

Answer 1

- (i) (a)
- (ii) (d)
- (iii) (d)
- (iv) (a)
- (v) (d)
- (vi) (c)
- (vii) (b)
- (viii) (a)
- (ix) (a)
- (x) (d)

Answer 2a –

Q 2 (a) Give a short note on VSEPR Theory giving at least three examples.

- This theory was proposed by Gillespie and Nyholm to predict the structure of molecular shapes and bond angle exactly.
- This theory may be summarized as follows:
 - The shape of molecules is determined by repulsions between all the electron pairs present in the valence shell.
 - A lone pair of electron possesses more space around the central atom than a bond pair.
 - Repulsion between two lone pairs is greater than repulsion a lone pair and a bond pair, which is actually greater than the repulsion between the two bond pair

$$lp-lp > lp-bp > bp-bp$$
 - Thus the presence of lone pairs on the central atom causes the slight distortion of the bond angles from the original shape.
 - If the angle between a lone pair, the central atom and a bond pair is increased then the actual bond angles between the atoms must be decreased
 - The magnitude of repulsions between bonding pairs of electrons depends upon the electronegativity difference between the central atom and the other atoms.
 - Double bonds cause more repulsions than single bonds and triple bonds cause more repulsion than a double bond.

Examples:

SnCl_2 : (2bp + 1lp), sp^2 hybridisation, V-shaped

NH_3 : (3bp + 1lp), sp^3 hybridisation, Pyramidal,

H_2O : (2bp + 2lp), sp^3 hybridisation, V-shaped

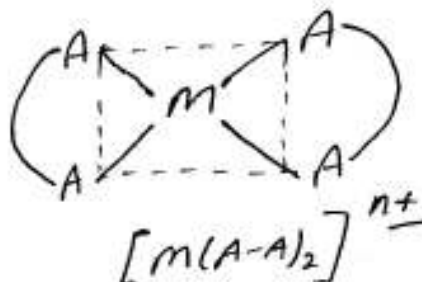
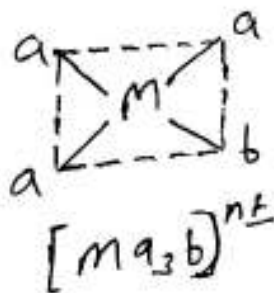
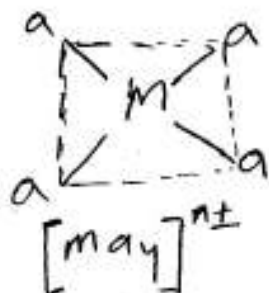
Answer 2b –

Q 2

(b) Which type of square planar complexes do not show the geometrical isomerism and why? Give the possible structures.

$[\text{Ma}_4]^{n+}$, $[\text{Ma}_3\text{b}]^{n+}$, $[\text{M}(\text{A}-\text{A})_2]^{n+}$ type of square planar complexes do not show the geometrical isomerism since every spatial arrangement of ligands around the metal ion is exactly equivalent

