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Grand Test	HSC EXAMINATION SET - A HINT & SOLUTION CHEMISTRY	M.Marks : 70 Duration : 3 Hrs

Note*: (1) All questions are compulsory

(2) Both the section are to be attempted in the same answer book.

(3) Figures to the right indicate full marks.

(4) Answer to every question, must be started on a new page.

(5) Every new question must be started on a new page.

(6) Use of logarithmic table is allowed.

Section – I

Q1 Select and write the most appropriate answer from the given alternatives for each sub-question **[07]**

(i) Sulphide ores are generally concentrated by (1)

    (a) Froth floatation process

(ii) Which solid will have the weakest intermolecular forces (1)

    (a) Ice

(iii) Which is responsible for electrical conduction of molten sodium chloride? (1)

    (b) Free ions

(iv) Which of these does not influence the rate of reaction _____ (1)

    (d) Molecularity of the reaction

(v) Molarity of $0.2N\ H_2SO_4$ is

    (d) 0.1

    [Hint:- Normality of acid = molarity × basicity *i.e.,* 0.2 = molarity × 2

    ∴ Molarity = 0.2/2 = 0.1]

(vi) For the reaction $CH_3COOH(l) + 2O_2(g) \rightleftharpoons 2CO_2(g) + 2H_2O(l)$ (1)

    at 298K and 1 *atm*. pressure, $\Delta H = -874$ kJ. Then the change in internal energy

    (ΔU) is

    $(a) -874$KJ   [$\Delta H = \Delta U + \Delta nRT$ ∴ For this reaction, $\Delta n = 0$ hence $\Delta U = \Delta H = -874$KJ.]

(vii) Which of the following is the most suitable drying agent for ammonia gas (1)

    (a) Calcium oxide

Q2 Attempt ANY SIX of the following : [12]

(i) Define. (a) Calcination (b) slag (2)

   (a) Calcination: - is a process in which the ore is heated to a high temperature below its melting point in the absence of air or in a limited supply of air.

   (b) Slag: - is defined as a waste product formed by combustion of a flux and gangue during the extraction of metals by smelting process.

(ii) Derive Van't Hoff equation for osmotic pressure of a solution. The equation (2)
expressing relationship between the osmotic pressure ( ), the concentration of the solution (C) and the absolute temperature T is called the van't hoff equation.

Or Van't Hoff general solution equation is represented as **= CRT**

Consider a volume V (in dm^3) of a dilute solution at an absolute temperature T. containing W grams of a substance having molecular weight M. Then, the number of

moles of the substance $= n = \dfrac{W}{M}$ and the concentration of the solution: $= C = \dfrac{n}{V}$

By van't Hoff-Boyle's law, at the constant temperature ……….. (I)

      $\propto C$

By Van't Hoff- Charles' law, at the constant concentration of the solution ………. (II)

      $\propto T$

      $\therefore$ From (I) and (II)

$\therefore \propto CT \quad \therefore = CRT$ This is called the Van't Hoff general solution equation

{Where R is the universal gas constant}

$\because C = \dfrac{n}{V}$ hence $= \dfrac{nRT}{V} \therefore V = nRT$

$\because n = \dfrac{W}{M}$

$V = \dfrac{WRT}{M}$

(iii)   Distinguish between hexagonal close packing and cubic close packing.   (2)

Hexagonal close packing	Cubic close packing
The arrangement of packing is ABAB type.	The arrangement of packing is ABCABC type.
In this three dimensional building of unit cell, spheres of third layer are placed on triangular shaped tetrahedral voids of the second layer.	In this three dimensional building of unit cell, the crest of spheres of third layer are placed in the positions of tetrahedral voids having apices upward.
In this, the spheres of third layer lie directly above the spheres of first layer.	In this, the spheres of third layer do not lie above the spheres of first layer.
In this first and third layers are identical.	In this first and third layers are different.
In this first and fourth layers are different.	In this first and fourth layers are identical.

(iv) State and explain Kohlrausch's law of independent migration of ions   (2)

Kohlrausch's law states that at infinite dilution of the solution. Each ion of an electrolyte migrates independently of its co-ions and contributes independently to the total molar conductivity of the electrolyte, irrespective of the nature of other ion present in the solution.

Explanation: Both the ions, cation and anion of the electrolyte make a definite contribution to the molar conductivity of the electrolyte at infinite dilution or zero concentration(Λ_0).

If $\}_+^0$ and $\}_-^0$ are the molar ionic conductivities of cation and anion respectively at infinite dilution, then $\Lambda_0 = \}_+^0 + \}_-^0$

(v) Write Arrhenius equation and explain the significance of terms involved in it.   (2)

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$k = A\,e^{-E_a/RT}$............(i)

The equation is called Arrhenius equation.

In which constant A is known as frequency factor. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and

R is the gas constant

Both A and E_a are collectively known as. Arrhenius parameters.

Taking logarithm equation (i) may be written as,

$\log k = \log A - \dfrac{E_a}{2.303RT}$

(vi)   What are the uses of   (A) H_2SO_4 and (B) Chlorine   (2)

    (A) Uses of H_2SO_4:-
            It is used as oxidizing agent.
            It is used in refining petroleum.
            It is used in preparation of important compounds like HCl, HNO_3
            It is used in the manufacture of dyes, ferlilizers.

    (B) Uses of Chlorine:-
   It is used in the manufacture of refrigerant such as Freon (i.e. CCl_2F_2).
            It is used in the extraction of metals like gold and platinum.
            It is used in the manufacture of bleaching powder.
            It is used as bleaching agent in textile and paper industry.

(vii) Explain fractional crystallisation?   (2)

Ultra pure metals and non-metals are obtained by **zone refining process.** It is **also called as fractional crystallization method** because this method is based on the principle that when an impure metal is melted and allowed to solidify, the impurities move away from the solid region and prefer to be distributed in the molten region.
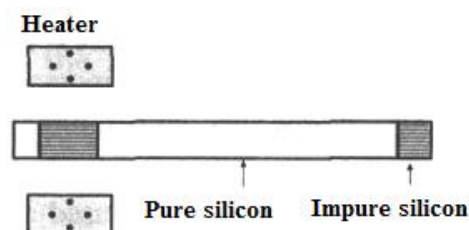
In this method one end of long rod of an element is heated using a small high frequency induction furnace so that a thin cross section of the metal is melted. When heating unit is moved slowly along the other end of the rod, the molten region solidifies. The impurities are more soluble in the molten liquid than in the solid.

