SECTION-A

a) What is the difference between scattering and reflection?

Ans. Scattering takes place due to the wave nature of matter whereas reflection is a consequence of the particle nature of matter. Scattering happens upon total absorption and emission of a particle or a photon, whereas in reflection the incident particle or wave only bounces off from a surface

b) What is the difference between oxidation number and oxidation state?

Ans. Oxidation number is the average of the charges present on all the atoms of an element in a molecule. But Oxidation state is the charge present on an individual atom in a molecule.

c) What do you understand by substitution/elimination ratio?

Ans. n a substitution reaction an existing group on the substrate is removed and a new group takes its place. In an elimination reaction the group is simply removed and no new group comes to take its place and this usually results in a double or triple bond forming in the substrate instead.

d) Which of the following will show IR spectrum?

O_2, N_2, HI, CO_2

Ans. O_2-IR inactive

N_2-IR inactive

HI-IR active

CO_2-IR active

e)What is standard reduction potential?

Ans. Standard reduction potential measures the tendency for a given chemical species to be reduced. The standard oxidation potential measures the tendency for a given chemical species to be oxidized as opposed to be reduced.

f)What information can be drawn from Ellingham diagrams?

Ans.An Ellingham diagram is a graph that depicts the temperature dependency of a compound's stability. This method is commonly used to assess the ease with which metal oxides and sulphides can be reduced.

g) Why d and f orbitals show poor shielding effect?

Ans.Since, atomic shielding depends on electron density in a shell and electron density is very less for d and f shells, hence it has poor shielding effect as compared to s and p shells.

h) List the factors on which Δ depends.

- Geometry (which changes the d-orbital splitting patterns)
- Number of d-electrons.
- Spin Pairing Energy.
- Ligand character (via Spectrochemical Series)

i)The following compounds show only one signal in NMR .Write their structural formula

$C_2H_4Br_2C_4H_6$.

j) Indicate R or S configuration at stereogenic center(s). Assign priorities to each group.
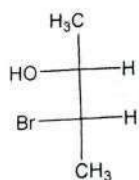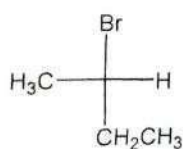
ANS. 1) R

2) S

SECTION-B

2) (a) Deduce the time-independent Schrodinger equation.

At Schrodinger wave equation is used to describe the wave motion of electrons. It uses the concept of energy conservation, i.e.,

Total Energy = Kinetic Energy + Potential Energy.

This equation is given by Erwin Schrodinger in 1926. It is a partial differential equation.

⇒ Now, As, $E = V + \dfrac{mv^2}{2}$ ——— (i)

where, E = Total energy

V = Potential energy

$mv^2/2$ = Kinetic energy

Divide and multiply both sides by m, we get,

$E = V + \dfrac{(mv)^2}{2m}$ ——— (ii)

⇒ According to debroglie, $\lambda = \dfrac{h}{mv}$ ⇒ $mv = \dfrac{h}{\lambda}$ ——— (iii)

where, h = plank's constant

λ = wavelength

m, v = mass and velocity of particle

Squaring both sides of equation (ii), we get,

$(mv)^2 = h^2/\lambda^2$ ——— (iv)

Substituting (iv) in (ii), we get,

$E = V + \dfrac{h^2}{2m\lambda^2}$

$= \dfrac{1}{\lambda^2} = \dfrac{2m(E-V)}{h^2}$ ——— (v)

⇒ The ~~wavelength~~ function of wave motion of electrons is given by,

$\Psi = A \sin \dfrac{2\pi x}{\lambda}$ ——— (vi)

⇒ Differentiating (vi) w.r.t. x, we get,

$$\frac{d\Psi}{dx} = A \cos \frac{2\pi x}{\lambda} \cdot \frac{2\pi}{\lambda}$$

Again differentiating, we get,

$$\frac{d^2\Psi}{dx^2} = A \cdot -\sin \frac{2\pi x}{\lambda} \cdot \left(\frac{2\pi}{\lambda}\right)^2$$

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \Psi \qquad \text{——— (vii)}$$

Substituting (v) in (vii), we get,

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2 \times 2m(E-V)}{h^2} \Psi$$

$$\boxed{\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m (E-V)}{h^2} \Psi = 0}$$

⇒ This is required Schrodinger wave equation for 1D.

(b) Give the significance of wave function.

At In quantum chemistry, Ψ is the wave function of electron. It is a mathematical description of an electron as a three dimentional standing wave. It has no physical significance.

