## BOARD ANSWER PAPER: MARCH 2013 CHEMISTRY

## SECTION - I

Q.1. Select and write the most appropriate answer from the given alternatives for each sub-question:
i. (A) $68 \%$
ii. (C) $\mathrm{atm} \mathrm{s}^{-1}$
iii. (B) Thiosulphuric acid
iv. (C) $0.5 \mathrm{M} \mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3}$
$0.5 \mathrm{M} \mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ shows maximum depression in freezing point since 0.5 mole of $\mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ will give the highest number of particles, i.e., 1 mole of $\mathrm{Al}^{3+}$ and 1.5 mole of $\mathrm{SO}_{4}^{2-}$ ions as compared to other solutions. 0.5 mole of $\mathrm{Li}_{2} \mathrm{SO}_{4}$ gives 1.5 mole of ions, 1 mole of NaCl gives 2 mole of ions and 0.5 mole of $\mathrm{BaCl}_{2}$ gives 1.5 mole of ions.
v. (C) 571.4 K

The reaction turns spontaneous, when $\Delta \mathrm{G}=0$
$\therefore \quad 0=\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$
$\therefore \quad \mathrm{T}=\frac{\Delta \mathrm{H}}{\Delta \mathrm{S}}=\frac{-20 \times 10^{3} \mathrm{~J}}{-0.035 \times 10^{3} \mathrm{~J} / \mathrm{K}}=571.4 \mathrm{~K}$
vi. (B) 0.337 V
$\mathrm{E}_{\text {cell }}^{\circ}=\mathrm{E}_{\text {cathode }}^{\circ}-\mathrm{E}_{\text {anode }}^{\circ}$
$=\mathrm{E}_{\mathrm{Ag}}^{\circ}-\mathrm{E}_{\mathrm{Cu}}^{\circ}$
$0.463 \mathrm{~V}=0.800 \mathrm{~V}-\mathrm{E}_{\mathrm{Cu}}^{\circ}$
$\mathrm{E}_{\mathrm{Cu}}^{\circ}=0.800 \mathrm{~V}-0.463 \mathrm{~V}=0.337 \mathrm{~V}$
vii. (D) CO

## Q. 2. Answer any SIX of the following:

i.

|  | Property | Crystalline solids | Amorphous solids |
| :--- | :--- | :--- | :--- |
| a. | Shape | They have definite <br> characteristic geometrical <br> shape due to the orderly <br> regular <br> arrangement of constituent <br> particles. | They have irregular shape and <br> lack characteristic geometrical <br> shape due to the short range <br> orderly arrangement of <br> constituent particles. |
| b. | Melting point | They have sharp and <br> characteristic melting point. | They do not have sharp melting <br> point. They gradually soften <br> over a range of temperature. |
| c. | Cleavage <br> property | When cut with a sharp edged <br> tool, they split into two pieces <br> and the newly generated <br> surfaces are plain and smooth. | When cut with a sharp edged <br> tool, they cut into two pieces <br> with irregular surfaces. |
| d. | Heat of fusion | They have a definite and <br> characteristic heat of fusion. | They do not have definite heat <br> of fusion. |


| e. | Anisotropy | They are anisotropic, i.e. have <br> different physical properties in <br> different direction. | They are isotropic, i.e. have <br> same physical properties in all <br> directions. |
| :--- | :--- | :--- | :--- |
| f. | Nature | They are true solids. | They are pseudo solids or super <br> cooled liquids. |
| g. | Order in <br> arrangement of <br> constituent particles | They have long range order. | They have only short range <br> order. |
|  | eg. | Copper, silver, iron, zinc <br> sulphide, common salt, <br> potassium nitrate, etc. | Glass, rubber, plastics, etc. |

(Any four distinguishing points) $\quad[1 / 2 \times 4]$
ii. Kohlrausch Law:
a. Kohlrausch law states that, "at infinite dilution, each ion migrates independently of its co-ion and makes its own contribution to the total molar conductivity of an electrolyte irrespective of the nature of other ion with which it is associated."
b. According to the law, both types of ions-cation and anion contribute a definite share to the molar conductivity of the electrolyte at zero concentration. In other words, $\wedge_{0}$ is the sum of two factors, one is the molar conductivity of cation and the other that of anion at infinite dilution. Thus,
$\wedge_{0}=\lambda_{+}^{0}+\lambda_{-}^{0}$
where, $\lambda_{+}^{0}$ and $\lambda_{-}^{0}$ are the molar conductivities of cation and anion respectively at infinite dilution.
iii. Cell reactions during discharge (cell functions as galvanic cell)
a. Oxidation reaction at anode (negative electrode):

At the anode, lead is oxidised to $\mathrm{Pb}^{2+}$ ions which accumulates on lead plates. The $\mathrm{Pb}^{2+}$ ions so formed, combine with $\mathrm{SO}_{4}^{2-}$ ions from $\mathrm{H}_{2} \mathrm{SO}_{4}$ and insoluble $\mathrm{PbSO}_{4}$ is formed.

