn-Hg with HCl	1
12	d. When two rates have a time interval equal to zero	1
13	d. $[Cr(H_2O)_6]Cl_3$	1
14	a. Copper will deposit at cathode.	1
15	D	1
16	A	1
17	A	1
18	C	1
19	$t_{99\%} = \frac{2.303}{K} \log\left(\frac{100}{1}\right) = \frac{2.303}{K} \log 10^2$ $= \frac{2.303 \times 2}{K}$ $t_{90\%} = \frac{2.303}{K} \log\left(\frac{10}{1}\right) = \frac{2.303}{K} \log 10$ $= \frac{2.303}{K}$ -(2) $\frac{(1)}{(2)} = \frac{t_{99\%}}{t_{90\%}} = \frac{2}{1}$ $\therefore t_{99\%} = 2\, t_{90\%}$ hence proved.	1 1
20	D-Glucose is treated with (a) HI – n Hexane is formed	1+1

	(b) with acidic anhydride - Glucose pentaacetate is formed OR (a) Because it is water soluble and is excreted out with sweat and urine. (b) Due to internal cycling, there is no free aldehydic group	
21	a. SP^2 hybridisation of chlorobenzene /partial double bond character b. Formation of $COCl_2$ i.e Phosgene OR a. p -Dichlorobenzene is more symmetrical than o -and m -isomers. For this reason, it fits more closely than o -and m -isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p -dichlorobenzene b. it is a racemic mixture	1+1
22.	(a) $[Co(en)_3]^{3+}$ & (c) cis-$[Co(en)_2Cl_2]^+$	1+1
23.	a. The Concentration of Zn^{2+} ions will increase and concentration of Ag + ions will decrease due to conversion in oxidized and reduced forms. b. completes the circuit & maintains neutrality of the cell	1+1
24.	Initial rate = $k[A][B]^2$ But [A] = 0.1 M, [B] = 0.2 M and k = 2.0×10^{-6} mol^{-2} L^2 s^{-1} Initial rate 2.0×10^{-6} mol^{-2} L^2 s^{-1} × 0.1 M × $(0.2\ M)^2$ = 8×10^{-9} M s^{-1} From the equation $2A + B \rightarrow A_2B$ it is clear that when 2 moles of A are used then 1 mol of B is used in the same time. Therefore, when A has been reduced to 0.06 M , 0.04 M of A and hence 0.02 M of B have reacted. Thus, Concentration of A left = [A] = 0.06 M. Concentration of B left = [B] = (0.2 M – 0.02 M) = 0.18 M Rate = $k[A][B]^2$ = 2.0×10^{-6} mol^{-2} L^2 s^{-1} × 0.06 M × $(0.18\ M)^2$ = 3.89×10^{-9} M s^{-1}	1 1
25.	a.  b. 	1 1
26.	a.Salicylaldehyde  	1+1+1

	b.Propan-1-ol  c. Tertiary butyl alcohol,R=Methyl  	
27.	d^2sp^3, magnetic moment **μ** =1.732BM , inner orbital complex	1+2
28.	a. due to formation of azeotropic mixture b. $\pi = \frac{n}{V}RT$ $= \frac{1}{185000} \times \frac{1}{0.45} \times 8.314 \times 10^3 \times 310K$ $\pi = 30.95Pa$	1+2
29.	**ANY THREE-** a. Aniline is acetylated, before nitration reaction in order to avoid formation of tarry oxidation products and protecting the amino group, so that p -nitro derivative can be obtained as major product. b. pKb of aniline is lower than the m-nitro aniline because basic strength of aniline is more that m-nitroaniline. pkb value is inversely proportional to basic strength. Presence of Electron withdrawing group decrease basic strength. c. The reaction of benzene sulphonyl chloride with secondary amine yields N, N-alkyl benzene sulphonamide. The product N,N-alkyl benzene sulphonamide has no acidic hydrogen. So, the product N-alkyl benzene sulphonamide cannot form hydrogen bonding with alkali and hence insoluble in alkali. d. Due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.	1+1+1
30.	(a)1-methyl cyclo hex-1 ene (b) 2-methyl but-2-ene (c) 3,4,4 trimethyl pent-2 ene OR Butane 1 ol $\xrightarrow{Red\ P4/I2}$ 1-iodo butane	1+1+1

	1 Chlorobutane $\xrightarrow{NaI+dry\ acetone/}$ 1-iodo butane But-1-ene $+HBr + peroxide \xrightarrow{NaI+dry\ acetone}$ 1-iodo butane	
31.	a. ii b. iii c. Reaction with Bromine water & nitric acid	1+1+2
32.	1) c 2). Higher the value of the K_H the lower is the solubility of a gas in the liquid. Hence the order of increasing solubility will be $Ar<CO_2<CH_4<HCHO$. 1kg of solvent contains $\frac{1000}{18} = 55.55$ moles. Mole fraction of H_2S is $\frac{0.195}{0.195+55.55} = \frac{0.195}{55.475} = 0.0035$ 3) Pressure of $H_2S = \frac{0.987}{0.0355} = 282bar$ (at STP pressure is 0.987bar.) OR (a) Molar mass of KI = 39 + 127 = 166 20% (mass/mass) aqueous solution of KI means 20 g of KI is present in 100 g of solution. That is, 20 g of KI is present in (100 - 20) g of water = 80 g of water molality= 1.506 m = 1.51 m (approximately	1+1+2
33.	a) Propanone, as it contains alpha hydrogen b)i)  ii)  iii)  	2+ 1+1+1

34.	a)(i) Mercury cell is used in hearing aids. (ii) Fuel cells was used in Apollo space programme. b) $M = 0.001\ mol/L = \frac{0.001}{10^{-3}}\ mol/cm^3$ $\therefore \lambda = 5 \times 10^{-5} \times \frac{1000}{10^{-3}} = 5 \times 10^{6} \times 10^{-5}$ $\Longrightarrow \lambda = 50$ Degree of dissociation, $\alpha = \frac{50}{390.5} = 0.128$ $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $c - c\alpha \qquad c\alpha \qquad c\alpha$ $K_a = \frac{c^2\alpha^2}{c - c\alpha} = c\alpha^2 \quad [c - c\alpha \approx c]$ $\therefore K_a = 10^{-3} \times (0.128)^2$ $\Longrightarrow K_a = 16.38 \times 10^{-6}$ Or a)i) From the reaction, 1 mol of $Cr_2O_7^{2-}$ require 6F $= 6 \times 96500 = 579000\ C$ $\therefore$ 579000 C of electricity are required for reduction of $Cr_2O_7^{2-}$ to Cr^{3+} ii) $H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$ $H_2O \rightleftharpoons H^+ + OH^-$ At cathode: $H^+ + e^- \longrightarrow H,$ $H + H \longrightarrow H_2(g)$ At Anode: $OH^- \longrightarrow OH + e^-$ $4OH \longrightarrow 2H_2O + O_2(g)$ Thus, H_2 gas is liberated at the cathode and O_2 gas at the anode. iii) $E^0_{cell} = +0.46v$ $E_{cell} = 0.46V - \frac{0.0591}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]}$ $E_{cell} = 0.46V - \frac{0.0591}{2}\log\frac{[10^{-3}]^2}{[10^{-1}]}$ $E_{cell} = +0.61V$ Thus the Emf of the reaction is +0.61V	1+1+3

35.	a. Strong metallic bonds b. surface area & ability to form complexes c. poorer shielding effect of 5f subshell d High third ionisation enthalpy. e. because of the presence of incomplete d-orbital (3d 1 4s 2) in its ground state. Or 1.Ce (Z = 58) Ce = 4f 1 5d 1 6s 2. It is a strong oxidising agent. ⇒ Formation of Ce 4+ is favoured because its noble gas configuration, but it is a strong oxidant due to the common +3 O.S 2.Correct equation 3.Correct balanced chemical reaction	1+1+1+1+1 1+2+2

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MODEL PAPER 3 RAIPUR RESION

CHEMISTRY THEORY (043)

MM:70 Time: 3 hours

General Instructions: Read the following instructions carefully.

a) There are 35 questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 short answer questions carrying 3 marks each.

e) SECTION D consists of 2 case- based questions carrying 4 marks each.

f) SECTION E consists of 3 long answer questions carrying 5 marks each.

g) All questions are compulsory.

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

Q1.The molar conductance of Ba^{2+} and Cl^{-} are respectively 127 and 76 ohm^{-1} cm^{-1} at infinite dilution. The equivalent conductance of $BaCl_2$ at infinite dilution will be

a. 139.5
b. 203
c. 279
d. 101.5

Q2. For a certain redox reaction, E° is positive. This means that
(a) ΔG° is positive, K is greater than 1
(b) ΔG° is positive, K is less than 1
(c) ΔG° is negative, K is greater than 1
(d) ΔG° is negative, K is less than 1

Q3.In the reaction $2A + B \rightarrow A_2B$ Rate = $k[A]^2[B]$, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will

a. increase 2 times
b. increase 4 times
c. decrease 2 times
d. remain the same

Q4.A catalyst alters, which of the following in a chemical reaction?

a. Entropy
b. Enthalpy
c. Internal energy
d. Activation energy

Q5. Which of the following isaffected on adding catalyst in a reaction
(a) ΔH (b) E_a (c) ΔG (d) K_c
Q6. Which of the following ions is coloured in aqueous solution?
(a) Ti^{4+}(b) Sc^{3+}(c) Cu^{2+} (d) Zn^{2+}

Q7. Which of the following will not give test for Cl^- with $AgNO_3$(aq) at 25°C?
(a) $COCl_3.5NH_3$
(b) $COCl_3.6NH_3$
(c) $COCl_3.3NH_3$
(d) $COCl_3.4NH_3$

Q8. The oxidation state of nickel in |($Ni(CO_4)$| is
(a) 1
(b) 0
(c) 2
(d) 3

Q9.Which of the following will not convert ethyl alcohol in to ethyl chloride?
a) PCl_5 (b) NaCl (c) $SOCl_2$ (d) $HCl/ZnCl_2$

Q10. Which of the following alcohols gives 2-butenc on dehydration byconc. H_2SO_4?
(a) 2-methyl propene-2-ol
(b) 2-methyl 1 -propanol
(c) Butane-2-ol
(d) Butane 1-ol

Question 11.Order of esterification of alcohols are
(a) 3° > 1° > 2°
(b) 2°> 3° > 1°
(c) 1 ° > 2° > 3°
(d) None of these

Q12. **The reaction of methanal with an excess of CH_3MgI followed by hydrolysis gives**

a. ethanol
b. n-propyl alcohol
c. propanal
d. isopropyl alcohol

Q13. When acetamide is converted to methylamine, what is the name of the reaction?
a) Friedel-Craft's reaction
b) Hofmann reaction
c) Hoffmann bromamide degradation reaction

d) Hinsberg reaction

Q14. By reacting with which of the following, primary amines can be distinguished from secondary and tertiary amines?

a) Chloroform alone

b) Methyl iodide

c) Chloroform and alcoholic KOH

d) Zinc dust

In the following questions15to 18, a statement of **assertion** followed by a statement of **reason** is given. Choose the correct answer out of the following choices
(A) If Assertion and reason are true and reason is the correct explanation of assertion
(B) If Assertion and reason both are true but reason is not correct explanation of the assertion
(C) If Assertion is true reason is false
(D) If Assertion is false reason is true

Qu15. **Assertion-**$CuSO_4$ solution can be kept in Zn pot.
Reason-Position of Zn is higher than copper in electrochemical series.

