Chemistry

Academic Year: 2016-2017 Marks: 70
Date & Time: 8th March 2017, 11:00 am
Duration: 3h

Question 1: Select and write the most appropriate answer from the given alternatives for each sub-question: **[7]**

Question 1.1: An antifriction alloy made up of antimony with tin and copper, which is extensively used in machine bearings is called _______. **[1]**

(A) Duralumin
(B) Babbitt metal
(C) Spiegeleisen
(D) Amalgam

Solution: (B) Babbitt metal

Question 1.2: Which of the following pairs is an intensive property? **[1]**

(A) Density, viscosity
(B) Surface tension, mass
(C) Viscosity, internal energy
(D) Heat capacity, volume

Solution: (A) Density, viscosity

Question 1.3: Fe2+ ions react with nitric oxide formed from reduction of nitrate and yields a brown coloured complex _____________. **[1]**

$[Fe(CO)_5NO]^{2+}$
$[Fe(NH_3)_5NO]^{2+}$
$[Fe(CH_3NH_2)_5NO]^{2+}$
$[Fe(H_2O)_5NO]^{2+}$

Solution: $[Fe(H_2O)_5NO]^{2+}$
An aqueous salt solution containing nitrate ion is mixed with ferrous sulphate and sulphuric acid solution. First nitric oxide is formed.
$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

Fe^{2+} ions react with nitric oxide formed from reduction of nitrate and yields a brown coloured complex $[Fe(H_2O)_5NO]^{2+}$

Thus, one mole of ferrous sulphate reacts with one mole of nitric oxide and five moles of water to form the complex $[Fe(H_2O)_5NO]^{2+}$
The balanced chemical reaction is shown below.
$FeSO_4 + NO + 5H_2O \rightarrow [Fe(H_2O)_5NO]SO_4$
This reaction is used for the detection of nitrate ion in the ring test.

Question 1.4: MnO_2 and $Ca_3(PO_4)_2$ present in iron ore get reduced to Mn and P in the zone of ______. **[1]**

(A) combustion
(B) reduction
(C) fusion
(D) slag formation

Solution: (C) fusion

Question 1.5: An ionic compound crystallises in FCC type structure with 'A' ions at the centre of each face and 'B' ions occupying corners of the cube. The formula of compound is ______. **[1]**

AB_4
A_3B
AB
AB_3

Solution: 'A' ions are at the centre of each face. There are six face centres and each contributes one half to the unit cell. Total number of A ions present per unit cell

$$= 6 \times \frac{1}{2} = 3.$$

'B' ions occupy corners of the cube. There are 8 corners and each contributes one eight to the unit cell.
Total number of B ions present per unit cell

$$= 8 \times \frac{1}{8} = 1.$$

The formula of a compound is A_3B

Hence, the correct answer is A_3B.

Question 1.6: On passing 1.5 F charge, the number of moles of aluminium deposited at cathode are ______ [Molar mass of Al = 27 gram mol^{-1}] **[1]**

(A) 1.0
(B) 13.5
(C) 0.50

(D) 0.75

Solution: (C) 0.50

The half reaction for the reduction of Al^{3+} ion is
$Al^{3+} + 3e^{-} \rightarrow Al$
The reaction indicate that 1 mole of Al is produced by the passage of 3 mole electrons. The charge of 3 mole electrons is 3 faraday.

3 F of charge produces 1 mole of Al.
1.5 F of charge produces 0.50 mole of Al.

Question 1.7: For a chemical reaction, A→ products, the rate of reaction doubles when the concentration of 'A' is increased by a factor of 4, the order of reaction is **[1]**

(A) 2
(B) 0.5
(C) 4
(D) 1

Solution: (B) 0.5

$Rate_1 = k[A]^x$ …(i)
$Rate_2 = k4^x[A]^x$ …(ii)
dividing (ii) by (i)

$Rate_2/Rate_1=4^X$

But, Rate2 = 2Rate1 (given)

$2Rate_1/Rate_1=4^X$

$2=4^X$

x = 1/2 or 0.5

Question 2: Answer any SIX of the following: **[12]**

Question 2.1.i: What are fuel cells? **[2]**

Solution: The galvanic cell in which two energy of combustion of fuels is directly connected into electrical energy Called fuel cell.
Reaction of cell :

Oxidation at anode :
At anode hydrogen gas is oxidized to H_2O.

$$2\,H_2\,(g) + 4\,OH^-\,(aq) \longrightarrow 4\,H_2O\,(l) + 4\,e^-$$

Reduction at cathode (+)

The electrons released at anode travel to cathode through the external circuit.

Here O_2(g) is reduced to $OH-$

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

Question 2.1.ii:

Write cathode and anode reaction in a fuel cell.

Solution: Cell reactions in a fuel cell:

Oxidation at the anode (-):

Oxidation of hydrogen gas to water occurs at the anode.
$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Reduction at the cathode (+):

Reduction of oxygen gas to OH– ions occurs at the cathode.
$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Question 2.2: Derive the relation between half life and rate constant for a first order reaction **[2]**

Solution: The integrated rate law for the first order reaction is given by the equation

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

Where $[A]_0$ = initial concentration of the reactant at t = 0

The concentration falls to $[A]_t$ at time t from the start of the reaction.

The concentration of the reactant falls to $[A]_0/2$ at time $t_{1/2}$.
Therefore, $t = t_{1/2}$
$[A]_t = [A]_0/2$
So, the equation can be written as

$$
\begin{aligned}
k &= \frac{2.303}{t_{\frac{1}{2}}}\log_{10}\frac{[A]_o}{\frac{[A]_o}{2}} \\
&= \frac{2.303}{\frac{t_1}{2}}\log_{10}2 \\
&= \frac{2.303}{\frac{t_1}{2}}\cdot 0.301 = \frac{0.693}{\frac{t_1}{2}} \\
t_{\frac{1}{2}} &= \frac{0.693}{k}
\end{aligned}
$$

Question 2.3: Explain magnetic separation process of ores with the help of a neat, labelled diagram. `[2]`

Solution: Magnetic separation process:

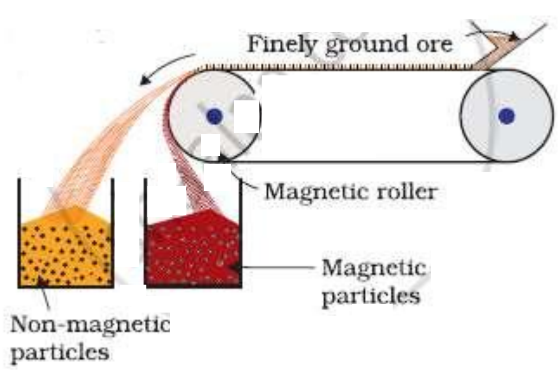
a. The magnetic separation process is based on the differences in magnetic properties of the ore components.

b. If either ore or the gangue is attracted by a magnet, then the ore can be separated from the impurities with the help of magnetic separation method.

c. It requires an electromagnetic separator which consists of a brass or leather belt moving over two rollers, one of which is magnetic in nature as shown in the figure.

d. Powdered ore is dropped over the moving belt at one end.

e. At the other end, the magnetic portion of the ore is attracted by the magnetic roller and falls nearer to the roller, while the non-magnetic impurities fall separately farther off.