| $\mathrm{Pb}_{\text {(s) }}$ $\longrightarrow \mathrm{Pb}_{\text {(aq) }}^{2+}+2 \mathrm{e}^{-}$ | (oxidation) <br> $\mathrm{Pb}_{(\mathrm{aq})}^{2+}+\mathrm{SO}_{4(\mathrm{aq})}^{2-}$ $\mathrm{PbSO}_{4(\mathrm{~s})}$ |
| :--- | :--- |

b. Reduction reaction at cathode ( positive electrode):

At the cathode, $\mathrm{PbO}_{2}$ is reduced to $\mathrm{Pb}^{2+}$ ions which also combines with $\mathrm{SO}_{4}^{2-}$ ions from $\mathrm{H}_{2} \mathrm{SO}_{4}$ and insoluble $\mathrm{PbSO}_{4}$ is formed that gets coated on the $\mathrm{PbO}_{2}$ electrode.
$\mathrm{PbO}_{2(\mathrm{~s})}+4 \mathrm{H}_{(\mathrm{aq})}^{+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Pb}_{(\mathrm{aq})}^{2+}+2 \mathrm{H}_{2} \mathrm{O}_{(l)} \quad$ (reduction)
$\mathrm{Pb}_{(\mathrm{aq})}^{2+}+\mathrm{SO}_{4(\mathrm{aq})}^{2-} \longrightarrow \mathrm{PbSO}_{4(\mathrm{~s})} \quad \quad$ (precipitation)
$\mathrm{PbO}_{2(\mathrm{~s})}+4 \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{SO}_{4(\mathrm{aq})}^{2-}+2 \mathrm{e}^{-} \longrightarrow \mathrm{PbSO}_{4(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{O}_{(l)} \quad$ (overall reduction at cathode)
c. Net cell reaction during discharge:

The net cell reaction when cell supplies current is obtained by adding oxidation half reaction at anode and reduction half reaction at cathode. Thus,

$$
\begin{array}{ll}
\begin{array}{l}
\mathrm{Pb}_{(\mathrm{s})}+\mathrm{SO}_{4(\mathrm{aq})}^{2-} \longrightarrow \mathrm{PbSO}_{4(\mathrm{~s})}+2 \mathrm{e}^{-} \\
\mathrm{PbO}_{2(\mathrm{~s})}+4 \mathrm{H}_{(\mathrm{aq})}^{+}+\mathrm{SO}_{4(\mathrm{aq})}^{2-}+2 \mathrm{e}^{-} \longrightarrow \mathrm{PbSO}_{4(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
\end{array} & \begin{array}{l}
\text { (oxidation at anode) } \\
\text { (reduction at cathode) }
\end{array} \\
\hline \mathrm{Pb}_{(\mathrm{s})}+\mathrm{PbO}_{2(\mathrm{~s})}+4 \mathrm{H}_{(\mathrm{aq})}^{+}+2 \mathrm{SO}_{4(\mathrm{aq})}^{2-} \longrightarrow 2 \mathrm{PbSO}_{4(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} & \text { (overall cell reaction) }  \tag{1}\\
\mathrm{OR} \\
\mathrm{~Pb}_{(\mathrm{s})}+\mathrm{PbO}_{2(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})} \longrightarrow 2 \mathrm{PbSO}_{4(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
\end{array}
$$

iv.


Pyramidal structure of $\mathrm{PCl}_{3}$


Bipyramidal structure of $\mathbf{P C l}_{5} \quad[1 / 2 \times 2]$

Geometry of $\mathrm{PCl}_{3}$ : Pyramidal
Geometry of $\mathrm{PCl}_{5}$ : Trigonal bipyramidal
v. a. $\Delta \mathrm{H}$ and $\Delta \mathrm{U}$ at constant pressure are related as,
$\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}$
For reactions involving solids and liquids, $\Delta \mathrm{V}$ is usually very small because solids and liquids do not expand or contract significantly as pressure changes. For such reactions neglecting P. $\Delta \mathrm{V}, \Delta \mathrm{H}=\Delta \mathrm{U}$
However, for reactions involving gases, $\Delta \mathrm{V}$ cannot be neglected. The equation,
$\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}$
$=\Delta \mathrm{U}+\mathrm{P}\left(\mathrm{V}_{2}-\mathrm{V}_{1}\right)$
$=\Delta U+P V_{2}-\mathrm{PV}_{1}$
where, $\mathrm{V}_{1}$ is the volume of gas-phase reactants (initial state) and $\mathrm{V}_{2}$ is the volume of gas-phase products (final-state).
b. If we assume that reactant and product gases are ideal, we can apply ideal gas equation, $\mathrm{PV}=\mathrm{nRT}$. Suppose that $\mathrm{n}_{1}$ moles of gaseous reactants produce $\mathrm{n}_{2}$ moles of gaseous products. Then,
$\mathrm{PV}_{1}=\mathrm{n}_{1} \mathrm{RT}$ and $\mathrm{PV}_{2}=\mathrm{n}_{2} \mathrm{RT}$
Substitution of equation (2) into equation (1) gives,
$\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{n}_{2} \mathrm{RT}-\mathrm{n}_{1} \mathrm{RT}$
$\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{RT}\left(\mathrm{n}_{2}-\mathrm{n}_{1}\right)$
$\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{RT} \cdot \Delta \mathrm{n}$ or $\Delta \mathrm{H}-\Delta \mathrm{U}=\mathrm{RT} \Delta \mathrm{n}$
where, $\Delta \mathrm{n}$ is the difference between the number of moles of gaseous products and that of gaseous reactants.
c. Conditions under which $\Delta \mathbf{H}=\Delta \mathbf{U}$ :

