2023	12	25	TS-C3	SEAT NUMBER				

IIT INSPIRE
ACADEMY OF SCIENCE
A Place for Excellence & Perfection

XI & XII Science (CBSE/state)
IIT- JEE (Mains + Advance)
NEET, MH-CET , NDA
Mo. No. 9595445177/9021445177

Branches : Chhatrapati Sq., Mangalmurti Sq.

2

(4 Pages)

calculator is not allowed.
5. All symbols having their usual meanings unless otherwise stated.
6. For each MCQ, correct answer must be written along with its alphabet.
7. Evaluation of each MCQ would be done for the first attempt only.

SECTION-A

Q.1 Select and write the correct answers to the following questions: **[10]**

1)Which of the following does not conduct electricity?_

Ans:

c) Solid NaCl **(1)**

2)When 10g of solute is dissolved in 950 ml of water, the mass percent of solute in solution is

Ans:

a) 1.04 **(1)**

3)The oxidation number of oxygen atom in superoxide is

Ans:

d) $-\frac{1}{2}$

(1)

4)Polythene is a/an_____ polymer

Ans:

a) thermoplastic **(1)**

5)But-2-en-1-al has

Ans:

b) 10σ bond and 2πbonds **(1)**

6)The oxidation number and coordination number of Co in ¿¿$(C_2O_4¿_3¿^{-3}$

Ans:

a) +3, 6 **(1)**

7)The rate constant for a reaction was found to be $1.55 \times 10^{-3} 5^{-1}$. The order of the reaction is

Ans:

b) first **(1)**

8)During the isothermal revisable expansion of 1 mol of an ideal gas from $2\,dm^3$ to $20\,dm^3$ at 300K, work done is _____ KJ.

Ans:

a) – 5.745 **(1)**

9)Acrolein is a/an _____.

Ans:

b) aldehyde **(1)**

10) The Glucose on prolonged heating with HI gives.

Ans:

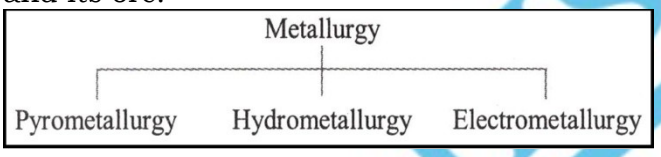
a) h-hexane **(1)**

Q.2 Answer the following questions in one sentence: [8]

1. Define metallurgy? (1)

Ans:

Commercial extraction of metals from their ores is called metallurgy. Different methods are used for their extraction depending on the nature of a metal and its ore.



2. What is the activation energy of a reaction? (1)

Ans:

For the reaction to occur the colliding reactant molecules must possess the minimum kinetic energy. This minimum kinetic energy is the activation energy.

3. Give molecular formulae of the following carbohydrates.

Glucose, sucrose, starch (1)

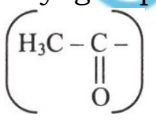
Ans:

1. Glucose $\left(C_6H_{12}O_6 \vee C_6\left(H_2O\right)_6\right)$
2. Sucrose $\left(C_{12}H_{22}O_{11} \vee C_{12}\left(H_2O\right)_{11}\right)$
3. Starch $\left[\left(C_6H_{10}O_5\right)_n \vee \left[C_6\left(H_2O\right)_5\right]_n\right]$

4. What is the acyl group? (1)

Ans:

Acyl group:



5. Explain the term: Semipermeable membrane (1)

Ans:

1. The osmotic pressure phenomenon involves the use of semipermeable membrane.
2. It is a film such as cellophane which has pores large enough to allow the solvent molecules to pass through them.
3. These pores are small enough not to allow the passage of large solute molecules or ions of high molecular mass through them.

4. The semi- permeable membrane selectively allows passage of solvent molecules.

6. What is electrolysis? **(1)**

Ans:

Electrolysis:

Electrolysis is breaking down of an ionic compound by the passage of electricity. Breaking down of an electrolyte during electrolysis is a chemical reaction where electrical energy is converted into chemical energy.

7. Explain: Molecularity of reaction **(1)**

Ans:

1. The molecularity of an elementary reactions refers to how many reactant molecules are involved in reactions.
2. The elementary reactions in which only one reactant molecules in involved are called unimolecular reactions.

   E.g., $O_{3(g)} \longrightarrow O_{2(g)} + O_{(g)}$

   $C_2H_5I_{(g)} \longrightarrow C_2H_{4(g)} + HI_{(g)}$
3. The elementary reactions in which two reactant molecules are involved are called bimolecular reactions

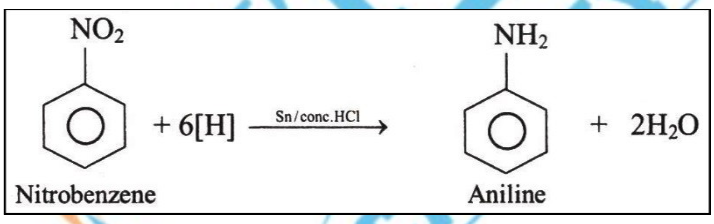
   E.g., $2\,NO_{2(g)} \longrightarrow 2\,NO_{(g)} + O_{2(g)}$

   $O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)}$
4. The molecularity of an elementary reaction is the number of reactant molecules taking part in it.

8. Predict the product of the following reaction. **(1)**

Nitrobenzene $Sn/conc.HCl$ *?*

Ans:



SECTION-B

Attempt any eight of the following questions: **[16]**

Q.3 Define of the following terms: **(2)**

1) Osmatic pressure

2) Hypertonic solution

Ans:

1. **Osmotic Pressure:** The hydrostatic pressure (on the side of solution) that stops osmosis is called an osmotic pressure of the solution.
2. **Hypertonic Solutions:** If two solutions have unequal osmotic pressures, the more concentrated solution with higher osmotic pressure is said to be hypertonic solution.

Q.4 Explain the following statement with the help of an example: **(2)**

'Salt of strong acid and strong base does not undergo hydrolysis.'

Ans:

1. NaCl is a salt of strong acid HCl and a strong base NaOH. When it is dissolved in water, it dissociates completely into its ions.
   $NaCl_{(aq)} \longrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$
2. The ions Na^{+} and Cl^{-} have no tendency to react with water. This is because the possible products, NaOH and HCl of such reactions are strong electrolytes and dissociate completely in aqueous solutions.
   In other words,
   $Na^{+}_{(aq)} + Cl^{-}_{(aq)} + H_2O \longrightarrow HCl_{(aq)} + NaOH_{(aq)}$
   (Strong acid) (Strong base)
   [Possible products]
   $HCl_{(aq)} + NaOH_{(aq)} + H_2O \longrightarrow H_3O^{+}_{(aq)} + Cl^{-}_{(aq)} + Na^{+}_{(aq)} + OH^{-}_{(aq)}$
   Thus, the reactants and the products are the same.
3. This implies that neither the cation no anion of the salt reacts with water or there is no hydrolysis.
4. Equality produced by ionization of water is not disturbed and solution is neutral. Therefore, the salt of strong acid and strong base does not undergo hydrolysis.