Question 2.4: Derive the relationship between relative lowering of vapour pressure and molar mass of nonvolatile solute. **[2]**

Solution: Let W_2 g of solute of molar mass M_2 be dissolved in W_1 g of solvent of molar mass M_1. Hence number of
mole of solvent n_1 and number of mole of solute n_2 in solution.

$$n_1 = \frac{W_1}{M_1} \text{ and } n_2 = \frac{W_2}{M_2} \left(\because \text{Number of moles (n)} = \frac{\text{mass of the substance}}{\text{molar mass of the substance}}\right)$$

The mole fraction of solute x_2 is given by

$$x_2 = \frac{n_2}{n_1 + n_2}$$

$$x_2 = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}} \text{ .....(1)}$$

For a solution of two components A1 and A2 with mole fraction x1 and x2 respectively, if the vapour pressure of pure component A1 is

P_1^0 and that of component A_2 is p_2^0 The relative lowering of vapour pressure is given by,

$$\frac{\Delta p}{p_0^1} = \frac{p_1^0 - p}{p_1^0}$$

$$\frac{\Delta p}{p_0^1} = \frac{p_1^0 x_2}{p_1^0}$$

$$\frac{\Delta p}{p_0^1} = x_2 \text{ .....(2)}$$

Combining equations (1) and (2)

$$\frac{\Delta p}{p_0^1} = \frac{p_1^0 - p}{p_1^0} = x_2 = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}}$$

For dilute solutions n1 >> n2. Hence n2 may be neglected in comparison with n1
in equation (1) and thus equation (3) becomes

$$\frac{\Delta p}{p_0^1} = \frac{n_2}{n_1} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}} = \frac{W_2 M_1}{W_1 M_2}$$

Knowing the masses of non-volatile solute and the solvent in dilute solutions and by determining experimentally vapour pressure of pure solvent and the solution, it is possible to determine molar mass of a non-volatile solute.

Question 2.5.i: Define the term 'enthalpy'. **[2]**

Solution: Enthalpy: Enthalpy of a system may be defined as the sum of the internal energy of the system and the energy that arises due its pressure and volume.

Question 2.5.ii: What will happen to the internal energy if work is done by the system?

Solution: First law of thermodynamics can be given as:
$\Delta U = q + W$
If work is done by the system on the surroundings (work of expansion), then W is negative (-W). The negative value of 'W' signifies that energy has left the system as work. Therefore, internal energy of the system decreases.

Question 2.6: Account for the following: Nitrogen does not form pentahalide. **[2]**

Solution 1: Group 15 elements form pentahalides when they have empty d-orbitals, which can be used for forming coordinate bonds. Since nitrogen does not have d-orbitals, it cannot form petahalides.

Solution 2: Nitrogen belongs to second period. Thus, it has only s- and p- orbitals available for bonding. Due to the absence of d-orbitals in nitrogen it cannot expand its covalency upto 5. It can have covalency maximum upto 4, like in the case of ammonium ion NH_4^+ (by donating all the lone pair of electrons). Thus, nitrogen does not form pentahalides.

Question 2.7: Calculate the percentage efficiency of packing in case of simple cubic cell. **[2]**

Solution: Simple cubic unit cell:
a. In a simple cubic lattice, the atoms are located only on the corners of the cube. The particles touch each other along the edge.
b. Thus, the edge length or side of the cube 'a', and the radius of each particle, 'r' are related as $a = 2r$
c. The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$
d. Since a simple cubic unit cell contains only 1 atom,
The volume of one atom (occupied space) = $4/3\ \pi r^3$

e. Packing efficiency = $\dfrac{\text{Volumeof oneatom}}{\text{Volumeof cubicunit cell}} \times 100\%$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.36\% \approx 52.4\%$$

f. The packing efficiency of simple cubic metal crystal is 52.4 %.

Question 2.8.i: Write the electronic configuration of the following elements: **[2]**

Sulphur (Z = 16)

Solution: Electronic configuration of sulphur (Z = 16) is, 16S -$1s^2 2s^2 2p^6 3s^2 3p4$ or $[Ne]3s^2 3p^4$

Question 2.8.ii: Write the electronic configuration of the following element:

Krypton (Z = 36)

Solution: Electronic configuration of krypton (Z = 36) is, 36Kr - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
or $[Ar]3d^{10} 4s^2 4p^6$

Question 3: Answer any THREE of the following: **[9]**

Question 3.1.i: How is phosphine prepared using the following reagent ? **[3]**
HCl
Solution: Preparation of Phosphine using HCl :
The reaction of calcium phosphide with dilute HCl gives phosphine.

$$\underset{\text{Calcium phosphide}}{Ca_3P_2} + 6\,HCl \longrightarrow \underset{\text{Calcium chloride}}{3\,CaCl_2} + \underset{\text{Phosphine}}{2\,PH_3} \uparrow$$

Question 3.1.ii: How is phosphine prepared using the following reagent?

H_2SO_4

Solution: Preparation of Phosphine using **H_2SO_4:**

The reaction of aluminum phosphide with dilute H_2SO_4 gives phosphine.

$$2AlP + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2PH_3 \uparrow$$

Aluminium phosphide   Aluminium sulfate   Phosphine

Question 3.1.iii: How is phosphine prepared using the following reagent?

Caustic soda

Solution: Preparation of Phosphine using **Caustic soda (NaOH)**
White phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2. It is the laboratory method.