1. When the reaction is carried out in a closed vessel so that the volume of the system remains constant, $\Delta \mathrm{V}=0$. Hence, equation, $\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}$ becomes $\Delta \mathrm{H}=\Delta \mathrm{U}$.
2. When the reactions involve only solids and liquids, $\Delta \mathrm{V}$ can be neglected and hence, $\Delta \mathrm{H}=\Delta \mathrm{U}$.
3. In the reactions in which the number of moles of gaseous reactants consumed is equal to the number of moles of gaseous products produced at constant temperature and pressure, i.e. $\mathrm{n}_{1}=\mathrm{n}_{2}, \Delta \mathrm{n}=0$. The equation $\Delta \mathrm{H}=\Delta \mathrm{U}+\mathrm{RT} \cdot \Delta \mathrm{n}$ becomes $\Delta \mathrm{H}=\Delta \mathrm{U}$.
(Any one condition)
vi. The ores of aluminium are:
a. Bauxite, $\mathrm{Al}_{2} \mathrm{O}_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$
b. Cryolite, $\mathrm{Na}_{3} \mathrm{AlF}_{6}$
c. Diaspore, $\mathrm{Al}_{2} \mathrm{O}_{3} \cdot \mathrm{H}_{2} \mathrm{O}$
d. Corundum, $\mathrm{Al}_{2} \mathrm{O}_{3}$
(Names of any two ores of aluminium) $\quad[1 / 2 \times 2]$
(Formulae of the two ores) [1⁄2 $\times 2]$
vii. a. Let $W_{2} g$ of non-volatile solute of molar mass $M_{2}$ be dissolved in $W_{1} g$ of solvent of molar mass $\mathrm{M}_{1}$.
b. The number of moles of solvent, $\mathrm{n}_{1}$ and number of moles of solute $\mathrm{n}_{2}$, in solution are given as,
$\mathrm{n}_{1}=\frac{\mathrm{W}_{1}}{\mathrm{M}_{1}}$ and $\mathrm{n}_{2}=\frac{\mathrm{W}_{2}}{\mathrm{M}_{2}} \quad\left(\because\right.$ Number of moles $\left.(\mathrm{n})=\frac{\text { mass of the substance }}{\text { molar mass of the substance }}\right)$
c. The mole fraction of solute, $x_{2}$ is given by,

$$
\begin{equation*}
x_{2}=\frac{\mathrm{n}_{2}}{\mathrm{n}_{1}+\mathrm{n}_{2}}=\frac{\mathrm{W}_{2} / \mathrm{M}_{2}}{\mathrm{~W}_{1} / \mathrm{M}_{1}+\mathrm{W}_{2} / \mathrm{M}_{2}} \tag{1}
\end{equation*}
$$

d. For a solution of two components $\mathrm{A}_{1}$ and $\mathrm{A}_{2}$ with mole fraction $x_{1}$ and $x_{2}$ respectively, if the vapour pressure of pure component $A_{1}$ is $p_{1}^{0}$ and that of component $A_{2}$ is $p_{2}^{0}=0$, The relative lowering of vapour pressure is given by,

$$
\begin{equation*}
\frac{\Delta \mathrm{p}}{\mathrm{p}_{1}^{\circ}}=\frac{\mathrm{p}_{1}^{\circ}-\mathrm{p}}{\mathrm{p}_{1}^{\circ}}=\frac{\mathrm{p}_{1}^{\circ} x_{2}}{\mathrm{p}_{1}^{\circ}}=x_{2} \tag{2}
\end{equation*}
$$

e. Combining equations (1) and (2)

$$
\begin{equation*}
\frac{\Delta \mathrm{p}}{\mathrm{p}_{1}^{\circ}}=\frac{\mathrm{p}_{1}^{\circ}-\mathrm{p}}{\mathrm{p}_{1}^{\circ}}=x_{2}=\frac{\mathrm{W}_{2} / \mathrm{M}_{2}}{\mathrm{~W}_{1} / \mathrm{M}_{1}+\mathrm{W}_{2} / \mathrm{M}_{2}} \tag{3}
\end{equation*}
$$