4.) (a) Explain the theory of NMR spectroscopy.

Ar The study of transition of nuclei from one spin to another spin state on absorption of radio frequency waves, when compound is placed in magnetic field is called NMR spectroscopy or Nuclear Magnetic Resonance spectroscopy.

NMR spectroscopy works on the principle that spin magnetic quantum number is the fixed property of nuclei and is denoted by I.

The nuclei having $I=0$, they are known as spin inactive or non-magnetic nuclei. They do not show NMP spectra.

The nuclei having $I>0$ are spin active or magnetic nuclei and they show NMR spectra.

To identify the nuclei which have $I=0$ or $I>0$, we have:

	Atomic no.	Mass no.	I	Example
if	even	even	0	$^4He_2$
if	odd	even	1, 2, 3..	$^{10}B_5$
if	odd or even	odd	$\frac{1}{2}, \frac{3}{2}, ...$	$^{23}Na_{11}$

⇒ Information from NMR spectroscopy:

ⓐ NMR spectroscopy is a powerful analytical technique used in chemistry, biochemistry and materials science for quantification and dynamic studies of molecules. Some of common applications are:

1. Number of signals: The number of signals in an NMR spectrum corresponds to the number of chemically distinct sets of protons or

nuclei in the molecule. For eg., CH_4 will give 1 signal, CH_3-OH will give two signals, etc..

2. **Position of signals :** The position of signals in an NMR spectrum provides information about the chemical environment of protons or nuclei. Protons or nuclei in different chemical environments will have different resonance frequencies and hence shows different positions in spectrum.

If shielding of protons is there, the graph between magnetic field and absorption shifts right side and left side in case of deshielding. It is also known as chemical shieft.

3. **Splitting of signals :** In NMR spectroscopy, it provides information about neighboring protons or nuclei. Protons or nuclei that are coupled to each other will split each other's signals into a pattern of peaks, and this pattern provides information about number and nature of neighboring protons or nuclei.

(b) What is the difference between diffraction and scattering?

Ar

| Diffraction	Scattering
(i) It occurs when waves encounter obstacles having size comparable to wavelength of the wave.	(i) It occurs when wave interact with particles in a medium, which can vary in size relative to wavelength.
(ii) It leads to bending and spreading of waves, resulting in a pattern of fringes.	(ii) It results in redirection of waves in multiple in multiple, often random directions without regular fringe pattern.
(iii) It is utilised in understanding wave properties.	(iv) It is used in wide range to study particle sizes and distribution, etc..

5. (a) Define excluded volume. Show that excluded volume, designated by b, is four times the actual volume of gas molecules.

At There is space between gas molecules which allows them to move. In other words, the volume occupied by one particle or molecule is excluded by one other particle from being occupied. It is designated as "b".

For n moles of gases = nb

⇒ Consider two molecules A and B. Taking the molecules to be spherical, if r is the radius of molecules, then - distant of closest approach between two molecules = 2r

Since, molecules cannot come closer than 2r, the excluded volume for molecule pairs
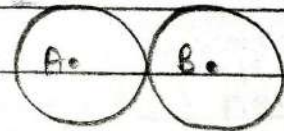
= volume of sphere of radius 2r

$$= \frac{4}{3} \pi (2r)^3 = \frac{8 \times 4}{3} \pi r^3$$

∴ Excluded volume per molecule (b)

$$= \frac{1}{2}\left(8 \times \frac{4\pi r^3}{3}\right) = 4 \times \frac{4\pi r^3}{3}$$

But $\frac{4\pi r^3}{3} = V_m$; i.e., the actual volume of gas molecule.

∴ $b = 4V_m$

(b) Calculate pressure exerted by one mole of CO_2 gas in 1.36 dm^3 vessel at 48°C using vander waals eq.. Given, $a = 3.59\ dm^6\ atm\ mol^{-2}$ and $b = 0.0427\ dm^3\ mol^{-1}$.

At According to vander waals equation;

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Since, $a = 3.59\ dm^6\ atm\ mol^{-2}$

$b = 0.0427\ dm^3\ mol^{-1}$

$V = 1.36\ dm^3$

$T = 48 + 273 = 321\ K$

∴, $P = \frac{RT}{(V-b)} - \frac{a}{V^2}$

$$= \frac{0.082 \times 321}{1.36 - 0.0427} - \frac{3.59}{(1.36)^2}$$

$$= 18.04\ atm$$

6.) (a) What is corrosion? Discuss mechanism of dry corrosion.