Qu16. **Assertion :** In Lucas test, 3º alcohols react immediately.
Reason : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

Q17. **Assertion :** Amines are basic in nature.
Reason : Amines have lone pair of electrons on nitrogen atom.

Q18. Assertion: Proteins are polypeptides.
Reason :α-Amino acids are organic compounds containing an amino group and carboxylic group as substituent on the α-carbon.

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

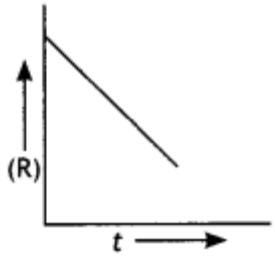
Q19. Given that the standard electrode potentials (E°) of metals are :
K^+/K = -2.93 V, Ag^+/Ag = 0.80 V, Cu^{2+}/Cu = 0.34 V,
Mg^{2+}/Mg = -2.37 V, Cr^{3+}/Cr = -0.74 V, Fe^{2+}/Fe = -0.44 V.
Arrange these metals in increasing order of their reducing power.

Q.20.For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
.

OR

The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value? (given: log 2 = 0.301)

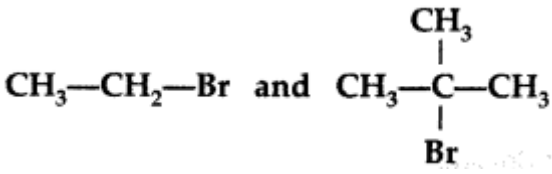
Q21. For a chemical reaction R → P, the variation in the concentration (R) vs. time (t) plot is given as



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

Q22. Explain why $[Fe(HO)_6]^{3+}$ has a magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

Q23. Which would undergo SN2 reaction faster in the following pair and why?

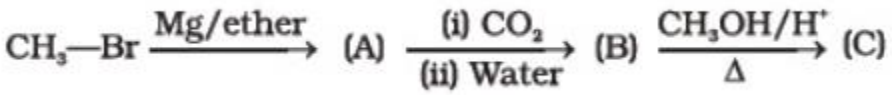


OR

Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
(ii) alkyl halides, though polar, are immiscible with water?

Q24. Identify the compounds A, B and C in the following reaction.



Q25. What is denaturation of proteins and its effect on the structure?

SECTION C

Q26.What mass of ethylene glycol (molar mass = 62.0 g mol^{-1}) must be added to 5.50 kg of water to lower the freezing point of water from 0 to – 10.0°C (k_f for water = 1.86 K kg mol^{-1}).

Q27. Describe the shape and magnetic behaviour of following complexes :
(i) $[Co(NH_3)_6]^{3+}$
(ii) $[Ni(CN)_4]^{2-}$ (At. No. Co = 27, Ni = 28)

Q28. How the following conversions can be carried out?
(i)Propene to propan-1-ol(ii) 1-butanol to 1-Iodobutane (iii) Aniline tochlorobenzene

Q29. How are the following conversions carried out?
(i) Propene to propan-1-ol
(ii) Ethylmagnesium chloride to propan-1-ol.
(iii) Benzyl chloride to benzyl alcohol,

Q30. Givereasons :
(a) Aniline is a weaker base than cyclohexyl amine.
(b) It is difficult to prepare pure amines by ammonolysis of alkyl halides
(c) Electrophiliic substitution in aromatic amines takes place more readily than benzene.

OR

In the following cases rearrange the compounds as directed :
(i) In an increasing order of basic strength :
$C_6H_5NH_2$, C_6H_5 $N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
(ii) In a decreasing order of basic strength :
Aniline, p-nitroaniline and p-toluidine
(iii) In an increasing order of pK_b values :
$C_2H_5NH_2$, C_6H_5 $NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

SECTION D

Q31.Read the passage given below and answer the following questions:

The concentration of a solute is very important in studying chemical reactions because it determines how often molecules collide in solution and thus indirectly determine the rate of reactions and the conditions at equilibrium. There are several ways to express the amount of solute present in a solution. The concentration of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution. Concentration can be expressed in terms of molarity, molality, parts per million, mass percentage, volume percentage, etc.A solution of glucose is prepared with 0.052 g at glucose in 80.2 g of water. (K_f = 1.86 K kg mol^{-1} and K_b = 5.2 K kg mol^{-1})

The following questions are multiple choice questions. Choose the most appropriate answer:
(i) Colligative properties depend on _____.
a) the nature of the solute particles dissolved insolution.
b) the number of solute particles in solution.
c) the physical properties of the solute particles dissolved in solution.
d) the nature of solvent particles.
(ii) Which of the following is temperature dependent?
(a) Molarity (b) Molality (c) mole fraction (d) Mass %
(iii)Molality of the given solution is –
(b) 0.0052m (b) 0.0036m (c) 0.0006m (d) 1.29m

OR

Mole fraction of glucose in the given solution is-
(c) 6.5×10^{-5} (b) 1.23×10^{-4} (c) 0.00625 (d) 0.00028
(iv) Which of the following is true for an aqueous solution of the solute in terms of concentration?

(a) 1 M = 1 m (b) 1M > 1m
(c) 1M < 1 m (d) Cannot be predicted

Q32. Read the passage given below and answer the following questions:

The sequence of bases along the DNA and RNA chain establishes its primary structure which controls the specific properties of the nucleic acid. An RNA molecule is usually a single chain of ribose-containing nucleotide. On the basis of X-ray analysis of DNA, J.D., Watson and F.H.C. crick (shared noble prize in 1962) proposed a three dimensional secondary structure for DNA. DNA molecule is a long and highly complex, spirally twisted, double helix, ladder like structure. The two polynucleotide chains or strands are linked up by hydrogen bonding between the nitrogeneous base molecules of their nucleotide monomers. Adenine (purine) always links with thymine (pyrimidine) with the help of two

hydrogen bonds and guanine (purine) with cytosine (pyrimidine) with the help of three hydrogen bonds. Hence, the two strands extend in opposite directions, i.e., are antiparallel and complimentary.

In these questions (i-iv), 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 correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.posite directions, i.e., are antiparallel and complimentary.

(i) Assertion: DNA molecules and RNA molecules are found in the nucleus of a cell.
Reason: There are two types of nitrogenous bases, purines and pyrimidines. Adenine (A) and guanine (G) are substituted purines; cytosine (C), thymine (T) and uracil (U) are substituted pyrimidines
(ii) Assertion: In both DNA and RNA, heterocyclic base and phosphate ester linkages are at C-l' and

C-5' respectively of the sugar molecule.
Reason: Nucleotides and nucleosides mainly differ from each other in presence of phosphate units.
(iii) Assertion: The backbone ofRNA molecule is a linear chain consisting of an alternating units of a heterocylic base, D-ribose and a phosphate.
Reason: The segment of DNA which acts as the instruction manual for the synthesis of protein is ribose.

Or

(iii) Assertion: The double helical structure of DNA was proposed by Emil Fischer.
Reason: A nucleoside is an N-glycoside of heterocyclic base.

iv) **Assertion:** sucrose is non reducing sugar

Reason: it has glycosidic linkage

SECTION E

Q33.a) The standard electrode potential for Daniel cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction. ($F = 96,500\ C\ mol^{-1}$)
b) Define the following terms :
(i) Fuel cell
(ii) Limiting molar conductivity (Λ°_m)

Or

a)The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity.

b) Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their Variation with change in temperature.

Q34. .Answer the following:

a. Why are all copper halides known except that copper iodide?

b. Why is the E^o (V^{3+}/V^{2+}) value for vanadium comparatively low?

c. Why HCl should not be used for potassium permanganate titrations? 11

d. Explain the observation, at the end of each period, there is a slight increase in the atomic radius of d block elements.

e. What is the effect of pH on dichromate ion solution.

Q35. a) Write the reactions involved in the following reactions:
(i) Clemmensen reduction
(ii) Cannizzaro reaction

b) Do the following conversions in not more than two steps:
(i) Benzoic acid to benzaldehyde
(ii) Ethyl benzene to Benzoic acid
(iii) Propanone to Propene

OR

a) Write notes on the following –

i) Aldol condensation

ii) Etard reaction

b) Write the chemical test to distinguish the following pairs of compounds –

i) Benzoic acid and phenol

ii) Acetone and acetaldehyde

iii) Propanone and pentan-3-one

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Chapter name	**MCQ 1MARKS**	**AR 1MARKS**	**VSA-1 2 MARKS**	**VSA-2 3 MARKS**	**LA 5MARKS**	**Case based 4 MARKS**	**TOTAL**
1.SOLUTION				**3(1)**		**4(1)**	**7(2)**
2.ELECTROCHEMISTRY	**2(2)**		**2(1)**		**5(1)**		**9(4)**
3.CHEMICAL KINETICS	**3(3)**		**4(2)**				**7(5)**
4.D & f BLOCK ELEMENTS	**1(1)**	**1(1)**			**5(1)**		**7(3)**
5.COORDINATION CHEMISTRY	**2(2)**		**2(1)**	**3(1)**			**7(4)**
6.HALOALKANES & HALOARENES	**1(1)**		**2(1)**	**3(1)**			**6(3)**
7.ALCOHOL PHENOL & ETHERS	**2(2)**	**1(1)**		**3(1)**			**6(4)**
8.ALDEHYDES KETONES & CABOXYLIC ACID	**1(1)**		**2(1)**		**5(1)**		**8(3)**
9.AMINES	**2(2)**	**1(1)**		**3(1)**			**6(4)**
10.BIOMOLECULES		**1(1)**	**2(1)**			**4(1)**	**7(3)**
	14(14)	**4(4)**	**14(7)**	**15(5)**	**15(3)**	**8(2)**	**70(35)**

SAMPLE PAPER (2022-23) CHEMISTRY THEORY (043) MARKING SCHEME SECTION A Q1 to 18 each correct answer 1 marks

1)(c)279

2.(c) $\Delta G°$ is negative, K is greater than 1

3) (a) increase 2 times

4) (d)Activation energy

5(b) Ea

6. (c) Cu^{2+}

7.(c) $[Co(NH_3)_3 Cl_3)$ does not have counter ions, so will not react with $AgNO_3(aq)$

8. (b)

9. (b) NaCl

10. (c) Butane-2-ol

11. (c) 1 ° > 2° > 3°

12. ethanol

13.c) Hoffmann bromamide degradation reaction

14. c) Chloroform and alcoholic KOH

15. D

16. **B**

17. A

18 B

Q19. $Ag^+/Ag < Cu^{2+}/Cu < Fe^{2+}/Fe < Cr^{3+}/Cr < Mg^{2+}/ Mg < K^+/K$
More negative the value of standard electrode potentials of metals is, more will be the reducing power.