f. For dilute solutions $n_{1} \gg n_{2}$. Hence $n_{2}$ may be neglected in comparison with $n_{1}$ in equation (1) and thus equation (3) becomes,

$$
\begin{equation*}
\frac{\Delta \mathrm{p}}{\mathrm{p}_{1}^{\circ}}=\frac{\mathrm{n}_{2}}{\mathrm{n}_{1}}=\frac{\mathrm{W}_{2} / \mathrm{M}_{2}}{\mathrm{~W}_{1} / \mathrm{M}_{1}}=\frac{\mathrm{W}_{2} \mathrm{M}_{1}}{\mathrm{~W}_{1} \mathrm{M}_{2}} \tag{1/2}
\end{equation*}
$$

g. 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.
viii. Pseudo first order reaction: The reactions that have higher order true rate law but are found to behave as first order are called pseudo first order reactions.

## Explanation:

a. Consider the hydrolysis of methyl acetate $\left(\mathrm{CH}_{3} \mathrm{COOCH}_{3}\right)$ in presence of an acidic medium.

b. The order of the reaction appears to be 2 as the solvent (water) participates in the reaction.
c. The rate law for the above reaction can be written as:

Rate $=\mathrm{k}^{\prime}\left[\mathrm{CH}_{3} \mathrm{COOCH}_{3}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]$
d. However, the given reaction is generally carried out by taking water in excess over methyl acetate. Thus, the concentration of water $\left[\mathrm{H}_{2} \mathrm{O}\right]$ remains constant.
e. So the rate of the reaction depends only upon the concentration of methyl acetate and the order of the reaction becomes one.
f. The new rate law for this reaction can be written as

$$
\text { Rate }=\mathrm{k}\left[\mathrm{CH}_{3} \mathrm{COOCH}_{3}\right] \quad\left(\because \mathrm{k}^{\prime}\left[\mathrm{H}_{2} \mathrm{O}\right]=\mathrm{k}\right)
$$

g. Therefore, hydrolysis of methyl acetate taking place in excess of water is called pseudo first order reaction or pseudo unimolecular reaction.

## Q.3. Answer any THREE of the following:

i. $\quad 12.2 \% \mathrm{HNO}_{3}$ means 12.2 g of $\mathrm{HNO}_{3}$ in 100 ml of water.

Number of moles of $\mathrm{HNO}_{3}=\frac{\text { Mass of } \mathrm{HNO}_{3}}{\text { Molar mass of } \mathrm{HNO}_{3}}=\frac{12.2}{63}=0.1937$ moles
Mass of $\mathrm{H}_{2} \mathrm{O}=100-12.2=87.8$
Number of moles of water $=\frac{\text { Mass of } \mathrm{H}_{2} \mathrm{O}}{\text { Molar mass of } \mathrm{H}_{2} \mathrm{O}}=\frac{87.8}{18}=4.8777$ moles
Total moles in solution $=\mathrm{n}_{\mathrm{H}_{2} \mathrm{O}}+\mathrm{n}_{\mathrm{HNO}_{3}}=4.8777+0.1937=5.0714$ moles
$\therefore \quad$ Mole fraction of $\mathrm{HNO}_{3}=\frac{0.1937}{4.8777+0.1937}=\frac{0.1937}{5.0714}=\mathbf{0 . 0 3 8 2}$
Molality of $\mathrm{HNO}_{3}=\frac{\text { Mass of } \mathrm{HNO}_{3}}{\text { Molar mass of } \mathrm{HNO}_{3} \times \text { mass of solvent }}$

$$
\begin{equation*}
=\frac{12.2 \times 10^{-3}}{63 \times 10^{-3} \times 87.8 \times 10^{-3}}=\mathbf{2 . 2 0 6 ~ m o l} / \mathbf{k g} \tag{1/2}
\end{equation*}
$$

ii. Rate of reaction $=-\frac{1}{3} \frac{\mathrm{~d}\left[\mathrm{I}^{-}\right]}{\mathrm{dt}}=-\frac{\mathrm{d}\left[\mathrm{S}_{2} \mathrm{O}_{8}^{-2}\right]}{\mathrm{dt}}=+\frac{\mathrm{d}\left[\mathrm{I}_{3}^{-}\right]}{\mathrm{dt}}=+\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{SO}_{4}^{-2}\right]}{\mathrm{dt}}$ $\frac{\mathrm{d}\left[\mathrm{SO}_{4}^{2-}\right]}{\mathrm{dt}}=2.2 \times 10^{-2} \mathrm{M} \mathrm{s}^{-1}$
Rate of formation of $\mathrm{SO}_{4}^{2-}=\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{SO}_{4}^{2-}\right]}{\mathrm{dt}}=\frac{1}{2} \times 2.2 \times 10^{-2}=\mathbf{1 . 1} \times \mathbf{1 0}^{-\mathbf{2}} \mathbf{M ~ s}^{-1}$
a. Rate of disappearance of $\mathrm{I}^{-}=-\frac{1}{3} \frac{\mathrm{~d}\left[\mathrm{I}^{-}\right]}{\mathrm{dt}}=\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{SO}_{4}^{2-}\right]}{\mathrm{dt}}$
$\therefore \quad$ Rate of disappearance of $\mathrm{I}^{-}=-\frac{1}{3} \frac{\mathrm{~d}\left[\mathrm{I}^{-}\right]}{\mathrm{dt}}=1.1 \times 10^{-2} \mathrm{M} \mathrm{s}^{-1}$
$\therefore \quad-\frac{\mathrm{d}\left[\mathrm{I}^{-}\right]}{\mathrm{dt}}=\mathbf{3 . 3} \times \mathbf{1 0}^{-\mathbf{2}} \mathbf{M ~ s}^{-1}$
b. Rate of disappearance of $\mathrm{S}_{2} \mathrm{O}_{8}^{2-}=-\frac{\mathrm{d}\left[\mathrm{S}_{2} \mathrm{O}_{8}^{2-}\right]}{\mathrm{dt}}=\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{SO}_{4}^{2-}\right]}{\mathrm{dt}}$