Ar The slow destruction of metal surface by the attack of atmospheric gases is called corrosion. It is a natural process that converts a refined metal into a more chemically stable oxide. Now, this gradual deterioration of materials by chemical or electrochemical reaction is explained below:

(i) Dry corrosion : The direct chemical attack of atmospheric gases due to which metal surface gets destructed in the absence of moisture is known as dry corrosion. It generally occurs at high temperature. Eg., In the absence of moisture, rusting is primarily a dry corrosion where iron reacts with oxygen to form iron oxide.

(ii) Wet corrosion : The electrochemical attack of atmospheric gases on metal surface in the presence of moisure is called wet corrosion. It can occur at room temperature. Eg., Rusting, Pitting corrosion, atmospheric corrosion, etc..
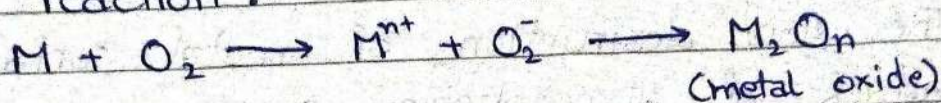
⇒ Mechanism of dry corrosion :

I Initially when oxygen attack the metal surface, the metal will loose its electrons and changes into its positive ions.

$$M \longrightarrow M^{n+} + e^-$$
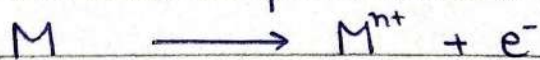
II The metal looses an electron which is gained by oxygen to form oxide ion

$$O_2 + e^- \longrightarrow O_2^-$$

Overall reaction :

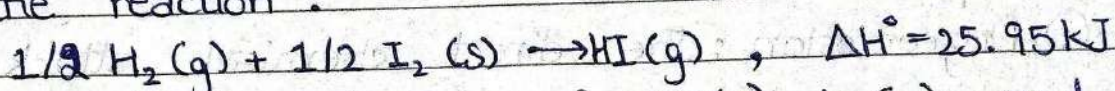$$M + O_2 \longrightarrow M^{n+} + O_2^- \longrightarrow M_2O_n$$
(metal oxide)

Further corrosion is possible or not, it depends on the nature of metal oxide layer.

(b) Calculate the standard free energy change (ΔG°) of the reaction :

$$\tfrac{1}{2} H_2 (g) + \tfrac{1}{2} I_2 (s) \longrightarrow HI (g) , \quad \Delta H^\circ = 25.95 kJ$$

The standard entropy of $HI(g)$, $H_2(g)$ and $I_2(s)$ are 206.27, 130.60 and 116.73 $J K^{-1} mol^{-1}$, respectively. Is this reaction feasible at standard state ?

Ar As we know, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

where $\Delta H^\circ = 25.95 \, kJ$ (given)

Now, Entropy (S°) of $HI = 206.27 \, J K^{-1} mol^{-1}$

      Entropy (S°) of $H_2 = 130.60 \, J K^{-1} mol^{-1}$

      Entropy (S°) of $I_2 = 116.73 \, J K^{-1} mol^{-1}$

$\therefore \quad \Delta S^\circ = \Sigma S^\circ (products) - \Sigma S^\circ (reactants)$

$$= (206.27 \times 1) - [(0.5 \times 130.6) + (0.5 \times 116.73)]$$

$$= 206.27 - 65.3 - 58.365$$

$$= 82.605 \, J K^{-1} mol^{-1}$$

Also, At standard condition, $T = 298K$

$\therefore \quad \Delta G^\circ = 25950 - [298 \times 82.605]$

$$= 25950 - 24615.49 \, J/mol$$

$$= 1334.51 \, J/mol$$

Thus, standard free energy change $(\Delta G^\circ) = 1334.51 \, J/mol$

7.)(a) Discuss molecular geometry of :

(i) NH₃

↠ Ammonia (NH₃) has a trigonal pyramidal or distorted tetrahedral structure. This is mainly due to the presence of a lone non-bonding pair which usually exerts greater repulsion on bonding orbitals. The bond angle is less than the standard 109.5° in ammonia. The bond angle is 107°.
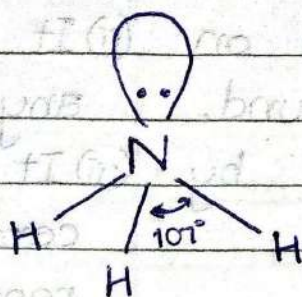
Pyramidal shape

(ii) SF₆

↠ Sulphur Hexafluoride (SF₆) has Octahedral structure. This means that the sulfur atom is located at the center of molecule with six fluorine atoms arranged symmetrically around it.
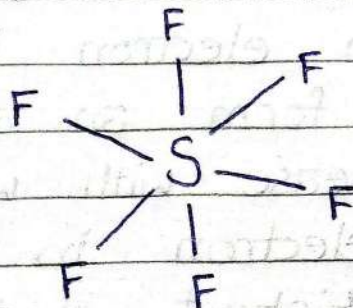
Octahedral structure

(b) What is the difference between oxidation number and oxidation state?