Q.5 Distinguish between isothermal process and adiabatic process. **(2)**

Ans:

No.	Isothermal process	No.	Adiabatic process
i.	It is a process in which temperature of the system remains constant throughout the transformation.	i.	It is a process in which there is no exchange of heat between system and surroundings.
ii.	Heat flows from the system to surroundings and vice versa. ($Q \neq 0$).	ii.	System is completely insulated with respect to heat from the surroundings. ($Q = 0$).
iii.	Temperature remains constant ($\Delta T = 0$):	iii.	Temperature may increase or decrease ($\Delta T \neq 0$).
iv.	Change in internal energy is zero ($\Delta U = 0$).	iv.	Internal energy may increase or decrease ($\Delta U \neq 0$).

Q.6 Calculate the packing efficiency of metal crystal that has fcc structure. **(2)**

Ans:

Step 1: Radius of particle/sphere

The corner particles are assumed to touch the particle at the centre of face ABCD as shown in figure.

The triangle ABC is right angled with $\angle ABC = 90^0$.

According to Pythagoras theorem,

$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$

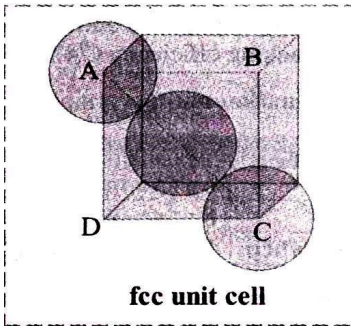
(Because AB = BC = a)

Hence, $AC = \sqrt{2}a$ ..... (1)

From the figure, $AC = 4r$

Substitution for AC from equation (1) gives

$\sqrt{2}a = 4r \vee r = \frac{\sqrt{2}}{4}a = \frac{a}{2\sqrt{2}}$ ..... (2)



fcc unit cell

Step 2: Volume of sphere

Volume of one particle $\frac{4}{3}\pi r^3$

Substitution for r from equation (2) gives

Volume of one particle ¿ $\frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3$

¿ $\frac{4}{3}\pi a^3 \times \left(\frac{1}{2\sqrt{2}}\right)^3 = \frac{\pi a^3}{3\sqrt{2}}$

Step 3: Total volume of particles

The unit cell of fcc lattice contains 4 particles.

Hence, volume occupied by particles in fcc unit cell ¿ $4 \times \frac{\pi a^3}{12\sqrt{2}} = \frac{\pi a^3}{3\sqrt{2}}$

Step 4: Packing efficiency:

Packing efficiency

¿ $\frac{\textit{Volume occupied by particles} \in \textit{unit cell}}{\textit{Total volume of unit cell}} \times 100$

¿ $\frac{\pi a^3}{3\sqrt{2}a^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$

Thus, in fcc/ccp/hcp crystal lattice, 74% of the total volume is occupied by particles and 26% is void volume or empty space.

Q.7 Write the general outer electronic configuration of the elements of group 16, group 17 and group 18 **(2)**

Ans:

Group	General outer electronic configuration
16	$ns^2 np^4$
17	$ns^2 np^5$
18	$ns^2 np^6$

Q.8 Write the electrode reactions during electrolysis of molten KC1. **(2)**

Ans:

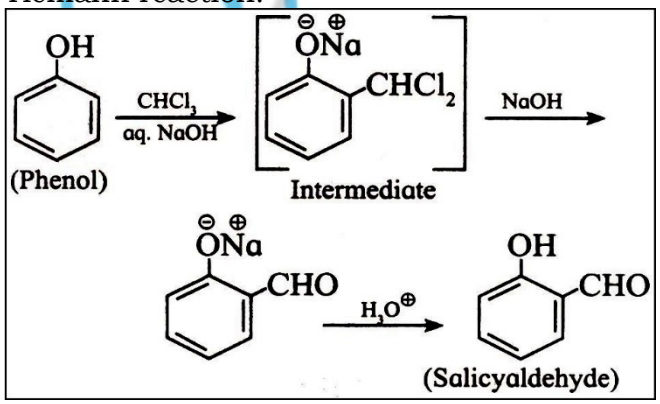
Electrode reactions during electrolysis of molten KCl are as follows:

¿¿

Q.9 Explain: Reimer-Tiemann reaction **(2)**

Ans:

When phenol is treated with chloroform in aqueous sodium hydroxide solution followed by hydrolysis with acid, salicylaldehyde is formed. This reaction is known as Reimer-Tiemann reaction.



If carbon tetrachloride is used in place of chloroform, salicylic acid is formed.

Q.10 What are the proteins? **(2)**

Ans:

Proteins are polypeptides having more than hundred amino acid residues linked by peptide bonds.

Q.11 a) Write a short note on Hofmann bromamide degradation. **(2)**

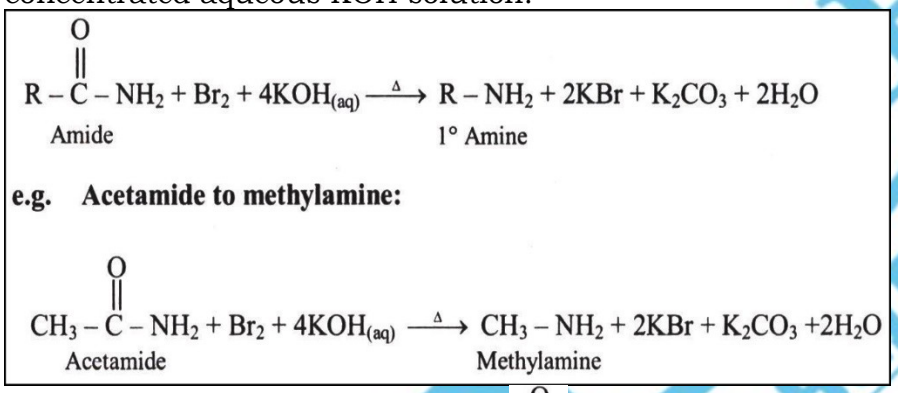
OR

b) Explain Gabriel phthalimide synthesis

a)

Ans:

1. This is a good laboratory method for the conversion of an amide into primary amine containing one carbon less.
2. The reaction is brought about by warming the amide with bromine and concentrated aqueous KOH solution.

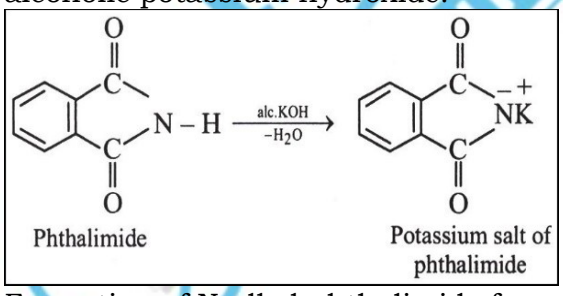


3. The overall result is removal of the $-\overset{O}{\overset{\|}{C}}-$ group from the amide.
   As the product contains one carbon atom less than the original amide. It is a step-down reaction.