Rate of disappearance of $\mathrm{S}_{2} \mathrm{O}_{8}^{2-}=-\frac{\mathrm{d}\left[\mathrm{S}_{2} \mathrm{O}_{8}^{2-}\right]}{\mathrm{dt}}=\mathbf{1 . 1} \times \mathbf{1 0}^{-\mathbf{2}} \mathbf{M ~ s}^{-1}$
c. Rate of formation of $\mathrm{I}_{3}^{-}=\frac{\mathrm{d}\left[\mathrm{I}_{3}^{-}\right]}{\mathrm{dt}}=\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{SO}_{4}^{2-}\right]}{\mathrm{dt}}$
$\therefore \quad-\frac{\mathrm{d}\left[\mathrm{I}_{3}^{-}\right]}{\mathrm{dt}}=-\mathbf{1 . 1} \times \mathbf{1 0}^{-\mathbf{2}} \mathbf{M ~ s}^{-1}$
iii. Number of moles $(\mathrm{n})=300 \mathrm{M} \mathrm{mol}=0.3 \mathrm{~mol}$

Initial volume $\left(\mathrm{V}_{1}\right)=13 \mathrm{~L}$
Increase in volume $=3 \mathrm{~L}$
Final volume $\left(\mathrm{V}_{2}\right)=13 \mathrm{~L}+3 \mathrm{~L}=16 \mathrm{~L}$
Temperature ( T ) $=320 \mathrm{~K}$
a. Isothermal expansion against a constant external pressure ( $\mathrm{P}_{\mathrm{ex}}$ ) of 0.20 atm :

$$
\begin{align*}
\text { Work done }(\mathrm{W}) & =-\mathrm{P}_{\mathrm{ex}} \Delta \mathrm{~V} \\
& =-0.20 \mathrm{~atm} \times 3 \mathrm{~L} \\
& =-0.60 \mathrm{~L} \mathrm{~atm} \\
& =-0.60 \times 101.3 \mathrm{~J} \quad(\because 1 \mathrm{~L} \mathrm{~atm}=101.3 \mathrm{~J}) \\
& =-\mathbf{6 0 . 7 8} \mathbf{~ J} \tag{1/2}
\end{align*}
$$

b. Isothermal and reversible process:

$$
\begin{align*}
\operatorname{Maximum} \text { work }\left(\mathrm{W}_{\max }\right) & =-2.303 \mathrm{nRT} \log _{10} \frac{\mathrm{~V}_{2}}{\mathrm{~V}_{1}}  \tag{1/2}\\
& =-2.303 \times 0.3 \times 8.314 \times 320 \log _{10} \frac{16}{13} \\
& =-\mathbf{1 6 5 . 8} \mathbf{~ J} \tag{1}
\end{align*}
$$

c. Expansion into vacuum:

External pressure $\left(\mathrm{P}_{\mathrm{ex}}\right)=0 \mathrm{~atm}$
Work done (W) $=-\mathrm{P}_{\mathrm{ex}} \Delta \mathrm{V}$

$$
=-0 \mathrm{~atm} \times 3 \mathrm{~L}
$$

$$
=0 \mathbf{J}
$$

iv. a. Excess of air:

Ammonia burns in excess of air to form dinitrogen. In presence of Pt at 1100 K , it is oxidized to NO .
$4 \mathrm{NH}_{3}+3 \mathrm{O}_{2} \longrightarrow 2 \mathrm{~N}_{2}+6 \mathrm{H}_{2} \mathrm{O}$
Ammonia Dinitrogen
b. Excess of chlorine:

Reaction of ammonia with excess of chlorine forms nitrogen trichloride.
\(\underset{Ammonia}{\mathrm{NH}_{3}}+\underset{\substack{Chlorine <br>

(Excess)}}{3 \mathrm{Cl}_{2}} \longrightarrow \underset{\)|  Nitrogen  |
| :--- |
|  trichloride  |\(}{\mathrm{NCl}_{3}}+\underset{\substack{Hydrogen <br>

chloride}}{3 \mathrm{HCl}}\)
c. Na metal:

Ammonia reacts with sodium metal to form sodamide.