Hence, they move towards the molten region. As the heating unit is moved to the other end of the rod, impurities also move to the same end.

This process is repeated, several times until purity of 99.999 (a purity of five nines) is achieved. The end portion is impure and can be rejected. A noble gas atmosphere is provided during the process in order to prevent the oxidation of the metal.

Elements like germanium, silicon and gallium which are used as semi conductors are refined by this process.

(viii)   Explain concept of maximum work?   (2)

Consider expansion of an ideal gas where work done is given by the formula
        $W = - P_{(ext)} \, V$
Work done in vacuum: **-** In vacuum external pressure is zero i.e.
        $P_{(ext)} = 0$
$\therefore W = (0 \times V)$ _OR_ $W = 0$ .....(1)
(It is called free expansion of gases)

Therefore as $P_{(ext)}$ increases the work done by the system also increases

But when $P_{(ext)}$ becomes equal to the pressure of the system then

$V = V_2 - V_1 = 0$

$\therefore W = -P_{(ext)} \times 0$ _OR_ $W = 0$ …..(2)

Therefore from above two statements we can conclude that more work is obtained if **P**$_{(ext)}$ & **P**$_{(system)}$ differ by **infinitesimally** small amount i.e. **if the process is carried out reversibly** …..(3)

According to the 1st law of thermodynamics

$U = q + W$

In an isothermal process, **U = 0** (at constant temperature)

Therefore q = –W

Which means, theoretically all the heat absorbed gets converted only into work, thus work done is more …..(4)

Thus from statements (3) & (4) it can be concluded that maximum work is obtained if the reaction is carried out **isothermally** (i.e. Constant temperature) and **reversibly.** The maximum work is denoted by **W$_{max}$.**

$$W_{max} = -2.303 n\, R\, T \log_{10}\left(\frac{V_2}{V_1}\right) \quad \textbf{OR} \quad W_{max} = 2.303 n\, R\, T \log_{10}\left(\frac{V_1}{V_2}\right)$$

$$W_{max} = -2.303 n\, R\, T \log_{10}\left(\frac{P_1}{P_2}\right) \quad \textbf{OR}$$

Q3 Attempt ANY THREE of the following :   **[09]**

(i) Explain the structure of SO_2 molecule on the basis of hybridization.   (3)

 i) SO_2 molecule has a bent V shaped structure with S-O-S bond angle 119^0 and bond dissociation enthalpy is 297 KJ mol^{-1}

 ii) Sulphur in SO_2 is sp2 hybridized forming three hybrid orbital's. Due to lone pair electrons. Bond angle is reduced from 120^0 to 119^0

 iii) In SO_2, each oxygen atom is bonded to sulphur by a   and   bond.

 iv)   bonds between S and O are formed by $Sp^2 - p$ overlapping. One of   bonds is formed by p – p overlapping while other   bond is   formed by p – p overlap

 v) Due to resonance both the bonds are identical having observed bond length 143 pm due to resonance.
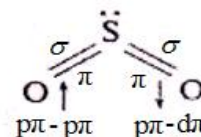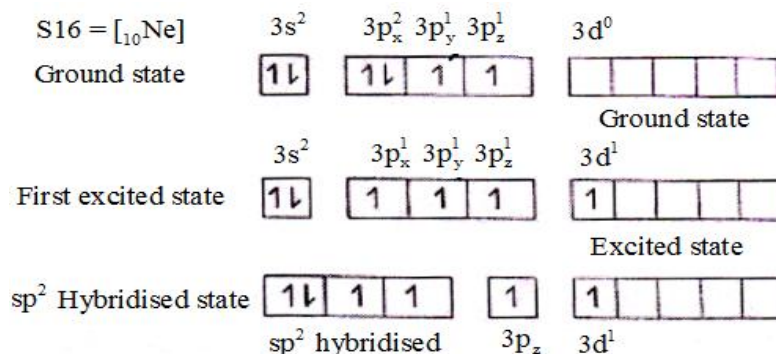
Partially filled $3p^1_z$ and $3d^1$ orbital's overlap to form   bonds with oxygen atoms.

(ii) The energy of activation for a first order reaction is 104 kj mol^{-1} (3)
The rate constant at 298 K is 3.7×10^{-5} S^{-1} what is rate constant at 303K

$E_a = 104$kj mol^{-1}, $k_1 = 3.7 \times 10^{-5}$ s^{-1}, $T_1 = 298$K, $T_2 = 303$ K,

$R = 8.314$ jk^{-1} mol^{-1} $k_2 = ?$

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

$$\log \frac{k_2}{3.7 \times 10^{-5} s^{-1}} = \frac{104\ k\ j\ mol^{-1}}{2.303 \times 8.314 \times 10^{-3} kj\ k^{-1} mol^{-1}} \left[\frac{303 - 298}{303 \times 298} \right]$$

$$\log \frac{k_2}{3.7 \times 10^{-5} s^{-1}} = \frac{104\ k\ j\ mol^{-1}}{2.303 \times 8.314 \times 10^{-3} kj\ k^{-1} mol^{-1}} \left[\frac{5\ k}{90924\ k^2} \right]$$

$$\log \frac{k_2}{3.7 \times 10^{-5} s^{-1}} = \frac{520}{2.303 \times 8.314 \times 90.924}$$

$$\log \frac{k_2}{3.7 \times 10^{-5} s^{-1}} = 0.2986$$

$$\therefore \frac{k_2}{3.7 \times 10^{-5} s^{-1}} = \text{Antilog } 0.2986$$

$$\therefore k_2 = 1.989 \times 3.7 \times 10^{-5} s^{-1} = 7.4 \times 10^{-5} s^{-1}$$

$$\begin{bmatrix} + \log 520 & = 2.7160 \\ - \log 2.303 & = 0.3623 \\ - \log 8.314 & = 0.9198 \\ - \log 90.924 & = \underline{1.9587} \\ & \overline{1}.4752 \end{bmatrix}$$

$$\begin{bmatrix} \text{Antilog } \overline{1}.4752 = 0.2987 \\ \log 3.7 \times 10^{-5} = \underline{\overline{5}.5682} \\ \overline{5}.8669 \\ \text{Antilog } \overline{5}.8669 = 7.4 \times 10^{-5} \end{bmatrix}$$

(iii) 2.8×10^2 mmole of a perfect gas occupies 127×10^{-1} L at 310 K (3)

Calculate the work done when the gas expands
(a) Isothermally against a constant pressure of 25×10^{-2} atm.
(b) Isothermally and reversibly
(c) Into vacuum until its volume has increased by 33×10^{-1} L

Solution: - (a) Isothermally against a constant pressure of 25 x 10-2 atm.