Q20. $t=2.303/k \log[A]_o/[A]$ using the formula prove $t_{99\%} = 2 \times t_{90\%}$ OR
Given,k=60 s^-.
Let a **$[A]_o$** be the initial concentration.
Final concentration will be[A]= **$[A]_o/16$**.
$t=2.303/k \log([A]_o[A])$
$t=2.303/60\log(16)$
$t=4.6\times10^{-2}$ seconds

21. (i) Zero order reaction
(ii) Slope = – k

22. $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$ involves sp^3d^2 hybridisation with five unpaired electrons. This difference is due to the presence of strong ligand CN^- and weak ligand H_2O in these complexes.

23. CH_3CH_2Br reacts faster because it is a primary halide (1° halide).

OR

(i)Due to presence of sp^2 hybridized carbon atom is chlorobenzene.

(ii) Because energy is required to overcome the attraction between the haloalkane molecule & break the H-bond between the water molecules.

24.**Answer:**

A= CH_3MgBr

B= CH_3COOH

C= CH_3COOCH_3

25. It destroys the primary structure of proteins.

26. $\Delta T_f = (Kf \times 1000 \times wB)/(wA \times MB)$

$K_f = 1.86$ K kg mol^{-1}, $w_A = 5.50$ kg = 5500 g

$W_B = ?$

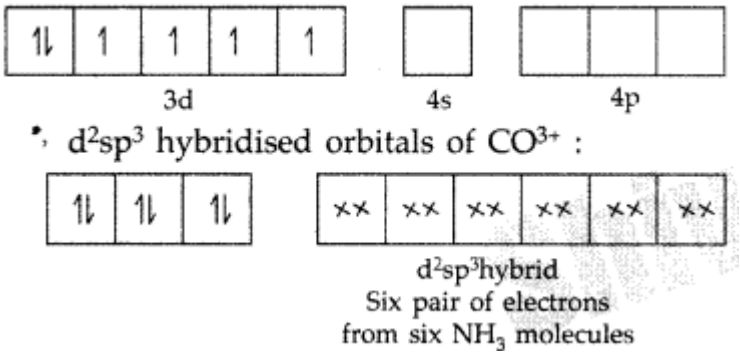
$M_B = 62.0$ g/mol, $\Delta T_f = 0 – (- 10) = 10°C$

$10 = 1.86 \times 1000 \times wB5500 \times 62$

$W_B = 10 \times 5500 \times 621.86 \times 1000$ = 1833.3 g = 1.833 kg

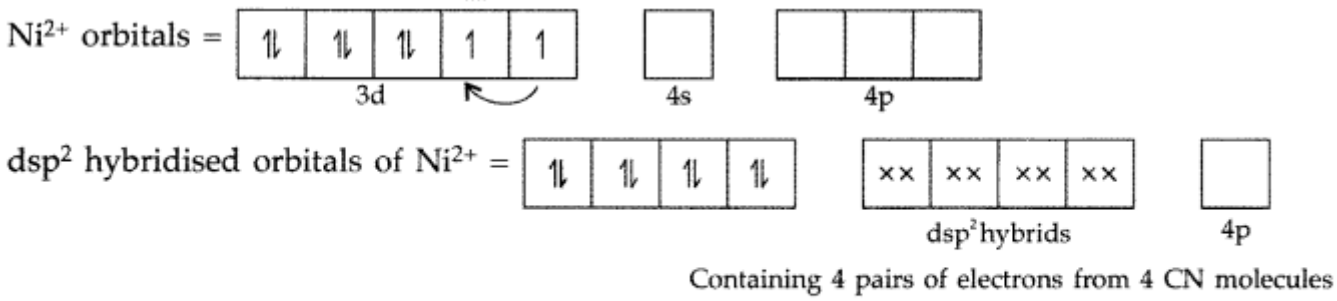
27. (i) $[CO(NH_3)_6]^{3+}$:

Orbitals of CO^{3+} ion :



Hybridization : d^2sp^3 Shape : Octahedral Magnetic behaviour : Diamagnetic (absence of unpaired electrons)

(ii) $[Ni(CN)_4]^{2-}$



Shape : Square planar
Hybridisation : dsp^2
Magnetic behaviour : Diamagnetic (no unpaired electrons)

Ans. (i) Propene to propan-2-ol

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{(Mark. add}^n\text{)}]{HBr} \underset{\text{Isopropyl bromide}}{CH_3-\overset{\overset{Br}{|}}{CH}-CH_3} \xrightarrow[\text{(Hydrolysis)}]{\text{Aq. KOH}, \Delta,\ -KBr} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3}$$

(ii) Ethyl magnesium chloride to propan-1-ol

$$\underset{\text{Ethyl Magnesium chloride}}{CH_3CH_2MgCl} \xrightarrow[\text{(Grignard Rx}^n\text{)}]{HCHO} \underset{\text{Addition product}}{[CH_3CH_2CH_2OMgCl]} \xrightarrow{H^+/H_2O} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + Mg(OH)Cl$$

Ans30.(a) In aniline, the lone pair of electrons on the N-atom is delocalised over the benzene ring. As a result, the electron density on the nitrogen decreases.
But in cyclohexylamine, the lone pair of electrons on N-atom is readily available due to absence of π-electrons. Hence aniline is weaker base than cyclohexylamine.
(b) Because the primary amine formed by ammonolysis itself acts as a nucleophile and produces further 2° and 3° alkyl amine.

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

or

(i) Order of basic strength :

$$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < \underset{\text{More +I effect}}{(C_2H_5)_2NH}$$

***(ii)* The decreasing order of basic strength :**

$$\underset{\text{(+I effect)}}{\text{p-toluidine}} > \text{aniline} > \underset{\text{(NO}_2\text{ is electron withdrawing group)}}{\text{p-nitroaniline}}$$

***(iii)* Increasing order of pK_b values :**

$$(C_2H_5)_2NH < C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$$

Since a stronger base has a lower pKb value therefore basic strength order.
$(C_2H_5)_2NH > C_2H_5NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$

Ans31
(i) (b):
(ii) (a)
(iii)(i) (b)
Or
(iii) (a)
(iv) (b):
Ans32. 1) D

ii) B

iii)C

or

iii) D

iv) B

Ans. 33.a) Given: $E° = 1.1V$, $F = 96,500\ C\ mol^{-5}$, $n = 2$
$Zn + Cu^{2} \rightleftharpoons Cu + Zn^{2+}$
Using $\Delta G° = -nFE° = -2 \times 96500 \times 1.1$
$= 212,300\ CV\ mol^{-1}$

b) **i) 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.
(ii) The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ°_{m}.

Or

a) Molar conductivity $\Lambda_m = 1000 \times \kappa M$
Given : $K = 0.025\ S\ cm^{-1}$, $M = 0.20\ M$
Hence, $\Lambda_m = 0.025 \times 10000.20 \therefore \Lambda_m = 125\ S\ cm^{2}\ mol^{-1}$

b) **Conductivity:** Conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section. It is represented by K.
Its unit is $S\ cm^{-1}$
Molar conductivity : Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in $V\ cm^{3}$ of the solution when the electrodes are 1 cm apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is represented by Λ_m.
Its unit is $S\ cm^{2}\ mol^{-1}$
Conductivity and molar conductivity of electrolytes increase with increasing temperature.

Ans.34. Cu2+ oxidizes iodide ion to iodine. (1)

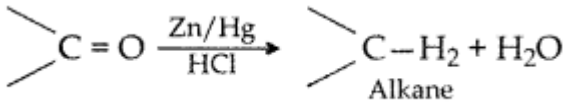
b. The low value for V is related to the stability of V2+ (half-filled t2g level) (1)

c. Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

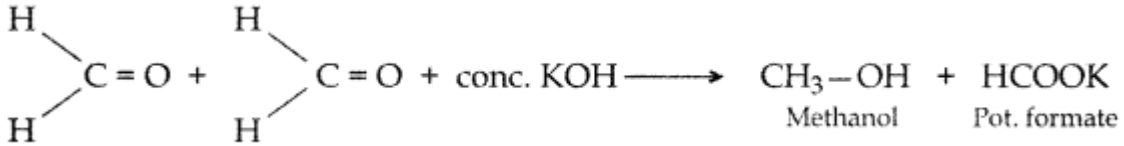
d. The d orbital is full with ten electrons and shield the electrons present in the higher s-orbital to a greater extent resulting in increase in size.

e. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. Increasing the pH (in basic solution)of dichromate ions a colour change from orange to yellow is observed as dichromate ions change to chromate ions

qu35.(i) Clemmensen reduction. The carbonyl group of aldehyde and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.



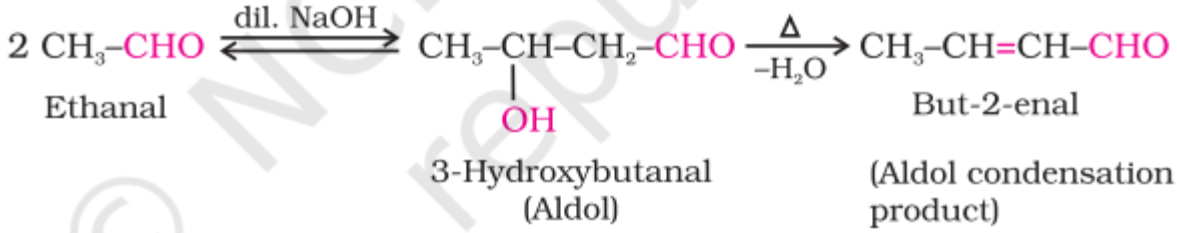
(ii) Cannizzaro reaction. Aldehydes, which do not have an a-hydrogen atom undergo self oxidation and reduction on treatment with cone, alkali and produce alcohol and carboxylic acid salt.



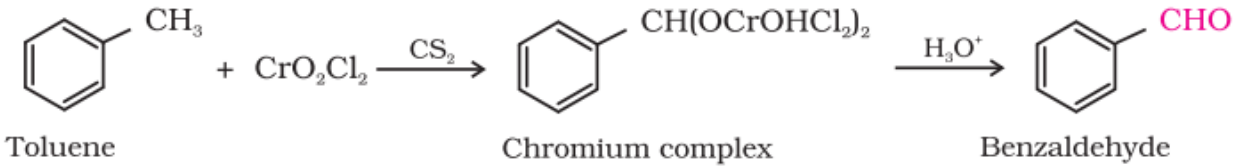
b)
OR

(a)

(i) Aldol condensation: Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively. This is known as **Aldol reaction.**



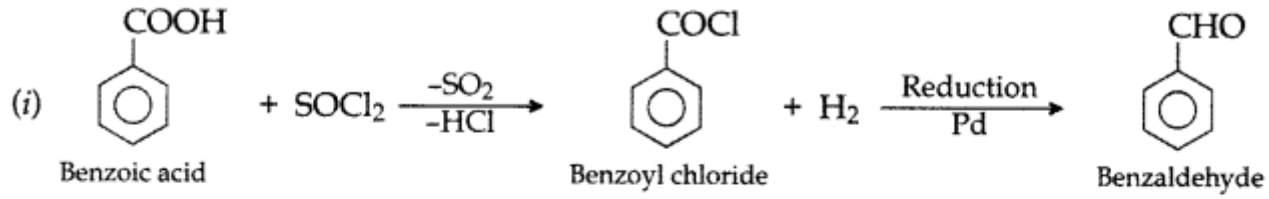
ii) Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called Etard reaction.