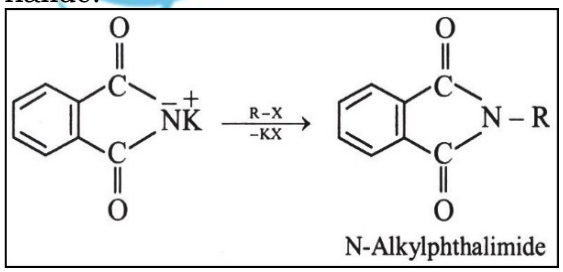
b)

This method is used for the synthesis of primary amine. It involves the following three stages.

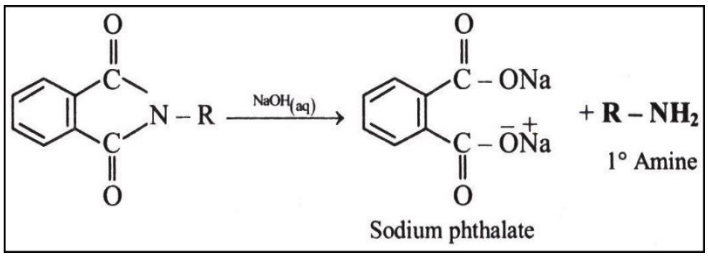
1. Formation of potassium salt of phthalimide from phthalimide on reaction with alcoholic potassium hydroxide.



2. Formation of N-alkyl phthalimide from the potassium salt by reaction with alkyl halide.



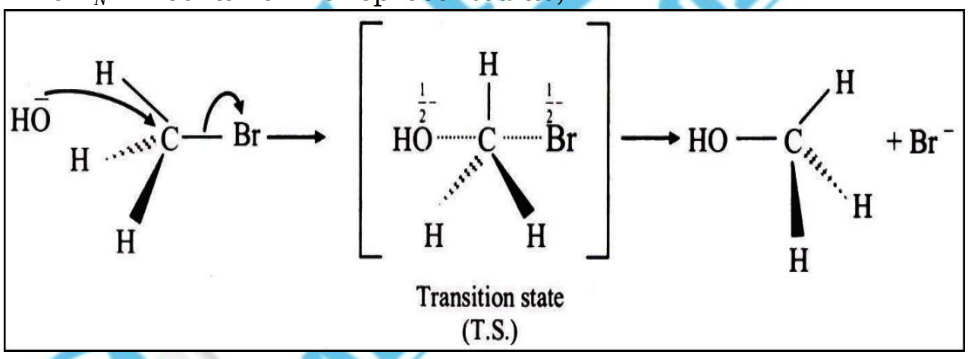
3. Alkaline hydrolysis of N-alkyl phthalimide to form the corresponding primary amine.



Q.12 Give a brief idea about S_N2 mechanism with the help of an example (2)

Ans:

1. S_N2 mechanism is a referred to as substitution nucleophilic bimolecular mechanism.
2. For example, the reaction between methyl bromide and hydroxide ion to give methanol.
   $CH_3-Br+OH^- \rightarrow CH_3-OH+Br^-$
   $Rate=k[CH_3Br]$
3. The reaction follows a second order kinetics.
   That is, the rate of this reaction depends on concentration of two reacting species, namely, methyl bromide and hydroxide ion. Hence, it is called substitution nucleophilic bimolecular mechanism (S_N2).
4. Rate of a chemical reaction is influenced by the chemical species taking part in the slowest step of its mechanism.
5. In the above reaction only two reactants are present and both are found to influence the rate of the reaction. This means that the reaction is a single step reaction which can also be called the slow step. This further implies that the two changes, namely, bond breaking and bond forming at the carbon take place simultaneously.
6. This S_N2 mechanism is represented as,



Q.13 Give the reagents and conditions necessary to prepare phenol from: (2)

1) Chlorobenzene 2) Benzene sulfonic acid

Ans:

1. **Chlorobenzene:**
   Reagents: NaOH, dil HCl
   Conditions: Temperature 623 K and Pressure 150 atm
2. **Benzene Sulphonic Acid:**
   Reagents: NaOH, Solid NaOH, dil HCl
   Conditions: Temperature 573 K

Q.14 Distinguish between thermosetting and thermoplastic resins. Write example of both the classes. (2)

Ans:

No.	Thermosetting resin	Thermoplastic resin
1	They do not soften on heating.	They soften on heating and harden on cooling.
2	They cannot be remoulded or reshaped.	These can be remoulded or reshaped.
3	They possess extensive cross-linking formed by covalent bonds.	They possess moderately strong intermolecular forces that are intermediate between elastomers and fibres.
4	They are rigid polymers.	They are not rigid polymers.
Eg:	Bakelite, urea-formaldehyde resins, etc.	PVC, polythene, polystyrene, etc.

SECTION-C

Attempt any eight of the following questions: **[24]**

Q.15 Write a short note on lanthanoid contraction. **(3)**

Ans:

1. As we move along the lanthanoid series, there is a decrease in atomic and ionic radii. This steady decrease in the atomic and ionic radii is called Lanthanoid contraction.
2. As we move from one element to another, the nuclear charge increases by one unit and one electron is added.
3. The new electrons are added to the same inner4f subshell. Thus, the 4f electrons shield each other from the nuclear charge poorly owing to their diffused nature.
4. With increasing atomic number and nuclear charge, the effective nuclear charge experienced by each 4f electrons increases. As a result, the whole of 4f electron shell contracts at each successive element.

Q.16 Find the values of ΔU under following conditions:

(3)

1) 30 kJ of heat is supplied to the system.

2) 20 kJ of work is done on the system.

3) A system releases 10 kJ of heat and performs 15 kJ of work on the surroundings.

Ans:

1. $30\,kJ$ of heat supplied to the system. It would be added to internal energy of the system.
   Hence, $\Delta U = +30\,kJ$
2. If $20\,kJ$ of work is done on the system, it is added to internal energy of the system.
   Consequently, $\Delta U = +20\,kJ$
3. Suppose a system release $10\,kJ$ of heat and performs $15\,kJ$ of work on the surroundings. These quantities are removed from internal energy of the system.
   Hence, $\Delta U = -25\,kJ$

Q.17 a) A reaction takes place in tow steps; **(3)**

a) $NO_{(g)} + CL_{(g)} \rightarrow NOCL_{2(g)}$

b) $NOCL_{2(g)} + NO_{(g)} \rightarrow 2\,NOCL_{(g)}$

1) Write the overall reaction.

2) Identify reaction intermediates.

3) What is the molecularity of each step?