$P_{ext} = 0.25 atm$ and $V = 3.3 L$

$w = -P_{ext} \cdot V$

$w = -0.25 atm \times 3.3 L = -0.825 L.atm = -0.825 L.atm \times \dfrac{101.3 J}{L. atm} = -83.6 J$

$w = -83.6 J$

(b) Isothermally and reversibly

$n = 280$ mmol $= 0.28$ mol $V_1 = 12.7$ L

$R = 8.314$ J K^{-1} mol^{-1} $V_2 = 12.7$ L $+ 3.3$ L $= 16$ L

$T = 310$ K

$W_{max} = -2.303 \, nRT \log_{10}\left(\dfrac{V_2}{V_1}\right)$

$W_{max} = -2.303 \times 0.28 \text{ (mol)} \times 8.314 \text{ (J K}^{-1} \text{ mol}^{-1}) \times 310 \text{ (K)} \log_{10}\left(\dfrac{16L}{12.7L}\right)$

cancelling the common units

$W_{max} = -2.303 \times 0.28 \times 8.314 \text{ (J)} \times 310 \log_{10}(1.26)$

$W_{max} = -2.303 \times 0.28 \times 8.314 \text{ (J)} \times 310 \times (0.1004)$

$W_{max} = -166.9 J$

(c) Into vacuum until its volume has increased by 33×10^{-1} L

in vaccum $P_{ext} = 0$ atm   and $V = 3.3 L$

$w = -P_{ext} \cdot V$

$w = -0$ (atm) $\times 3.3$ (L) $= 0$

$w = 0$

(iv) Boiling point of a solvent is 80.2^0C. When 0.419 gram of the solute of molar (3) mass 252.4 g mol^{-1} is dissolved in 75 gram of the above solvent, the boiling point of the solution is found to be 80.256^0C. Find the molal elevation constant.

Boiling point of solvent $T^0 = 80.2^0$C   Molar mass of solute $= M_2 = 252.4$ g mol^{-1}

Boiling point of solution $T = 80.256^0$C   Weight of solute $= 0.4190$ g

Weight of solvent $= 75$ g

Increase in boiling point $=$ $Tb = T - T^0$

$$Tb = 80.256\ ^0C - 80.2\ ^0C = 0.056\ ^0C$$

$$k_b = \frac{T_b \times M_2 \times W_1}{W_1 \times 1000} = \frac{0.0560K \times 75\ g \times 252.49\ g\ mol^{-1}}{0.419\ g \times 1000}$$

$$k_b = 2.53\ K\ Kg\ mol^{-1}$$

Q4 Attempt ANY ONE of the following: [07]

(A) (i) Define mole fraction. State and explain Hess's law of constant heat summation. (4)
Write its two applications.

Ans : <u>mole fraction (x)</u> :- It is defined as the ration of numbers of moles of the component present in the solution to the total number of moles of all the components of the solution.

<u>Statement of Hess's law of constant heat summation</u> : It states that, the heat of a reaction or the enthalpy change in a chemical reaction depends upon initial state of reactants and final state o products and independent of the path by which the reaction is brought about (i.e. in single step or in series of steps).

Heat of reaction is same whether it is carried out in one step or in several steps.

<u>Explanation:</u>

The Hess's law is a direct consequence of the fact that the enthalpy is a state the conversion of the reactant A into the final product C. Let   rH0 be the enthalpy function, hence enthalpy change is independent of the path of the reaction. Consider change for the direct conversion

          A   C $_rH^0$

The same conversion can be carried out in two steps as,
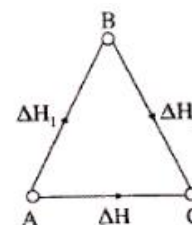
 Reaction   Enthalpy change
  A   B $_rH_1^0$
  B   C $_rH_2^0$

Consider the formation of $CO_{2(g)}$

 In one step : $C_{(g)} + O_{2(g)}$ $CO_{2(g)}$ H = –394 k J

 In two steps : $C_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ Δ $H_1 = -83$ k J

                $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ Δ $H_2 = -311$ k J

∴   H = H_1 + H_2
–394 kJ = –83 kJ + (–311) kJ

Hence law treats thermo chemical equations mathematically i.e. then can be added subtracted or multiplied by numerical factors like algebraic equations.

Applications : Hess's law is used for :
  1) To calculate heat of formation, combustion. Neutralization, ionization, etc.
  2) To calculate heat of reaction this may not take place normally or directly.
  3) To calculate heats of extremely slow or fast reactions.
  4) To calculate enthalpies of reactants and products.

(ii)   Calculate the equilibrium constant for the redox reaction at 298K   (3)

$$Sr_{(s)} + Mg^{2+}_{(aq)} \quad Sr^{2+}_{(aq)} + Mg_{(s)}$$

that occurs in a galvanic cell. Write the conventional cell representation for it.

$(E^0_{Mg} = -2.37 \text{ V and } E^0_{sr} = -2.89 \text{ V.})$

Ans: Cell reaction:

$E^0_{Mg^{2+}/Mg} = -2.37$ V ; $E^0_{Sr^{2+}/Sr} = -2.89$ V

Equilibrium constant K =?

