Chemistry

Academic Year: 2012-2013 Marks: 70
Date: October 2012

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

Question 1.1: In Van Arkel method of refining metal, impure zirconium is converted to unstable volatile compound by heating it with ______. [1]

(A) oxygen
(B) chlorine
(C) bromine
(D) iodine

Solution: iodine

Question 1.2: The temperature at which vapour pressure of a liquid becomes equal to the atmospheric pressure is ______. [1]

(A) melting point
(B) boiling point
(C) 273 K
(D) 373 K

Solution: boiling point

Question 1.3: Which of the following parameters are correct for triclinic lattice? [1]

(A) $\alpha = \beta = \gamma = 90°$ and $a = b = c$
(B) $\alpha \neq \beta \neq \gamma = 90°$ and $a \neq b \neq c$
(C) $\alpha = \gamma = 90°$, $\beta \neq 90°$ and $a \neq b \neq c$
(D) $\alpha \neq \beta \neq \gamma \neq 90°$ and $a \neq b \neq c$

Solution: $\alpha \neq \beta \neq \gamma \neq 90°$ and $a \neq b \neq c$

Question 1.4: Which mixture is used for respiration by deep sea divers? [1]

(A) $He + O_2$
(B) $Ne + O_2$
(C) $Ar + O_2$
(D) $Kr + O_2$

Solution: $He + O_2$

Question 1.5: For the reaction, $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ in liquid bromine, which of the following rate equation is INCORRECT? **[1]**

a) $-\frac{1}{2}\frac{d[N_2O_5]}{dt}$
b) $-\frac{1}{4}\frac{d[NO_2]}{dt}$
c) $\frac{d[O_2]}{dt}$
d) $\frac{1}{4}\frac{d[NO_2]}{dt}$

Solution:

$$-\frac{1}{4}\frac{d[NO_2]}{dt}$$

The instantaneous rate of the reaction is $-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{\mathrm{dt}}$

Question 1.6: For a certain reaction, $\Delta H = -50$ kJ and $\Delta S = -80$ J K^{-1}, at what temperature does the reaction turn from spontaneous to non-spontaneous? **[1]**

(A) 6.25 K
(B) 62.5 K
(C) 625 K
(D) 6250 K

Solution: 625 K

The reaction turns from spontaneous to non-spontaneous when $\Delta G = 0$.

$\therefore 0 = \Delta G = \Delta H - T \Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-50 \times 10^3 J}{-80 J K^{-1}} = 625 \text{ K}$$

Question 1.7: What is the ratio of volumes of H2 and O2 liberated during electrolysis of acidified water? **[1]**

(A) 1 : 2
(B) 2 : 1
(C) 1 : 8
(D) 8 : 1

Solution: 2 : 1

The reaction occurring during electrolysis of acidified water is

$$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

Thus the ratio of number of moles (n) of H2 and O2 liberated is 2 : 1

But volume V ∝ n (∵ PV = nRT)

∴ The ratio of volumes of H2 and O2 liberated is 2 : 1

Question 2: Answer any THREE of the following: [9]

Question 2.1: [3]

Calculate ΔH° for the following reaction:

$2H_3BO_{3(aq)} \rightarrow B2O_{3(s)} + 3H_2O_{(l)}$

a) $H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)}$, $\Delta H_1^o = -0.02$ kJ

b) $H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}$, $\Delta H_2^o = 17.3$ kJ

c) $H_2B_4O_{7(s)} + H_2O_{(l)} \rightarrow 4HBO_{2(aq)}$, $\Delta H_3^o = -11.58$ kJ

Solution: Given: Given equations are

$H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)}$, $\Delta H_1^o = -0.02$ kJ ....(i)

$H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(l)}$, $\Delta H_2^o = 17.3$ kJ....(ii)

$H_2B_4O_{7(s)} + H_2O_{(l)} \rightarrow 4HBO_{2(aq)}$, $\Delta H_3^o = -11.58$ kJ.....(iii)

To find: The standard enthalpy of the reaction, ΔH°

Calculation: Multiply equation (i) by (2),

$2H_3BO_{3(aq)} \longrightarrow 2HBO_{2(aq)} + 2H_2O_{(l)}$, ΔH° = −0.04 kJ .... (iv)

Multiply equation (ii) by ½

$$\frac{1}{2}H_2B_4O_{7(s)} \longrightarrow B_2O_{3(s)} + \frac{1}{2}H_2O_{(l)},\ \Delta H^\circ = 8.65\ \text{kJ} \qquad \ldots.\ (v)$$

Reverse equation (iii) and multiply by $\frac{1}{2}$,

$$2HBO_{2(aq)} \longrightarrow \frac{1}{2}H_2B_4O_{7(s)} + \frac{1}{2}H_2O_{(l)},\ \Delta H^\circ = 5.79\ \text{kJ} \qquad \ldots.\ (vi)$$

Now add equations (iv), (v), and (vi)

$$2H_3BO_{3(aq)} \longrightarrow 2HBO_{2(aq)} + 2H_2O_{(l)},\ \Delta H^\circ = -0.04\ kJ$$

$$\frac{1}{2}H_2B_4O_{7(s)} \longrightarrow B_2O_{3(s)} + \frac{1}{2}H_2O_{(l)},\ \Delta H^\circ = 8.65\ kJ$$

$$2HBO_{2(aq)} \longrightarrow \frac{1}{2}H_2B_4O_{7(s)} + \frac{1}{2}H_2O_{(l)},\ \Delta H^\circ = 5.79\ kJ$$

$$2H_3BO_{3(aq)} \longrightarrow B_2O_{3(s)} + 3H_2O_{(l)}$$

$$\Delta H^\circ = -0.04 + 8.65 + 5.79$$
$$= +\ 14.4\ kJ$$

∴The ΔH° of the reaction = +14.4 kJ

Question 2.2: Calculate molarity and molality of 6.3% solution of nitric acid having density 1.04 g cm^{-3}. (H = 1, N = 14, O = 16) **[3]**

Solution: Given: Density of 6.3% HNO_3 = 1.04 g cm^{-3}

To find: a. Molarity b. Molality

Formulae:

a) Molarity = Number of moles of solute/Volume of solution in L b) Molality = Number of moles of solute/Mass of solvent in kg

Calculation: Density of solution = Mass of solution/Volume of solution

$$\therefore \text{Volume of solution} = \frac{100}{1.04} = 96.15\ cm^3 = 96.15 \times 10^{-3}\ dm^3$$

$$\text{Molarity} = \frac{\text{Massof solute}}{\text{Molar mass of solute} \times \text{Volume of solution in L}}$$

$$\therefore \text{Molarity} = \frac{6.3 \times 10^{-3}}{63 \times 10^{-3} \times 96.15 \times 10^{-3}} = 1.04\ mol/dm^3$$

b) 6.3% HNO3 is present means 6.3 g of HNO3 is present in 100 g of solution.