Ar

| Oxidation number	Oxidation state
(i) In any coordination compound, if central metal atom is bonded in ionic form then charge on central atom signifies oxidation number.	(i) An electron can lose, gain or share electrons with another atom, and that particular state is called oxidation state.
(ii) It can be applied on coordination compound.	(ii) It can be applied on any element or compound.
(iii) It is represented by roman numerals.	(iii) It gives charge on central atom and represented by Arabic numerals.
(iv) Example; Oxidation no. of Mn in $[Mn(H_2O)_6]^{2+}$ is +2.	(iv) Example; Oxidation state no. of carbon in CO_2 is +4.

(c) What is electron affinity? Which element has highest electron affinity?

Ar Electron affinity is the amount of energy released when an electron is added to a neutral atom to form an anion. It is also defined as the ease with which an element can accept an electron in gaseous state.

⇒ Chlorine (Cl) has highest electron affinity among elements. This is due to its large atomic radius, or size and its 3p outermost orbital.

8) (a) Discuss the following :

(i) Enantiomers : Enantiomers are chiral molecules that are mirror images of one another and are not superimposable. A chiral molecule has an image that is not the same as its mirror image and is typically characterized by a carbon centre with 4 different atoms bonded to it. They have identical physical and chemical properties. They rotate the plane polarised light to the opposite side but to same extent. They can't be separated by fractional distillation. Eg., Bromochloroethane.

$$H—\overset{Cl}{\underset{Br}{C}}—H \qquad H—\overset{Cl}{\underset{Br}{C}}—H$$
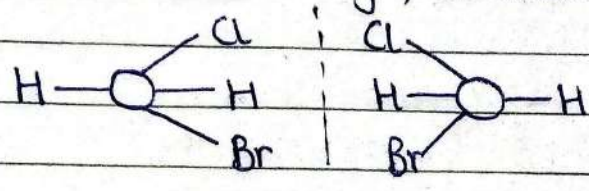
(ii) Diastereomers : Diastereomers are stereoisomer compounds with molecules that do not have a mirror image relationship. They do not have similar physical and chemical properties. They rotate the plane polarised light to the same side but unequal extent. They can be separated by fractional distillation. Eg., Structure of D-glucose and D-altrose.
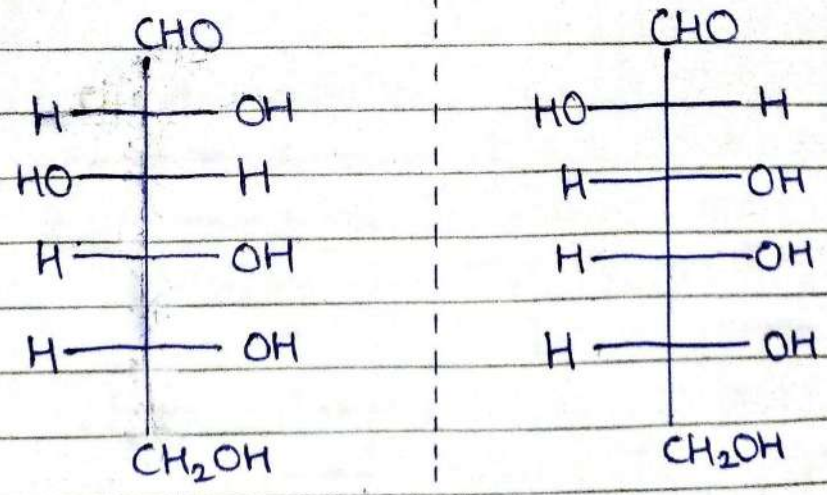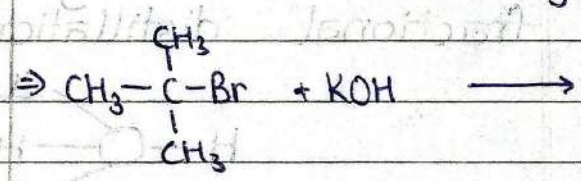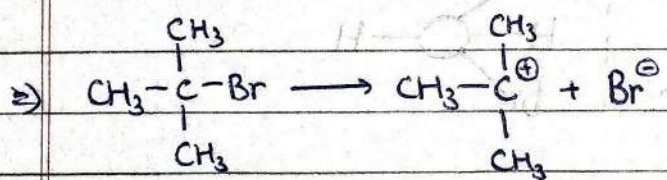
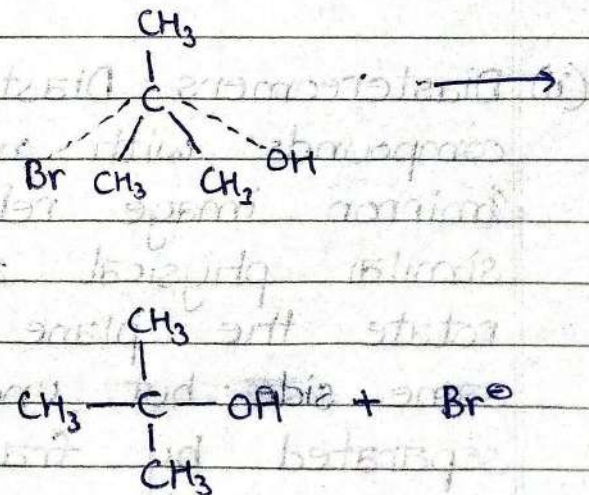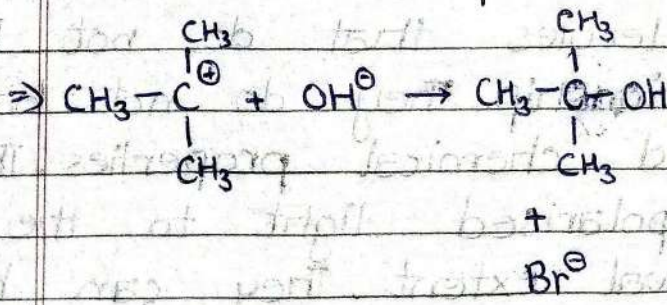| CHO		CHO
H——OH		HO——H
HO——H		H——OH
H——OH		H——OH
H——OH		H——OH
CH_2OH		CH_2OH
D-Glucose		D-Altrose