$P_4 +$	$3NaOH + 3H_2O$	$\rightarrow PH_3 +$	$3NaH_2PO_2$
White phosphorus	Sodium hydroxide	Phosphine	Sodium hypophosphite

Question 3.2: 0.05 M NaOH solution offered a resistance of 31.6 Ω in a conductivity cell at 298 K. If the cell constant of the cell is 0.367 cm^{-1}, calculate the molar conductivity of NaOH solution. **[3]**

Solution: Given:

Cell constant (b) = 0.367 cm^{-1}
Molar concentration (C) = 0.05 M
Resistance (R) = 31.6 Ω

To find: Molar conductivity (^)

Formulae:

a. Cell constant, (b) = k x R

b. Molar conductivity (∧)=1000K/C

solution:

Cell constant, b = k x R

0.367=k x 31.6

$$k = \frac{0.367}{31.6} = 11.61 \times 10^{-3}\Omega^{-1}cm^{-1}$$

from formula b

$$\text{Molar conductivity}(\wedge) = \frac{1000K}{C}$$

$$= \frac{1000 \times 11.61 \times 10^{-3}}{0.05}$$

$$= 232.2\Omega^{-1}cm^2mol^{-1}$$

Question 3.3: Calculate ΔH° for the reaction between ethene and water to form ethyl alcohol from the following data: **[3]**

$\Delta cH^\circ\ C_2H_5OH_{(l)} = -1368$ kJ
$\Delta cH^\circ\ C_2H_{4(g)} = -1410$ kJ
Does the calculated ΔH° represent the enthalpy of formation of liquid ethanol?

Solution: Given:

The standard enthalpy of combustion of $C_2H_5OH_{(l)}$ i.e. $\Delta c\ H^\circ\ C_2H_5OH_{(l)} = -1368$ kJ
The standard enthalpy of combustion of ethene i.e. $\Delta c\ H^\circ\ C_2H_{4(g)} = -1410$ kJ
To find: ΔH° for the enthalpy of formation of liquid C_2H_5OH

Calculation: Given equations are,

$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$; $\Delta cH^\circ = -1368$ kJ ...(1)
$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}$; $\Delta cH^\circ = -1410$ kJ ...(2)
The required equation is,
$C_2H_{4(g)} + H_2O_{(l)} \rightarrow C_2H_5OH_{(l)}$,
To get required equation, reverse equation (1) and add to equation (2).

$$\cancel{2CO_{2(g)}} + 3H_2O_{(l)} \longrightarrow C_2H_5OH_{(l)} + \cancel{3O_{2(g)}} \qquad \Delta_cH^\circ = +1368\text{ kJ}$$
$$C_2H_{4(g)} + \cancel{3O_{2(g)}} \longrightarrow \cancel{2CO_{2(g)}} + 2H_2O_{(l)} \qquad \Delta_cH^\circ = -1410\text{ kJ}$$
$$\overline{C_2H_{4(g)} + H_2O_{(l)} \longrightarrow C_2H_5OH_{(l)} \qquad \Delta H^\circ = +1368\text{ kJ} - 1410\text{ kJ}}$$
$$= -42\text{ kJ.}$$

The calculated ΔH° = – 42 kJ is not the enthalpy of formation of liquid ethanol because the reaction does not involve the formation of liquid ethanol from its constituent elements.

Question 4: Answer any ONE of the following: **[7]**

Question 4.1.i: State the first law of electrolysis **[7]**

Solution 1: First law : It states that the amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.

Solution 2: It is one of the primary laws of electrolysis. It states, during electrolysis, the amount of chemical reaction which occurs at any electrode under the influence of electrical energy is proportional to the quantity of electricity passed through the electrolyte.

Question 4.1.ii:

Write any two uses of H_2SO_4

Solution: Uses of sulphuric acid:
1. Sulphuric acid is used in the manufacture of fertilizers. eg. Ammonium sulfate,

superphosphate.
2. It is used in petroleum refining.
3. It is used in manufacture of pigments, paints and dyestuff intermediates.
4. It is used in detergent industry.
5. It is used in storage batteries.
6. It is used in the manufacture of explosives. eg. T.N.T., nitroglycerine, green cotton, etc.
7. It is a laboratory reagent.
8. Sulphuric acid is used in the preparation of important chemicals like HNO3, HCl, H3PO4, Na2CO3, sulphates, alums, ether, etc.
9.It is a dehydrating agent and used for drying wet gases which do not react with acid.
10. It is used as an oxidizing agent.
11.Sulphuric acid is also used as a pickling agent. Pickling is an industrial process for removing layers of basic oxides from metals like Fe and Cu before electroplating, enameling, galvanizing and soldering.

Question 4.1.iii:

Write any two uses of Chlorine.

Solution: Uses of chlorine:
1. Large quantities of chlorine are used industrially for bleaching wood pulp (required for the manufacture of paper and rayon), bleaching cotton and textiles.
2. It is used in the extraction of gold and platinum.
3. It is used for the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, refrigerants, etc.
4. It is used in sterilising drinking water.
5. It is used in preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($Cl.C_2H_4$-S - C_2H_4Cl).
6. It is used in the manufacture of DDT and BHC which are important insecticide.
7. It is used in the manufacture of vinyl chloride which is starting material for polyvinyl chloride plastics.
8. It is used in the manufacture of bleaching powder, aluminium chloride, hydrogen chloride, hypochlorites, chlorates, perchlorates, etc., which are important industrial compounds.

Question 4.1.iv:

Distinguish between crystalline solid and amorphous solid

Solution:

	Crystalline solid		Amorphous solid

(i)	They have a definite geometrical shape	(i)	They have an irregular shape
(ii)	They have a sharp melting point	(ii)	They melt over a range of temperature
(iii)	They are anisotropic	(iii)	They are isotropic
(iv)	They are pure solid	(iv)	They are supercooled liquid.
(v)	They have long-range order of regular pattern of arrangement of constituent particles.	(v)	They have short-range order of regular pattern of arrangement of constituent particles.
(vi)	They have definite heat of fusion.	(vi)	They do not have a definite heat of fusion.

Question 4.1.v:

A solution of a substance having mass 1.8 x 10^{-3} kg has the osmotic pressure of 0.52 atm at 280 K. Calculate the molar mass of the substance used.
[Volume = 1 dm^3, R = 8.314 J K^{-1} mol^{-1}]

Solution: Given: Volume (V) = 1dm^3 = 1L
Mass of substance (W_2) = 1.8 x 10^{-3} kg = 1.8g
Osimotic pressure (π) = 0.52 atm
R = 8.314 J K^{-1} mol^{-1} or R = 0.082 L atm K^{-1} mol^{-1}
Temperature (T) = 280K

$$\pi = \frac{W_2RT}{M_2V}$$

$$M_2 = \frac{W_2RT}{\pi V}$$

$$M_2 = \frac{1.8 \times 0.082 \times 280}{0.52 \times 1}$$

$$M_2 = 79.47 gmol^{-1}$$

Question 4.2.i: Define Leaching. **[7]**

Solution: Leaching:

Leaching is the process of extracting a soluble material from an insoluble solid by dissolving out in a suitable solvent.

Question 4.2.ii:

Define Metallurgy

Solution: Metallurgy:

The process of extraction of a metal in a pure state from its ore is called metallurgy.