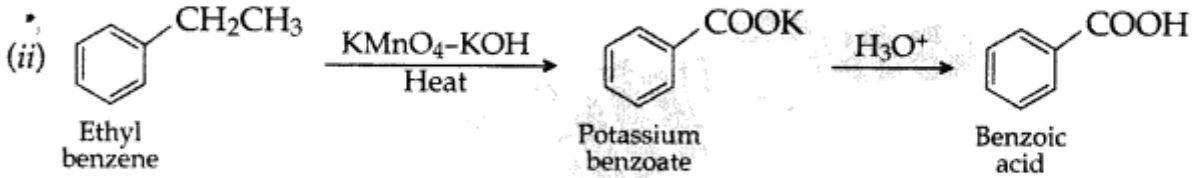


b) (i) phenol gives $FeCl_3$ test

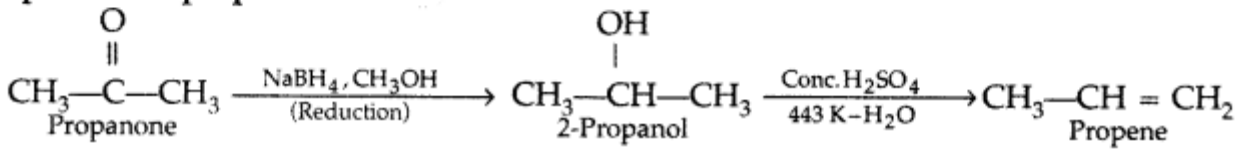
(ii) Acetaldehyde gives Tollens reagent test or Fehlings test.

(iii) Propanone gives Iodoform test.





(*iii*) **Propanone to propene**



KENDRIYA VIDYALAYA SANGATHAN RAIPUR REGION

MODEL PAPER4 (2022-23)CHEMISTRY THEORY (043)

MM:70 Time: 3 hours

General Instructions:

Read the following instructions carefully.

a) There are 35 questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 short answer questions carrying 3 marks each.

e) SECTION D consists of 2 case- based questions carrying 4 marks each.

f) SECTION E consists of 3 long answer questions carrying 5 marks each.

g) All questions are compulsory.

h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple-choice questions with one correct answer. Eachquestion carries 1 mark. There is no internal choice in this section.

1.The process of converting alkyl halides into alcohols involves_____.
(a) addition reaction
(b) substitution reaction
(c) dehydrohalogenation reaction
(d) rearrangement reaction

2.Toluene reacts with a halogen in the presence of iron (iii) chloride givingng ortho and para halo compounds. The reaction is
(a) Electrophilic elimination reaction
(b) Electrophilic substitution reaction
(c) Free radical addition reaction
(d) Nucleophilic substitution reaction

3.Which of the following oxidition state is common for all lanthanoids?
(a) +2
(b) +3
(c) +4
(d) +5

4. Which of the following statements as not correct about order of a reaction.
(a) The order of a reaction can be a fractional number.
(b) Order of a reaction as experimentally determined quantity.

(c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
(d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

5. An electrochemical cell can behave like an electrolytic cell when _____.
(a) Ecell = 0
(b) Ecell > Eext
(c) Eext > Ecell
(d) Ecell = Eext

6.Rate law for the reaction A + 2B → C as found to be Rate = k [A][B] Concentration of reactant 'B' as doubled, keeping the concentration of 'A' constant, the value of rate constant wall be_____.
(a) the same
(b) doubled
(c) quadrupled
(d) halved

7. The correct IUPAC name for CH_2 ==$CHCH_2$ $NHCH_3$ is
(a) Allylmethylamine
(b) 2-amino-4-pentene
(c) 4-aminopent-1-ene
(d)N-methylprop-2-en-1-amine

8. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)6]^{3+}$
(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$
(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

9. What would be the major product of the following reaction?

C_6H_5 -CH_2-OC_6H_5 + HBr A + B►

(a)A= $C_6H_5CH_2OH$, B= C_6H_6
(b)A=$C_6H_5CH_2OH$,B= C_6H_5Br
(c)A=$C6H_5CH_3$,B= C_6H_5Br
(d)A=$C_6H_5CH_2Br$, B= C_6H_5OH

10. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?
(a) H_2 (excess)/Pt
(b) $LiAlH_4$ an ether
(c) Fe and HCl
(d) Sn and HCl

11.Using the data given below find out the strongest reducing agent.
E^0 $Cr_2O_7^{2-}$ Cr =1.33V
E^0 Cl^-/Cl = 1.36V
E^0 MnO_4^- /Mn^{2+} = 1.51V

$E^{o}Cr^{3+}/Cr = -0.74V$
(a) Cl^-
(b) Cr
(c) Cr^{3+}
(d) Mn^{2+}

12. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?
(a) 1.26×10^{15} s
(b) 2.52×10^{14} s
(c) 2.52×10^{28} s
(d)infinite

13. When 1 mol CrCl3 ·6H2O as treated with excess of $AgNO_3$, 3 mol of AgCl are obtained. The formula of the complex is :
(a) $[CrCl_3(H_2O)_3]\cdot 3H_2O$
(b) $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2\cdot H_2O$
(d) $[Cr(H_2O)6]Cl_3$

14. Which of the following compounds will give butanone on oxidation with alkaline KMnO4 solution?
(a) Butan-1-ol
(b) Butan-2-ol
(c) Both of these
(d) None of these

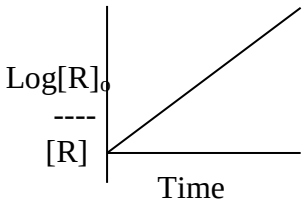
Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): An ether as more volatile than an alcohol of comparable molecularmass.
Reason (R): Ethers are polar in nature.
Select the most appropriate answer from the options given below:
a.Both A and R are true and R as the correct explanation of A
b.Both A and R are true but R as not the correct explanation of A.
c.A is true but R as false.
d.A is false but R as true.

15. Assertion : p-nitrophenol is more acidic than phenol.
Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.
16. Assertion : Vitamin D can be stored in our body.
Reason : Vitamin D is fat soluble vitamin.
17. Assertion : Separation of Zr and Hf is difficult.
Reason : Because Zr and Hf lie in the same group of the periodic table.
18. Assertion :N-Ethylbenzene sulphonamide is soluble in alkali.
Reason :Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

SECTION-B

19. For a chemical reaction R→ P, the variation in the Concentration log[R0]/[R] vs time (t) plot is given below
i) Predict the order of the reaction.
ii) What is the slope of the curve?



OR

In a first order reaction , the units of the rate constant do not depend upon the concentration of the reactants? justify.

20. Write two differences between following pairs Globular protein and Fibrous protein

21.Explain why
i) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
ii) Alkyl halides, though polar, are immiscible with water?
22. Answer the following questions:
.(i) $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic.
(ii) $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

OR

Draw figure to show the splitting of d- orbitals in an octahedral crystal field
23. Calculate ΔrG 0 for the reaction $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
Given : E^0 cell = 2.71 V 1 F = 96500 C Mol^{-1}
24. The half life for radioactive decay of 14 C is 5730 years. An archaeological artifact contained wood that had only 80% of the 14 C found in living tree. Estimate the age of the sample.

25 Give chemical test to distinguish between : i) Isopropyl alcohol and n-propylalcohol. ii) Phenol and ethyl alcohol

SECTION –C

26. Write the equations for the following reaction:
a. Salicylic acid is treated with acetic anhydride in the presence of conc. H_2SO_4
b. Tert butyl chloride is treated with sodium ethoxide.
c. Phenol is treated with chloroform in the presence of NaOH
27. (a) Write the IUPAC name for $[Co(en)_3]_2(SO_4)_3$
(b) How many geometrical isomers are possible in the coordination entity $[Co (NH3)_3(NO_3)_3]$?
(c) Give the number of unpaired electrons in $[Ni(CN)_4]^{-2}$. (Atomic no of Ni = 27)

OR

Predict hybridization, shape, magnetic properties of hexachloridochromate(III) ion on the basis of VBT
28. State Raoult's law. What is meant by positive and negative deviations from Raoults law and how is the sign of Δmix H related to positive and negative deviations from Raoults law?
29. Arrange in the increasing order of the property mentioned against each

(a) $C_2H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$, $(C_2H_5)_2NH$ (pKb)

(b) n-$C_4H_9NH_2$, C_2H_5 -$N(CH_3)_2$, $(C_2H_5)_2NH$, C_4H_9OH (boiling point)

(c) $C_6H_5N_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$. (Solubility in water)

30. Do the following conversions:

(i) Methyl bromide to acetone.

(ii) Benzyl chloride to 2-phenyl acetic acid.

(iii) Chloroethane to Flouroethane

SECTION –D

31. Read the following passage and answer the questions that follow:

Solutions are homogeneous mixture of two or more substances. Ideal solution follow Raoult's law. The vapour pressure of each component is directly proportional to their mole fraction if both solute and solvent are volatile. The relative lowering of vapour pressure is equal to mole fraction of solute if only solvent is volatile. Non-ideal solution form azeotropes which cannot be separated by fractional distillation. Henry's law is special case of Raoult's law applicable to gases dissolved in liquids. Colligative properties depend upon number of particles of solute. Relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure are colligative properties

which depend upon mole fraction of solute, molality and molarity of solutions. When solute undergoes either association or dissociation, molecular mass determined by colligative property will be abnormal. van't Hoff factor is used in such cases which is ratio of normal molecular mass over observed molar mass.

(a) 50 ml of an aqueous solution of glucose (Molar mass 180 g/mol) contains 6.02×10^{22} molecules. What is molarity?

(b) Identify which liquid has lower vapour pressure at 90°C if boiling point of liquid 'A' and 'B' are 140°C and 180° respectively.

(c) What type of azeotropes are formed by nonideal solution showing negative deviation from Raoult's law?

OR

Why 0.1 M KCl has higher boiling point than 0.1 M glucose solution?

32. Read the given passage and answer the questions that follow.

Biomolecules are complex molecules which build up living organisms and required for their growth, maintenance and ability to reproduce. Carbohydrates are polyhydroxy aldehydes and ketones which are major sources of energy. Monosachharides are simple sugars which cannot be hydrolysed. Oligosachharide, on hydrolysis give 2 to 10 molecules of monosachharides. Polysachharides like starch and cellulose on hydrolysis give large number of molecules of glucose a-glucose and b-glucose (Anomers). Proteins are complex nitrogeneous polymers of amino acids connected through peptide bonds. The sequence in which amino acids are linked is called Primary structure. Secondary structures are of 2 types a-helix in globular proteins and b-pleated structure in fibrous proteins involving H-bonds. Tertiary structure has H-bonds, disulphide linkage, ionic bonding and van der Waals' forces. Insulin is hormone for metabolism of glucose, has quarternary structure. Denaturation of protein destroys secondary and tertiary structure, loss of biological activity but primary structure remaining the same. Enzymes are highly specific, work at specific pH, moderate temperature and catalyse biochemical reactions. Hormones perform specific functions and secreated by endocrine glands. Vitamins are essential for healthy body. A, D, E, K are fat soluble vitamins. Vitamin C and B1, B2, B6 are water soluble. B12 is neither water, nor fat soluble. Nucleic acids are polymer of nucleotides. RNA consist of m-RNA, t-RNA, r-RNA. RNA has Adenine, Cytosine, Uracil and Guanine. It helps in protein synthesis. It cannot replicate. DNA contains deoxyribose, A, C, G and Thymine. It transfers genetic characteristics. DNA has double helix structure and undergoes replication

(a) Name a disachharide which on hydrolysis give glucose and galactose.