OR

b) In the first order reaction, the concentration of reactant decreases from 20 mmol dm^{-3} to 8 mmoldm^{-3} in 38 minutes. What is the half life of reaction?

Ans:

a)

1. The overall reaction: $2\,NO_{(g)} + Cl_{2(g)} \longrightarrow 2\,NOCl_{2(g)}$
2. Since, $NOCl_2$ is formed in the first step and consumed in the second step. Hence, it is the reaction intermediates.
3. The molecularity of each step is 2 because two reactants are involved in each of the steps.

b)

Given: $[A]_0 = 20$ mmol dm^{-3}, $[A]_t = 8$ mmol dm^{-3}, t = 38 min

To find: Half life of reaction $\left(t_{1/2}\right)$

Formulae: i. $k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$ ii. $t_{1/2} = \frac{0.693}{k}$

Calculation: Substituting given value in

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

$$k = \frac{2.303}{38\text{ min}}\log_{10}\frac{20}{8}$$

$$= \frac{2.303}{38\text{ min}}\log_{10}(2.5)$$

$$= \frac{2.303}{38\text{ min}} \times 0.3979 = 0.0241\text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0241} = 28.7\text{ min}$$

Q.18 The gold crystallizes, it forms face-centred cubic cells. The unit cell edge length is 408 pm. Calculate the density of gold. Molar mass of gold is 197 g/mol. (3)

Ans:

Given: Edge length (a) = 408 pm = 408×10^{-12} m = 4.08×10^{-8} cm

Molar mass of gold = M = 197 g mol^{-1}

$N_A = 6.022 \times 10^{23}$ atoms mol^{-1}

To find: Density (ρ)

Formula: Density (ρ) = $\frac{M\,n}{a^3\,N_A}$

Calculation: For an fcc lattice, number of atoms per unit cell is 4.

$\therefore$ n = 4

From formula,

Density, $\rho = \frac{M\,n}{a^3\,N_A}$

$\therefore$ $\rho = \frac{197\text{ g mol}^{-1} \times 4\text{ atom}}{\left(4.08 \times 10^{-8}\right)^3\text{ cm}^3 \times 6.022 \times 10^{23}\text{ atom mol}^{-1}}$

$= \mathbf{19.27\ g/cm^3 = 19.27 \times 10^3\ kg/m^3}$

Q.19 How are xenon fluorides $XeF_2, XeF_4 \wedge Xef_6$ *obtained ? Give suitable reactions.* **(3)**

Ans:

Xenon fluorides are generally prepared by direct reaction of xenon and fluorine in different ratios and conditions, such as temperature, electric discharge and photochemical reaction.

i. $Xe + F_2 \xrightarrow[400\ °C]{\text{Sealed Ni tube}} XeF_2$
Xenon Fluorine Xenon difluoride

ii. $Xe + 2F_2 \xrightarrow[400\ °C\ 5\text{-}6\ atm]{\text{Sealed Ni tube}} XeF_4$
Xenon Fluorine (1:5) Xenon tetrafluoride

iii. $Xe + 2F_2 \xrightarrow[-80\ °C]{\text{Electric discharge}} XeF_4$
Xenon Fluorine Xenon tetrafluoride

iv. $Xe + 3F_2 \xrightarrow[\text{Low temp.}]{\text{Electric discharge}} XeF_6$
Xenon Fluorine Xenon tetrafluoride

Q.20 Derive the relation between elevation of boiling point and molar mass of the solute. (3)

Ans:

1. The boiling point elevation is directly proportional to the molality of the solution. Thus,
   $\Delta T_b = K_b m$ ..... (1)
2. Suppose we prepare a solution by dissolving $W_2 g$ of solute in $W_1 g$ of solvent.
   Moles of solute in $W_1 g$ of solvent $¿ \frac{W_2}{M_2}$
   Where, M_2 is the molar mass of solute
   Mass of solvent $¿ W_1 g = \frac{W_1 g}{1000\, g/kg} = \frac{W_1}{1000} kg$
3. The molality is expressed as,
   $m = \frac{Moles\ of\ solute}{Mass\ of\ solvent \in kg}$
   $m = \frac{W_2/M_2 mol}{W_1/1000\, kg}$
   $m = \frac{1000\, W_2}{M_2 W_1} mol\, kg^{-1}$ ..... (2)
4. Substitution equation (2) in equation (1), we get,
   $\Delta T_b = \frac{1000\, K_b W_2}{M_2 W_1}$
   Hence,
   $M_2 = \frac{1000\, K_b W_2}{\Delta T_b W_1}$

Q.21 Explain the role of green chemistry. **(3)**

Ans:

The green chemistry approach recognize that the Earth does have a natural capacity for dealing with much of the waste and pollution that society generates. It is only when that capacity us exceeded that we become unsustainable.

Following is the role of Green Chemistry:

1. To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.
2. The green chemistry helps to capital expenditure, to prevent pollution.
3. Green chemistry incorporates pollution prevention practices in the manufacture of chemicals and promotes pollution prevention and industrial ecology.
4. Green chemistry is a new way of looking at chemicals and their manufacturing process to minimize any negative environmental effects.
5. Green chemistry helps to protect the presence of ozone in the stratosphere essential for the survival of life on the earth.
6. Green chemistry is useful to control greenhouse effect (Global warning).

Q.22 1. Write a note on: Halogen exchange reactions (Finkelstein reaction) (3)

OR

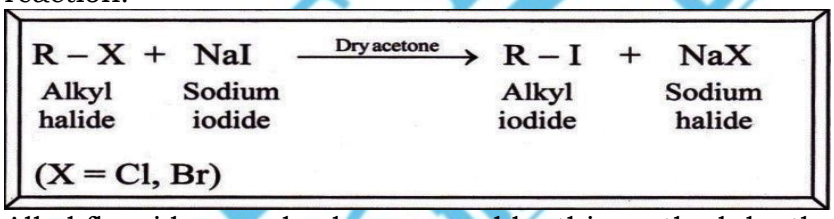
2. Explain Markownikoff's and Antimarkownikoff's rule with example.

1)

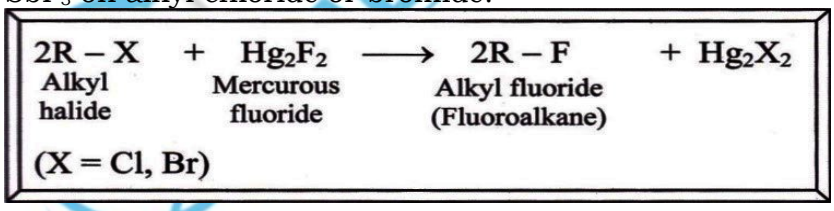
Ans:

1. Halogen Exchange Reactions:

1. This method is used for the preparation of alkyl iodides. Alkyl chlorides or bromides are heated with solution of sodium iodide in dry acetone to give corresponding alkyl iodide. The reaction is known as "Finkelstein reaction".
2. Sodium bromide and sodium chloride are less solution in dry acetone and thus they get precipitated.
3. These precipitates are removed by filtration and thus backward reaction is also prevented.
4. Primary alkyl bromides and primary alkyl chlorides give best results by this reaction.