Question 4.2.iii:

Define anisotropy.

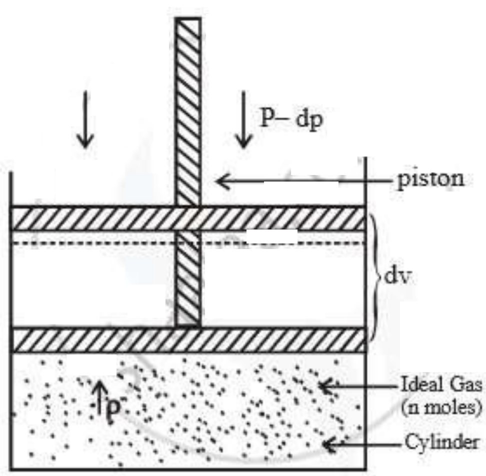
Solution: Anisotropy:

The ability of crystalline solids to change values of physical properties when measured in different directions is called anisotropy.

Question 4.2.iv:

Derive an expression for maximum work in isothermal reversible expansion of two moles of an ideal gas.

Solution:



a. Consider the expansion of 'n' moles of an ideal gas enclosed in a cylinder fitted with a weightless and
frictionless piston at a constant temperature T.
b. Let the pressure of the gas be P which is equal to the external pressure.
c. Let the external pressure be reduced by an infinitesimally small amount dp so that the new external pressure becomes (P-dp).
d. Let the corresponding small increase in volume by dv.
e. Therefore amount of work done in the expansion of the gas, dw = - [(p dp)dv] = -[pdv - dp.dv] ..(i)
f. Since dp and dv are very small, their product (dp.dv) will be much smaller and can be neglected ∴ dw = -pdv ...(ii)
g. During expansion of the gas, if the initial volume V_1 changes to volume V_2 then total amount of work alone (Wmax) can be obtained by integrating the work, dw between the two limits, V_1 and V_2.

$$\therefore W_{max} = \int_{v_2}^{v_1} -dw$$

$$= \int_{v_1}^{v_2} -pdv \quad ...(iii)$$

But pv = nRT (Ideal gas Equation for n moles of a gas)

$$\therefore p = \frac{nRT}{v}$$

Substitute pressure value in equation (iii)

$$\therefore W_{max} = \int_{v_1}^{v_2} -\frac{nRT}{v} dv$$

$$= nRT \int_{v_1}^{v_2} \frac{dv}{v} \quad \text{(n,R,T are constatnt)}$$

$$= -nRT \left[\log v\right]_{v_1}^{v_2}$$

$$= -nRT \ln \frac{v_2}{v_1}$$

$$\therefore W_{max} = -2.303nRT \log \frac{v_2}{v_1}$$

($\ln = 2.303 \log_{10}$) ...(iv)

Question 4.2.v:

The boiling point of benzene is 353.23 K. When 1.80 gram of non-volatile
solute was dissolved in 90 gram of benzene, the boiling point is raised to 354.11 K.
Calculate the molar mass of solute.
[Kb for benzene = 2.53 K kg mol^{-1}]

Solution: Given:

Kb for benzene = 2.53 K kg mol^{-1}
Mass of solute = W2 = 1.8 g = 1.8 x 10^{-3} kg
Mass of solvent = W1 = 90 g = 90 x 10^{-3} kg
Boiling point of solution = Tb = 354.11 K

Boiling point of pure solvent = T_b' = 353.23 K

To Find: Molar mass of solute (M2)

$$\Delta T_b = \frac{K_b \times W_2}{M_2 \times W_1}$$

→ Elevation in boiling point (ΔTb) = $T_b - T_b'$

$$\Delta T_b = 354.11 - 353.23$$

$$\Delta T_b = 0.88K$$

From Formula

$$M_2 = \frac{K_b \times W_2}{\Delta T_b \times W_1}$$

$$M_2 = \frac{2.53 \times 1.8 \times 10^{-3}}{0.88 \times 90 \times 10^{-3}} = \frac{4.554}{79.2}$$

=0.0575 kg mol^{-1}

=57.5 g mol^{-1}

Question 5: Select and write the most appropriate answer from the given alternatives for each sub-question: [7]

Question 5.1: When primary amine reacts with CHCl3 in alcoholic KOH, the product is ______. [1]

(A) aldehyde
(B) alcohol
(C) cyanide
(D) an isocyanide

Solution: (D) an isocyanide

Question 5.2: [1]

$CH_3 - CH_2 - Br \xrightarrow{\text{Alcoholic KOH}} > B \xrightarrow{\text{HBR}} > C \xrightarrow{\text{Na/Eather}} > D$, the Compound D is

(A) ethane
(B) propane
(C) n-butane
(D) n-pentane

Solution: (C) n-butane

$$CH_3 - CH_2 - Br \xrightarrow{\text{Alcoholic KOH}} > CH_2 = CH_2 \xrightarrow{\text{HBR}} > CH_3 - CH_2 - Br \xrightarrow{\text{Na/Eather}} > Ch_3 - CH_2 - CH_2 - CH$$

Question 5.3: Cisplatin compound is used in the treatment of ______. **[1]**

(A) malaria
(B) cancer
(C) AIDS
(D) yellow fever

Solution: (B) cancer

Question 5.4: A gas when passed through $K_2Cr_2O_7$ and dil. H_2SO_4 solution turns it green, the gas is **[1]**

(A) CO_2
(B) NH_3
(C) SO_2
(D) Cl_2

Solution: (C) SO_2
Sulphur dioxide gas is oxidized to sulphuric acid when passed through acidified potassium dichromate solution. The colour of the solution changes from orange to green because potassium dichromate is reduced to chromic sulphate.

Question 5.5: The alcohol used in thermometers is ______. **[1]**
(A) methanol

(B) ethanol
(C) propanol
(D) butanol

Solution: (B) ethanol
Ethanol is used in thermometers as it has low freezing point.