(b) What tyhpe of protein is albumin?

(c) Name one non-reducing sugar.

OR

(c) Which linkage by which nucleotide are joined together between 5′ and 3′ atoms of pentose sugar?

SECTION -E

33.(a) Calculate e.m.f of the cell at 298K.

$Cr / Cr^{3+} // Fe^{2+} / Fe$ 0.1M 0.01M

Given: $E°(Cr^{3+}/Cr) = -0.75V$, $E°(Fe2+/Fe) = -0.45V$

(b) If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

OR

a) Calculate the charge in coulombs required for the oxidation of 2 mole of water to oxygen? (Given 1F = 96500 C/mol-1)

b) Zn/AgI oxide cell is used in hearing aids and electric watches where following reactions occur: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$ $E^0 (Zn^{2+}(aq)/ Zn = -0.76V$

$Ag_2S + H_2O + 2e \rightarrow 2Ag + 2OH^-$ $E^0 (Ag^{+1}/Ag) = 0.344V$

Calculate the

i)Standard potential of the cell

ii) standard Gibb's energy.

34.(a) Arrange the following in the increasing order of:

i) Methanal, Propanal, Butanone, Ethanal, Propanone (nucleophilic addition reaction)

ii) Formaldehyde, Acetone, Acetaldehyde (reactivity towards HCN)

b.How are the following conversions carried out –

i. Ethanol to But-2-enal

ii. Propanone to propene

iii. Benzoic acid to m-Nitrobenzyl alcohol

OR

a.Give chemical test to

ii.Phenol and benzoic acid

b.An organic compound 'A' molecular formula $C_8H_{16}O_2$ was hydrolysed with dil. H_2SO_4 to give a carboxylic acid 'B' and an alcohol 'C'. Oxidation of 'C' with chromic acid also produced 'B'. On dehydration 'C' gives but-1-ene. Write the equations for the reactions involved.

35. How would you account for the following:

a)Of the d^4 species, Cr^{2+} is strongly reducing while Mn(III) is strongly oxidizing

b)Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized.

c)Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

d) Complete the following reactions:

(i) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow$

(ii) $MnO_4^- + 3e + H^+ \rightarrow$

OR

a) The enthalpies of atomization of the transition metals are high because the atoms in these elements are held together by strong metallic bonds.

b)Transition metals generally form coloured compounds because of presence of unpaired electrons in d sub shell.

c)Transition and their many compounds act as good catalysts because of variable oxidation-state they form intermediate compounds with reactants and provide a low activation energy path for reaction.

d) Complete the following reactions:

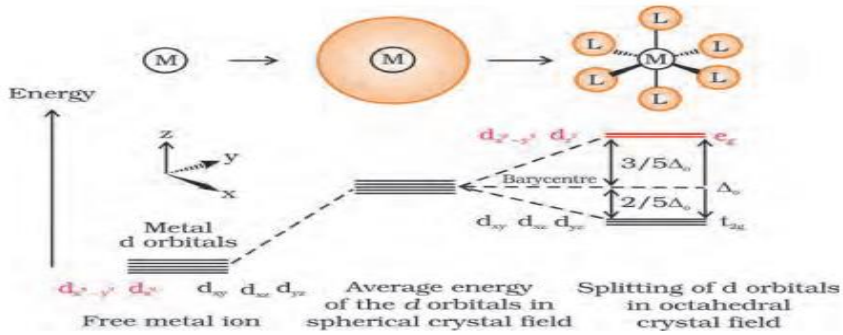
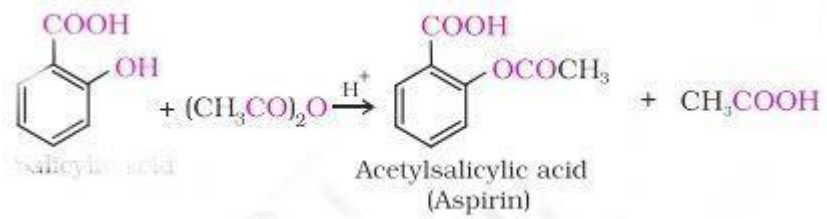
(i) $Cr_2O_4^{2-} + H^+ \rightarrow$

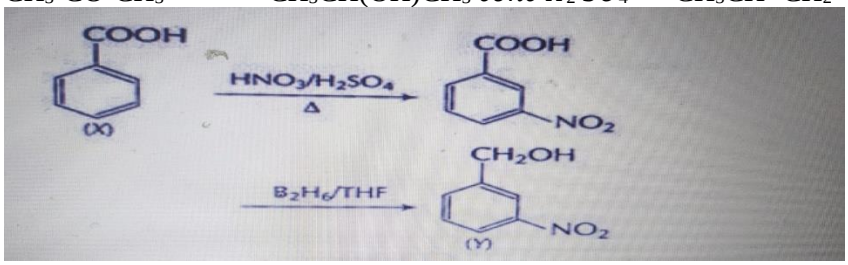
(ii) $MnO_4^- + I^- + H_2O \rightarrow$

BLUE PRINT							
Chapter name	MCQ 1MARKS	AR 1MARKS	VSA-1 2 MARKS	VSA-2 3 MARKS	LA 5MARKS	Case based 4 MARKS	TOTAL
1.SOLUTION				3(1)		4(1)	7(2)
2.ELECTROCHEMISTRY	2(2)		2(1)		5(1)		9(4)
3.CHEMICAL KINETICS	3(3)		4(2)				7(5)
4.D & f BLOCK ELEMENTS	1(1)	1(1)			5(1)		7(3)
5.COORDINATION CHEMISTRY	2(2)		2(1)	3(1)			7(4)
6.HALOALKANES & HALOARENES	1(1)		2(1)	3(1)			6(3)
7.ALCOHOL PHENOL & ETHERS	2(2)	1(1)		3(1)			6(4)
8.ALDEHYDES KETONES & CABOXYLIC ACID	1(1)		2(1)		5(1)		8(3)
9.AMINES	2(2)	1(1)		3(1)			6(4)
10.BIOMOLECULES		1(1)	2(1)			4(1)	7(3)
	14(14)	4(4)	14(7)	15(5)	15(3)	8(2)	70(35)

MARKING SCHEME

S. No.	SECTION A	
1.	**B**	**1**
2.	**B**	**1**
3.	**B**	**1**
4.	**C**	**1**
5.	**C**	**1**
6.	**B**	**1**
7.	**D**	**1**
8.	**C**	**1**
9.	**D**	**1**
10.	**B**	**1**
11.	**B**	**1**
12.	**D**	**1**
13.	**D**	**1**
14.	**B**	**1**
15.	**A**	**1**
16.	**A**	**1**
17.	**B**	**1**
18.	**D**	**1**
	SECTION- B	
19.	Ist order Reaction Slope= $\frac{K}{2.303}$ **OR** Rate equation for the first order reaction is : k = $\frac{2.303}{t}\log\frac{a}{a-x}$ here a is initial concentration of the reactants & (a-x) is concentration afer time t. since the units of a & (a-x) are to cancel out, therefore, units of rate constant (k) do not depend upon the concentration of the reactants	**1+1**
20.	Globular protein - They have folded ball – like structure They may have three dimensional Shapes Fibrous protein - Their molecules have long thread like structure. They have helical or sheet structures	**1+1**
21.	. i) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride because in chlorobenzene C- Cl bond is less polar due to sp2 hybridisation of carbon and shorter due to partial double bond nature. ii) Alkyl halides, though polar, are immiscible with water.because alkyl haides are unable to form H-bond with water as well as unable to break the existing H-bonds among water molecules.	**1+1**
22.	(i) $[Fe(H_2O)_6]^{3+}$ involves $sp^3 d^2$ hybridisation and have five unpaired electrons while $[Fe(CN)_6]^{3-}$ involves $d^2 sp^3$ hybridisation and have only one unpaired electron. (ii) In $Co(NH_3)_6]^{3+}$,Co is in +3 oxidation state and has six electrons in 3d sub shell. In the presence of NH3 the 3d electrons pair up leaving two d orbitals empty to be involved in $d^2 sp^3$ hybridisation forming an inner orbital complex. In $Ni(NH_3)_6]^{2+}$,Ni is in +2 oxidation state and has d8 configuration.The hybridization involved is sp3 d 2 forming the outer orbital complex. **OR**	**1+1**

		
23.	$\Delta rG^0 = -nFE^0$ cell =-2x2.71x96500 =-523030J	**1+1**
24.	Decay constant k= $\frac{0.693}{t1/2} = \frac{0.693}{5730}$ year^{-1} k= $\frac{2.303}{t}\log\frac{[A]0}{[A]}$ =1845 years	**1+1**
25.	i) Isopropyl alcohol and n-propyl alcohols: On adding NaOH/I_2 and NaOI and heating isopropyl alcohol forms yellow ppt. of iodoform (CHI_3) or any other Whereas n-propyl alcohol does not. ii)Phenol and alcohol : On adding neutral FeCl3 solution, phenol red- violet complex whereas alcohol does not.	**1+1**
	SECTION_ C	
26.	**SALICYLIC ACID TO ASPIRIN**  (ii) $(CH_3)_3CCl$ sodium ethoxide $(CH_3)_2C=CH_2$ 2-methylpropene (iii) o-hydroxybezaldehyde will be formed(Reimer Tiemen Reaction)	**1+1+1**
27.	(i) Tris(ethan-1,2-diamine)cobalt(III) sulphate (ii) 2 (fac and mer) (iii) zero unpaired electron dsp^2 – square planar OR $d^2 sp^3$ apply VBT then answer, Octahedral , paramagnetic because of 3 unpaired electrons. Magnetic moment = 3.9 BM	**(1+1+1)**
28.	It states that for a solution of volatile liquids, the partial vapor pressure of each component of the solution is directly proportional to the mole fraction present in the solution. Non ideal solutions show positive and negative deviation from Raoult's law. Δmix = -ve solution show negative deviation from Raoult's law Δmix = +ve solution show positive deviation from Raoult's law	(1+1+1)
29.	(a) $(C_2H_5)_2$ NH < $C_2H_5NH_2$ < $C_6H_5NH_2$ (pKb) (b) C_2H_5-$N(CH_3)_2$ < $(C_2H_5)_2$ NH < n-$C_4H_9NH_2$,< C_4H_9OH (boiling point) (c) (c) $C_6H_5NH_2$< $(C_2H_5)_2$ NH < $C_2H_5NH_2$. (solubility in water)	(1+1+1)
30.	(i)$CH_3Br + Mg \rightarrow CH_3MgBr + C\ H_3CHO \xrightarrow{H2O} CH_3CH(OH)CH_3 \xrightarrow{Cu-573\ K} \rightarrow (CH_3)_2CO$ (ii)$C_6H_5CH_2Cl\ KCN \rightarrow C_6H_5CH_2CN \xrightarrow{H2O} C_6H_5CH_2COOH$ (iii) CH_3CH_2Cl + AgF $\rightarrow$ CH_3CH_2F + AgCl	(1+1+1)