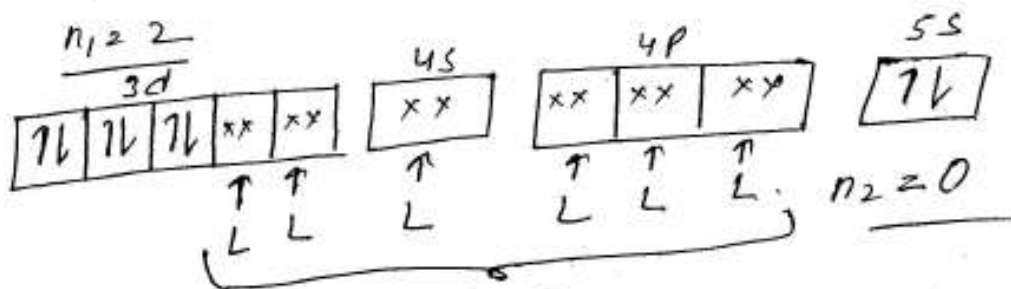
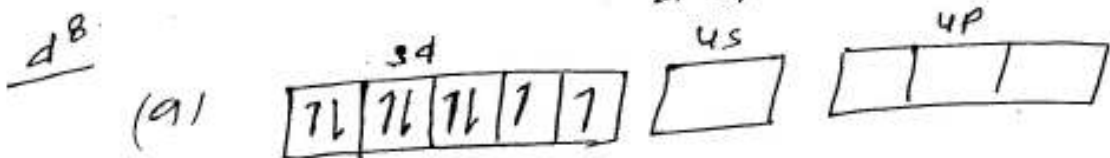
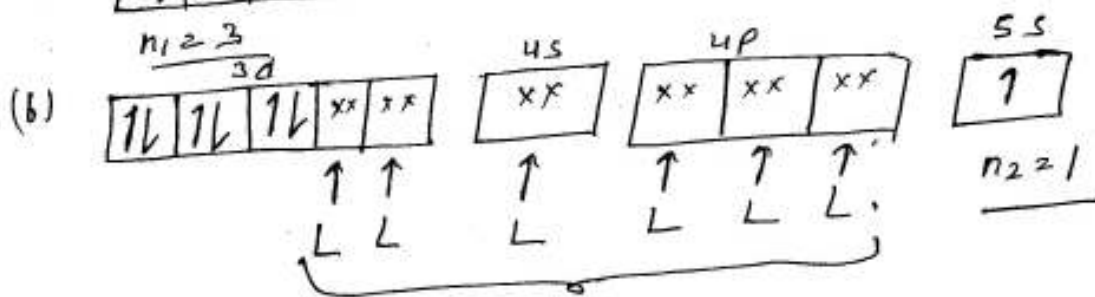
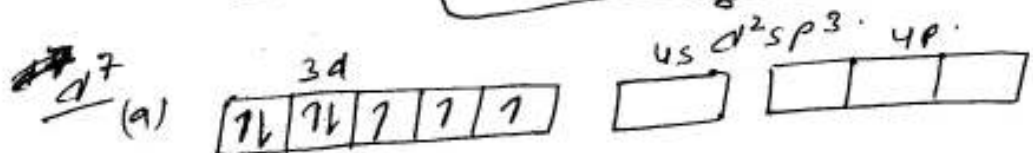
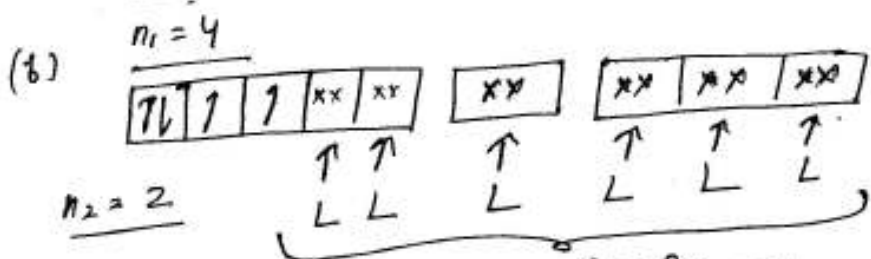
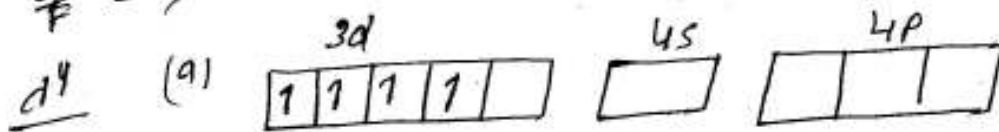
Note: where a and b are the monodentate ligands like -Cl, H_2O , Py, NO_2 etc, and A-A is a bidentate ligand like ethylene diamine (en)



Answer 2c -

Q 2 (c) Show the formation of inner and outer orbital octahedral complexes ions containing d^4 , d^7 and d^8 electrons.