Question 5.6: Which of the following vitamins is the vitamin of alicyclic series? **[1]**

(A) Vitamin C
(B) Vitamin K
(C) Vitamin B
(D) Vitamin A

Solution: (D) Vitamin A

Question 5.7: Which of the following is the first oxidation product of secondary alcohol? **[1]**

(A) Alkene
(B) Aldehyde
(C) Ketone

(D) Carboxylic acid

Solution: (C) Ketone

6. **[12]**

Question 6.1: How is diethyl ether prepared by continuous etherification process? **[2]**

Solution: When an excess of ethyl alcohol is distilled with concentrated H_2SO_4 at 413 K (140 °C), diethyl ether is formed.
This reaction takes place in two steps:

Step-I: Formation of ethyl hydrogen sulphate:

When excess of ethyl alcohol is heated with concentrated H_2SO_4, ethyl hydrogen sulphate is obtained.

$$C_2H_5 - OH + H - O - SO_3H \rightarrow C_2H_5 \_ O - SO_3H + H_2O$$

Ethyl alcohol Conc.sulphuric acid Ethyl hydrogen sulphate

Step-II: Formation of diethyl ether: Ethyl hydrogen sulphate then reacts with excess of ethyl alcohol at 413 K and forms diethyl ether.

$$C_2H_5 - O - SO_3H + OH - C_2H_5 \overset{413\mathrm{K}}{\overline{\qquad}} > C_2H_5 - O - C_2H_5 + H_2SO_4$$

Ethyl hydrogen sulphate Ethyl Alcohol Diethyl ether

Question 6.2: Write the chemical equations involved in the following reactions:(i) Hoffmann-bromamide degradation reaction **[2]**

Solution 1: a. Primary amine can be prepared by reaction of the amide with bromine and aqueous or alcoholic
sodium hydroxide. This reaction is known as Hoffmann bromamide degradation

b. It involves molecular rearrangement.

c. An alkyl or aryl group migrates from the carbonyl carbon to the adjacent nitrogen atom.

d. This reaction is useful for decreasing the length of carbon chain by one carbon atom.

$$\mathrm{CH_3 - CO - NH_2 + 4\,NaOH + Br_2 \longrightarrow CH_3 - NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}$$

Solution 2:

$$\mathrm{R - CH_2 - CO - NH_2 + 4\,NaOH + Br_2 \longrightarrow R - CH_2 - NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}$$

$$\mathrm{CH_3 - CH_2 - CO - NH_2 + 4\,NaOH + 2\,NaBr + 2\,H_2O \longrightarrow CH_3 - CH_2 - NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}$$

Question 6.3: How is ethanoic acid prepared from dry ice? **[2]**

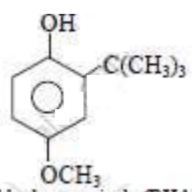
Solution: When the solution of methyl magnesium iodide (Grignard reagent) in dry ether is added to solid carbon dioxide (dry ice), it gives an adduct (magnesium salt of carboxylic acid), which on acid hydrolysis gives ethanoic acid or acetic acid.

Example:

$$\begin{array}{ccccccc} O{=}C{=}O & + & CH_3-Mg-I & \xrightarrow{\text{Dry ether}} & CH_3-\underset{\underset{O}{\|}}{C}-OMgI & \xrightarrow{H_3O^+} & CH_3-\underset{\underset{O}{\|}}{C}-OH + Mg(OH)I \\ \text{Dry ice} & & \text{Methyl} & & \text{Adduct} & & \text{Acetic acid} \\ \text{(Solid carbon} & & \text{Magnesium} & & & & \text{(Ethanoic acid)} \\ \text{dioxide)} & & \text{iodide} & & & & \end{array}$$

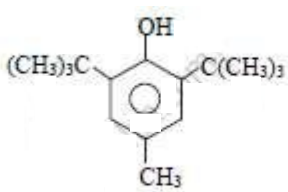
Question 6.4: Write the molecular and structural formula of BHA and BHT. **[2]**

Solution: a. Butylated hydroxy anisole (BHA)
Molecular formula: $C_{11}H_{16}O_2$



Butylated hydroxy anisole (BHA)

b. Butylated hydroxy toluene (BHT)
Molecular formula: $C_{15}H_{24}O$



Butylated hydroxy toluene (BHT)

Question 6.5: Describe laboratory method for preparation of glucose. **[2]**

Solution: Preparation of glucose

Glucose can be prepared in the laboratory by boiling sucrose (cane sugar) with dilute hydrochloric acid or sulphuric acid for about two hours. This hydrolyzes sucrose to glucose and fructose. In order to separate glucose from fructose, alcohol is added during cooling. Glucose is almost insoluble in alcohol. It crystallizes out first, while fructose is more soluble. It remains in the solution. The solution is filtered to obtain the crystals of glucose.

By boiling sucrose with dilute HCl or H_2SO_4 in alcoholic solution

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} > C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose Glucose Fructose

By boiling starch with dilute H_2SO_4, at 393 K, under pressure

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{393k,2-3 atoms}]{H^+} > nC_6H_{12}O_6$$

starch or cellulose Glucose

Question 6.6: Write the factors which are related to the colour of transition metal ions. **[2]**

Solution: Factors responsible for colour of a transition metal ions :
(a) The presence of incompletely filled d – orbitals in metal ions. [1/2 M]
(b) The presence of unpaired electrons in d – orbitals. [1/2 M]
(c) d – d transition of electrons due to absorption of radiation in the visible region. [1/2 M]
(d) Type of hybridisation in metal ion in the complex. [1/2 M]
(e) Geometry of the complex containing transition metal ion.

Question 6.7.i: Explain the given terms: Homopolymers **[2]**

Solution: Homopolymers: Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers.
Ex: – Polythene (prepared by using only one type of monomer i.e. ethene)

Question 6.7.ii: Explain the given terms : Elastomers **[2]**

Solution: Elastomers: The polymers that have the elastic character like rubber are called elastomers.
Elastomers are soft & stretchy used to make rubber bands.
Ex: Neoprene, Vulcanized rubber etc.

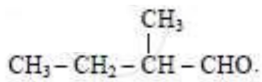
Question 6.8.i: Define racemic mixture. **[2]**

Solution: Recemic mixture:

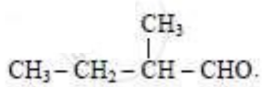
When equimolar quantities of dexto and leavo isomer are mixed, then resulting mixture is found to be optically inactive due to external compensation .such optically inactive mixture known as recemate or recemic mixture.

Question 6.8.ii:

Give IUPAC name of :



Solution: IUPAC name :



2-methyl -1-butanal

Question 7: Answer any THREE of the following: **[9]**

Question 7.1.i: What is ‘effective atomic number’ (EAN)? **[3]**

Solution: It is total number of electrons around the central metal ion present in a complex and calculated as the sum of electrons on the metal ion and the number of electrons donated by ligands. It can be calculated using formula,
EAN =Z-X+Y
where Z = Atomic number of metal.
X = Number of electrons lost during the formation of metal ion from its atom.
Y = Number of electrons donated by the ligands.