## Q. 4. Answer any ONE of the following:

i. a. 1. $\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \longrightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}$

Entropy decreases because number of moles of gaseous reactants > number of moles of gaseous products.
$\therefore \quad$ Disordered state of gaseous reactants > Disordered state of gaseous products
$\therefore \quad \Delta \mathrm{S}$ is negative.
2. $\mathrm{CO}_{2(\mathrm{~g})} \longrightarrow \mathrm{CO}_{2(\mathrm{~s})}$

Entropy (disordered state) decreases as reactants are in gaseous state and
products are in solid state.
$\therefore \quad \Delta \mathrm{S}$ is negative.
b. 1. Smelting:

Smelting is the process of extracting the impure molten metal from its ore at a high temperature using suitable flux and a reducing agent like carbon, hydrogen, aluminium, etc.
2. Flux:

A flux is a chemical substance added to the concentrated ore during smelting in order to remove the gangue to form easily fusible slag.
c. Unit cell of fcc type gold contain $=\frac{1}{8} \times 8+6 \times \frac{1}{2}=4$ atoms

Mass of unit cell of fcc type $=4 \times \frac{197}{6.023 \times 10^{23}}=130.83 \times 10^{-23} \mathrm{~g}$
Density of gold $=19.3 \mathrm{~g} \mathrm{~cm}^{-3}$
Density $=\frac{\text { mass of unit cell }}{\text { volume of unit cell }}$
Volume of unit cell,

$$
\begin{align*}
\mathrm{V} & =\frac{130.83 \times 10^{-23}}{19.3 \mathrm{~g} \mathrm{~cm}^{-3}} \\
& =6.78 \times 10^{-23} \mathrm{~cm}^{3} \\
\mathrm{~V} & =\mathrm{a}^{3}=6.78 \times 10^{-23} \mathrm{~cm}^{3} \\
\therefore \quad \mathrm{a} & =\sqrt[3]{6.78 \times 10^{-23}} \\
& =4.08 \times 10^{-8} \mathrm{~cm} \tag{1/2}
\end{align*}
$$

where, $a$ is the edge of unit cell
$\mathrm{a}=\sqrt{8} \mathrm{r}$

$$
\begin{align*}
& \text { Hence } r=\frac{a}{\sqrt{8}}  \tag{1/2}\\
& =\frac{4.08 \times 10^{-8} \mathrm{~cm}}{\sqrt{8}} \\
& =1.44 \times 10^{-8} \mathrm{~cm} \\
& =144 \mathrm{pm} \text {. } \tag{1/2}
\end{align*}
$$

ii. a. 1. Atomic and ionic radii:
i. On going from group 15 element to group 16 element in a period, the atomic radii decreases due to increase in the nuclear charge which results in a greater nuclear pull.
ii. On moving down the group, a new shell is added for each element. This results in increase in the atomic and ionic radii.
2. Density:
i. On moving down the group 16, the atomic size and the atomic mass increase. But the increase in the atomic size is smaller than the increase in the atomic mass. Hence the density increases on moving down the group.
ii. On moving down the group, the lattice becomes more compact as the magnitude of van der Waals forces of attraction increase. Hence, density also increases.
3. Ionisation enthalpy:
i. Group 16 elements have quite high ionisation enthalpy. It is difficult to remove an electron from the valence shell. On moving down the group, the ionization enthalpy decreases.
ii. On going from group 15 element to group 16 element in a period, for lighter elements ( $\mathrm{O}, \mathrm{S}$ and Se ), the first ionization enthalpy unexpectedly decreases.

## 4. Electronegativity:

i. On going from group 15 element to group 16 element in a period, the effective nuclear charge increases. This increases the electronegativity.
ii. On moving down the group, the atomic size increases which decreases the effective nuclear charge. Hence electronegativity decreases from O to Po.
d, the
b. Given: $\quad$ Mass of Ag deposited $=0.7 \mathrm{~g}$

Molar mass of $\mathrm{Ag}=107.9 \mathrm{~g} \mathrm{~mol}^{-1}$
To find: $\quad$ Quantity of electricity required (in coulomb)
Formula: $\quad$ Moles of substance produced $=\frac{\text { Mass of the substance produced }}{\text { Molar mass of thesubstance }}$
Calculation: From formula,

$$
\begin{align*}
\text { Moles of Ag produced } & =\frac{\text { Mass of Ag produced }}{\text { Molar mass of substance }} \\
& =\frac{0.7 \mathrm{~g}}{107.9 \mathrm{~g} \mathrm{~mol}^{-1}} \\
& =6.4874 \times 10^{-3} \mathrm{moles} \tag{1/2}
\end{align*}
$$