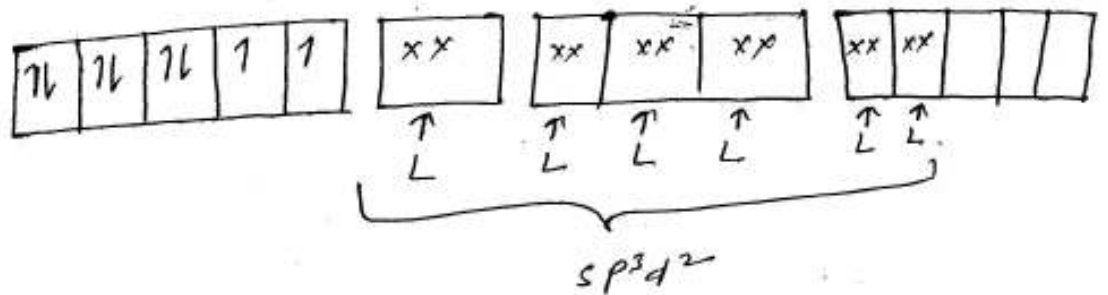
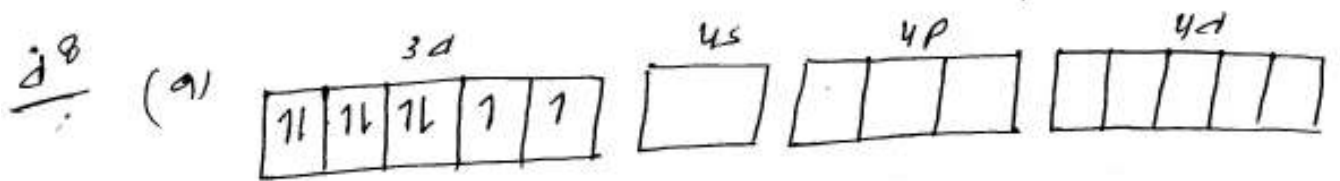
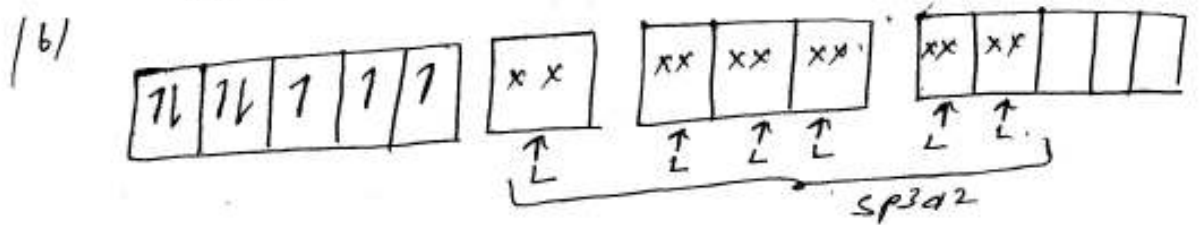
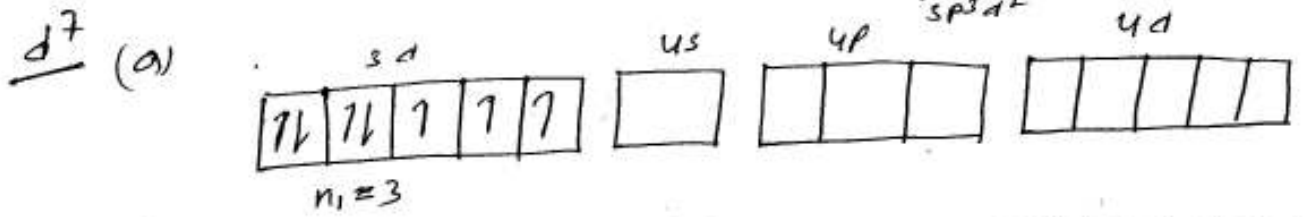
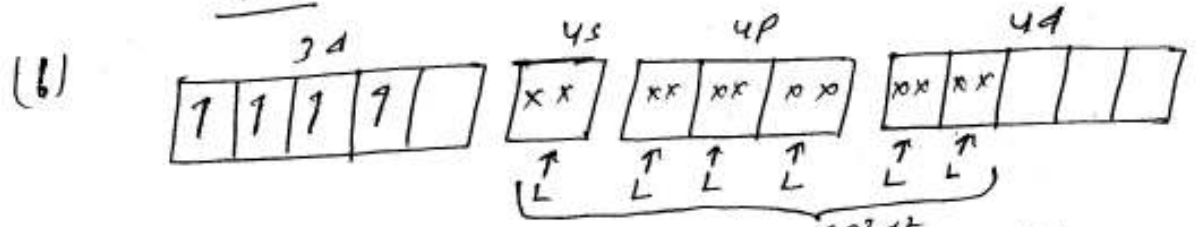
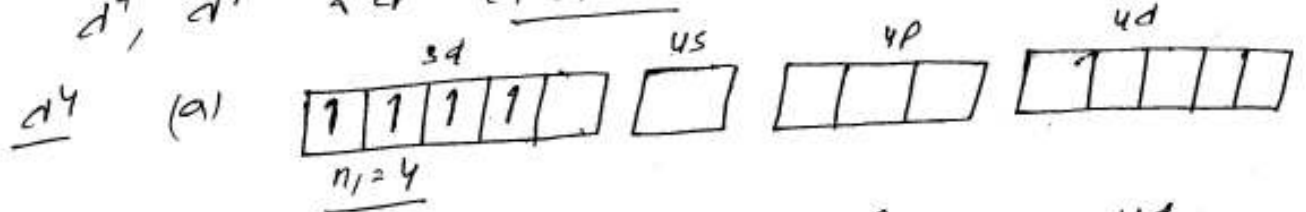
→ Formation of inner-orbital octahedral complexes (d^2sp^3) containing d^4 , d^7 & d^8



d^2sp^3

(2A)

Formation of outer-orbital complexes (sp^3d^2) containing d^4 , d^7 & d^8 electrons



Inductive effect:

In a covalent bond if ~~the~~ both the atoms have same electronegativity, the shared electron pair occupy a central position and such type of bonds are called non-polar covalent bond ex. H-H, Cl-Cl.

But if there is difference in electronegativity of covalently bonded atoms the shared electron pair electrons are shifted or displaced towards more electronegative atom. and the more electronegative atom bears partial -ve charge and other partial +ve charge. Such type of electron displacement through a chain of atom in a sigma bond is called as inductive effect.

This is a permanent effect.

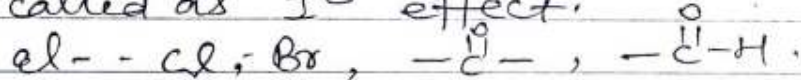
* There are two types of inductive effect.

- ① +I effect
- ② -I effect

①. Those atoms or groups which releases electrons more strongly towards carbon atom or more ~~more~~ strongly than H. is are called I^+ group and process is called I^+ group effect
ex. $-CH_3$,

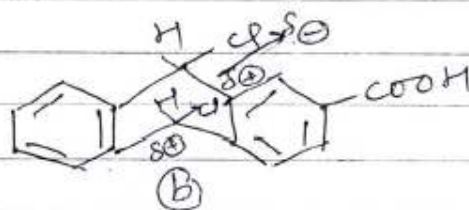
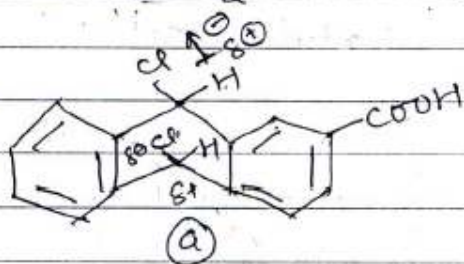
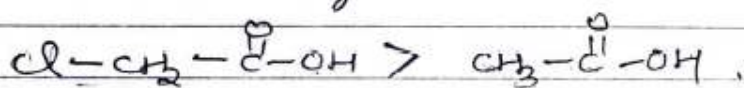
2) Those atoms or groups which attracts

electrons more strongly than Hydrogen are called as I^{\ominus} groups and effect is called as I^{\ominus} effect.