Question 7.1.ii: Calculate the effective atomic number of the central metal atom in the following compounds: $K_4Fe(CN)_6$ Fe(Z=26) **[3]**

Solution: $K_4Fe(CN)_6$

Z=26, X=2, Y=12

EAN=Z-X+Y=26-2+12=36

Question 7.1.iii: Calculate the effective atomic number of the central metal atom in the following compounds: **[3]**

$Cr(CO)_6$ Cr(Z=24)

Solution: $Cr(CO)_6$

Z=24, X=0,Y=12

EAN=Z-X+Y=24-0+12=36

Question 7.2: Write the different oxidation states of iron **[3]**

Solution: (a) The different oxidation states shown by Fe are +2, +3, +4, +5, +6.

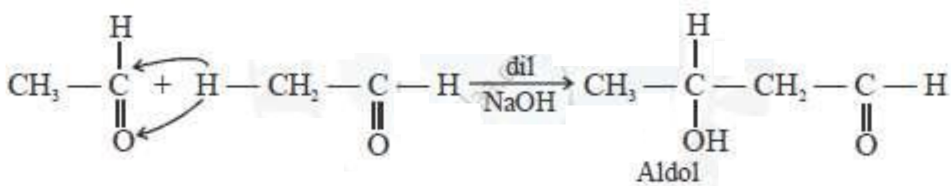
Question 7.3: Write a note on ‘aldol condensation’. **[3]**

Solution: (a) It is a characteristic reaction of aldehydes and ketones containing active α – H atoms. The carbon atom adjacent to carbonyl carbon is called α –C and the H-atom attached to α –C is known as α – H atoms.

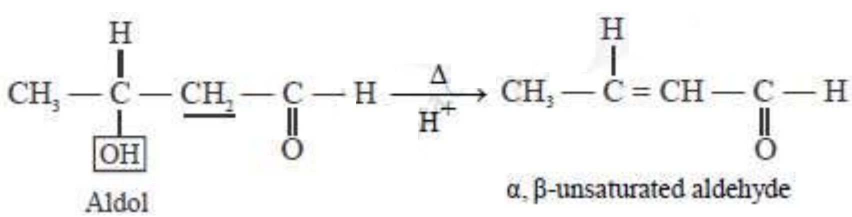
(b) When two molecules of Aldehyde or Ketones containing active α – H atom are warmed in presence of dilute base or dilute acid, they undergo self-condensation to given β Hydroxy aldehyde (aldol) or β Hydroxy ketone (ketol) respectively. This reaction is known as aldol condensation. The Aldol or Ketol undergoes dehydration on heating to form unsaturated aldehyde or ketone.

Eg. Aldol condensation of Acetaldehyde

Step I: Addition



Step II: Condensation



Question 7.4.i: What are nucleic acids? Mention their two important functions. [3]

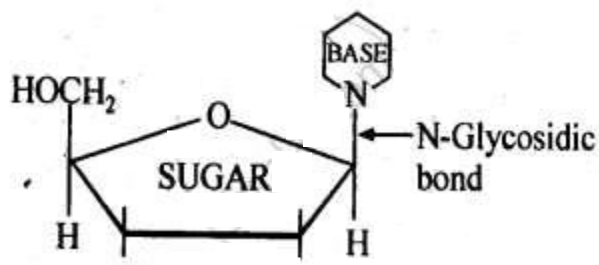
Solution 1: Nucleic acids are biomolecules found in the nuclei of all living cells, as one of the constituents of chromosomes. There are mainly two types of nucleic acids – deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Nucleic acids are also known as polynucleotides as they are long-chain polymers of nucleotides.

Two main functions of nucleic acids are:

(i) DNA is responsible for the transmission of inherent characters from one generation to the next. This process of transmission is called heredity.

(ii) Nucleic acids (both DNA and RNA) are responsible for protein synthesis in a cell. Even though the proteins are actually synthesised by the various RNA molecules in a cell, the message for the synthesis of a particular protein is present in DNA.

Solution 2: Nucleic acids are biomolecules which are found in the nuclei of all living cell in form of nucleoproteins or chromosomes (proteins contains nucleic acids as the prosthetic group).



Nucleic acids are of two types: deoxyribonucleic acid (DNA) and ribonucleic acid.(RNA).

The two main functions of nucleic acids are:

(a) DNA is responsible for transmission of hereditary effects from one generation to another. This is due to its unique property of replication, during cell division and two identical DNA strands are transferred to the daughter cells.

(b) DNA and RNA are responsible for synthesis of all proteins needed for the growth and maintenance of our body. Actually the proteins are synthesized by various RNA molecules (r-RNA, m-RNA) and t-RNA) in the cell but the message for the synthesis of a particular protein is coded in DNA.

Question 7.4.ii: Define complex lipids

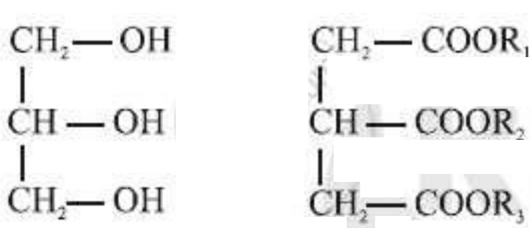
Solution: Complex lipids : -

(a)They are esters of long chain fatty acids. It can be hydrolysed.

(b) They include triglycerides (animal fats and vegetable oils), glycolipids, phospholipids and waxes.

(c) Triglycerides are the triesters of glycerol with higher fatty acids.

(d) They are also called triacylglycerols (TAG).



Fats and oil are mixture of triacylglycerols. R1, R2 and R3 may be same or different and may be saturated or unsaturated.

Question 7.4.iii:

Mention 'two' functions of lipids

Solution: Functions :-

(i) Fats and oils have a convenient and concentrated means of storing food energy in plants and animals.

(ii) Glycolipids are components of cell membrane. Glycolipids occur in bacterial cell wall.

(iii) In plants, glycolipids are principal lipid constituents of chloroplasts.

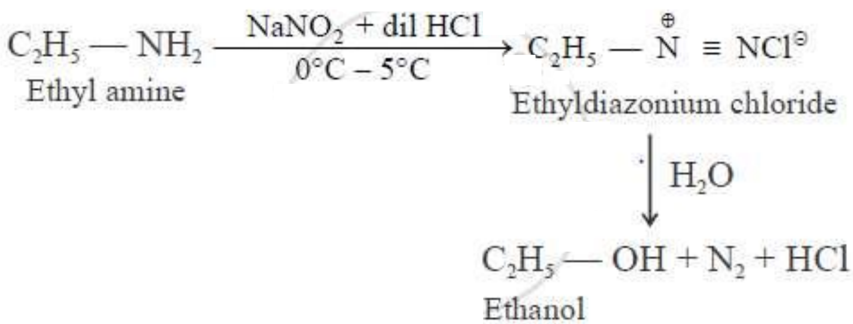
(vi) Waxes provide vital waterproofing for body surface. Waxes are water repelling solids that are protective coatings on leaves, fruits, berries, animal fur and feather of birds.