9.)(a) Compare and contrast the S_{N1} and S_{N2} mechanism of substitution of alkylhalides.

A. Unimolecular Substitution reaction S_{N1}	Bimolecular Substitution reaction S_{N2}.
(i) It is a unimolecular reaction.	(i) It is a bimolecular reaction.
(ii) S_N^1 involves two steps.	(ii) S_N^2 is a single-step process.
(iii) In it, rate of reaction depends on concentration of substrate.	(iii) Rate of reaction depends on concentration of both substrate and nucleophile.
(iv) S_N^1 reactions are favoured by weak nucleophiles.	(iv) S_N2 reactions are favoured by strong nucleophiles.
(v) The mechanism is of double steps. where in first step, formation of carbocation take place and in second step, attack of nucleophile takes place. Eg., I: formation of carbocation:	(v) The mechanism is of single step in which both leaving groups leave and nucleophiles makes bond in a single step through transition state. Eg.,

$$\Rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^{\oplus} + Br^{\ominus}$$

II: Attack of nucleophile:

$$\Rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^{\oplus} + OH^{\ominus} \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

$$+$$

$$Br^{\ominus}$$

$$\Rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + KOH \longrightarrow$$

$$\underset{Br\ \ CH_3\ \ CH_2\ \ \ OH}{\overset{CH_3}{\underset{|}{C}}} \longrightarrow$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + Br^{\ominus}$$

(b) Write short notes on following organic reactions:
(i) Cyclization reactions:
Cyclization is a chemical reaction where a molecule forms a ring structure by bonding with its own functional groups. An example is the interamolecular aldol condensation, where a ketone or aldehyde reacts with itself to form a cyclic compound. For instance, acetylacetone can undergo intramolecular aldol condensation to yield cyclopentenone.

(ii) Reduction reaction:
Reduction is a chemical process involving the gain of electrons or a decrease in oxidation state. An example is the reduction of alkenes to alkanes using hydrogen gas and a catalyst (such as platinum). For instance, reduction of ethene (C_2H_4) results in ethane (C_2H_6) through addion of hydrogen atom.