- stability of Carbanion, carbocation and free radicals.

1. Acidity: I^{\ominus} group increases acidity of an acid while I^{\oplus} group decreases acidity.



a is more acidic than b

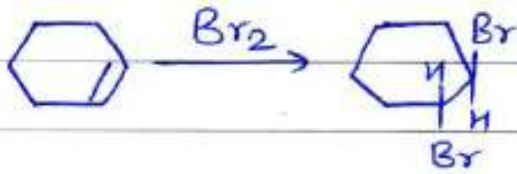
Field Effect

This effect arises from polarity of bond. This effect doesn't operate through covalent bond like in inductive effect. But it operates through environment that is through regulating molecule or space.

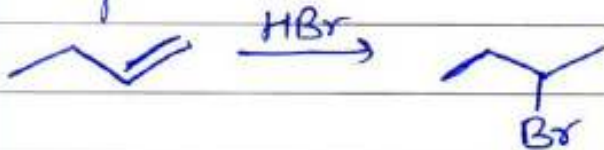
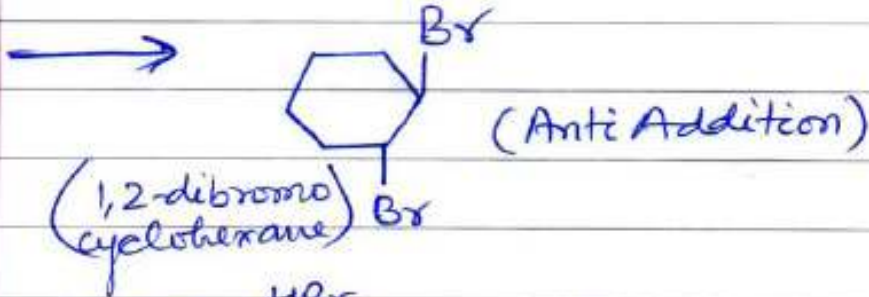
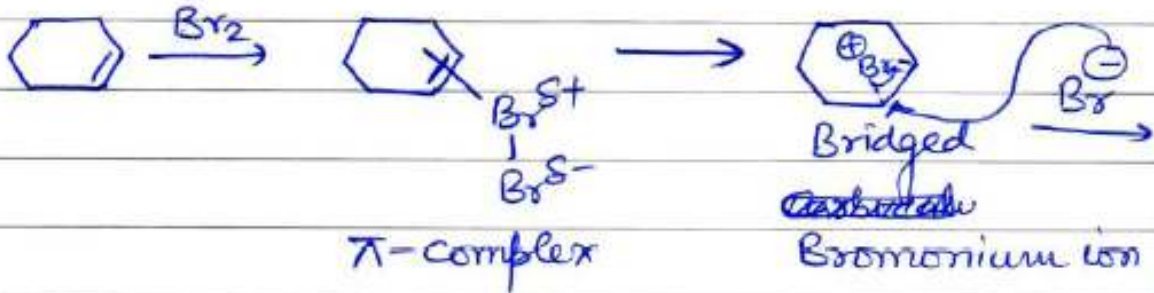
In the given example both the acids may not be differentiated on the basis of inductive effect but applying field effect, these two acids may be differentiated. and a is more acidic than b. This is because ^{in (a)} the negative end of dipole is far away.

But in (b) negative end of dipole is towards.