	SECTION-D	
31.	.(a) M = $\frac{\text{No.of Moles}}{\text{Litre of solution}}$ =6.022X10^{22}/6.022X10^{23}X 1000/50 =2M (b) 'B' will have lower vapour pressure because its boiling point is higher. (c) Maximum boiling azeotropes. OR (c) It is because KCl dissociates into ions, it has double particles as compared to glucose. Therefore, elevation in boiling point is double.	(1+1+2)
32.	(a) Lactose. (b) Globular protein. (c) Sucrose OR (c) Phosphodiester linkage	(1+1+2)
	SECTION -E	
33.	(a) Cr → Cr^{3+} + 3 e- , Fe $^{2+}$ + 2e- → Fe 2Cr $^{+3}$ Fe $^{2+}$ → 2 Cr^{3+} + 3 Fe ie n=6 , Ecell°= E° - E° = +0.30 V $Ecell = +0.30 - 0.0591\ 6\ log\ \frac{[0.1]\ 2}{[0.01]\ 3}$ Answer = +0.2606V (b) Q=It= 0.5X 2X60X60=3600 C 3600C is equivalent to flow of electrons=6.022 X10^{23} X$\frac{3600}{96500}$=2.246X10^{22} ELECTRONS **OR** (a)2H_2O → 4H+ +O_2 +4e- 2mol 4mol or 4F Therefore , charge (Q) required for converting 2 moles of H2O to Oxygen =4F= 4 × 96500C mol-1 = 386000C mol-1 (b)Zn(s) → Zn^{2+} (aq) +2e b) Ag_2O +H_2O +2e- → 2Ag +2OH Zn(s) +Ag_2O +H_2O → Zn^{2+} (aq) + 2Ag + 2OH^- . i) E_0 cell = E_0Cathode - E_0 anode= 0.344-(.76V) = 1.104V ii) ΔG_0 = -nFE_0Cell = -2×96500×1.104 = -2.13 ×105 $Jmol_{-1}$	**3+2**
34.	(a(i) Butanone <Propanone<Propanal<Ethanal (2+3) (ii) Acetone< Acetaldehyde< Formaldehyde. (b) i. 2CH_3-CHO $\xrightarrow{OH-}$ $CH_3CH(OH)CH_2CHO$ $\xrightarrow{\Delta H+}$ $CH_3CH=CHCHO$ ii. CH_3-CO-CH_3 $\xrightarrow{LiAlH4}$ $CH_3CH(OH)CH_3$ $conc\ H_2\ SO_4 \xrightarrow{\Delta}$ $CH_3CH=CH_2$ iii.  **OR** a. i. Iodoorm test (add I_2 + NaOH) - Yellow ppt for ethanal whereas no formation of yellow ppt for propanal ii. $NaHCO_3$ test (add $NaHCO_3$) – Brisk effervescence for benzoic acid b.CH_3-CH_2-CH_2-COO-CH_2-CH_2-CH_2-CH_3 (A) + H_2O $\xrightarrow{conc\ H2\ SO4}$ → $CH_3CH_2CH_2COOH$ (B) + CH_3-CH_2-CH_2-CH_2-OH (C) CH_3-CH_2-CH_2-CH_2-OH (C) $\xrightarrow{CrO3}$ CH_3-CH_2-CH_2-COOH (B)	**2+3**

	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$ (C) $\xrightarrow[\Delta]{\text{conc H2 SO4}}$ $CH_3\text{-}CH_2\text{-}CH{=}CH_2 + H_2O$	
35.	a) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a halffilled t_2g level. On the other hand, the change from Mn^{2+} to Mn^{3+} results in the halffilled (d^5) configuration which has extra stability. b) Cobalt (III) has greater tendency to form complex than Cobalt (II)Hence in the presence of ligands Cobalt (II) changes to Cobalt (III) i.e. is easily oxidized. c) Due to poor shielding by 5f electrons in actinoid as compared to that by 4f electrons in the lanthanoids. d) (i) $Cr_2O_7^{2-} + 6\ Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7\ H_2O$ (ii) $MnO_4^- + 5e + 8H^+ \rightarrow Mn^{2+} + 4H_2O$	(1+1+1+2)

KENDRIYA VIDYALAYA SANGATHAN, RAIPUR REGION

SAMPLE PAPER – 5

SUBJECT – CHEMISTRY (043)

CLASS – XII

TIME – 3.00 Hours **MAX. MARKS – 70**

General Instructions –

- **This question paper contains 35 questions of 70 marks.**
- **Section A consists of 18 MCQs carrying 1 mark each.**
- **Section B consists of 7 questions carrying 2 marks each.**
- **Section C consists of 5 questions carrying 3 marks each.**
- **Section D consists of 2 case based questions carrying 4 marks each.**
- **Section E consists of 3 questions carrying 5 marks each.**
- **All questions are compulsory, internal choices are given in few questions.**
- **Use of calculator and log table is not allowed.**

SECTION – A

This section contains 18 multiple choice questions with one correct answer and there is no internal choice.

1. The limiting molar conductivities of CH_3COOH, KCl & HCl are 390, 150 & 425 S cm^2/mol respectively. Molar conductivity of CH_3COOK would be –
   (a) 100 S cm^2/mol (b) 125 S cm^2/mol (c) 115 S cm^2/mol (d) 150 S cm^2/mol
2. For a reaction A + 2B ---------> Product, order of reaction wrt both A & B is 2. What will be effect on reaction rate if the concentration of the reactants A is doubled and B is halved?
   (a) Remains same (b) Increases four times
   (c) Decreases four times (d) Increases two times
3. Actinoid contraction from element to element is greater than Lanthanoid contraction, due to –
   (a) Poor shielding effect of 5f orbitals (b) Lower effective nuclear charge
   (b) Greater shielding effect of 5f orbitals (d) All of the above
4. 0.1 mol of a coordination compound $CoCl_3.5NH_3$ gives 0.2 mol equivalent of precipitate of AgCl with excess of $AgNO_3$. The correct formula of the complex is –
   (a) $[CoCl_3(NH_3)_3]Cl$ (b) $[Co(NH_3)_5Cl]Cl_2$
   (c) $[Co(NH_3)_5]Cl_3$ (d) $[Co(NH_3)_5Cl_2]Cl$
5. Major product that would be formed by the dehydrohalogenation of the compound 2-chloro-2-methyl butane with alcoholic KOH.
   (a) 2-methylbut-2-ene (b) 2-methylbut-1-ene
   (c) 3-methylbut-2-ene (d) 3-methylbut-1-ene
6. The C-O bond length in phenol is less than that in methanol, due to-
   (a) Partial double bond character (b) sp^2 hybrid state of C
   (b) sp^3 hybrid state of C (d) both (a) & (b)
7. The correct order of acidic strength is-
   (a) Phenol< Ethanol< Chloroacetic acid< Acetic acid
   (b) Phenol> Ethanol> Chloroacetic acid> Acetic acid
   (c) Ethanol< Phenol< Acetic acid< Chloroacetic acid
   (d) Acetic acid< Phenol< Ethanol< Chloroacetic acid

8. An organic compound **A** on treatment with NH_3 gives **B** which on heating gives **C**. **C** gives ethanamine upon Hoffmann bromamide degradation. Compound **A** would be-

(a) $CH_3CH_2CH_2COOH$ (b) CH_3COOH
(c) CH_3CH_2COOH (d) $(CH_3)_2CHCOOH$

9. The rate constant for a first order reaction is equal to the initial rate of the reaction when the initial concentration of the reactant is –

(a) 0.01M (b) 1M (c) 10M (d) 0.1M

10. Which statement regarding $[Cr(NH_3)_6]^{3+}$ is incorrect?

(a) It has octahedral geometry (b) It has d^2sp^3 hybridization
(c) It is diamagnetic (d) It is a low spin complex

11. The major product of acid catalyzed hydration of Propene is –

(a) 1- propanol (b) 2-propanol
(c) Ethanol (d) 2- methylpropan-1-ol

12. Which of the following is primary battery?

(a) Lead storage battery (b) Nickle Cadmium cell
(c) Dry cell (d) None of these

13. Which of the following will not give Hinsberg's test?

(a) N-methylethanamine (b) N,N-dimethylethanamine
(b) N-ethyl ethanamine (d) Propanamine

14. The role of a catalyst to change –

(a) Gibb's energy of reaction (b) Enthalpy of reaction
(c) Activation energy of reaction (d) Equilibrium constant

Answer assertion reason questions. Read following & carefully give the answer.

(a) Both A & R are true and R is the correct explanation of A.
(b) Both A & R are true and R is not the correct explanation of A.
(c) A is correct and R is not the correct statement.
(d) A is not correct and R is the correct statement.

15. **ASSERTION (A)** - In transition elements ns orbital is filled first and (n-1) d afterwards, and during ionisation, ns electron are lost prior to (n-1) d electrons.

REASON (R) - The Effective nuclear charge felt by (n-1) d electron is higher as compared to that by ns electrons.

16. **ASSERTION (A)** - p- nitrophenol is more acidic than Phenol.

REASON (R) – Nitro group stabilize the conjugate base as it is electron withdrawing.

17. **ASSERTION (A)** – Basic strength of secondary amine is greater than primary & tertiary amines in both aqueous and gaseous phase.

REASON (R) – Positive inductive effect is responsible for basic strength of amines in gaseous phase.

18. **ASSERTION (A) -** DNA has double strand alpha helix structure.

REASON (R) – DNA contains cytosine and thymine as pyrimidine base.

SECTION – B

This section contains 7 questions carrying two marks each with internal choice in two questions.

19. The energy of combustion of fuels like hydrogen, methane etc. is directly converted into electrical energy. This cell was first used in the Apollo space programme. Write the reaction occurred in a H_2-O_2 fuel cell at anode and cathode.
20. Show that in a 1st order reaction, the time required for completion of 99.9% is 10 times of half-life of the reaction.
21. The rate of a reaction quadruples when the temperature changes from 293 K to 303 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

    (Log 4 = 0.6021)
22. Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is –
    (i) Diamagnetic (iii) Outer orbital complex
    (ii) More stable (iv) Low spin complex
23. Write the mechanism of the following reaction –

    $(CH_3)_3C\text{-}Br + KOH\ (aq) \text{----------}> (CH_3)_3C\text{-}OH + KBr$

    OR

    (a) Nucleophilic substitution of chlorobenzene becomes easier when $–NO_2$ group is attached at ortho- or para-positions. Explain giving resonating structures.
    (b) Out of chlorobenzene and cyclohexyl chloride which one has higher dipole moment and why?
24. Give example of the formation of (i) an Oxime and (ii) a Cyanohydrin from either Ethanal.
25. What happens when D- glucose is oxidized with (i) Br_2 water & (ii) conc. HNO_3? Write chemical equations.

    OR

    (a) Give evidence for each of the followings (giving chemical equations) –
    (i) Glucose has six carbon chains in its molecule.
    (ii) Glucose reduces Tollen's as well as Fehling's solutions.

SECTION – C

This section contains 5 questions carrying three marks each with internal choice in one question.