The formulation of the cell:

$Sr \mid Sr^{2+}_{(aq)} (1 \text{ m}) \parallel Mg^{2+}_{(aq)} (1M) \mid Mg$

LHE $Sr_{(s)} \qquad Sr^{2+}_{(aq)} + 2e^-$ (Oxidation at anode)

RHE $Mg^{2+}_{(aq)} + 2e \qquad Mg_{(s)}$ (Reduction at cathode)

_____

$Sr_{(s)} + Mg^{2+}_{(aq)} \qquad Sr^{2+}_{(aq)} + Mg_{(s)}$ (overall cell reaction)
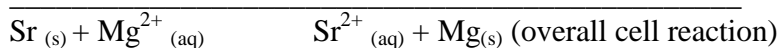
$\therefore n = 2$

$E^0_{cell} = E^0_{Mg^{2+}/Mg} - E^0_{Sr^{2+}/Sr} = -2.37(-2.89)$

$\qquad = 0.52$ V

$E^0_{cell} = \dfrac{0.0592}{n} \log_{10} k$

$\therefore \log_{10} k = \dfrac{n \times E^0_{cell}}{0.0592} = \dfrac{2 \times 0.52}{0.0592} = 17.568$

$K = Al\ 17.568 = 3.698 \times 10^{17}$

Ans: equilibrium constant = $K = 3.698 \times 10^{17}$

(B)   (i)   Explain the trends in ionization enthalpy of noble gases? Write uses of Krypton.   (4)

Ans: Groups 18 elements (Noble gases) possess very high values of ionization enthalpies the enthalpy of each noble gas is the highest in the period.

The ionization enthalpy decreases down the group. The very large ionization enthalpies of noble gases are due to their very stable closed shell electronic configuration as it requires a very large amount of energy to remove an electron from a completely filled outermost shell.

On moving down the group, the size of atom increases and consequently the valance electron experience less force of attraction by the nucleus. Hence ionization energy decreases from He to Rn.

Uses of krypton

i)   It is used in filling discharge tubes and electric bulbs.

ii)   It is used in high efficiency miner's cap lamps .

iii)   It is used in signal lights on run ways of airports since it produces bright white light during electric discharge.

iv)   Krypton 85 is used to measure thickness of sheets of metals and plastics.

(ii) Niobium is found to crystalline with bcc structure and found to have density of (3) 8.55 g cm^{-3}. Determine the atomic radius of niobium if its atomic mass is 93

Ans: Density of Niobium (Nb) crystal = 8.55 g cm^{-3} Crystalline structure is bcc.

Atomic mass of Nb = 93 g mol^{-1}, Avogadro number = N_A = 6.022 x 10^{23} mol^{-1}

Atomic radius of Niobium =?

In bcc unit cell, there are 8 atoms at 8 corners and 1 atom at the body centre.

$\therefore$ Number of Nb atoms = $\dfrac{1}{8}$ × 8 + 1 = 1 + 1 = 2.

Mass of one Nb atmo = $\dfrac{93}{6.022 \times 10^{23}} = 1.544 \times 10^{-22} g$

Mass of unit cell = Mass of 2Nb atoms = 3.088 x 10^{-22} g

If is edge length of bcc unit cell, Volume of unit cell = ^{3}

$\text{density} = \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}} \quad d = \dfrac{3.088 \times 10^{-22}}{r^3}$

$\therefore r^3 = \dfrac{3.088 \times 10^{-22}}{d} = \dfrac{3.088 \times 10^{-22}}{8.55}$

$= 0.361 \times 10^{-22} \, cm^3 = 36.1 \times 10^{-24} \, cm^3$

$\therefore r = (36.1 \times 10^{-24})^{\frac{1}{3}} = 3.3 \times 10^8 \, cm$

If r is the radius of 1 Nb atom, then in bcc structure

$r = \dfrac{\sqrt{3}}{4} r = \dfrac{\sqrt{3}}{4} = 3.3 \times 10^{-8} = 1.43 \times 10^{-8} \, cm$

$= 14.3 nm \, (1cm = 10^9 nm)$

SECTION-II

Q5 **Select and write the most appropriate answer from the given alternatives for each** [07]
sub-question

(i) Chlorobenzene can be obtained by benezene diazonium chloride by _____ (1)

   c) Gatterman's reaction

(ii) Insulin is a _____ (1)

   (a) hormone

(iii) Acidified potassium dichromate cannot be oxidize by _____ (1)

   c) ferric sulphate

(iv) Molecular formula of 'Urotropine' is _____ (1)

   a) $C_6H_{12}N_4$

(v) Phenol gives characteristic colour with _____ (1)

   d) aqueous ferric chloride solution

(vi) Which of the following complex will not show colour? (1)

   c) $[Sc(H_2O)_6]^{3+}$

(vii) Identify the compound 'B' in the following series of reactions. (1)
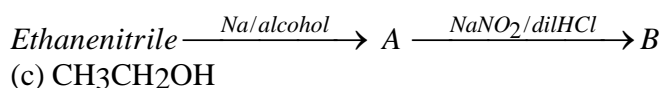
   $Ethanenitrile \xrightarrow{Na/alcohol} A \xrightarrow{NaNO_2/dilHCl} B$
   (c) CH_3CH_2OH

Q6 **Attempt ANY SIX of the following:** [12]

(i) What is the action of following compounds on cyclohexanone in presence of (2)
   dry hydrogen chloride?