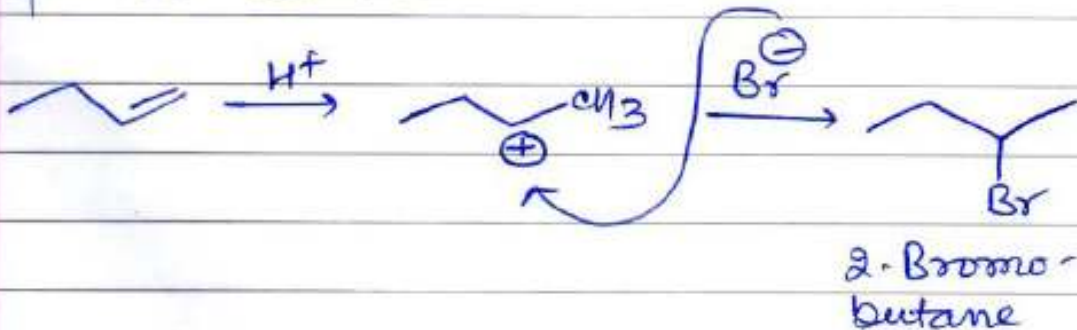
Answer 3b -



Mechanism :-



It is Markonikoff Addition and involves open chain carbocation

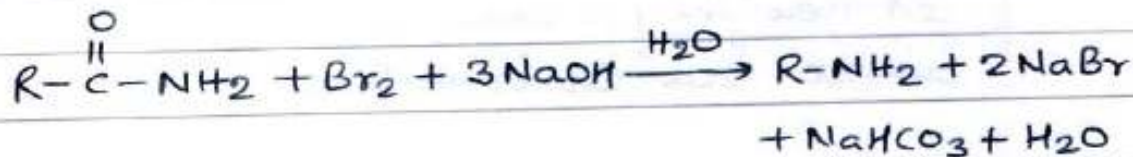


Answer 3c -

Hofmann Rearrangement

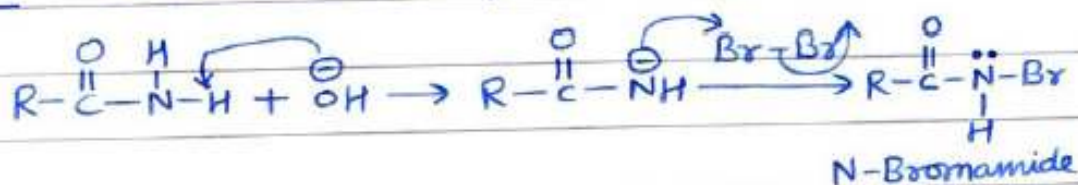
[Also called as Hofmann bromamide reaction]

This is the conversion of an amide into a primary amine with one carbon less in presence of bromine and alkali.

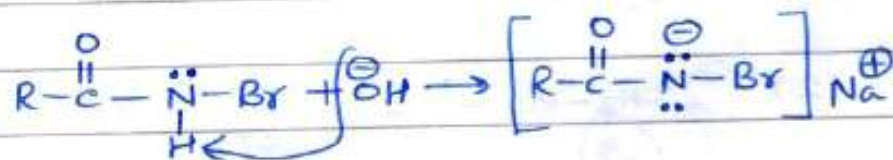


Mechanism:- The reaction takes place in following steps -

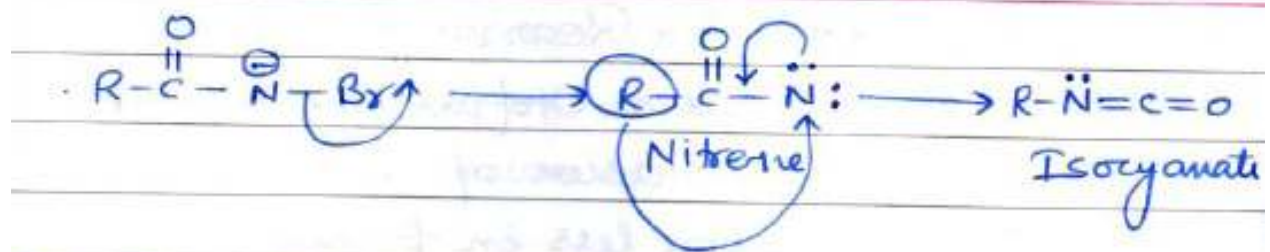
Step 1:- It involves the formation of N-bromamide



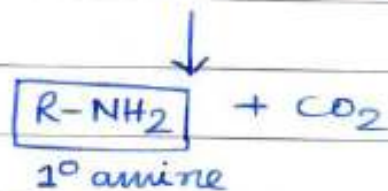
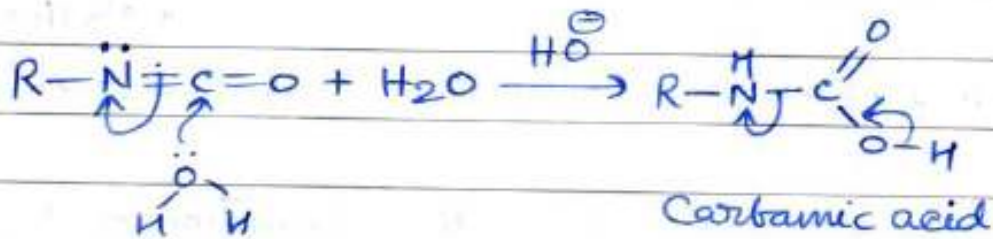
Step 2:- In this step, N-bromoamide forms a sodium salt



Step 3. The anion loses bromine to form a species having electron deficient nitrogen, which rearranges to give an isocyanate.



Step IV : The isocyanate reacts with water in the presence of base to give an amine via carbamate salt.



Answer 4a –

Entropy of fusion, $\Delta S_f = \Delta H_f / T_f$

Where, ΔH_f = molar heat of fusion

T_f = fusion temperature

ΔH_f and T_f are obtained as following –

$$\Delta H_f = (80 \text{ cal g}^{-1}) (4.184 \text{ J cal}^{-1}) (1000 \text{ g kg}^{-1})$$

$$T_f = 0^\circ \text{C} = 273 \text{ K}$$

$$\Delta S_f = \Delta H_f / T_f$$

$$= (80 \text{ cal g}^{-1}) (4.184 \text{ J cal}^{-1}) (1000 \text{ g kg}^{-1}) / 273 \text{ K}$$

$$= 1226 \text{ J K}^{-1} \text{ kg}^{-1}$$

Thus entropy change is **1226 J K⁻¹ kg⁻¹**.