26. (a) State Henry's law.
    (b) The vapour pressure of pure liquids **A** and **B** are 450 and 700 mm Hg respectively. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg.
27. Using valence bond theory explain the complex $[NiCl_4]^{2-}$ is tetrahedral and paramagnetic whereas the complex $[Ni(CN)_4]^{2-}$ is square planer and diamagnetic.
28. (a) Identify the major product formed when 1-chloro-1-methylcyclohexane is dehydrohalogenated with alcoholic KOH.
    (b) Out of following pairs which will be more reactive towards Nucleophilic substitution reactions? Give reason in short.
    (i) Chloroethane and chlorobenzene
    (ii) Vinyl chloride and allyl chloride

    OR

    (a) What is the product when an alkyl halide reacts with $AgNO_2$? Write the chemical equation.
    (b) Out of CH_3-CH_2-Br and $(CH_3)_3C$-Br, which will give S_N^2 reaction faster and why?
29. (a) What happens when salicylic acid is acetylated?
    (b) Ortho nitrophenol is steam volatile whereas para isomer does not. Why?
    (c) How will you convert phenol into 2-hydroxy benzenecarbaldehyde?
30. (a) Give a chemical test to distinguish between ethanamine and N-methylethanamine.

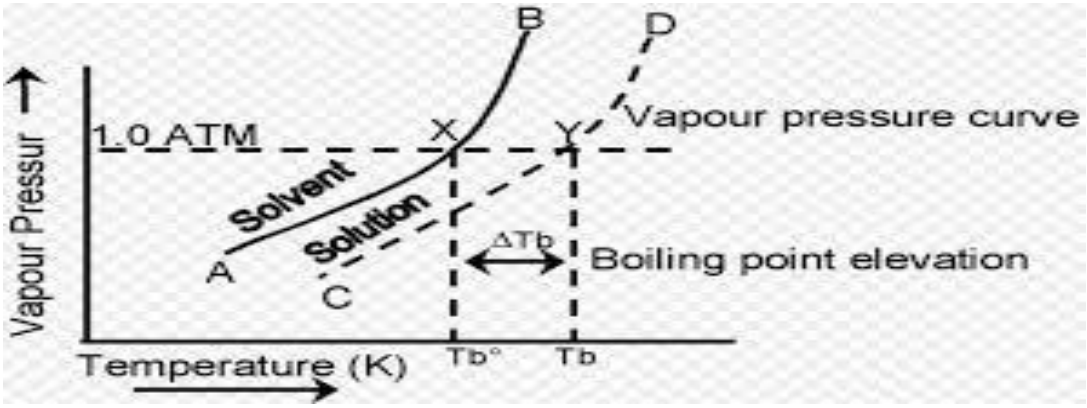
(b) Arrange them in decreasing order of their pKb value- C_2H_5-NH_2, $(C_2H_5)_2NH$ & $(C_2H_5)_3N$.

(c) Aniline gives appropriate yield of Meta nitro benzene upon nitration along with ortho & para isomers. Why?

SECTION – D

The following questions are case based questions. Each question has three questions of 1+1+2 = 4 marks.

31. Observe the graph and give the answers of questions followed.



(a) Boiling point of which solution is lower, 1M glucose solution OR 1M NaCl solution?

(b) If a solution of a salt has observed boiling point nearly doubled to its calculated boiling point. It's Observed molar mass would be either twice of its calculated molar mass OR half of its calculated molar mass. Justify.

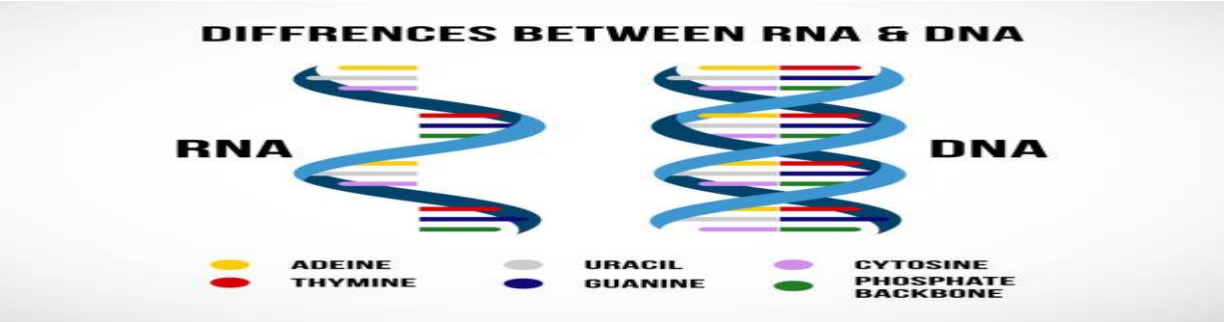
(c) 1 Molal solution has boiling point 374.15 K. What would be the boiling point of the same salt solution if its molality becomes 2.5 times? (boiling point of pure solvent = 373.15 K)

OR

(c) Compare the boiling point of NaCl solution (1 molal) assuming that NaCl is (i) 100% ionized and (ii) 0% ionized.(Kb for water = 0.52 K. Kg mol-1. (boiling point of pure solvent = 373.15 K)

32. Read the following paragraphs and give the answers of the questions followed.

1. Nucleic acids are of two types – DNA & RNA. Both are having nitrogenous bases as Adenine, Guanine, Cytosine, Thymine and Uracil. Out of these Thymine is not found in RNA. Intermolecular H – bonds are present in between A-T and G-C pair. More number of H- bonding is present in between G-C pair.



2. Proteins are the polymers of alpha amino acids. The simplest amino acid is 2-aminoethanoic acid called Glycine. Nature of amino acid solutions depends upon relative numbers of $–NH_2$ & -COOH groups.

(a) A sample of DNA has higher boiling point as compared to another sample. Which pair of nitrogenous pair would you expect more in this sample?

(b) How is a nucleoside different from a nucleotide?

(c) What would you infer from the following observations?

(i) A nucleic acid sample has unequal % composition of Purine and Pyrimidine. Is it DNA single strand or double strand?

(ii) A nucleic acid sample has uracil as one of the nitrogenous base. Identify the nucleic acid.

OR

(c) How is RNA structurally different from DNA? Give any two points.

SECTION – E

This section contains 3 questions carrying five marks each with internal choice in two questions.

33. (a) The electrolyte solution used in a lead storage battery is essentially changing in a regular interval of time. What is the reason behind it?

(b) Write the reaction taking place at the electrodes and the product of electrolysis of aqueous solution of NaCl.

(c) Write the Nernst equation and find the EMF of the cell at 298K.
$Mg(s) / Mg^{2+}$ (0.001M) // Cu^{2+} (0.001M) / Cu(s), (given is EMF^0cell is 2.71V)

OR

(a) Suggest a formula to find the limiting molar conductivity of water.

(b) A solution of $AgNO_3$ is electrolyzed for 10 minutes with a current of 2 amperes. What mass of Ag is deposited at the cathode? (atomic mass of Ag = 108u)

(c) Calculate the ΔG^0 for the following reaction. State whether the reaction becomes spontaneous or not?
Cu(s) + Zn2+(aq) ---------> Cu2+(aq) + Zn(s) , E^0Cu^{2+}/Cu= 0.34V & E^0Zn^{2+}/Zn= - 0.76V

34. Answer the following questions – (any five)

(a) Silver atom has $4d^{10}$ $5s^1$ electronic configuration in its ground state. Can you consider it as a transition element?

(b) Cr has higher Δ_iH^0 (II) than Mn. Why?

(c) Why is Cr^{2+} reducing in nature whereas Mn^{3+} is oxidizing when both are having $3d^4$ configuration?

(d) The chemistry of actinoids is more complex. Why?

(e) What is the effect of pH change on dichromate ion?

35. (a) An alkene **A** (C_3H_6) on ozonolysis gives two compounds **B** & **C**. **B** gives α, β- unsaturated aldehyde when reacting with dilute NaOH whereas **C** gives self-oxidation and reduction when treated with conc. NaOH. Identify **A**, **B** & **C** and write the name reactions involved.

(b) Comment upon the reactivity of Ethanal, propanone and benzene carbaldehyde.

OR

(a) A Grignard's reagent **R**-Mg-X when reacts with CO_2 gives a carboxylic acid **X** of molecular formula ($C_3H_6O_2$). **X** has less acidic strength than acetic acid. On decarboxylation **X** gives ethane. Identify **X** and the Grignard's reagent and write the chemical reactions involved.

(b) Write a chemical test to distinguish between the following pairs of compounds.

(i) Phenol and Benzoic acid (ii) Acetophenone and benzophenone.

KENDRIYA VIDYALAYA SANGATHAN, RAIPUR REGION

BLUE PRINT

SAMPLE PAPER – 5

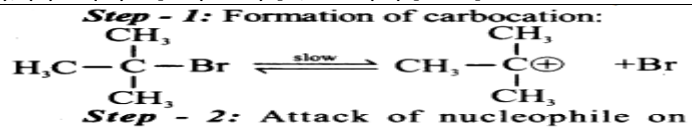
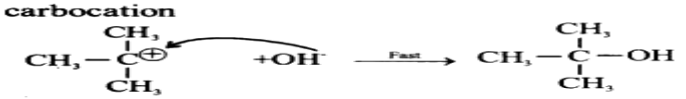
CHEMISTRY – XII 2022-23

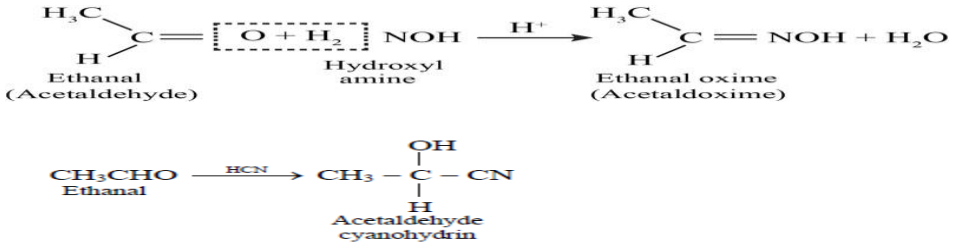
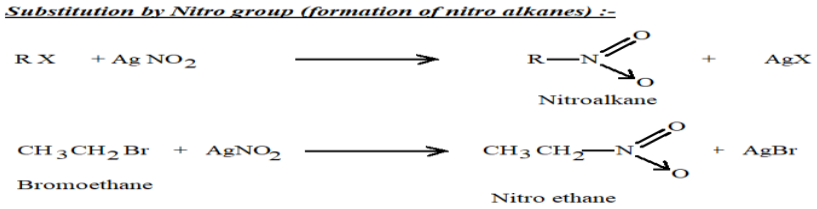
MAXIMUM MARKS = 70 TIME = 3 HOURS