Mass of H_2O = 100 − 6.3 = 93.7 g

Molality of HNO_3 = Massof HNO_3/Molar mass of HNO_3 ×Massof solvent in kg

$$= \frac{6.3 \times 10^{-3}}{63 \times 10^{-3} \times 93.7 \times 10^{-3}}$$

= 1.067 mol/kg

Question 2.3.i: What is the action of chlorine (Cl) on the following: **[3]**

Cold and dilute caustic soda

Solution: Action of Cl_2 on cold and dil. NaOH:

When chlorine is passed through cold and dilute caustic soda solution, a mixture of sodium hypochlorite and sodium chloride is formed.

$$\underset{}{Cl_2} + \underset{\text{(cold and dilute)}}{2NaOH} \longrightarrow \underset{\substack{\text{Sodium}\\\text{chloride}}}{NaCl} + \underset{\substack{\text{Sodium}\\\text{hypochlorite}}}{NaOCl} + H_2O$$

Question 2.3.ii:

What is the action of chlorine (Cl) on the following:
Hot and concentrated caustic soda

Solution: Action of Cl_2 on hot and conc. NaOH:

Chlorine reacts with hot and conc. NaOH to produce sodium chlorate and sodium chloride.

$$3Cl_2 + \underset{\substack{\text{(hot and}\\\text{conc.)}}}{6NaOH} \longrightarrow \underset{\substack{\text{Sodium}\\\text{chloride}}}{5NaCl} + \underset{\substack{\text{Sodium}\\\text{chlorate}}}{NaClO_3} + 3H_2O$$

Question 2.3.iii:

What is the action of chlorine (Cl) on the following:
Potassium bromide solution

Solution: Action of Cl_2 on potassium bromide solution:

Chlorine reacts with KBr, to form potassium chloride, displacing bromine.

$$\underset{\substack{\text{Potassium}\\\text{bromide}}}{2KBr_{(aq)}} + Cl_2 \longrightarrow \underset{\substack{\text{Potassium}\\\text{chloride}}}{2KCl} + Br_2$$

Question 2.3.iv:

Calculate the number of atoms present in 2 gram of crystal which has face-centred cubic
(FCC) crystal lattice having edge length of 100 pm and density 10 gcm−3

Solution: Given: Density (d) = 10 g cm^{-3}

Edge length (a) = 100 pm = 100×10^{-10} cm.

Mass of crystal = 2 g

To find: Number of atoms

Formula: Density = Mass/Volume

Calculation: Density = Mass/Volume

∴ Volume = Mass/Density

$$\therefore \text{Volume} = \frac{2\text{g}}{10gcm^{-3}} = 0.2\ \text{cm}^3$$

Volume of unit cell = $a^3 = (100 \times 10^{-10}\ \text{cm})^3 = 1 \times 10^{-24}\ \text{cm}^3$

Number of unit cells in 2 g of crystal = total volume/volume of unit cell

$$\frac{(0.2cm)^3}{1 \times 10^{-24} cm^4}$$

The given unit cell is of fcc type, therefore, it contains 4 atoms.

0.2×10^{24} unit cells will contain $4 \times 0.2 \times 10^{24} = 0.8 \times 10^{24}$ atoms

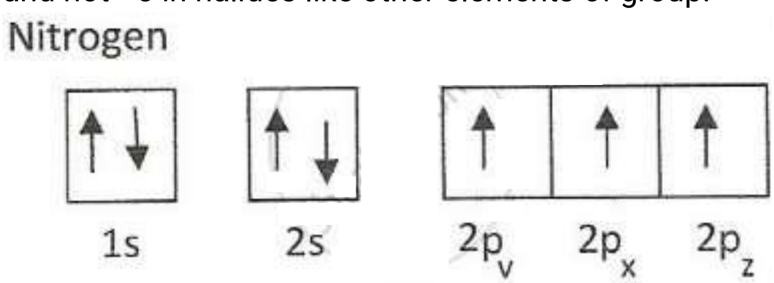
$= 8 \times 10^{23}$ atoms

Number of atoms present in 2g of crystal is 8×10^{23} atoms

Question 3: Answer any SIX of the following: [12]

Question 3.1: NF_3 is possible, but NF_5 is not. Why? [2]

Solution: According to the electronic configuration of nitrogen, it does not have 3d orbital that's why it can't expand the valency up to 5 and does not form NF_5. N does not have vacant d orbitals. Hence, there is no excitation of ns2 electron to vacant orbitals. Thus, has only three unpaired electrons in p-orbitals showing +3 oxidation state and not +5 in halides like other elements of group.



Question 3.2.i: State second law of electrolysis [2]

Solution: Second law : It states that when the same amount of electricity is passed through different cells containing different electrolytes and arranged in series, the amount of substances oxidized or reduced at the represive electrode are directly proportional to their chemical equavalent masses

Question 3.2.ii:

Explain Faraday's second law of electrolysis

Solution: Explanation:

Two cells are connected in series. They contain different electrolytes. Same quantity of electricity is passed through them. In other words, the number of moles of electrons passed through two electrolytes is same.

Moles of A produced in one cell = moles of electrons actually passed × mole ratio of A half reaction

Mole of B produced in other cell = moles of electrons actually passed × mole ratio of B half reaction

Hence, $\frac{\text{moles of A produced}}{\text{moles of B produced}} = \frac{\text{mole ratio of A half reaction}}{\text{mole ratio of B half reaction}}$

Question 3.3: Describe 'froth floatation process' for concentration of sulphide ore. **[2]**

Solution: Froth floatation process:

1) Froth floatation process is based on the principle of difference in the wetting properties of the ore and gangue particles with water and oil.

2) It is used for the extraction of those metals in which the ore particles are preferentially wetted by oil and gangue by water

3) This method has been used for removing gangue from sulphide ores. eg. Galena (PbS), zinc blende (ZnS), copper pyrites (CuFeS2), etc.

4) In this method, a suspension of the powdered ore is made with water. To this suspension small quantities of collectors and froth stabilizers are added. Collectors (eg. pine oil, eucalyptus oil, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilizers (eg. cresols, aniline) help in stabilization of the froth. The mineral ore particles become wet by oil, while the gangue (impurities) particles by water.

5) In the floatation tank, a current of compressed air is circulated through the water. A rotating paddle agitates the mixture and draws air into it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles. The gangue material is wetted by water and settles at the bottom.

6) In the floatation tank, a current of compressed air is circulated through the water. A rotating paddle agitates the mixture and draws air into it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles. The gangue material is wetted by water and settles at the bottom.

7) Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using ‘depressants’. eg. In case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come wi th the fr oth, whi ch can be further removed.

Question 3.4: Distinguish between: Order and Molecularity of reaction [2]

Solution:

ORDER OF A REACTION	MOLECULARITY OF A REACTION
It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It need not be a whole number i.e. it can be fractional as well as zero.	It is always a whole number.
It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules of the slowest step.
It is for the overall reaction and no separate steps are written to obtain it.	The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.
Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalance equation.	For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation.
It may be an integer, fraction or zero	IIt is always an integer and never a fraction or zero

Question 3.5.i: What are the conditions for spontaneous and non-spontaneous reactions in terms of free energy change? [2]

Solution: Conditions for spontaneous and non-spontaneous reactions in terms of free energy change:

a) For a spontaneous process, $\Delta G < 0$ means the Gibbs energy of the system decreases during the process. The end of the spontaneous process is equilibrium which corresponds to minimum in G.

b) Hence the change in Gibbs energy, ΔG must be zero for the process at equilibrium. Thus if,

a) $\Delta G < 0$, the process is spontaneous

b) $\Delta G > 0$, the process is non-spontaneous.

c) $\Delta G = 0$, the process is at equilibrium.

Question 3.5.ii:

Define entropy.

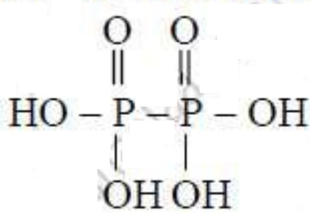
Solution: Conditions for spontaneous and non-spontaneous reactions in terms of free energy change:
a. For a spontaneous process, $\Delta G < 0$ means the Gibbs energy of the system decreases during the process. The end of the spontaneous process is equilibrium which corresponds to minimum in G.
b. Hence the change in Gibbs energy, ΔG must be zero for the process at equilibrium.
Thus if,
a. $\Delta G < 0$, the process is spontaneous.
b. $\Delta G > 0$, the process is non-spontaneous.
c. $\Delta G = 0$, the process is at equilibrium.

Definition of entropy: The property of a system which measures the degree of disorder or randomness in the system is called entropy. It is denoted by letter S.