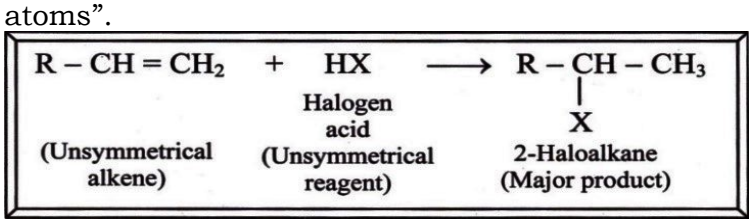


5. Alkyl fluoride can also be prepared by this method, by the action of mercurous fluoride (Hg_2F_2), silver fluoride (AgF), cobalt fluoride (CoF_3) or antimony trifluoride SbF_3 on alkyl chloride or bromide.



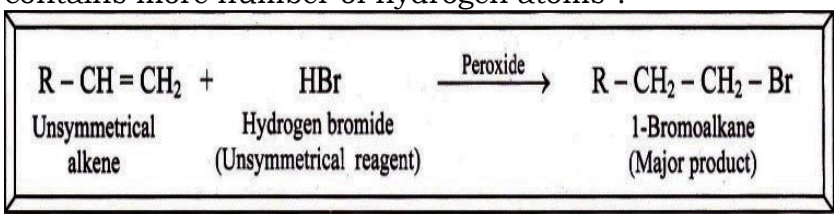
2)

1. **Markownikoff's Rule:**
   Statement: "When an unsymmetrical alkene is treated with an unsymmetrical reagent (HX), then the negative part of the reagent (-X) gets added to that unsaturated carbon of the double bond, which contains lesser number of hydrogen atoms".



2. **Anti-Markownikoff's Rule**

Statement: "When an unsymmetrical alkene is treated with an unsymmetrical reagent (HX), in the presence of peroxide such as Na_2O_2, the negative part of the reagent (-X) gets added to that unsaturated carbon of the double bond which contains more number of hydrogen atoms".

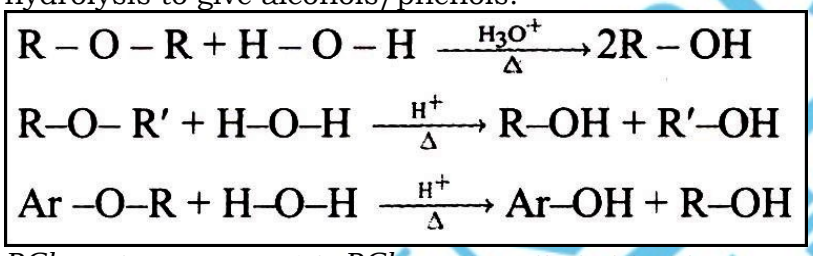


Q.23 What happens when ether is treated with the following reagents?

1) Dil. Sulphuric acid (hot) 2) PCL_5 3) Conc. HI or HBr (hot) (3)

Ans:

1. **Dil. sulphuric acid (hot):** Ethers when heated with dilute sulfuric acid undergo hydrolysis to give alcohols/phenols.



2. **PCl_5:** Ethers react with PCl_5 to give alkyl chlorides

$$R-O-R^{'}+PCl_5 \xrightarrow{\Delta} R-Cl+R^{'}-Cl+POCl_3$$

3. **Conc. HI or HBr (hot):** Alkyl ethers react with hot and concentrated HI and HBr to give an alcohol and an alkyl halide.

$$R-O-R+HX \rightarrow R-X+R-OH \xrightarrow{HX} R-X$$

$$R-OH \xrightarrow{HX} R-X+H_2O$$

Q.24 a) Explain vulcanization of rubber.

b) How is Nylon 6,6 prepared? Mention properties and uses of Nylon 6,6. (3)

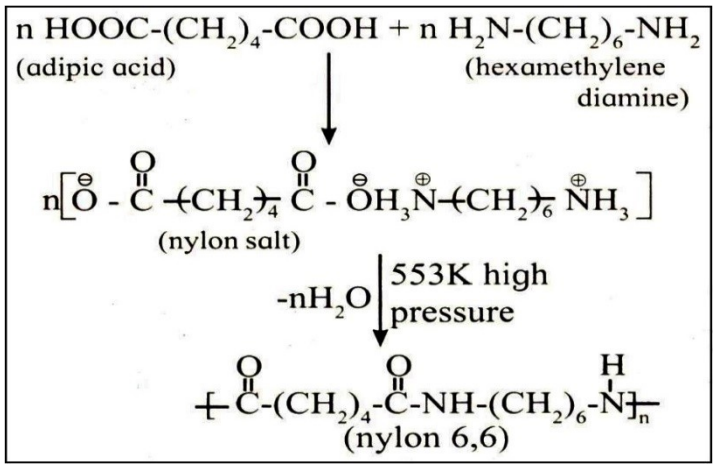
Ans:

a)

1. The process by which a network of cross links is introduced into an elastomer is called vulcanization.
2. Vulcanization of rubber is carried out to improve the physical properties of natural rubber.
3. The profound effect of vulcanization enhances the properties like tensile strength, stiffness, elasticity, toughness; etc. of natural rubber.
4. Sulfur vulcanization is the most frequently used process. Sulfur forms crosslinks between polyisoprene chains which results in improved properties of natural rubber.

   Note: In 1839 Charles Goodyear, an American inventor invented the process of Vulcanization.

b)



1. The monomers adipic acid and hexamethylendiamine on mixing forms nylon salt, which upon condensation polymerization under conditions of high temperature and pressure give the polyamide fibre nylon 6,6.
2. The numerals 6,6 in the name of this polymer stand for the number of carbon atoms in the two bifunctional monomers, namely, adipic acid and hexamethylenediamine.

Properties of Nylon 6,6:

1. Nylon 6,6 is high molecular mass (12000 50000 u) linear condensation polymer.
2. It possesses high tensile strength.
3. It does not soak in water.

Uses: It is used for making sheets, bristles for brushes, surgical sutures, textile fabrics, etc.