UNIT NO	**CHAPTER**	SECTION – A MCQ	SECTION –A A/R	SECTION – B SA -I	SECTION – C SA - II	SECTION – D CBQ	SECTION – E LA	TOTAL
1	SOLUTIONS				1(3)	1(4)		2(7)
2	ELECTRO CHEMISTRY	2(2)		1(2)			1(5)	3(9)
3	CHEMICAL KINETICS	3(3)		2(4)				5(7)
4	d - & f – BLOCK ELEMENTS	1(1)	1(1)				1(5)	3(7)
5	COORDINATION COMPOUNDS	2(2)		1(2)	1(3)			4(7)
6	HALOALKANES & HALOARENES	1(1)		1(2)	1(3)			3(6)
7	ALCOHOLS, PHENOLS & ETHERS	2(2)	1(1)		1(3)			4(6)
8	ALDEHYDES, KETONES & CARBOXYLIC ACIDS	1(1)		1(2)			1(5)	3(8)
9	AMINES	2(2)	1(1)		1(3)			5(6)
10	BIOMOLECULES		1(1)	1(2)		1(4)		3(7)
TOTAL		**14(14)**	**4(4)**	**7(14)**	**5(15)**	**2(8)**	**3(15)**	**35(70)**

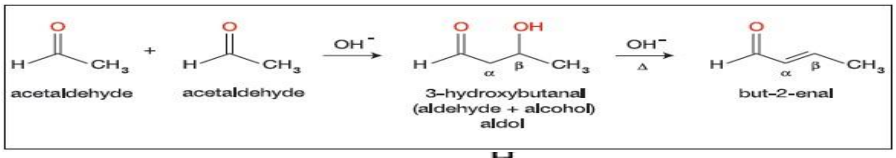
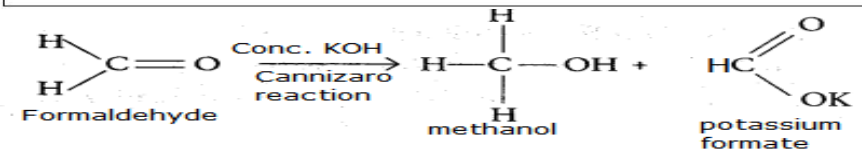
NOTE: - * **OPTIONS ARE GIVEN IN TWO QUESTIONS OF SECTION B, ONE QUESTION IN SECTION C AND TWO QUESTIONS OF SECTION E.**

KENDRIYA VIDYALAYA SANGATHAN, RAIPUR REGION
MARKING SCHEME – SAMPLE PAPER – V
CHEMISTRY (043)

Q.No	VALUE POINTS	MARKS
1	(c) 115 S cm^2/mol	1
2	(a) Remains same	1
3	(a) Poor shielding effect of 5f orbitals	1
4	(b) $[Co(NH_3)_5Cl]Cl_2$	1
5	(a) 2-methylbut-2-ene	1
6	(d) both (a) & (b)	1
7	(c) Ethanol< Phenol< Acetic acid< Chloroacetic acid	1
8	(c) CH_3CH_2COOH	1
9	(b) 1 M	1
10	(c) It is diamagnetic	1
11	(b) 2-propanol	1
12	(c) Dry cell	1
13	(b) N,N-dimethylethanamine	1
14	(c) Activation energy of reaction	1
15	(a) Both A & r are correct and R is the correct explanation of A	1
16	(a) Both A & r are correct and R is the correct explanation of A	1
17	(d) A is not correct but R is the correct statement.	1
18	(b) Both A & r are correct and R is not the correct explanation of A	1
19	Anode – $2H_2(g) + 4OH^-(aq)$ ---------> $4H_2O(l) + 4e^-$ Cathode – $O_2(g) + 2H_2O(l) + 4e^-$ ----------> $4OH^-(aq)$	1+1
20	$t_{1/2} = \frac{2.303}{K} log2$ .....(1) $t_{99.9\%} = \frac{2.303}{K} log\frac{100}{0.1}$ $= \frac{2.303}{K} log10^3$ $= \frac{2.303}{K} 3\, log\, 10$ .....(2) From equation (1) & (2) $t_{99.9\%} = 10 \times t_{1/2}$	2
21	Use correct formula log K_2/K_1 = Ea/2.303R .[T_2-T_1/T_1xT_2] = 0.5 mark Putting correct values = 0.5 mark Calculation & result = 1 mark i.e. Ea = 102.34 KJ/mol	2
22	(i), (ii) & (iv) = $[Co(C_2O_4)_3]^{3-}$, and (iii) $[CoF_6]^{3-}$	0.5 x 4 = 2
23	***Step - 1:*** **Formation of carbocation:**  ***Step - 2:*** **Attack of nucleophile on carbocation**  each correct step = 1 mark OR	1+1 = 2

	(a) The nitro group stabilizes the intermediate anion by withdrawing electrons when it is attached at ortho & para positions. (b) Cyclohexyl chloride has greater dipole moment because difference in electronegativity of Cl and sp3 hybrid C is more.	1+1=2
24	Oxime  	2
25	(i) Gluconic acid HOOC-$(CHOH)_4$-CH_2OH is formed. (ii) Saccharic acid HOOC-$(CHOH)_4$-COOH is formed. OR (i) On reacting with HI gives n-hexane. (ii) Glucose is an aldohexose i.e. it has an aldehyde group at C1.	1+1 = 2 1+1=2
26	(a) Statement of Henry's law. $p_{Total} = p_A + p_B$ $= (1 - x_B)\, p_A^0 + x_B\, p_B^0$ $= p_A^0 + (p_B^0 - p_A^0)\, x_B$ $600 = 450 + (700 - 450)x_B$ $600 - 450 = 250x_B$ $150 = 250x_B$ $x_B = \frac{150}{250} = 0.60$ (b) $\Rightarrow x_A = 1 - 0.60 = 0.40$	1+2 = 3
27	Complex $[NiCl_4]^{2-}$ has unpaired electrons and sp^3 hybridization whereas the complex $[Ni(CN)_4]^{2-}$ has no unpaired electrons and dsp^2 hybridization.	1.5x2= 3
28	(a) Methyl cyclohexene (b) (i) Chloroethane because C-Cl bond is weaker in cyclohexyl chloride and C-Cl bond in chlorobenzene is stronger due to partial double bond character. (ii) Allyl chloride has stable intermediate carbo cation through resonance. OR (a) Nitroalkane is formed.  (b) CH_3-CH_2-Br will give SN^2 faster because of less +I effect and less stearic hindrance.	1+1+1=3 2+1=3
29	(a) Acetyl salicylic acid (Asprin) is formed. (b) Less boiling point due to intra molecular H bonding. (c) By treating phenol with NaOH then reacting with CO_2 followed by acidification. (Kolbe reaction)	1+1+1=3
30	(a) Ethanamine reacts with Heinsberg's reagent and the product is soluble in alkali whereas the product of N-methylethanamine with the same reagent is insoluble in	1+1+1=3

	alkali. Better to write with chemical equation OR Ethanamine gives carbyl amine with chloroform and KOH whereas N-methylethanamine does not OR anuother test. (b) C_2H_5-NH_2> $(C_2H_5)_3N$ >$(C_2H_5)_2NH$ (c) Anilinium ion is formed in sufficient amount and it directs the attack of -NO_2 group at meta position.	
31	(a) 1M glucose solution has is lower because glucose molecules do not associated or dissociated whereas NaCl molecules dissociated and elevate the boing point more. (b) Observed molar mass is inversely related with the elevation of boiling point so observed molar mass will find half of its calculated molar mass. (c) Compare and calculate T_b of 2.5 molal solution i.e. 375.65 K. $\Delta T_{b1} = Kb.m_1$ eq 1 $\Delta T_{b1} = T_b - T_b°$ = 374.15 – 373.15 = 1.0 Kelvin For 2.5 molal solution $\Delta T_{b2} = K_b, m_2$ eq 2 Compare eq 1 and eq 2 ΔT_{b2} = 2.5 K $\Delta T_{b2} = T_b - T_b°$ 2.5 K = T_b - 373.15 K T_b = 375.65 K OR (c) B.P. of NaCl solution (if it is 100% ionised) $\Delta T_{b1} = K_b . m.i$ ΔT_{b1} = 0.52 x 1 x 2 (i=2 for Na Cl 100% ionised) ΔT_{b1} = 1.04 K (eq 1) B.P. of NaCl solution (if it is unionised) ΔT_{b2} = 0.52 x 1 (i= 1 if NaCl is unionised) Compare ΔT_{b1} and ΔT_{b2} $\Delta T_{b1} = 2 \times \Delta T_{b2}$	1+1+2=4
32	(a) G≡C pair is more in the given sample because of more number of H- bonding. (b) Nucleoside consists of nitrogenous pair and pentose sugar whereas nucleotide consists of nucleoside and phosphate group. (c) (i) The DNA has single strand structure. (ii) RNA because it has only Uracil. OR (c) Any two structural difference between DNA & RNA.	1+1+2=4
33	(a) After some time the sulphuric acid solution becomes dilute therefore this has to be changed. (b) $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ (cathodic reduction) $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ (anodic oxidation) $2H_2O_{(l)} + 2Cl^-_{(aq)} \rightarrow H_{2(g)} + 2OH^-_{(aq)} + Cl_{2(g)}$ (Overall cell reaction) (c) Ecell = E^0cell – 2.303 RT/nF . log $[Cu^{2+}]/[Mg^{2+}]$, Since the concentration of both the solutions are equal therefore Ecell becomes equal to E^0cell. OR (a) $\Lambda^0m(H_2O) = \Lambda^0m(HCl) + \Lambda^0m(NaOH) - \Lambda^0m(NaCl)$ (b) W(Ag) = Z.I.t = 108 x 2 x 600 / 96500 = 1.34 Ag	1+2+2=5 1+2+2=5

	(c) $\Delta G° = -nFE°cell$ $E°cell = E°cathode - E°anode$ $E°cell = -0.76 – (0.34) = -1.10$ V $= -(2 \times 96500 \times -1.1)$ $= -212.3$ kJ $\Delta G°$ is found negative, therefore the reaction becomes non spontaneous.	
34	(a) Yes because in its +2 oxidation state it has an unpaired electron. (b) Cr has 6 unpaired electrons in 3d & 4s orbitals whereas Mn has 5 unpaired electrons so Cr has stronger metallic bonding. (c) After losing an electron Cr^{2+} becomes more stable due to t_2g^3 stable electronic configuration whereas Mn^{3+} acquires stability $3d^5$ after gaining an electron. (d) Because – veriety of oxidation states and radioactive nature. (e) On increasing pH $Cr_2O_7^{2-}$ ion (orange) changes into CrO_4^{2-} ion (yellow) and vice versa.	1*5=5
35	(a) A= CH_3-CH=CH_2, B = CH_3-CHO, C = HCHO   (b) Order of reativity = Propanone < Banzaldehyde < Ethanal with proper explanation. OR (a) X = CH_3-CH_2-COOH & Grignard's reagent = C_2H_5-Mg-Br $CH_3CH_2MgBr + CO_2 \rightarrow CH_3CH_2CO_2MgBr$ Ethylmagnesium bromide $CH_3CH_2CO_2MgBr \xrightarrow{HCl} CH_3CH_2COOH + Mg(Br)Cl$ Propanoic acid (b) (i) Phenol gives violet colouration with neutral $FeCl_3$ whereas benzoic acid does not. OR Benzoic acid gives brisk effervescence with $NaHCO_3$ whereas phenol does not or any other test. (ii) Acetophenone gives yellow precipitate with I_2 and NaOH (iodoform test) whereas benzophenone does not. Its better to write chemical equation of the tests.	3+2=5