Question 8: Answer any ONE of the following: [7]

Question 8.1.i:

What will be the action of the mixture of sodium nitrite and dilute hydrochloric acid on ethyl amine

Solution:

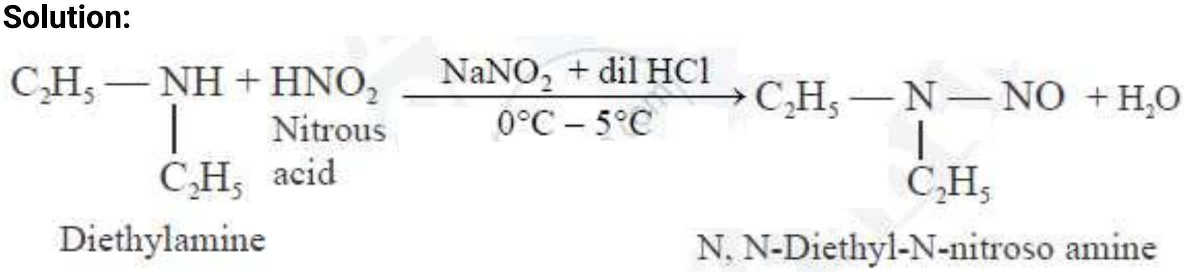


Ethyl amine reacts with $NaNO_2$ + dil HCl to give diazonium salt which decomposes and forms ethanol

Question 8.1.ii:

What will be the action of the mixture of sodium nitrite and dilute hydrochloric acid on aniline

Solution:

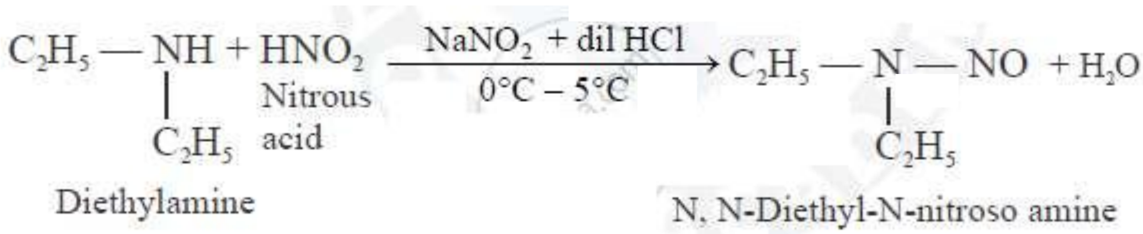


Diethylamine reacts with $NaNO_2$ + dil HCl to give N-Nitro so compound.

Question 8.1.iii:

What will be the action of the mixture of sodium nitrite and dilute hydrochloric acid on diethyl amine

Solution:



Diethylamine reacts with $NaNO_2$ + dil HCl to give N-Nitroso compound.

Question 8.1.iv:

How is Nylon 6, 6 prepared?

Solution 1: Nylon-6,6 is prepared by the method of condensation polymerisation process. Hexamethylenediamine combines with adipic acid to give the macromolecule Nylon-6,6 with the elimination of water molecule.

$$n\,\underset{\text{Adipic acid}}{HOOC-(CH_2)_4-COOH} + n\,\underset{\text{Hexamethylediamine}}{H_2N-(CH_2)_6-NH_2} \xrightarrow[\text{High pressure}]{553\text{ K}} \underset{\text{Nylon 6,6}}{[-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{||}}{C}(CH_2)_4-\overset{\overset{O}{||}}{C}-]n}$$

Used in making sheets, bristles for brushes and in the textile industry.

Solution 2: Nylon -6,6 is synthesized by polycondensation of hexamethylenediamine and adipic acid. Equivalent amounts of hexamethylenediamine and adipic acid are combined with water in a reactor. This is crystallized to make nylon salt, an ammonium/carboxylate mixture. The nylon salt goes into a reaction vessel where polymerization process takes place either in batches or continuously.

> n $HOOC\text{-}(CH_2)_4\text{-}COOH$ + n $H_2N\text{-}(CH_2)_6\text{-}NH_2 \rightarrow [\text{-}OC\text{-}(CH_2)_4\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}]_n$ + (2n-1) H_2O

Removing water drives the reaction toward polymerization through the formation of amide bonds from the acid and amine functions. Thus molten nylon 66 is formed. It can either be extruded and granulated at this point or directly spun into fibers by extrusion through a spinneret (a small metal plate with fine holes) and cooling to form filaments.

Question 8.1.v:

What are 'antacids'?

Solution: Antacids : The chemical substances which neutralize excess of acid in gastric juices and give relief from acid indigestion, acidity, heart burns and gastric ulcers and are called antacids.
Eq. Magnesium Hydroxide, Sodium bicarbonate

Question 8.1.vi:

Write any ‘two’ side effects of tranquilizers.

Solution: Side effects of tranquilizers:
(i) It is addictive
(ii) It produces drowsiness
(iii) It produces defect in memory.

Question 8.2.i: [7]

Explain the mechanism of alkaline hydrolysis of tert-butyl bromide with energy profile diagram.

Solution: Mechanism of Alkaline hydrolysis of tert-alkyl halide.

Consider the action of aqueous sodium hydroxide or potassium hydroxide on a tertiary alkyl halide such as t-butyl bromide.

$$(CH_3)_3\,CBr + KOH \qquad\qquad (CH_3)_3\,COH + KBr$$

The ionic form of the reaction is:

$$(CH_3)_3\,CBr + \;:\bar{O}H \qquad\qquad (CH_3)_3\,COH + Br^-$$

During this hydrolysis the stronger nucleophile, $:OH^-$
has displaced the weaker nucleophile, Br^- and therefore, it is nucleophilic substitution (SN) reaction.

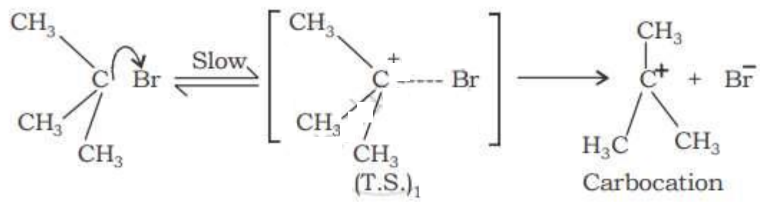
Kineties of reaction: Experimentally is observed that the rate of the reaction depends only on the concentration of $(CH_3)_3CBr$ and is independent of the concentration of the OH^- ions, i.e.,

Rate = k $[(CH_3)_3CBr]$

Therefore, this reaction is first order nucleophilic substitution reaction SN^1 reaction.