Answer 4b –The potential of an electrode, at a given temperature, depends upon the concentration of the ions in the surrounding solution. If the concentration of the ions is unity and the temperature is 25 °C, the potential of the electrode is termed as the **standard electrode potential** (E°_{e1}). The standard electrode potentials of a number of electrodes may be arranged in a table given as following. These values are said to be on hydrogen scale, because in these determinations the potential of the standard hydrogen electrode, used as the reference electrode, has been taken as zero. The values of standard electrode potentials arranged in the decreasing order, is called as the **Electrochemical Series**.

Electrochemical Series:-

The series consists of values of standard reduction potential of metals in decreasing order.

		<u>SRP (V)</u>
(1)	$Li^+ + e^- \rightarrow Li$	-3.05
(2)	$K^+ + e^- \rightarrow K$	-2.93
(3)	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
(4)	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.71
(5)	$Na^+ + e^- \rightarrow Na$	-2.36
(6)	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
(7)	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
This reaction is used for the reduction of H_2O		
(8)	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
(9)	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.75
(10)	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
(11)	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
(12)	$H^+ + e^- \rightarrow H_2$	0.00
(13)	$Cu^{2+} + 2e^- \rightarrow Cu$	0.15
(14)	$Ag^+ + e^- \rightarrow Ag$	0.22
(15)	$Hg^{2+} + 2e^- \rightarrow Hg$	0.79
(16)	$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
(17)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.33
(18)	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	1.4
This reaction is used for the oxidation of water		
(19)	$Au^{3+} + 3e^- \rightarrow Au$	1.5
(20)	$F_2 + 2e^- \rightarrow 2F^-$	2.87

SRP increases
↓
Decreases

Answer 4c –

Q4

(c) Describe the wet corrosion and dry corrosion with the help chemical reactions.

Dry corrosion or Chemical corrosion:

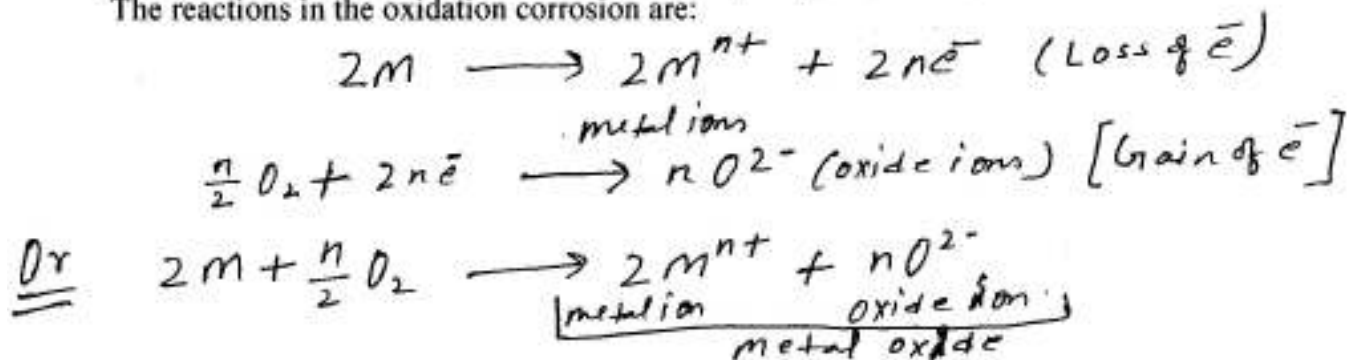
➤ This type of corrosion occurs mainly through the direct chemical action of atmospheric gases such as oxygen, hydrogen sulphide, sulphur dioxide, halogens etc. There are three main types of chemical corrosion

1. Oxidation corrosion is brought about by the direct action of oxygen at low or high temp. on metals, usually in the absence of moisture.

Alkali metals (Li, Na, K, Rb etc.) and alkaline earth metals (Ba, Ca, Sr, etc.) are rapidly oxidized even at low temp.

At high temperature almost all the metals (except Ag, Au, and Pt) are oxidized.

The reactions in the oxidation corrosion are:



2. Corrosion by other gases like SO₂, CO₂, Cl₂, H₂S etc. The extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.

3. Liquid metal corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy

Wet or Electrochemical corrosion:

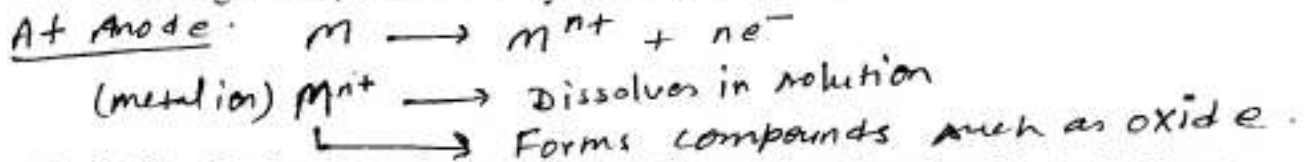
This type of corrosion occurs;

(i) When a conducting liquid is in contact with metal or

(ii) When two dissimilar metals or alloys are either immersed partially in a solution.