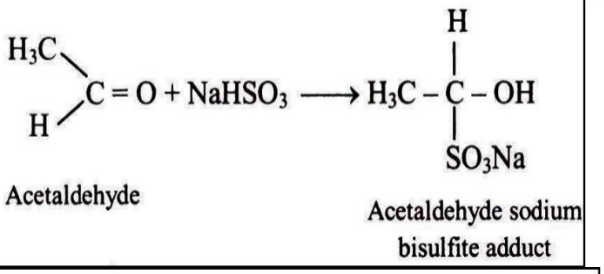
Q.25 What is the action of sodium bisulfite ($NaHSO_3$) on aldehydes and ketones? (3)

Ans:

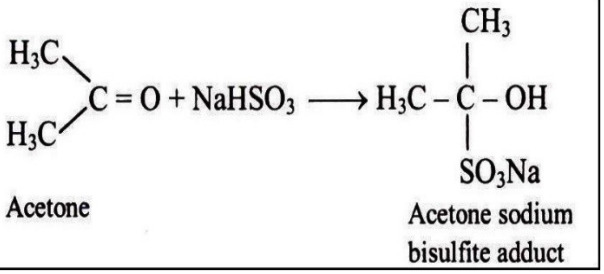
Aldehydes and ketones react with saturated aqueous solution of sodium bisulfite to give crystalline precipitate of sodium bisulfite adduct (addition compound).

e.g.

i.



ii.

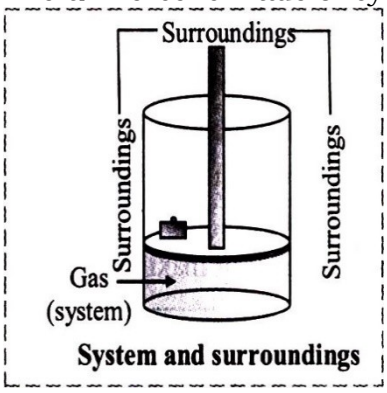


Q.26 Explain the term system and surrounding with the help of a diagram. (3)

Ans:

1. Consider a gas enclosed in a cylinder equipped with a movable piston as shown in figure.

2. Suppose we undertake study of change in volume of a gas and the amount of energy released or gained by a gas when the pressure is varied by putting certain mass on the piston.
3. In this case, a gas under study is called the system. A part of the universe under thermodynamic investigation is called the system. All other parts of the universe outside the system such as cylinder, room and others, are surroundings.
4. The universe is made of system plus surroundings.



SECTION-D

Attempt any three of the following question: **[12]**

Q.27 a) What is Kohlrausch law of independent migration of ions? How is it useful in obtaining molar conductivity at zero concentration of a week electrolyte explain with an example.

b) Calculate emf of the cell at $25^0\,C$. $Zn_{(s)}|Zn^{2+}¿|0.08\,M||Cr^{3+}¿|0.1\,M|Cr_{(s)}¿$

$E^0_{Zn}=-0.76\,V$, $E^0_{Cr}=0.74\,V$ **(4)**

Ans:

a)

1. Kohlrausch law states that, "at infinite dilution each ion migrates independent of co-ion and contributes to total molar conductivity of an electrolyte irrespective of the nature of other ion to which it is associated."
2. Both cation and anion contribute to molar conductivity of the electrolyte at zero concentration and thus Λ_0 is sum of molar conductivity of cation and that of the anion at zero concentration.
   Thus, $\Lambda_0=n_{+¿}\lambda_{+¿}^0+n_{-¿}\lambda_{-¿}^0¿$
   Where, $\lambda_{+¿¿}$ and $\lambda_{-¿¿}$ are molar conductivities of cation and anion, respectively, and $n_{+¿¿}$ and $n_{-¿¿}$ are the number of moles of cation and anion specified in the chemical formula of the electrolyte.
3. Determination of molar conductivity of weak electrolyte at zero concentration:
   The theory is particularly useful in calculating Λ_0 values of weak electrolytes from those of strong electrolytes.
   For example, Λ_0 of acetic acid can be calculated by knowing those of HCl, NaCl and CH_3COONa as described below:
   $\Lambda_0(HCl)+\Lambda_0(CH_3COONa)-\Lambda_0(NaCl)$
   $¿\lambda_{H^+¿}+\lambda_{Cl^-¿}+\lambda_{CH_3COO^-¿}+\lambda_{Na^+¿}-\lambda_{Cl^-¿}¿$ $¿\lambda_{H^+¿}+\lambda_{CH_3COO^-¿}=\Lambda_0|CH_3COOH|¿$
   Thus, $\Lambda_0(CH_3COOH)=\Lambda_0(HCl)+\Lambda_0(CH_3COONa)-\Lambda_0(NaCl)$
   Because Λ_0 values of strong electrolytes, HCl, CH_3COONa and NaCl, can be determined by extrapolation method, the Λ_0 of acetic acid can be obtained.

b)

Given: $E^{\circ}_{Zn} = -0.76\ V,\ E^{\circ}_{Cr} = -0.74\ V$

To find: Emf of the cell (E_{cell})

Formulae: i. $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

ii. $E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{n} \log_{10} \frac{[Product]}{[Reactant]}$

Calculation: **Cell reaction:**

$[Zn_{(s)} \longrightarrow Zn^{2+}_{(0.08M)} + 2e^{-}] \times 3$ (oxidation at anode)

$[Cr^{3+}_{(0.1M)} + 3e^{-} \longrightarrow Cr_{(s)}] \times 2$ (reduction at cathode)

$3Zn_{(s)} + 2Cr^{3+}_{(0.1M)} \longrightarrow 3Zn^{2+}_{(0.08M)} + 2Cr_{(s)}$ (overall reaction)

Using formula (i),

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$E^{\circ}_{cell} = E^{\circ}_{Cr} - E^{\circ}_{Zn} = -0.74\ V - (-0.76\ V) = 0.02\ V$

Using formula (ii),

The cell potential is given by

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{n} \log_{10} \frac{[Product]}{[Reactant]}$$

$$= 0.02 - \frac{0.0592\ V}{6} \log_{10} \frac{(0.08)^3}{(0.1)^2}$$

$$= 0.02 + 0.0127 = \mathbf{0.0327\ V}$$

OR

(a) +What is the mass of Cu metal produced at the cathode during the passage of 5 ampere current through $CuSO_4$ solution for 100 minutes? Molar mass of Cu is $63.5\,g\,mol^{-1}$.

(b) Sketch and describe the operation of standard hydrogen electrode. Give its application.

Ans:

a)

Given:

Current (I)= 5A

Time (t)= 100 min

100 × 60= 6000sec

Molar mass of Copper= 63.5 g/mol

We have to calculate the mass of copper produced at the cathode according to Faraday's first law of electrolysis.

According to this law,

The mass of substance deposited at an electrode is directly proportional to the amount of electric current passed through the electrolyte.

We have W=ZIT

W- Amount the substance deposited

Z- Electrochemical equivalent

I- Current passed

T- Time taken

Also,

$Z = \frac{M}{nF}$

M- Molecular mass

n- moles of electrons

F- Faraday's constant

Step by step working:

W= $\frac{63.5}{2\times 96500}\times 5\times 6000$

W= $\frac{63.5}{193000}\times 30000$

W= 9.87 g

b)

1. Construction:

a. SHE consists of a platinum plate, coated with platinum black used as electrodes.

b. Platinum plate is connected to the external circuit through sealed narrow glass tube containing mercury. It is surrounded by an outer jacket.

c. The platinum electrode is immersed in 1M H^{+} ion solution which is kept saturated with dissolved H_2 by bubbling hydrogen gas under 1 atm pressure through the side tube of the jacket.

d. In this electrode, Platinum does not take part in the electrode reaction. It is inert electrode and serves as the site for electron transfer.