The half reaction for the formation of Ag is,

$$
\begin{align*}
& \mathrm{Ag}_{(\mathrm{aq})}^{+}+\mathrm{e}^{-} \longrightarrow \mathrm{Ag}_{(\mathrm{s})} \\
& \text { Mole ratio }=\frac{\text { moles of } \mathrm{Ag}}{\text { moles of electrons }}=\frac{1(\mathrm{~mol} \mathrm{Ag})}{1\left(\mathrm{~mol} \mathrm{e}^{-}\right)}=1 \mathrm{~mole} \mathrm{Ag} / \mathrm{mol} \mathrm{e}^{--} \\
& \text {Moles of electrons actually passed }=\frac{\text { moles of } \mathrm{Ag}}{\text { mole ratio }} \\
& \\
& =\frac{6.4874 \times 10^{-3} \mathrm{moles} \text { of } \mathrm{Ag}}{1 \mathrm{~mole} \mathrm{Ag} / \mathrm{mol} \mathrm{e}^{-}}  \tag{1/2}\\
& \\
& =6.4874 \times 10^{-3} \mathrm{~mol} \mathrm{e}
\end{align*}
$$

c. The spontaneous and unidirectional flow of solvent molecules through a semipermeable membrane, into the solution or flow of solvent from a solution of lower concentration to the solution of higher concentration through a semi-permeable membrane is called osmosis.

## SECTION - II

Q.5. Select and write the most appropriate answer from the given alternatives for each sub-question:
i. (C) fluorides and oxides
ii. (C) $\mathrm{CH}_{3}-\mathrm{CH}_{2}-\stackrel{\oplus}{\mathrm{C}} \mathrm{H}_{2}$
iii. (D) acetal
iv. (A) linkage isomer
v. (B) Vitamin $\mathrm{B}_{2}$
vi. (C) n-propyl alcohol

(B)
vii. (A) $\mathrm{LiAlH}_{4}$
Q.6. Answer any SIX of the following :
i. Atomic number $=26$

Electronic configuration of Fe atom $=[\mathrm{Ar}] 3 \mathrm{~d}^{6} 4 \mathrm{~s}^{2}$.
Electronic configuration of $\mathrm{Fe}^{2+}=[\mathrm{Ar}] 3 \mathrm{~d}^{6}$
So d-orbital has following distribution of electrons.


There are 4 unpaired electrons.
$\therefore \quad$ Spin only magnetic moment $(\mu)=\sqrt{n(n+2)}$ B.M.

$$
\begin{align*}
& =\sqrt{4(4+2)} \text { B.M. } \\
& =4.89 \mathrm{~B} . \mathrm{M} . \tag{1/2}
\end{align*}
$$

ii. Ethanol is prepared by the action of methyl magnesium iodide on methanal in dry ether, followed by the hydrolysis of the complex using dilute acid.

iii.



Novolac linear polymer
iv. The presence of electron withdrawing $-\mathrm{NO}_{2}$ group at p - position with respect to chlorine atom greatly activates p - nitrochlorobenzene to undergo nucleophilic displacement reactions.
eg. p - nitrochlorobenzene easily undergoes nucleophilic attack of $\mathrm{OH}^{-}$to give $\mathrm{p}-$ nitrophenol.

p-Nitrochlorobenzene
Resonating structures
[11/2]


The carbanion formed by the attack of $\mathrm{OH}^{-}$gets stabilized because of $\pi$ electrons of benzene ring as well as negative charge on C -atom attached to electron withdrawing $\mathrm{NO}_{2}$ group.
v. Primary nitroalkanes can form mono-and dihalo derivatives, whereas secondary nitroalkanes form only monohalo derivative. Tertiary nitroalkanes do not react with halogens. In this reaction, $\alpha$-hydrogen atoms of nitroalkanes are successively replaced by halogen atoms.
a.


vi. Antioxidant: Antioxidant is a substance which when added to food, retards or prevents oxidative deterioration of food.
eg. The most common antioxidants used are, Butylated hydroxy toluene (BHT) and Butylated hydroxy anisole (BHA).
vii.


viii. 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. They are present in very small amounts and regulate the vital functions of the body.
c. The word hormone is derived from Greek word 'Hormaein' which means 'to gear up' or 'to excite'.
d. The parts of the body organs where hormone are produced are called effectors and where they act on cells are called targets.
e. Hormones are derivatives of amino acids, peptides, proteins, steroids etc.
f. The molecular weights of hormones are low and they are easily diffusible.
eg. Thyroxine, Insulin, Androgens, Estrogens and Progesterone.

## Structure of simple triglycerides:



## Q.7. Answer any THREE of the following:

i. Oxidation states of Mn:
$+2,+3,+4,+5,+6$ and +7 .