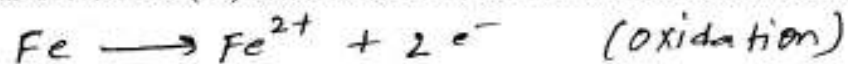
This corrosion occurs due to the existence of separate 'anodic' and 'cathodic' areas/parts between which current flows through the conducting solution.

- At anodic area, oxidation reaction takes place, as a result anodic metal is corroded by either dissolving. Hence, corrosion always occurs at anodic areas.



- On the other hand, at cathodic areas, reduction reaction takes place. So at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions (like OH⁻, O²⁻).

- The metallic ions (at anodic part) and non-metallic ions (formed at cathodic part) diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode
- At the anodic areas of the metal (Fe) dissolves as ferrous ions with liberation of electrons.



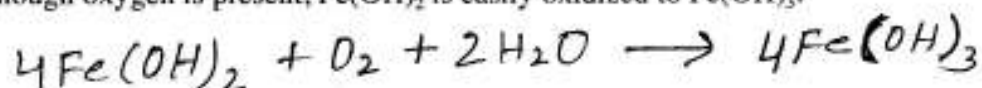
- The liberated e^{-} flows from anodic to cathodic areas, through iron metal, where e^{-} are intercepted by the dissolved oxygen as:



- The Fe^{2+} ions (at anode) and OH^{-} ions (at cathode) diffuse and $\text{Fe}(\text{OH})_2$ is precipitated.



- If enough oxygen is present, $\text{Fe}(\text{OH})_2$ is easily oxidized to $\text{Fe}(\text{OH})_3$.



- This product is called yellow rust actually corresponds to $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
- If the supply of O_2 is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4 .

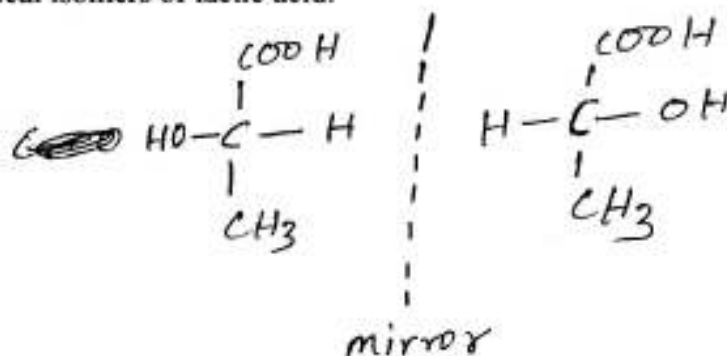
Answer 5a –

Q 5 (a) What are differences between enantiomers and diastereomers. Explain it further by giving the examples.

Enantiomers:

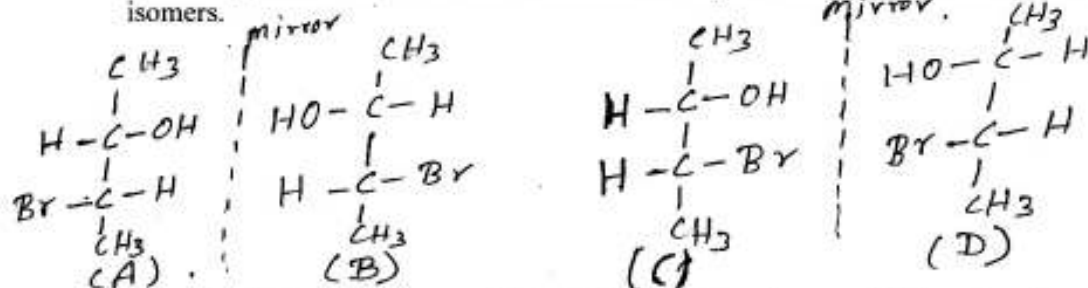
- Optical isomers that are mirror images are called enantiomers. These always exist as discrete pairs.
- Enantiomers have identical properties in all respects except in their interaction with plane of polarized light. They have same melting point, density, solubility, color, and reactivity.
- Both rotate the plane of polarized light to exactly the same extent (same angle) but one rotates the plane to the right (clockwise: called dextrorotatory), while the other rotates the plane to the left (anticlockwise: called laevorotatory).
- Enantiomers are stable, isolable, compounds that differ from each other in 3-D spatial arrangement. They cannot be interconverted under ordinary conditions

Example: Two optical isomers of lactic acid.



Diastereomers:

- Stereoisomers that are not mirror image of each other are called Diastereomers.
- Diastereomers have different properties. They have different melting point, boiling point, solubilities, and reactivity.
- For example 3-bromo-2-butanol which has two asymmetric carbon atoms shows four isomers.



- Where A is the mirror image of B, and C is the mirror image of D. Thus four isomers are two pairs of enantiomers.
- But A and C are neither superimposable nor mirror image, called diastereomers.
- A and D are also diastereomers, as are B and C, and B and D.

Answer 5b –

Q 5 (b) Describe the classification of polymers based on their intermolecular forces.

The polymers are classified into three categories based upon the strength of intermolecular forces holding the polymeric chain in polymers.