Question 3.6.i: Draw the structure of $H_4P_2O_6$ hypo phosphoric acid **[2]**

Solution:

Structure of $H_4P_2O_6$:



Hypophosphoric acid($H_4P_2O_6$)

Question 3.6.ii:

What is the action of heat on potassium permanganate?

Solution: Action of heat on $KMnO_4$:

KMnO4 when heated to 473 K, readily decomposes giving oxygen.

$$2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$$

At red heat, potassium permanganate decomposes into potassium manganate (K2MnO3) and oxygen.

$$2K_2MnO_4 \xrightarrow{\text{Red heat}} 2K_2MnO_3 + O_2$$

Question 3.7.i: State Henry’s law. **[2]**

Solution 1: Henry's law: The mass of a gas dissolved in a given volume of the liquid at constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid.

Solution 2: Henry's law relates solubility of a gas with external pressure. The law states that, "the solubility of a gas in liquid at constant temperature is proportional to the pressure of the gas above the solution".

f S is the solubility of the gas in mol dm−3, then according to Henry's law,

$S \propto P$ i.e. $S = KP$

where, P is the pressure of the gas in atmosphere, K is constant of proportionality and has the unit of mol dm^{-3} atm^{-1}.

Question 3.7.ii: How does solubility of a gas in water varies with the temperature? **[2]**

Solution: Effect of temperature:

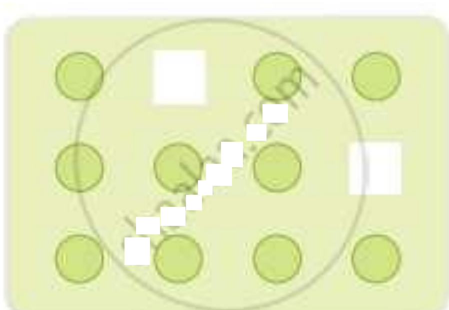
According to Charle's law, volume of a given mass of a gas increases with increase in temperature. Therefore, volume of a given mass of dissolved gas in solution also increases with increase in temperature, so that it becomes impossible for the solvent in solution to accommodate gaseous solute in it and gas bubbles out. Hence solubility of gas in liquid decreases with increase of temperature.

Question 3.8.i: Define the following term **[2]**

Schottky defect

Solution 1: Schottky defect is defined as the one in which equal number of cations and anions are missing from their lattice positions in an ionic compound.

Solution 2: Schottky defect: Schottky defect is basically a vacancy defect shown by ionic solids. In this defect, an equal number of cations and anions are missing to maintain electrical neutrality. It decreases the density of a substance. Significant number of Schottky defects is present in ionic solids. For example, in NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature. Ionic substances containing similar-sized cations and anions show this type of defect. For example: NaCl, KCl, CsCl, AgBr, etc.



Solution 3: Schottky defect:

1) Sometimes during crystallisation, some of the places of the constituent particles remain unoccupied and the defect generated is called vacancy defect or Schottky defect

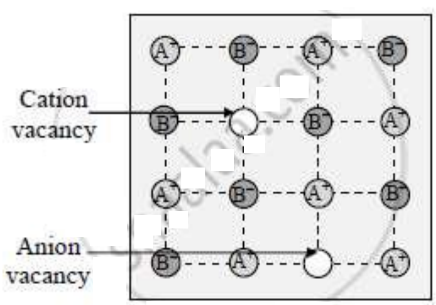
2) The unoccupied positions are called vacancies

3) It results in the decrease in density of the substance.

4) In case of ionic solids, cations and anions in stoichiometric proportions remain absent from their position to maintain electrical neutrality.

5) In Ionic compounds, this defect is known as Schottky defect

6) The defects are observed in solids with cations and anions having almost equal size like NaCl, KCl, CsCl, etc.



Schottky defect

Question 3.8.ii: What are Frenkel defect [2]

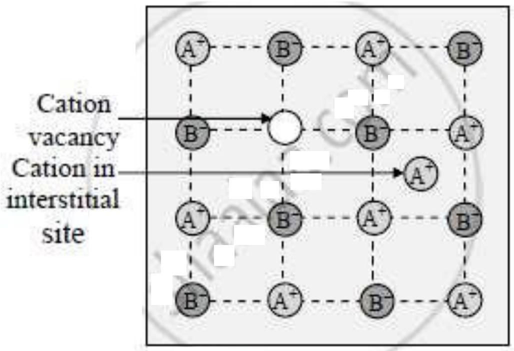
Solution: Frenkel defect:

1) When cation or anion from ionic solid leaves its regular site and moves to occupy a place between the lattice site called interstitial position, the defect is called interstitial defect or Frenkel defect.

2) The presence of this defect does not alter the density of the solid.

3) This defect is common when the difference in ionic radii of cations and anions is large

4) This defect is observed in AgCl solid because of Ag+ ions or ZnS solid because of Zn++ ions.



Frenkel defect

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

Question 4.1.i: Write electrode reaction and net cell reaction for fuel cell. Calculate e.m.f. of the following cell at 25 °C. [7]

$$Zn_{(s)}\,|\,\underset{0.1M}{Zn^{++}_{(aq)}}\,||\,\underset{0.5M}{Cu^{++}_{(aq)}}\,|\,Cu_{(s)}$$

Standard reduction potential (SRP) of Zn and Cu are – 0.76 V and 0.334 V respectively

Solution: Cell reactions for fuel cell:

1) Oxidation at anode (–):

At anode, hydrogen gas is oxidized to H_2O.

$$2H_{2(g)} + 4OH^-_{aq} \rightarrow 4H_2O_{(l)} + 4e^-$$

2) Reduction at cathode (+):

The electrons released at anode travel to cathode through the external circuit.
Here O2 gas is reduced to OH^-

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$$

3) Net cell reaction

The overall cell reaction is the sum of oxidation at anode and reduction at cathode.
Thus,

$$\begin{array}{ll} 2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^- & \text{(anodic oxidation)} \\ O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)} & \text{(cathodic reduction)} \\ \hline 2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} & \text{(overall reaction)} \end{array}$$

4) Calculation of e.m.f.:

E^0_{Cu} = 0.334 V

E^0_{Zn} = −0.76 V

The overall cell reaction is the redox reaction which is the sum of oxidation half reaction at anode and reduction half reaction at cathode.

$$\begin{array}{ll} Zn_{(s)} \longrightarrow Zn^{2+}(0.1M) + 2e^- & \text{(oxidation half reaction at anode)} \\ Cu^{2+}(0.5M) + 2e^- \longrightarrow Cu_{(s)} & \text{(reduction half reaction at cathode)} \\ \hline Zn_{(s)} + Cu^{2+}(0.5M) \longrightarrow Zn^{2+}(0.1M) + Cu_{(s)} & \text{(overall cell reaction)} \end{array}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$= 0.334 - (-0.76) = 1.094\ V = \mathbf{1.1\ V}$$
$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Product]}{[Reactant]}$$
$$= 1.1 - \frac{0.059}{2} \log \frac{0.1}{0.5}$$
$$= \mathbf{1.1206\ V}$$

Question 4.1.ii:

Define isotonic solutions

Solution: Isotonic solutions: Two or more solutions exerting the same osmotic pressure are called isotonic solutions.

eg. 0.05 M (3.0 g L^{-1}) urea solution and 0.05 M (17.19 g L^{-1}) sucrose solution are isotonic because their osmotic pressures are the same. If these solutions are separated by a semipermeable membrane, there is no flow of solvent in either direction.

Question 4.1.iii:

Derive the relation ΔH − ΔU = ΔnRT.

Solution: Derivation for the relation ΔH − ΔU = ΔnRT:

1) ΔH and ΔU at constant pressure are related as,

ΔH = ΔU + PΔV

For reactions involving solids and liquids, ΔV is usually very small because solids and liquids do not expand or contract significantly as pressure changes. For such reactions neglecting PΔV, ΔH = ΔU

However, for reactions involving gases, ΔV cannot be neglected. The equation
ΔH = ΔU + PΔV

= ΔU + P (V_2 − V_1)
= ΔU + PV_2 − PV_1 ….. (1)

where, V1 is the volume of gas-phase reactants (initial state) and V2 is the volume of gas-phase products (final-state).