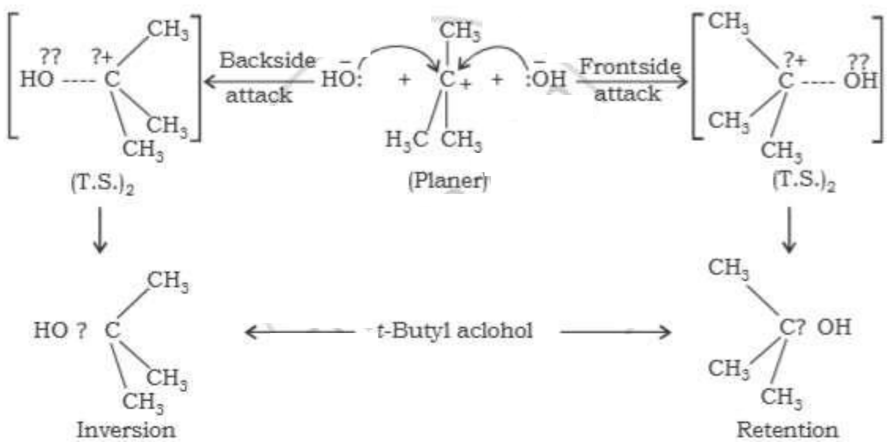
Mechanism: This nuclephilic substitution takes place in two steps which can be represented as follows.

Step (i): Ionization of t-butyl bromide:



The three methyl groups of tert-butyl bromide sterically hinder the approach of the nucleophile and thus prevent the backside attack. Therefore in the first step C–Br bond ionizes to give t-butyl carbocation and bromide ion.
Due to gradual breaking of the bond a transition state $(T.S)_1$ is formed. The electron repelling inductive effect of the methyl groups facilitates the ionization, by stabilising, carbocation.

Step (ii): Attack of nucleophile $(:\overline{O}H)$

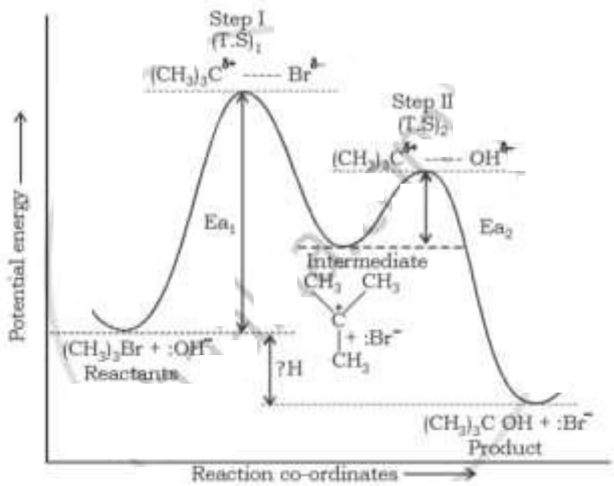


The nucleophile $(:\overline{O}H)$ attacks the carbocation forming t-butyl alcohol. But due to gradual formation of the C–OH bond a transition state $(T.S)_2$ is first formed. The carbocation has planar configuration, hence it can be attacked by the nucleophile from either side.

The frontside attack results in the product with retention of configuration. However, the backside attack results in the product with inversion of configuration. Since the attack from either side is equally probable, there will be retention in 50% of the molecules and inversion in the 50% of the molecules.

Energy profile diagram is obtained by plotting the potential energies of all the species against the reaction co-ordinates. The two-humps in the graph indicates two steps in the reaction.

Activation energy is the energy which must be supplied to reactants in order to form the transition state. It is equal to difference in potential energies of reactants and the transition state. The step-(i) has a higher activation energy, hence it is slow. The step-(ii) has lower activation energy, hence it is fast.



Energy profile diagram of alkaline hydrolysis of *t*-butyl bromide by SN^1 mechanism.

Ea_1 = Energy of activation for step 1

Ea_2 = Energy of activation for step 2

?H = Heat of reaction.

In multi-step reactions the slowest step determines the overall rate of reaction. This is called the rate controlling step. In the slow step only t-butyl bormide takes part and not the nucleophile. Hence it is a first order reaction.

Question 8.2.ii:

Define carbolic acid.

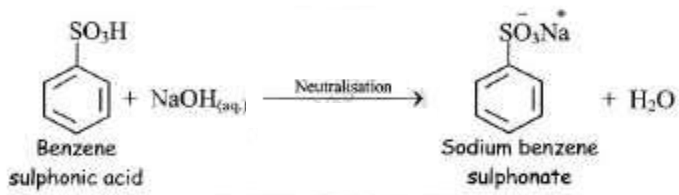
Solution: Phenols are organic aromatic, hydroxyl compounds, in which one or more hydroxyl (-OH) groups are directly attached to the aromatic nucleus (i.e., benzene like ring).

Question 8.2.iii:

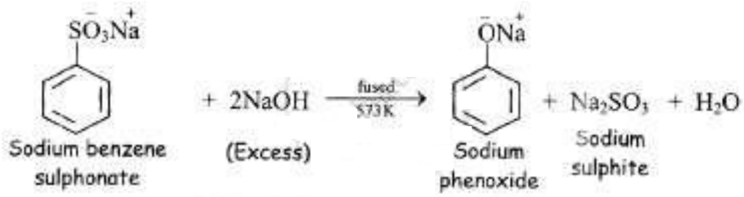
How carbolic acid is prepared from benzene sulphonic acid?

Solution: Preparation of Carbolic acid (Phenol) from Benzene sulphonic acid ($C_6H_6SO_3H$):

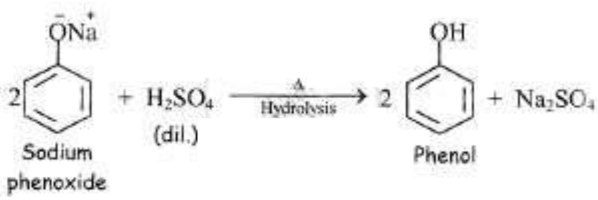
a) When benzene sulphonic acid is neutralised by aqueous sodium hydroxide (NaOH), sodium benzene sulphonate is obtained.



b) Dry sodium benzene sulphonate when fused with excess of sodium hydroxide at 573K, sodium phenoxide is obtained along with sodium sulphite (Na_2SO_3).



c) sodium phenoxide when hydrolysed by heating with dilute sulphuric acid, phenol is obtained.



When a current of carbon dioxide is passed through aqueous sodium phenoxide, phenol is obtained as product.