3. Formulation:

The standard hydrogen electrode is represented as: $H^{+}(1\,M)\,|\,H_2(g, 1\,atm)\,|\,Pt$

4. Electrode Reactions:

The platinum black capable of adsorbing large quantities of H_2 gas, allows the change from gaseous to ionic form and the reverse process to occur.

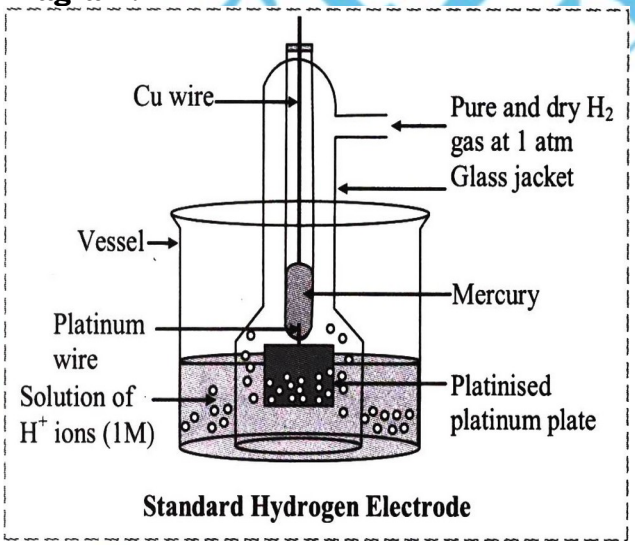
The reduction half reaction at electrode is

$2\,H^{+}(1\,M) + 2e^{-} \rightarrow H_2(g, 1\,atm);\ E^{0}_{H_2} = 0.0\,V$

5. Application:

SHE is used as a primary reference electrode to determine the standard potentials of other electrodes.

6. Diagram:



Standard Hydrogen Electrode

Example: To determine the standard potential of $Zn^{2+}(1\,M)\,|\,Zn_{(s)}$ electrode, it is combined with SHE to a galvanic cell.

$Zn_{(s)}\,|\,Zn^{2+}(1\,M)\,\|\,H^{+}(1\,M)\,|\,H_2(g, 1atm)\,|\,Pt$

The standard cell potential, E^{0}_{cell}, is measured.

$E^{0}_{cell} = E^{0}_{H_2} - E^{0}_{Zn} = -E^{0}_{Zn}$, because $E^{0}_{H_2}$, is zero.

Thus, the measured emf of the cell is equal to standard potential of $Zn^{2+}(1\,M)\,|\,Zn_{(s)}$ electrode.

Q.28 (a) Florine shows only -1 oxidation state while other halogens show -1, +1, +3, +5 and +7 oxidation states. Explain.
(b) State the general characteristics of interhalogen compounds. **(4)**

Ans:

a)

1. Fluorine atom has no d-orbitals in its valence shell and therefore, cannot expand its octet. Thus, fluorine being most electronegative exhibits -1 oxidation state only.
2. Cl, Br and I exhibit -1, +1, +3, +5 and +7 oxidation states. This is because they are less electronegative than F and possess empty d-orbitals in the valence shell and therefore, can expand the octet.

b)

1. The compound is considered as the halide of X. For example, ClF. Here the halogen having larger size is chlorine, it is more electropositive than F and hence the interhalogen compound is named as chlorine monofluoride. (n) is the number of atoms of X' attached to X.
2. As the ratio [radius of X : radius of X'] increases the value of n also increases.
3. Interhalogen compounds have even number of atoms 2, 4, 6, 8. For example, ClF_3 has 4 atoms.
4. The properties of interhalogen compounds are generally intermediate between those of the halogens from which they are made.
5. The central halogen exhibits different oxidation states in different interhalogen compounds.
6. Number of X' atoms in the compounds is always odd.
7. They are all diamagnetic.

Q.29 a) State and explain Henry's law. **(4)**
b) Define colligative properties. Give examples.

Ans:

a)

1. Henry's law: It states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution.
   Thus,
   $S \propto P \vee S = K_H P$
   Where, S is the solubility of the gas in mol L^{-1}, P is the pressure of the gas in bar over the solution. K_H, the proportionality constant is called Henry's law constant and its unit is $mol\,L^{-1}$ ¿¯¹¿.
2. When $P = 1$ bar, $K_H = S$. Thus, K_H is the solubility of the gas in a liquid when its pressure over the solution is 1 bar.

b)

The physical properties of solutions that depend on the number of solute particles in solutions and not on their nature are called colligative properties. These are

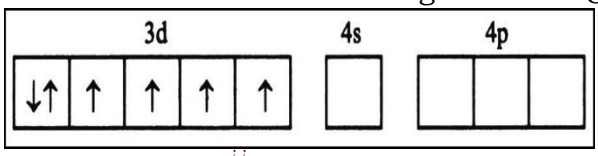
1. Vapour pressure lowering
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure

Q.30 (a) Explain the structure of octahedral high spin complex: ¿¿. **(4)**
(b) Explain linkage isomers giving one example.

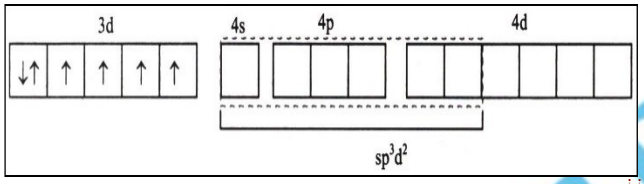
Ans:

a)

1. Oxidation state of central metal Co is +3.
2. Valence shell electronic configuration of $Co^{3+¿¿}$ is



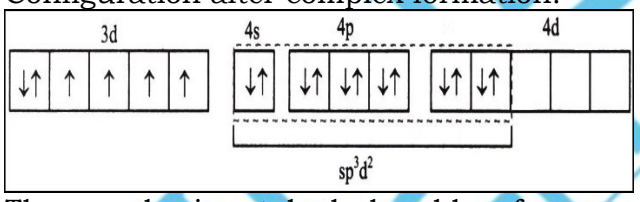
3. Six fluorides $F^{-¿¿}$ ligands, thus the number of vacant metal ion orbitals required for bonding with ligands would be six.
4. Complex is high spin that means pairing of electrons will not take place prior to hybridization.
5. Electronic configuration would remain the same as in the Free State shown above.
6. Six orbitals available for the hybridization. Those are one 4s, three 4p, two of 4d orbitals



Six metal orbitals after bonding with six $F^{-¿¿}$ ligands led to the sp^3d^2 hybridization. The d orbitals participating in hybridization for this complex are nd.