If we assume that reactant and product gases are ideal, we can apply ideal gas equation, PV = nRT. Suppose that n1 moles of gaseous reactants produce n_2 moles of gaseous products. Then,

$PV_1 = n_1RT$ and $PV_2 = n_2RT$ ….. (2)

Substitution of equation (2) into equation (1) gives,

$\Delta H = \Delta U + n_2RT - n_1RT$

$= \Delta U + (n_2 - n_1)RT$

$= \Delta U + \Delta nRT$

Where, Δn is the difference between the number of moles of gaseous products and that of gaseous reactants

$\therefore \Delta H - \Delta U = \Delta n\, RT$

Question 4.2.i: Define activation energy. [7]

Solution: Activation energy: The activation energy (Ea) is defined as the minimum kinetic energy required for a molecular collision to lead to reaction.

Question 4.2.ii:

Calculate activation energy for a reaction of which rate constant becomes four times when temperature changes from 30 °C to 50 °C. (Given R = 8.314 JK^{-1} mol^{-1}).

Solution: Calculation of activation energy:

Given: T_1 = 30° C = 303 K, T_2 = 50° C = 323 K

Rate constant becomes four times when temperature changes from 30° C to 50° C.

$\therefore k_2 = 4k_1$

or $\frac{k_2}{k_1} = 4$

To find: Activation energy (E_a)

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

Calculation: $\log_{10} \frac{4k_1}{k_1} = \frac{E_a}{2.303R}\left[\frac{323 - 303}{323 \times 303}\right]$

$$\log_{10} 4 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{97869}$$

$$\therefore \quad E_a = \frac{0.60206 \times 2.303 \times 8.314 \times 97869}{20} = 5.641 \times 10^4 \text{ J/mol}$$

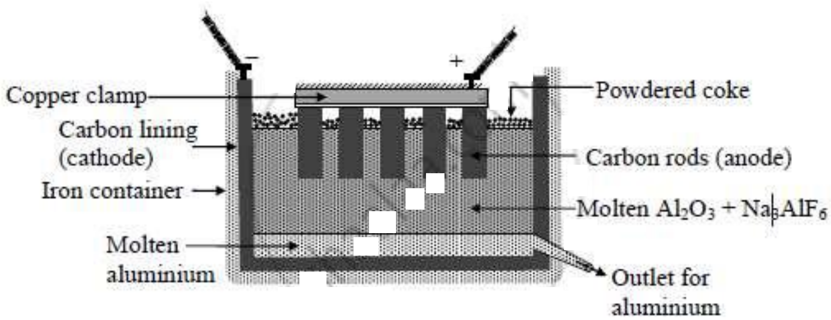
$$= 56.41 \text{ kJ/mol}$$

The activation energy for the given reaction is **56.41 kJ/mol.**

Question 4.2.iii:

Draw a neat, well labelled diagram of electrolytic cell for extraction of aluminium

Solution: Electrolytic cell for the extraction of aluminium:



Electrolytic cell for the extraction of aluminium

Question 4.2.iv:

Write electronic configuration and two uses of neon. (Z = 10)

Solution: Electronic configuration of Neon gases:

Element		Atomic number	Electronic configuration
Neon	Ne	10	$1s^2 2s^2 2p^6$

Uses of neon:

a) Neon bulbs are used in botanical gardens and in green houses

b) Neon is used in,

1) Neon lights. Neon lights are glass tubes filled with neon or mixture of neon and other gases at about 2mm pressure. They glow on electric discharge. They are attractive and have a great penetrating power in mist and fog. When the composition of gaseous mixture and the colour of tube is changed, various shades of neon light are observed.

2) Warning signals, spark plug and in television sets

3) Safety devices, voltage stabilizers and rectifiers.

Question 5: Select and write the most appropriate answer: [7]

Question 5.1: When KOH solution is added to potassium dichromate solution the colour of solution changes to yellow, because ______ [1]

(A) chromate ion changes to dichromate ion
(B) dichromate ion changes to chromate ion
(C) oxidation number of chromium changes from + 6 to + 4
(D) oxidation number of chromium changes from + 4 to +6

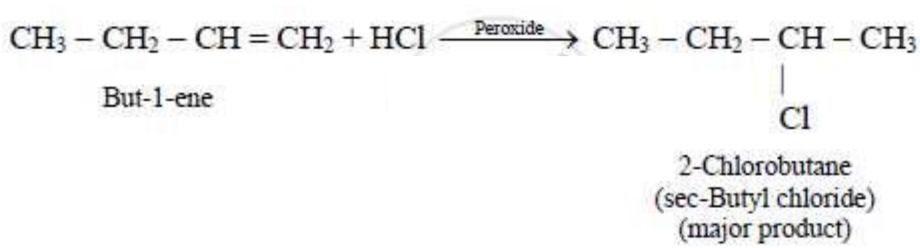
Solution: dichromate ion changes to chromate ion.

Question 5.2: But-1-ene on reaction with HCl in the presence of sodium peroxide yields ______. [1]

n-butyl chloride
isobutyl chloride
secondary butyl chloride
tertiary butyl chloride

Solution: Secondary butyl chloride

HCl always add according to Markownikoff's rule even in presence of peroxide



Question 5.3: 3-Methylbutane-2-ol on heating with HI gives ______ [1]

2-iodo-3-methylbutane
2-iodo-2-methylbutane
1-iodo-3-methylbutane

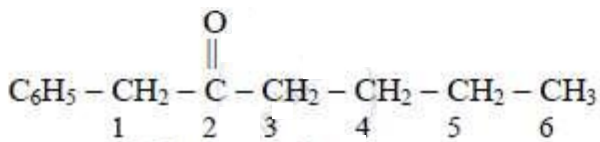
1-iodo-2-methylbutane

Solution: 2-iodo-2-methylbutane

Question 5.4: IUPAC name of is $C_6H_5 - CH_2 - C - CH_2 - CH_2 - CH_2 - CH_3$ is _______ [1]

(A) 1-Phenylhexan-2-one
(B) 6-Phenylhexan-5-one
(C) 1-Benzylhexan-5-one
(D) Dodecan-5-one

Solution: 1-phenylhexan-2-one



1-Phenylhexan-2-one

Question 5.5: Iodoform is used as an _______. [1]

antiseptic
antibiotic
insecticide
anaesthetic

Solution: antiseptic

Question 5.6: Stachyose is an example of _______. [1]

(A) monosaccharides
(B) disaccharides
(C) trisaccharides
(D) tetrasaccharides

Solution: tetrasaccharides

Question 5.7: The Zieglar-Natta catalyst is used in the preparation of _______. [1]

(A) LDPE
(B) PHBV
(C) PAN
(D) HDPE

Solution: HDPE

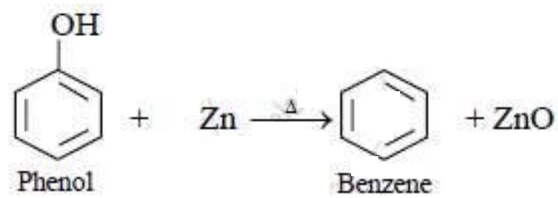
Question 6: Answer any THREE of the following: [9]

Question 6.1.i: How is phenol converted into the following? [3]

benzene

Solution: Conversion of phenol into benzene:

When phenol is heated with zinc dust, it gets converted to benzene

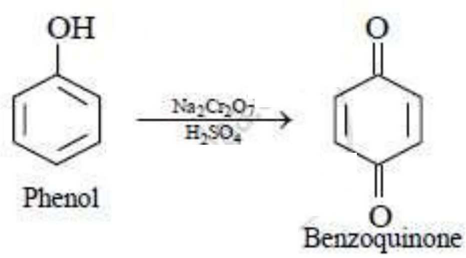


Question 6.1.ii:

How is phenol converted into the following?
benzoquinone

Solution: Conversion of phenol into benzoquinone:

Phenol on oxidation with Na2Cr2O7 (chromic acid) in H2SO4, gives conjugated diketone known as benzoquinone, which is dark coloured

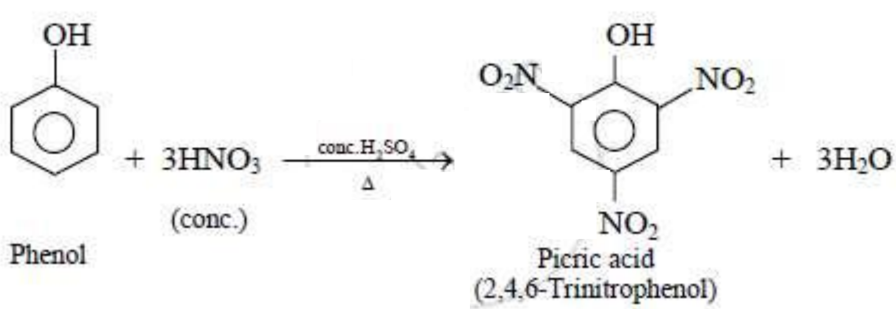


Question 6.1.iii:

How is phenol converted into the following?
picric acid

Solution: Conversion of phenol into picric acid:

When phenol is treated with hot and conc. HNO3 in the presence of conc. H2SO4 (nitrating mixture), yellow coloured picric acid, i.e. 2,4,6-Trinitrophenol is obtained

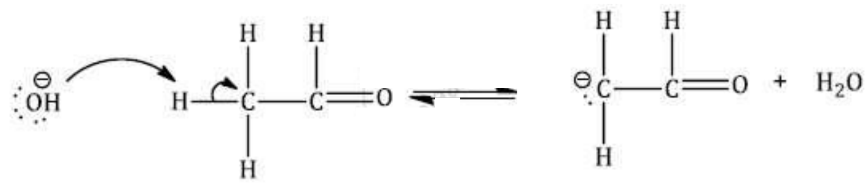


Question 6.2: Write mechanism of Aldol addition reaction. **[3]**

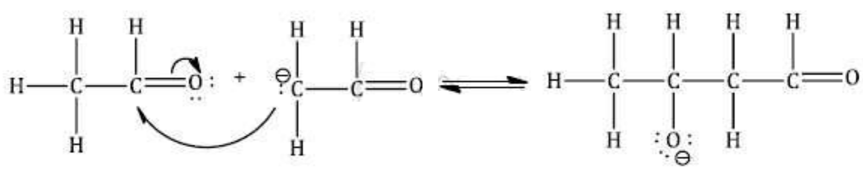
Solution: Aldol addition reaction:-

'Aldol' is an abbreviation of aldehyde and alcohol. When the enolate of an aldehyde or a ketone reacts at the α-carbon with the carbonyl of another molecule under basic or acidic conditions to obtain β-hydroxy aldehyde or ketone, the reaction is called an aldol reaction.

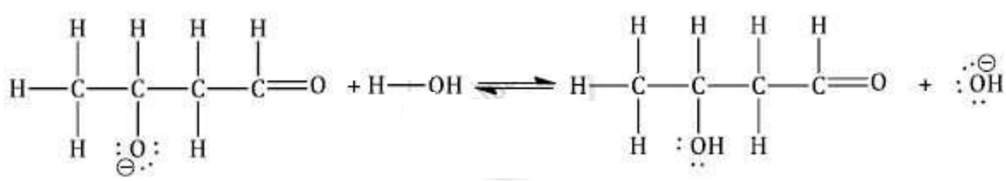
Step I: Base OH− ion abstracts a hydrogen atom from an α-carbon of aldehyde to form carbanion.



Step II: The nucleophilic carbanion or enolate ion attacks the electrophilic carbonyl carbon of the second aldehyde molecule to form an intermediate alkoxide ion. A new C–C bond is formed.



Step III: Alkoxide ion abstracts a hydrogen ion from water to form β-hydroxy aldehyde. Base OH− ion is regenerated.



Question 6.3: Enlist the properties of glucose that cannot be explained on the basis of open chain structure of it **[3]**

Solution: Although the open chain structure of D (+) – Glucose explains most of its reactions, it fails to explain the following facts:

a) D (+)-Glucose does not undergo certain characteristic reactions of aldehydes

eg., Glucose does not form NaHSO3 addition product, aldehyde-ammonia adduct 2, 4 – DNP derivative and does not respond to Schiff’s reagent test.

b) Glucose reacts with NH2OH to form an oxime but glucose pentaacetate does not react with NH2OH, which implies that the free aldehyde group is absent in glucose pentaacetate

c) D(+)-Glucose exists in two stereoisomeric crystalline forms, i.e. α-glucose and β-glucose, called anomers. α-D(+)-Glucose is obtained when a concentrated aqueous or alcoholic solution is crystallised at 303 K. It has a melting point of 419 K and has a specific rotation of +111° in a freshly prepared aqueous solution.

However, when glucose is crystallised from water above 371 K, β-D(+)-glucose is obtained. It has a melting point of 423 K and has a specific rotation of +19.2° in a freshly prepared aqueous solution. This behaviour could not be explained by the open chain structure of glucose.

Question 6.4.i: How is nitromethane prepared from the following? **[3]**

alkyl halide

Solution: Preparation of nitromethane from alkyl halide:

Bromomethane reacts with silver nitrite (AgNO2), to give nitromethane

$$\underset{\text{Bromomethane}}{CH_3-Br} + \underset{\text{Silver Nitrite}}{AgNO_2} \longrightarrow \underset{\text{Nitromethane}}{CH_3-NO_2} + AgBr$$

Nitromethane is obtained in good yield by action of sodium or potassium nitrite on bromomethane, in presence of solvent dimethyl sulphoxide or N,N-dimethylformamide

eg.

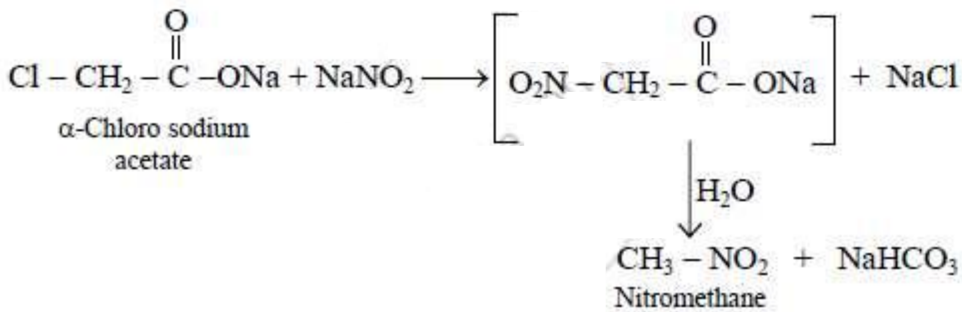
$$\underset{\text{Bromomethane}}{CH_3-Br} + \underset{\text{Sodium/potassium nitrite}}{NaNO_2/KNO_2} \xrightarrow[\text{N,N-Dimethylformamide}]{\text{dimethyl sulphoxide or}} \underset{\text{Nitromethane}}{CH_3-NO_2} + NaBr/KBr$$

Question 6.4.ii: How is nitromethane prepared from the following? **[3]**

α-halogen carboxylic acid

Solution: Preparation of nitromethane from α-halogen carboxylic acid:

Nitromethane is obtained by boiling aqueous sodium nitrite with sodium salt of α-chloro acetic acid