   (a) Ethyl alcohol   (b) Ethylene glycol

   (a) Cyclohexanone reacts with one equivalent of monohydric ethyl alcohol to from
       hemiketal, which   further adds another molecule of alcohol to form a gem-
   dialkox compound known as ketal.
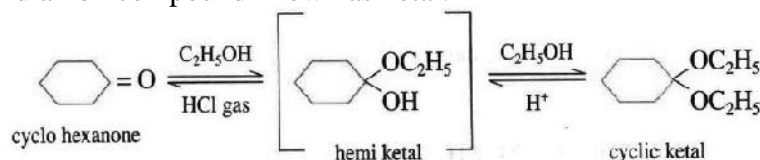
(b) Cyclohexanone reacts with ethylene glycol to form cyclic ketal.
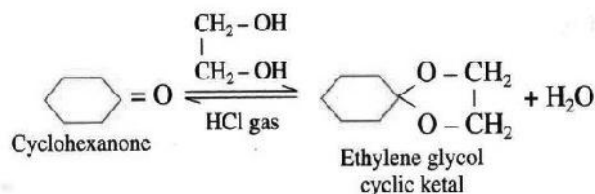
(ii) Explain structures of nucleoside and nucleotide? (2)

A nucleoside contains two basic components of nucleic acids i.e. a pentose sugar and a nitrogenous base. It is represented by sugar base. A nucleoside is formed when 1- position of a pyrimidine (crytosine, thymine, or uracil) or 9-position of guanine or ademine base is attached to C -1 of sugar by   - linkage.
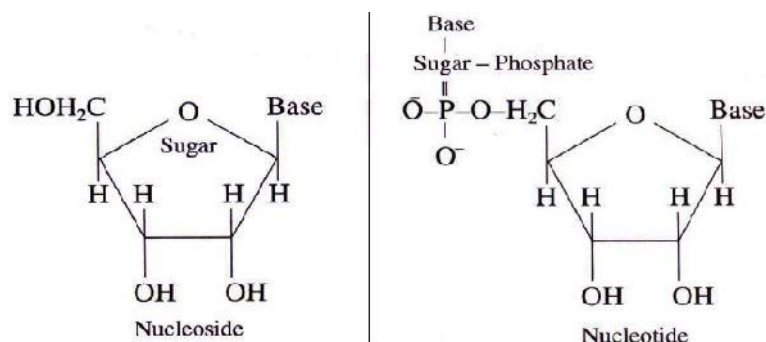

A nucleotide contains all three basic components of nucleic acids i.e. a pentose sugar, a phosphoric acid and a nitrogenous base. These are obtained by etherification of C5 – OH group of the pentose sugar by phosphoric acid. Nucleotides' are joined together through phosphate ester linkage.

(iii)   How is nylon -6 prepared? (2)

It is prepared from the monomer, Ɛ-caprolactum, which is obtained from Omega-amino- caproic acid (6-amino hexanoic acid)
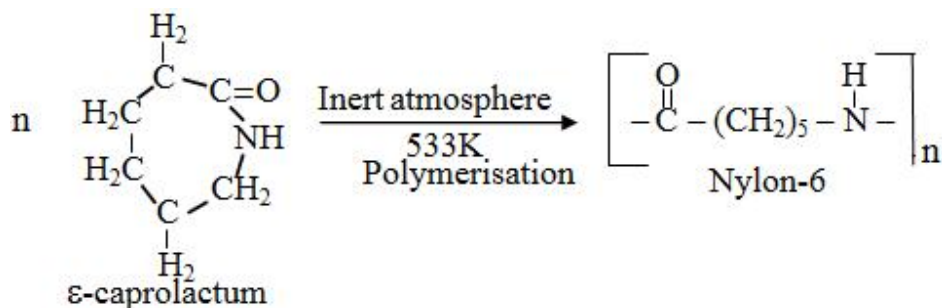$H_2N–CH_2–CH_2–CH_2–CH_2–CH_2–COOH$.
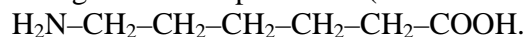
-aminocaproic acid, when heated undergoes dehydration to give Ɛ-caprolactum
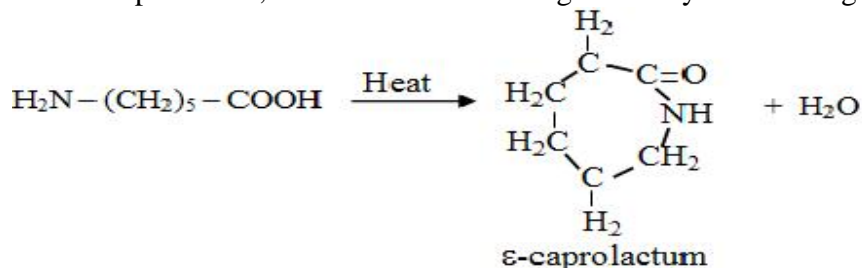
Ɛ-caprolactum is heated to about 533K in an inert atmosphere of nitrogen for

about 4 to 5 hours; when it gets polymerized to give Nylon-6.

It is called Nylon-6 because the monomer ε-caprolactum contains 6-carbon atoms.

(iv) What is the action of KOH on $K_2Cr_2O_7$ and HCl on K_2CrO_4? (2)

When alkali (KOH) is added to an orange coloured potassium dichromate, $K_2Cr_2O_7$ solution, yellow solution of potassium chromate, K_2CrO_4 is obtained.
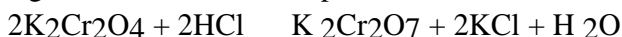
$K_2Cr_2O_7 + 2KOH (aq) \qquad 2K_2CrO_4 + H_2O$

Orange   Yellow

When acid (HCl) is added to yellow solution of potassium chromate K_2CrO_4 Orange coloured solution of potassium dichromate $K_2Cr_2O_7$ is obtained.

$2K_2Cr_2O_4 + 2HCl \qquad K_2Cr_2O_7 + 2KCl + H_2O$

(v) What are soaps? How are they prepared? (2)

Soaps are sodium or potassium salts of higher fatty acids which contain more than twelve carbon atoms. When fat or oil is hydrolysed using sodium or potassium hydroxide solution, soap obtained remains in colloidal form. Soap and glycerol are separated by adding sodium chloride. Soap precipitates out due to common ion effect, and glycerol remains in the solution can be recovered by fractional distillation.
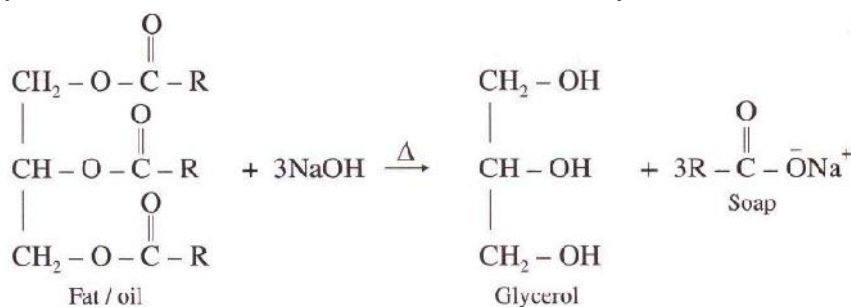
(vi) Write the structure and give IUPAC names of following (2)