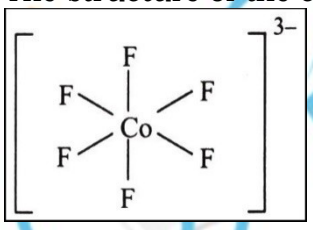
Six vacant sp^3d^2 hybrid orbital of $Co^{3+¿¿}$ overlap with six orbitals of fluoride forming Co - F coordinate bonds.

7. Configuration after complex formation.



8. The complex is octahedral and has four unpaired electrons and hence, is paramagnetic.

The structure of the complex is:



b)

1. Linkage isomers are formed when the ligand has two different donor atoms.
2. It coordinates to the metal via different donor atoms.

Eg:

The nitrite ion ¿ having two donor atoms shows isomers as:

$\left[Co\left(NH_3\right)_5\left(NO_2\right)\right]^{2+¿¿}$ and $\left[Co\left(NH_3\right)_5\left(ONO\right)\right]^{2+¿¿}$

The nitro complex has Co-N bond and the nitrito complex is linked through Co-O bond. These are linkage isomers.

Q.31 (a) Explain Gatterman-Koch formylation of arene. **(4)**

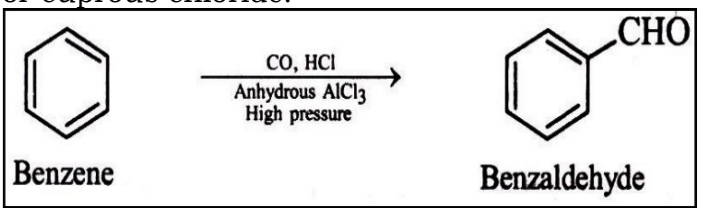
(b) Write a note on the haloform reaction.

(c) What is the action of hydrazine on cyclopentanone in presence of KOH in ethylene glycol?

Ans:

(a)

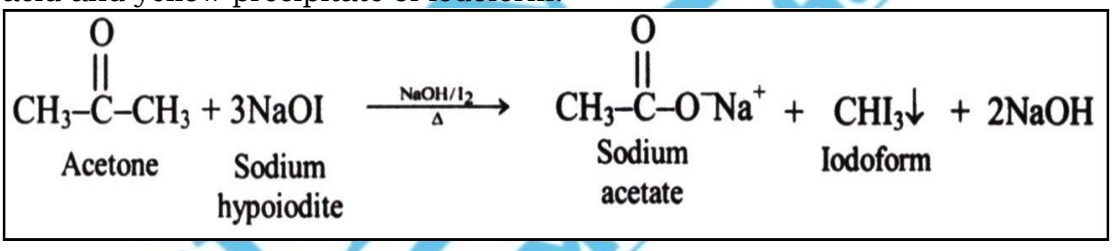
Gatterman –Koch Formylation of Arene: Benzene or substituted benzene is treated under high pressure with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride or cuprous chloride to give benzaldehyde or substituted benzaldehyde. The reaction is carried out in presence of anhydrous aluminium chloride or cuprous chloride.



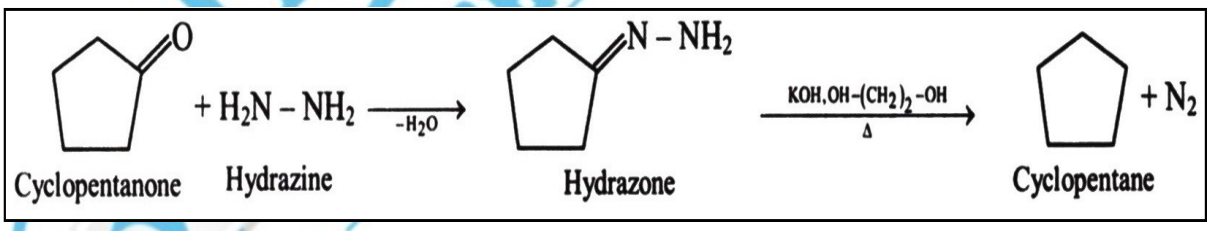
(b)

Haloform Reaction:

1. This reaction is given by acetaldehyde, all methyl ketones (CH_3-CO-R) and all alcohols containing $CH_3(CHOH)-¿$ group.
2. When an alcohol or methyl ketone is warmed with sodium hydroxide and iodine, a yellow precipitate is formed. Here the reagent sodium hypoiodite is produced in situ.
3. During the reaction, sodium salt of carboxylic acid is formed which contains one carbon atom less than the substrate.
4. The methyl group is converted in to haloform.
5. For example: Acetone is oxidized by sodium hypoiodite to give sodium salt of acetic acid and yellow precipitate of iodoform.



(c)



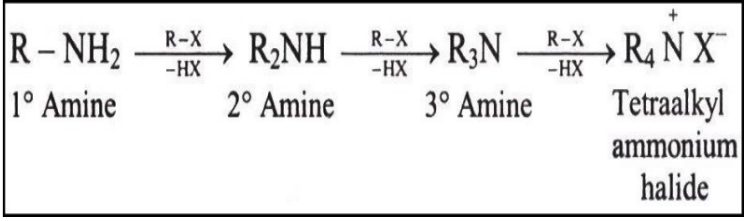
OR

a) Explain in details: Homann's exhaustive alkylation or alkylation of amines.

b) How many moles of methylbromide are required to convert ethanamine to N,N-dimethylethanamine?

Ans:

1. When a primary amine is heated with excess of primary alkyl halide it gives a mixture of secondary amine, tertiary amine along with tetraalkylammonium halide. This can be given as,



2. If excess of alkyl halide is used tetraalkyl ammonium halide is obtained as major product. The reaction is known as exhaustive alkylation of amines.

3. The tetraalkylammonium halides are called quaternary ammonium salts which are crystalline solids.
4. They are the derivatives of ammonium salts in which all the four hydrogen atoms attached to nitrogen in $NH_4^{+¿¿}$ are replaced by four alkyl groups (same or different).
5. Primary, secondary and tertiary amines consume three, two and one moles of alkyl halide respectively to get converted into quaternary ammonium salt.
6. The reaction is carried out in presence of mild base $NaHCO_3$, to neutralize the large quantity of HX formed.
7. If the alkyl halide is methyl iodide, the reaction is called exhaustive methylation of amines.

For Example: When methylamine is heated with excess methyl iodide, it gives tetramethyl ammonium iodide.

$$CH_3 - NH_2 + CH_3 - I \xrightarrow{\Delta} (CH_3)_2NH + HI$$

Methylamine Methyl iodide Dimethylamine

$$(CH_3)_2 - NH + CH_3 - I \xrightarrow{\Delta} (CH_3)_3N + HI$$

Trimethyl amine

$$(CH_3)_3N + CH_3 - I \xrightarrow{\Delta} (CH_3)_4\overset{+}{N}I^-$$

Tetramethyl ammonium iodide

b) Two moles of methyl bromide are required to convert ethanamine to N,N-dimethylethanamine.