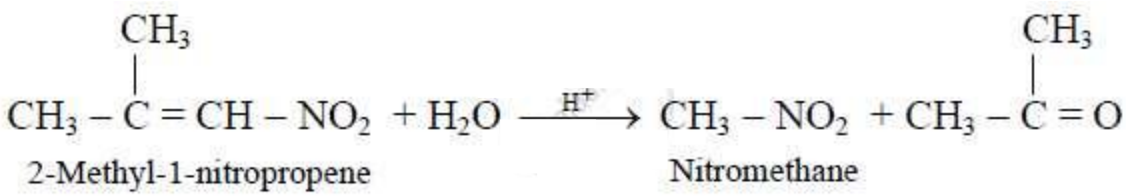


Question 6.4.iii:

How is nitromethane prepared from the following?
α-nitroalkene

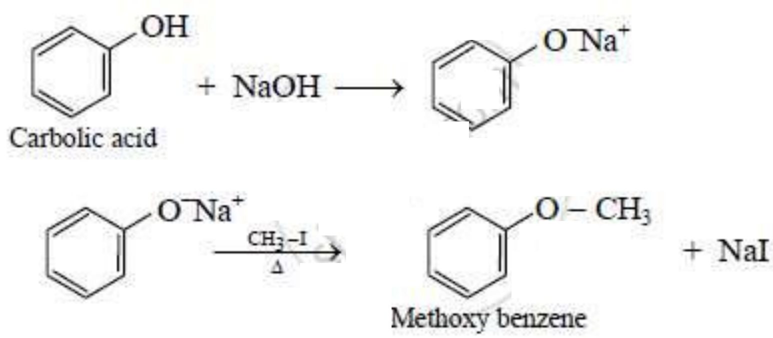
Solution: Preparation of nitromethane from α-nitroalkene:

Nitromethane is prepared by hydrolysis of 2-methyl-1-nitropropene in acidic medium.



Question 7.1: How is methoxy benzene prepared from carbolic acid? **[2]**

Solution:



Question 7.2: State the superiority of crystal field theory over valence bond theory. **[2]**

Solution: Superiority of Crystal Field Theory over Valence Bond Theory:

a) Magnetic properties of complexes and variation with temperature are explained by crystal field theory. Valence bond theory cannot explain these.

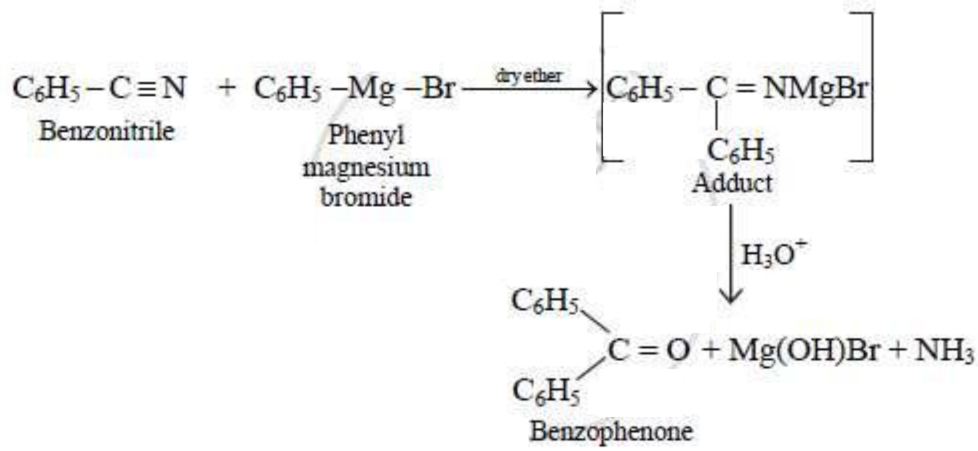
b) Crystal field theory gives the quantitative measure of the stability of complexes. It predicts the geometry of complexes. It is not possible by valence bond theory

c) Kinetic and thermodynamic properties of some complexes are explained by crystal field theory but not by valence bond theory.

d) Crystal field theory explains d-d transitions and colour of complexes. This is not explained by valence bond theory.

Question 7.3: How is Benzonitrile converted to Benzophenone? **[2]**

Solution: Benzonitrile reacts with phenyl magnesium bromide in equimolecular proportion in the presence of dry ether to give an adduct, which on acid hydrolysis gives benzophenone



Question 7.4: Write a short note on Hoffmann bromamide degradation. **[2]**

Solution 1: (a) **Hoffmann Bromanide degradation**

(1) The conversion of amides into amine in presence of bromine and alkali is known on Hoffmann degradation of amides.

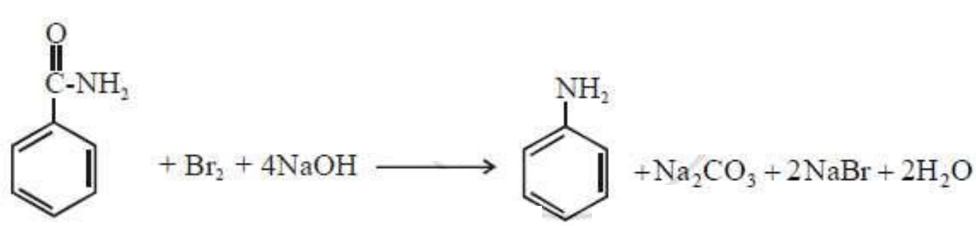
(2) An important characteristic of this reaction is that on amine with one carbon less than those in the amide is formed.

(3) This reaction is an example of molecular rearrangement and involves migration of an alkyl or aryl group from the carbonyl carbon to this adjacent nitrogen atom.

Example:

$$H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2+Br_2+4NaOH\longrightarrow H_3C-CH_2-NH_2+Na_2CO_3+2NaBr+2H_2O$$

Propanomide



Question 7.5.i: What are hormones? **[2]**

Solution: Hormones:

a) Hormones are the chemicals secreted by the ductless glands (endocrine glands) and transported by the blood stream, to different parts of the body where they control different physiological actions of the body.

b) The blood provides the required chemicals in the form of raw materials for secretion of hormones and also act as a vehicle for transport of hormones to reach the specific organs of the body

c) The parts of the body organs where hormones are produced are called effectors and where they act on cells are called targets

d) Hormones are easily diffusible, have low molecular weight and affect biological processes

e) Hormones are normally derived from amino acid derivatives or peptides and proteins or steroids.

eg. Thyroxine, Insulin, Androgens, Estrogens and Progesterone.

Question 7.5.ii:

State the function of insulin.

Solution: Function of insulin:

Insulin is a peptide hormone, secreted in pancreas and controls carbohydrate metabolism by increasing glycogen in muscles and oxidation of glucose in tissue and also lowers the blood sugar.

Question 7.6: How are polymers classified on the basis of polymerisation process? **[2]**

Solution: On the basis of mode of polymerisation, polymers are classified into the following groups:

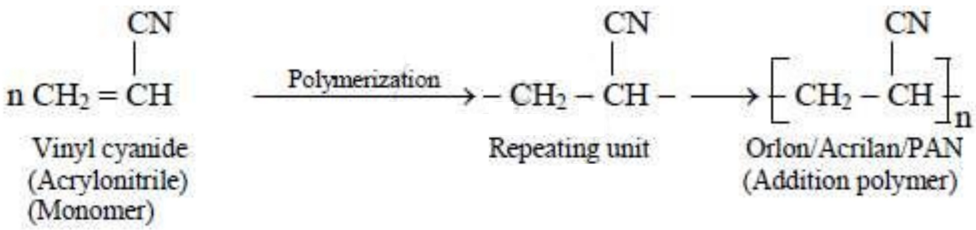
Addition polymers or chain growth polymers:

1) A polymer formed by direct addition of repeated monomers without the elimination of byproduct molecules is called addition polymer.