(a) Salicylic acid   (b) Isobutyric acid
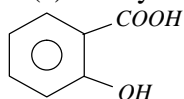
(a) Salicylic acid

2-Hydroxybenzoic acid   or   2-Hydroxybenzene-carboxylic acid

Salicylic acid

(b) Isobutyric acid

$(CH_3)_2CHCOOH$ 2- Methylpropanoic acid

(vii)   What are the antacids and antihistamines?   (2)

Antacids: Antacid is a base which neutralizes excess of acid in the stomach sodium bicarbonate and metal hydroxides of magnesium and aluminium are used as antacids which neutralize the excess of acid secreted. These chemicals control the symptoms and not the cause.

Antihistamines:- Histamine in the stomach stimulates the secretion of hydrochloric acid and pepsin. they work on receptors in stomach wall. Antihistamines are chemical drugs which prevent the interaction between histamine and receptors in the stomach wall, releasing less of amount of acid. They compete with histamines in binding with receptors in stomach wall. Hence decrease the secretion of acid.

(viii)   Write uses of CCl_4 and CHI_3

Uses of CCl_4:-
    It is used as a dry cleaning agent.
    It is used as a pesticide to kill insects in stored grains.
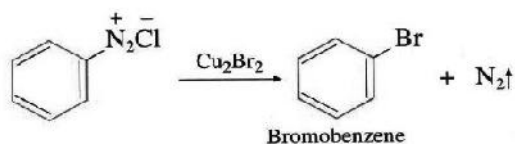   It is used as a solvent.
Uses of CHI_3 :-
    It is used as a disinfectant
   It is used in medicine as a healing agent and antiseptic, dressing of wounds and sores.

Q7   Attempt ANY THREE of the following: [09]

(i)   Explain Sandmeyer's reaction.   (3)
The replacement of diazonium group by –Cl or –Br using cuprous salt is called nitrite, a diazonium salt (benzene diazonium chloride) is formed. When diazonium salt is treated cuprous chloride or cuprous bromide, aryl halide (chlorobenzene or bromobenzene) is formed.
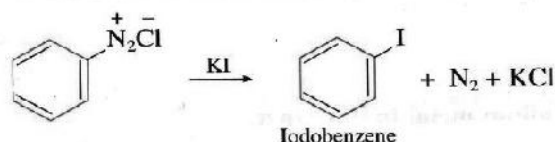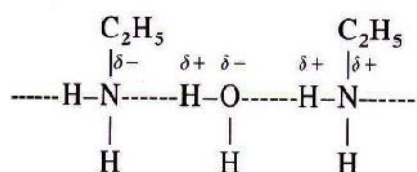
(ii) Explain: - (3)

    a) Ethylamine is soluble in water whereas aniline is not .

    b) Anlilne cannot be prepared by Gabriel Phthalimide synthesis.

    c) Triethylamine amines cannot be acylated.

a)   Ethylamine is soluble in water whereas aniline is not.

Ethyl amine is soluble in water due to intermolecular hydrogen bonding resulting in the formation of C_2H_5 NH_3 ion. Whereas **in aniline the hydrogen bonding** with water **is negligible** due to the **phenyl group (C_6H_5) is bulky and has – I effect**. Therefore, aniline is nearly insoluble in water.

b)   Anlilne cannot be prepared by Gabriel Phthalimide synthesis.

In Gabriel-phthalimide synthesis of aniline, potassium phthalimide requires the treatment with chlorobenzene or bromobenzene. Since **aryl halides do not undergo nucleophilic substitution reaction**. Therefore, chlorobenzene or bromobenenzene **does not react with potassium phthalimide** to give N-phenyl phthalimide and hence aniline cannot be prepared by Gabriel phthalimide synthesis.

c)   Triethylamine amines cannot be acylated.

Tertiary amines do not react with acetic anhydride or acetyl chloride i.e. they can be acylated because they do not contain a H-atom on the N-atom.

(iii) What are actanoids? Explain the compounds of copper (II) are coloured but (3)

those of zinc are colourless.

The series of elements from Thorium(Z = 90) to Lawrencium(Z = 103) in which 5f orbitals are progressively filled are called Actanoids.

The electronic configuration: $_{29}$Cu $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$ or $[Ar]\ 3d^{10}, 4s^1$

and Cu^{+2} $[Ar]\ 3d^9$

In copper compounds Cu^{+2} ions have incompletely filled 3-d orbital. Due to presence of one unpaired electron in 3-d orbital, Cu^{+2} ions absorb red light from visible spectrum and emit blue radiation **due to d   d transition**. Therefore, copper compounds are coloured. In case of zinc,($_{30}$Zn)the configuration is

$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2$ or $[Ar]\ 3d^{10}, 4s^2$

Since 3d subshell is completely filled and there is no unpaired electron, **d   d transition is not possible** and hence Zn^{2+} ions does not absorb radiation in visible region. Therefore, the compounds of Zn are colourless.