## Electronic configuration of Mn :

$1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 d^{5} 4 s^{2}$
Due to the presence of half filled ' d ' orbital, the +2 oxidation state of manganese is more stable.
ii. a. Treatment of benzene or its derivative with carbon monoxide and hydrogen chloride under high pressure in presence of a catalyst gives benzaldehyde or substituted benzaldehyde. The catalyst used is a mixture of anhydrous aluminium chloride and
cuprous chloride. This reaction is known as Gatterman-Koch synthesis and is widely benzaldehyde. The catalyst used is a mixture of anhydrous aluminium chloride and
cuprous chloride. This reaction is known as Gatterman-Koch synthesis and is widely used to synthesize aryl halides.


b. Treatment of benzene or its derivatives with acyl chloride $(\mathrm{RCOCl})$ in the presence of anhydrous aluminium chloride, yields corresponding ketones. This reaction is called Friedel-Crafts acylation reaction.

c. Hydrogenation of acyl chlorides (acid chlorides) in presence of a catalyst gives corresponding aldehydes. The catalyst generally used is palladium supported on barium sulphate. The reaction is known as 'Rosenmund reaction'.


Benzoyl chloride


Benzaldehyde

## iii. Complex lipids:

The esters of long chain fatty acids which can be easily hydrolyzed are complex lipids.

## Structure of a nucleoside and nucleotide:

a. Nucleoside is a base - sugar unit and nucleotide is a base - sugar - phosphoric acid unit.
b. A nucleoside is formed when 1-position of a pyrimidine (cytosine, thymine or uracil) or 9-position of a purine (guanine or adenine) base is attached to C -1 of sugar (ribose or deoxyribose) by a $\beta$-linkage. Thus, in general, nucleosides may be represented as: Sugar-Base. For example, structure (I) represents a nucleoside.
c. A nucleotide contains all the three basic components of nucleic acids, i.e., a phosphoric acid group, a pentose sugar and a nitrogenous base. These are obtained by esterification of $\mathrm{C}_{5}^{\prime}$ - OH group of the pentose sugar by phosphoric acid. Thus, in general, a nucleotide is represented as:


(I)

Nucleoside

(II) Nucleotide
iv. a. $\mathrm{Na}_{3}\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{6}\right]$
b. $\quad\left[\mathrm{CrCl}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right] \mathrm{Cl}$
c. $\mathrm{K}\left[\mathrm{Au}(\mathrm{CN})_{4}\right]^{-} \quad[1 \times 3]$

## Q.8. Answer any ONE of the following:

i. a. 1. Homopolymers:

Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers.
eg. Polythene (prepared by using only one type of monomer, i.e., ethene), PVC (monomer: vinyl chloride), Polystyrene (monomer: styrene), etc.
2. Elastomers:

The polymers that have elastic character like rubber are called elastomers.
When a small stress is applied the polymer chains get easily stretched. During stretching, polymers do not tear as cross linking is present. When the stress is removed, the polymer chains regain the original shape. This property is known as elasticity. Elastomers are soft and stretchy. They are used for making rubber bands.
eg. Neoprene, vulcanized rubber, etc.
b. 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. This forms oil in water type emulsion. The anions at the outer end of micelle repel each other and hence they do not precipitate. When the cloth is rubbed, big molecules of oil and soap break into small emulsified oil droplets. 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
c. 1. Action of phosphorus trichloride on propan-2-ol:

2. Action of hydrogen bromide on styrene in the presence of a peroxide:

3. Action of methyl bromide on silver propanoate:

Methyl bromide on heating with silver propanoate forms methyl propanoate.

ii. a. Hoffmann bromamide degradation:

1. Primary amine can be prepared by reaction of amide with bromine and aqueous or alcoholic sodium hydroxide.

eg. Ethanamine is prepared by reaction of propanamide with bromine and aqueous or alcoholic sodium hydroxide.

2. This reaction is known as Hoffmann bromamide degradation. It involves molecular rearrangement. An alkyl or aryl group migrates from the carbonyl carbon to the adjacent nitrogen atom.
3. Aniline is prepared by reaction of benzamide with bromine and aqueous or alcoholic sodium hydroxide.

4. This reaction is useful for decreasing the length of carbon chain by one carbon atom.
b. 3-methylbutan-2-ol is converted into 2-iodo-2-methylbutane by the action of hydrogen iodide.


## Mechanism:

The reaction takes place in three step as follows. ( $\mathrm{SN}^{1}$ mechanism)
Step I: The alcohol is protonated by the acid


Step II: It involves the formation of a carbocation.


Step III: Secondary carbocation rearranges to a stable tertiary carbocation by a hydride ion shift. Nucleophile I- ion attacks tertiary carbocation to give tertiary alkyl iodide.

c. Uses of propan-2-one:

1. Acetone and ethyl methyl ketone are common industrial solvents.
2. Many ketones are well known for their odours and flavours (for example acetophenone).
3. Acetone is also used as one of the constituents of liquid nail polish. It is used in manufacture of explosives, lacquers, paint removers, plastics, drugs, adhesives and disinfectants.
(Any two uses) $\quad[1 / 2 \times 2]$