2) In this, the monomers are alkenes, alkadienes (or their derivatives) or alkynes

3) All the atoms of monomers are present in the addition polymer and they have the same empirical formula as their monomer.

eg. Orlon/ acrilan / polyacrylonitrile (PAN):



Condensation polymers or step growth polymers:

1) A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, methyl alcohol, hydrogen chloride, ammonia, etc. is called condensation polymer.

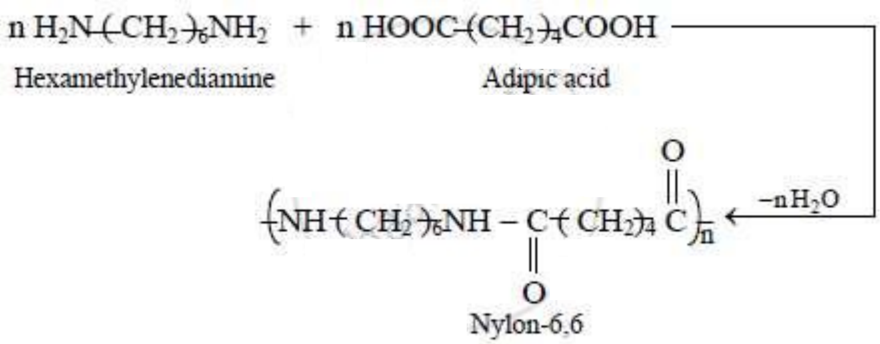
2) In this, bifunctional or trifunctional monomeric units undergo condensation.

3) All the atoms of monomers are not present in the condensation polymer.

4) There are ester or amide linkages in the condensation polymer.

5) Condensation polymer is formed in a stepwise manner (dimer, tetramer, … and so on).

eg.
Nylon-6,6:



Question 7.7: Explain any two chemical methods of food preservation. **[2]**

Solution: Chemical methods used to preserve food:

a) Addition of sugar: In this method, sugar is added and then food is heated. This method is used for the preparation of jams, jellies and marmalades. Fruits like apples, mangoes, strawberries, carrots, etc are preserved by this method

b) Addition of salt: Common salt has antimicrobial activity. Salt is added to food to control the growth of fungus and micro-organisms. When salt is added, bacterial cell loses water due to osmosis. Due to this, the cell either remains dormant or dies. This helps in storage of food. This method of preservation of food by addition of salt is called salting. It is used for preservation of fish products, meat and for the preparation of pickles of lemon, chillies, raw mangoes, etc. It is also used in the preservation of amla, beans, tamarind, etc.

c) Addition of vinegar: Vinegar is added to preserve food like pickles, salad dressings, mustard, fish, etc.

d) Addition of other chemicals: Chemicals like sodium benzoate, salts of sorbic acid and propionic acid etc., are used as preservatives.

Question 7.8: Write observed electronic configuration of elements from first transition series having half filled d-orbitals. **[2]**

Solution:

Elements	Symbols	Atomic Number	Expected Electronic Configuration	Observed Electronic Configuration
Chromium	Cr	24	[Ar] $3d^4\ 4s^2$	[Ar] $3d^5\ 4s^1$
Manganese	Mn	25	[Ar] $3d^5\ 4s^2$	[Ar] $3d^5\ 4s^2$

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

Question 8.1.i: What is lanthanoid contraction?

Solution: Lanthanoid contraction:
The atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. It is known as Lanthanoid contraction.

Question 8.1.ii: Explain the cause of lanthanoid contraction?

Solution: Cause of the lanthanoid contraction:

1) As the atomic number of the members of lanthanoids series increases, the positive charge on nucleus increases by +1 unit and one more electron enters in the same 4f subshell.

2)There is inadequate shielding of one electron by another electron in the same 4f subshell.

3) The shielding of 4f electrons is less effective than the shielding of 5d electron as 4f orbital is more diffused in shape than 5d orbital

4) Thus, greater effective nuclear charge is experienced with the increase in the atomic number. This results in slight pull of the valence shell towards the nucleus.

5)Thus, the atomic and ionic radii decrease slightly with increase in the atomic number, thereby causing lanthanoid contraction

Question 8.1.iii:

Explain effects of lanthanoid contraction

Solution 1: Effects of lanthanoid contraction:-

(a) Effects on the basic strength of hydroxides: As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases. Thus, the basic strength decreases. Hence, $La(OH)_3$ is most basic, while $Lu(OH)_3$ is the least basic.

(b) Ionic radii of post lanthanoids: The elements which follow the lanthanoids in the third transition series are known as post lanthanoids. As a result of lanthanoid contraction, the atomic radii (size) of the elements which follow lanthanum (Hf, Ta, W etc.) are similar to those of the elements of the previous period.

There is normal increase in size from Sc to Y to La. This trend disappears after the lanthanoids, and pairs of elements Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc–Re (group 7) have almost identical sizes. These atoms possess similar number of valence electrons and similar properties.

These pairs of elements are called 'chemical twins'. The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.

Group / Series	4	5	6	7
1st transition series	Ti (132 pm)	V (122 pm)	Cr (106 pm)	Mn (94 pm)
2nd transition series	Zr (145 pm)	Nb (134 pm)	Mo (129 pm)	Tc (114 pm)
3rd transition series	Hf (144 pm)	Ta (134 pm)	W (130 pm)	Re (114 pm)

(c) Difficulty in separation of lanthanoids:- Because the changes in ionic radii (size of the ions) in the lanthanoids are very small, their chemical properties are similar. This makes the separation of the lanthanoids in the pure state difficult. However, lanthanoid contraction results in slight difference in the size of the lanthanoids which results in the differences in properties such as solubility, complex formation, hydration, basic character of their hydroxides etc. Because of these differences, the lanthanoids can be separated by the ion exchange method.

Solution 2: Effects of the lanthanoid contraction:

1) Decrease in Basicity:

a) As per Fajan’s principle, “With increase in the size of cation, the tendency of the hydroxide to dissociate, increases. This increases the strength of base.”

b)The size of Ln^{3+} cation decreases with increase in the atomic number, due to lanthanoid contraction.

c) This decreases the ionic character of M–OH bond and gradually increases the covalent character of M–OH bond.

d)Therefore the basic strength of the corresponding hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

e) Thus, $La(OH)_3$ is most basic and $Lu(OH)_3$ is least basic.

2) Ionic radii of post lanthanoids:

a) The elements which follow the lanthanoids in the third transition series are known as post-lanthanoids

b) There is a regular increase in size from Sc to Y to La.

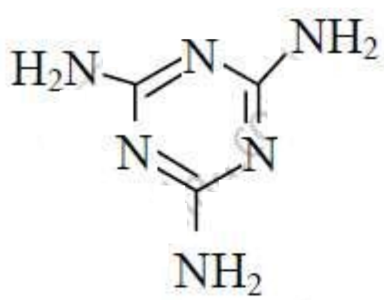
c) But after the lanthanoids, the increase in radii from second to third transition series almost vanishes.

d) Pairs of elements such as Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc-Re (group 7) possess almost same size. These pair of elements are called ‘chemical twins’. The properties of these elements are also similar. So due to lanthanoid contraction, elements of second and third series resemble each other.

Question 8.1.iv:

Write the structure of melamine.

Solution: The structure of melamine:

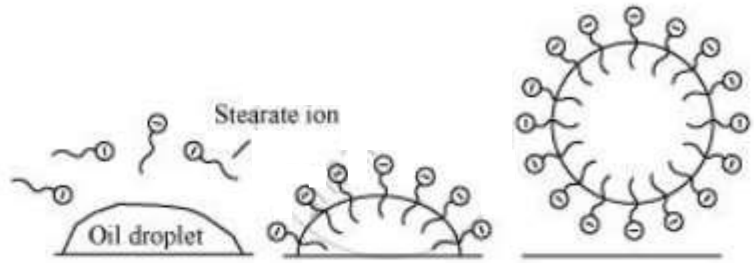


Melamine

Question 8.1.v:

Explain the cleansing action of soaps.