(iv) What are linkage and hydrated isomerism? Give example. 3

Linkage isomerism: The phenomenon of isomerism in which the coordination compounds have same metal atom or ion and same ligand but bonded through different atoms or linkages is known as linkage isomerism. For example:
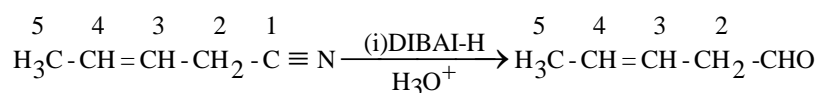
$[Co\ (NH_3)_5\ \mathbf{NO_2}]\ Cl_2$ and $[Co\ (NH_3)_5\ \mathbf{ONO}]\ Cl_2$
  (Yellow)   (Red)
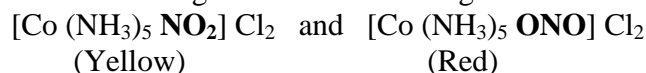
Hydrated isomerism: The phenomenon of isomerism in the coordination sphere of the complex is known as hydrate isomerism. For example:

$[Cr\ (H_2O)_6]Cl_3$
$[Cr\ (H_2O)_5\ Cl]Cl_2.H_2O$
$[Cr\ (H_2O)_4Cl_2]Cl.2H_2O.$
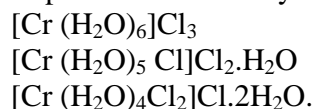
Q8 Attempt ANY ONE of the following: **[07]**

(i) **(A)** How will you bring following conversions? (7)

1) pent-3-ennitrile to pent-3-enal

$$\overset{5}{H_3C} - \overset{4}{CH} = \overset{3}{CH} - \overset{2}{CH_2} - \overset{1}{C} \equiv N \xrightarrow[H_3O^+]{(i)DIBAl\text{-}H} \overset{5}{H_3C} - \overset{4}{CH} = \overset{3}{CH} - \overset{2}{CH_2} - CHO$$
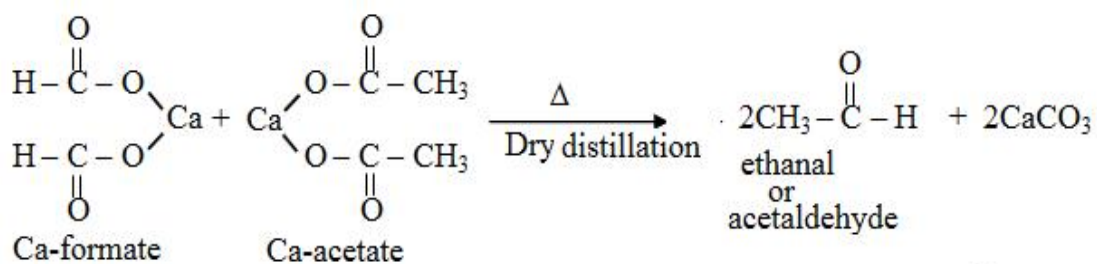
Pent – **3** – **ennitrile**   **Pent** – **3** – **en** al

2) Calcium salt of fatty acid to acetaldehyde

When an equimolar mixture of calcium formate and Ca-salt of any other acid (Other than formic acid) is dry distilled then an aldehyde is formed.

Ca-formate   Ca-acetate → ethanal or acetaldehyde + 2CaCO₃

3) Benzene to benzaldehyde

When benzene is treated under high pressure with arbon monoxide and hydrogen chloride in the presence of a catalyst consisting of a mixture of anhydrous aluminium chloride and cuprous chloride it gives benzaldehyde. This reaction is called Gatterman-Koch formylation

Benzene   Benzaldehyde
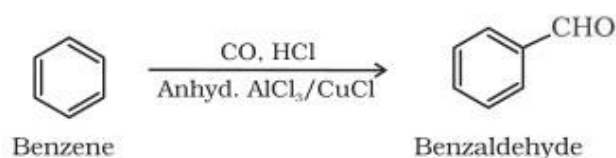
4) Calcium acetate to dimethyl ketone.

When Ca-salt of fatty acid other than calcium formate on dry distillation, then a symmetrical ketone is formed.
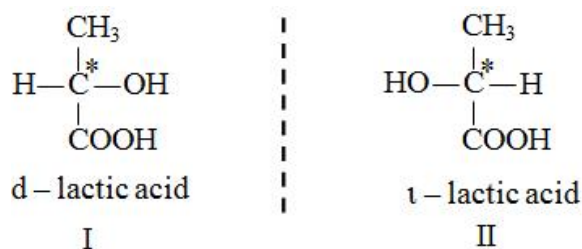

Ca-acetate
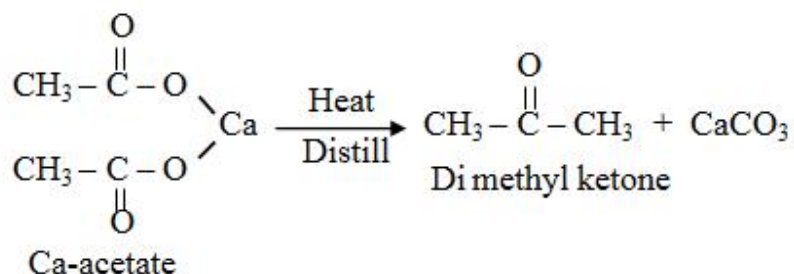
(B) What is chirality? Explain the optical activity of lacticacid.   (7)

A molecule containing asymmetric carbon atom and which has non- super imposable mirror images is said to be chiral and this property is called chirality. All chiral molecules exhibit optical activity.

Lactic acid contains one asymmetric carbon atom. Hence the molecule can exist in two isomeric forms.

The number of optical isomers is given by the formula $a = 2^n$ where 'a' is the number of isomers and 'n' is the number of asymmetric carbon atoms.

Hence Lactic acid exists in two isomeric forms ($a = 2^n = 2^1 = 2$)

$$CH_3 \qquad\qquad\qquad CH_3$$
$$H-\overset{*}{C}-OH \qquad\qquad HO-\overset{*}{C}-H$$
$$COOH \qquad\qquad\qquad COOH$$

d – lactic acid $\qquad\qquad$ ι – lactic acid

I $\qquad\qquad\qquad$ II

The two structures are <u>non-super imposable mirror images</u> of each other and are called enentiomers.

Structure I represents <u>dextroform</u> as it rotates the plane of polarized light to the Right (clockwise).
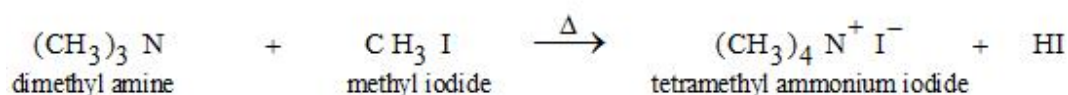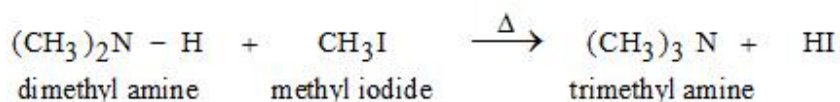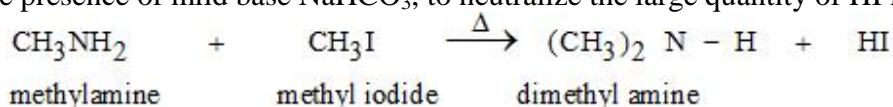
Structure II represents the <u>laevo form</u> as it rotates the plane of polarized light to the left (anticlock wise).

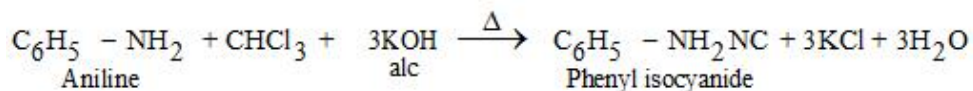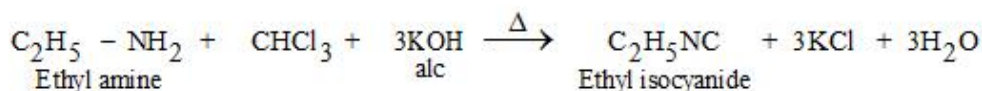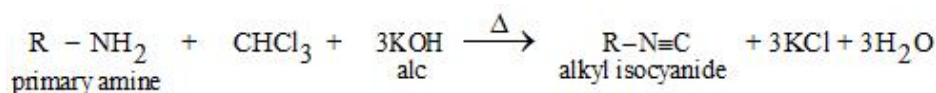The above optical isomers are also known as <u>Enantiomers</u>.

A mixture of equal amounts of dextro and laevo forms of Lactic acid are called <u>racemic form</u> and it is optically inactive due to external compensation.

(ii) (A) Explain Hoffmann's exhaustive methylation and Hoffmann's carbyl amine test. $\qquad$ (7)

Methylation of amine : The reaction in which a hydrogen atom attached to nitrogen atom of amines is replaced by methyl group is called methylation of amines. Hoffmann's Exhaustive Methylation: The process of converting primary, secondary or tertiary amine into quaternary ammonium halilde by heating them with excess of methyl iodide, is called exhaustive methylation or Hoffmann's exhaustive methylation. Thus when methyl amine is heated with excess of methyliodide it forms dimethylamine (Secondary amine), then trimethylamine (a tertiary amine) and finally of quaternary ammonium iodide (quaternary ammonium salt). The reaction is carried out in the presence of mild base $NaHCO_3$, to neutralize the large quantity of HI formed.

$$CH_3NH_2 + CH_3I \xrightarrow{\Delta} (CH_3)_2 N-H + HI$$
methylamine $\qquad$ methyl iodide $\qquad$ dimethyl amine

$$(CH_3)_2N-H + CH_3I \xrightarrow{\Delta} (CH_3)_3 N + HI$$
dimethyl amine $\qquad$ methyl iodide $\qquad$ trimethyl amine

$$(CH_3)_3 N + CH_3 I \xrightarrow{\Delta} (CH_3)_4 \overset{+}{N} \overset{-}{I} + HI$$
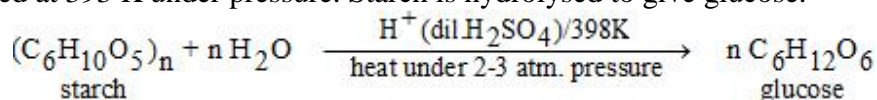dimethyl amine $\qquad$ methyl iodide $\qquad$ tetramethyl ammonium iodide

Aliphatic or aromatic primary amines on heating with chloroform and alcoholic potassium hydroxide solution form carbyl amines or isocyanides with extremely unpleasant smell. Secondary and tertiary amines do not give this test.

$$\underset{\substack{\text{primary amine}}}{R - NH_2} + CHCl_3 + \underset{\substack{\text{alc}}}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{alkyl isocyanide}}}{R-N{\equiv}C} + 3KCl + 3H_2O$$

$$\underset{\substack{\text{Ethyl amine}}}{C_2H_5 - NH_2} + CHCl_3 + \underset{\substack{\text{alc}}}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{Ethyl isocyanide}}}{C_2H_5NC} + 3KCl + 3H_2O$$

$$\underset{\substack{\text{Aniline}}}{C_6H_5 - NH_2} + CHCl_3 + \underset{\substack{\text{alc}}}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{Phenyl isocyanide}}}{C_6H_5 - NH_2NC} + 3KCl + 3H_2O$$

(B)   What are carbohydrates? How is glucose prepared on commercial scale?

Carbohydrates are optically active polyhydroxy aldehyde or polyhydroxy Ketones, or the compounds which on hydrolysis produce polyhydroxy aldehyde or polyhydroxy Ketones. Example: Glucose, sucrose, fructose.

Commercially, on a large scale, glucose is prepared by hydrolysis of starch with dilute sulphuric acid, starchy material is mixed with water and dilute sulphuric acid and heated at 393 K under pressure. Starch is hydrolysed to give glucose.

$$\underset{\substack{\text{starch}}}{(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow[\text{heat under 2-3 atm. pressure}]{H^+(\text{dil.}H_2SO_4)/398K} \underset{\substack{\text{glucose}}}{n\,C_6H_{12}O_6}$$

When hydrolysis is complete, calcium carbonate (chalk powder) is added. Chalk powder neutralizes excess of acid.

$$H_2SO_4 + CaCO_3 + 3KOH \xrightarrow{\Delta} CaSO_4 + H_2O + CO_2$$
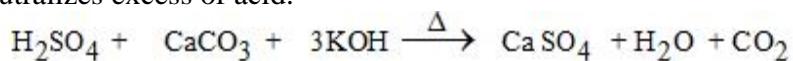
To the solution, activated charcoal is added which removes coloured impurities by adsorption. The solution is then filtered to remove insoluble impurities, the solution is then concentrated, when glucose is obtained in the crystalline form. Pure crystal of glucose is obtained by recrystallization.