Solution 1: Soap molecules form micelles around an oil droplet (dirt) in such a way that the hydrophobic parts of the stearate ions attach themselves to the oil droplet and the hydrophilic parts project outside the oil droplet. Due to the polar nature of the hydrophilic parts, the stearate ions (along with the dirt) are pulled into water, thereby removing the dirt from the cloth.

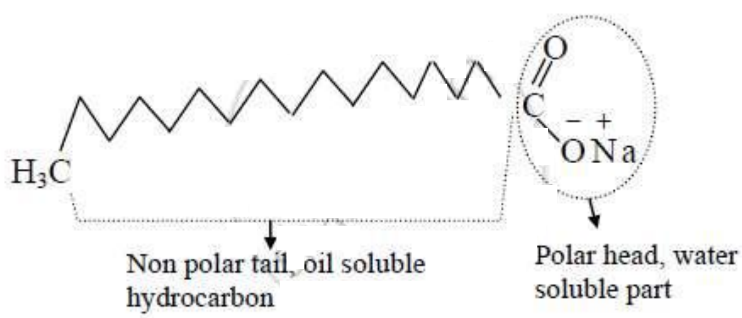


Solution 2: Cleansing action of soaps : Soaps contain two parts, a large hydrocarbon which is a hydrophobic (water repelling) and a negative charged head, which is hydrophillic (water attracting). In solution water molecules being polar in nature, surround the ions & not the organic part of the molecule. When a soap is dissolved in water the molecules gather together as clusters, called micelles. The tails stick inwards & the head outwards.

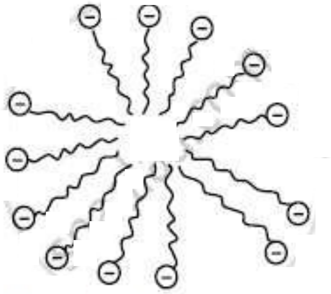
The hydrocarbon tail attaches itself to oily dirt. When water is agitated, the oily dirt tends to lift off from the dirty surface & dissociates into fragments. The solution now contains small globules of oil surrounded detergent molecules. The negatively charged heads present in water prevent the small globules from coming together and form aggregates. Thus the oily dirt is removed from the object.

Solution 3: The mechanism of cleansing action of soap:

1) A molecule of soap has two dissimilar ends. The hydrophobic end of the hydrocarbon chain is water repellent, while the hydrophilic end is polar and water soluble due to presence of carboxylate anion. Thus a soap molecule may be represented as:

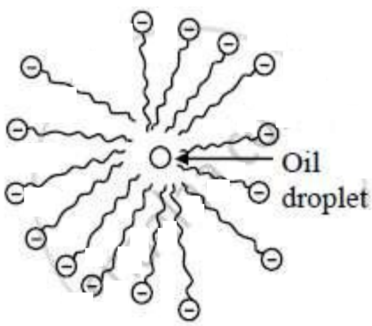


2) When a soap is dissolved in water, many molecules come together and form a group called micelle because their hydrocarbon chains come together and the polar ends are projected outward.



Micelle formation

3) When a cloth with a spot of oil and dirt is soaked into the soap solution, soap dissolves a tiny oil droplet by the hydrophobic end in the middle of the micelle. Due to the outwardly projected polar ends, these micelles dissolve in water and are washed away. Thus the clothes get cleaned.

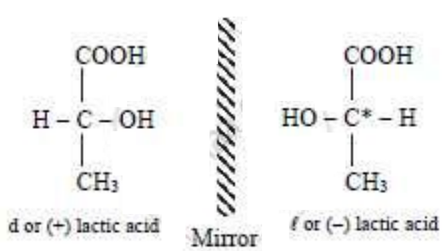


Oil droplet in the middle of the micelle

Question 8.2.i: Explain optical activity of lactic acid **[7]**

Solution: The optical activity of lactic acid can be discussed as:
1. Presence of asymmetrical carbon atom:
i. Lactic acid contains one asymmetrical carbon atom.
ii. According to van’t Hoff’s rule: a = 2^n, where, a is the number of isomers and n is the number of asymmetric carbon atom.
iii. Thus, two isomers of lactic acid are possible.

2. Non-superimposable mirror image structures:



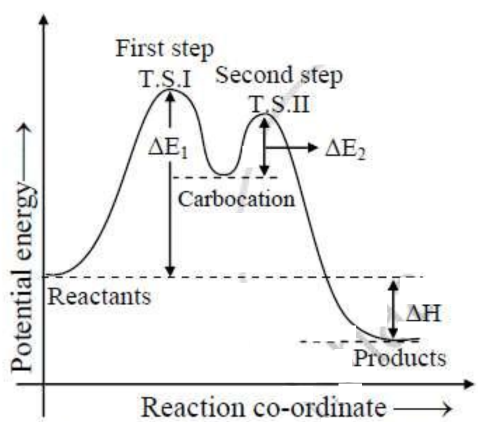
Hence, lactic acid can exist as d-form and l-form which are non-superimposable mirror images of each other.

3. (dl) Racemic mixture and its optical inactivity:
A mixture containing equal moles of the d and l forms of lactic acid is a racemic mixture which is optically inactive i.e., dl or (±) form. This inactivity arises due to external compensation.

Question 8.2.ii:

Draw a neat, labelled energy profile diagram for SN^1 reaction mechanism.

Solution: Energy profile diagram for SN1 reaction mechanism:



Energy profile diagram for S_N1 mechanism

where,
ΔE_1 = Activation energy for T.S. I
ΔE_2 = Activation energy for T.S. II
ΔH = Heat of reaction
T.S. I = Transition state of first step
T.S. II = Transition state of second step

Question 8.2.iii:

Write applications of co-ordination compounds in medicine and electroplating.

Solution: Applications of coordination compounds:

1) In medicine:

- Cisplatin [PtCl2(NH3)2] is useful in treatment of cancer.
- EDTA is useful in treatment of poisoning by lead.

2) In electroplating

Stable complexes with very small dissociation in solution are used for electroplating with silver and gold.

- The complex $K[Ag(CN)_2]$ is used for electroplating with silver
- The complex $K[Au(CN)_2]$ is used for electroplating with gold

Question 8.2.iv:

Applications of coordination compounds:

1) In medicine:

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- The complex $K[Ag(CN)_2]$ is used for electroplating with silver
- The complex $K[Au(CN)_2]$ is used for electroplating with gold

Question 8.2.v:

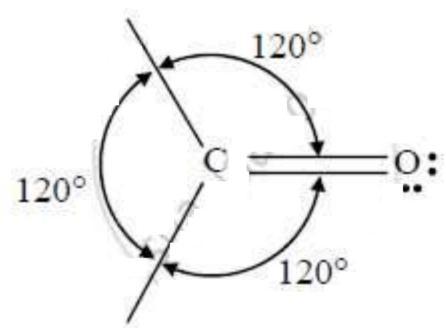
Explain the structure of carbonyl functional group

Solution: Structure of the carbonyl functional group:

1) In aldehydes and ketones, the carbonyl carbon atom is sp2 hybridised and bonded to three other atoms by sigma (σ) bonds. One of the sigma bond is formed with oxygen atom and other two with hydrogen and/or with carbon atoms. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane.

2) The remaining unhybridized 2p orbital of carbon overlaps with 2p orbital of oxygen to form pi (π) bond. This results in double bond between carbon and oxygen.

3) The bond angles are approximately 120° as expected of a trigonal coplanar structure as shown in the figure.



The oxygen atom carries two lone pairs of electrons. The π-electron cloud lies above and below the plane of the rest of the atoms.