Fibrous polymers or synthetic fibers:

- These polymers have long chain linear chains with very strong intermolecular forces between the chains. The forces which hold the polymeric chain together are strong intermolecular forces like H-bonding, dipole-dipole interaction etc.
- Due to these strong intermolecular forces, the polymeric chains in fibrous polymers are closely packed.
- Example: polyamides such as Nylon 66 shows high tensile strength, high modulus and high melting point due to H-bonding between the chains.

Thermoplastic polymers:

- These polymers are usually linear polymers with no cross-links
- They are generally soluble in organic solvents.
- The intermolecular forces of attraction in thermoplastic polymers are intermediary to those in elastomers and fibrous polymers.
- Due to not so strong intermolecular forces, thermoplastic polymers get soften on heating and harden on cooling. Therefore thermoplastic polymers can be easily moulded by heating
Example: Polyethylene, PVC etc.

Elastomers (Rubber like):

- In elastomers, the polymer chains are held together by the weakest intermolecular forces.
- Elastomers become soft on heating and can be moulded into any desired shape.
- The weak intermolecular forces permit the polymers to be stretched by using a small force
- Example: Natural Rubber

Answer 5c –

Q 5 (c) Discuss the preparation and uses of the following polymers

(i) HDPE,

High density polyethylene is synthesized by using the low pressure method. In this process, the ethylene is dissolved in a hydrocarbon solvent such as cyclohexane, and further it is polymerized by using a supported metal oxide catalyst (5% of CrO₃ on a finely divided silica alumina base, which is activated by heating to about 250°C) at 1.4-3.5 MPa pressure and at about 130-160°C. The solvent serves to dissolve the polymer as it is formed and as a heat transfer medium. Finally, polymer is obtained by either flushing off the solvent or precipitating the polymer by cooling.

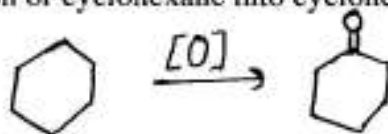
Applications:

- HDPE film is used as wrapping, and packing materials
- HDPE is used for the manufacture of crates, industrial container, and over-head tanks
- It can be used for domestic water and gas piping.
- It is also used as bottles for milk, chemical and house hold items

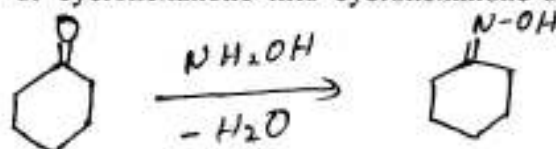
(ii) Nylon 6,

Synthetic fibers of polyamides are also termed as Nylons, Nylon 6 is the most important polymers of this categories. Synthesis of Nylon 6 is performed in the following steps

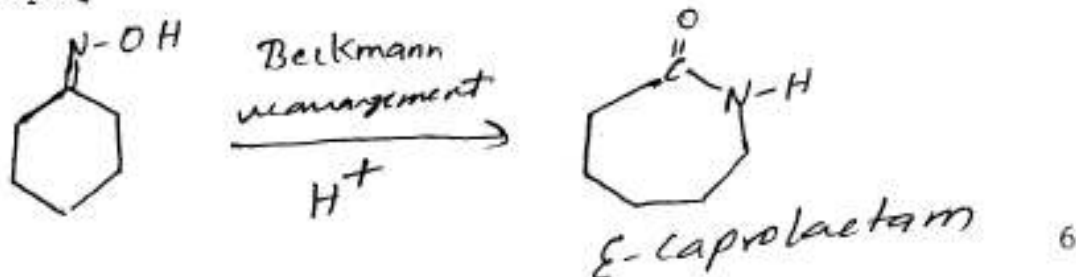
Step 1: Conversion of cyclohexane into cyclohexanone via oxidation



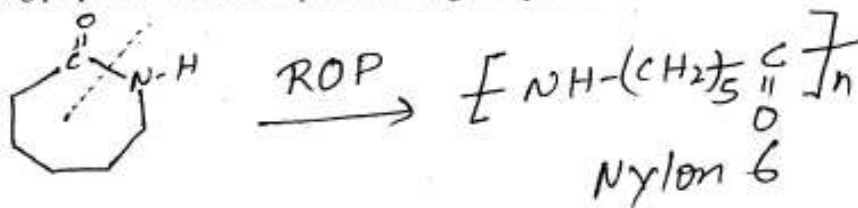
Step 2: Conversion of cyclohexanone into cyclohexanone-oxime by treatment with hydroxylamine (H₂NOH)



Step 3: Conversion of cyclohexanone-oxime into ε-caprolactam by Beckmann rearrangement in the presence of H₂SO₄



Step-4 Ring opening polymerization of ϵ -caprolactam to give Nylon 6.



Applications:

- These types of polymers are mainly used as fibers in textile industries.
- Nylon 6 is mainly used for moulding purposes for gears, bearings, electrical mountings etc. Nylon bearings and gears work quietly without any lubrication
- They are also used for making filaments for ropes, bristles for tooth brushes, and tyre cords etc.

Answer 6a –

Structure I:

Base value	= 207 nm
03 exocyclic double bonds	= 15 nm
1 r.r. at α position	= 10 nm
1 r.r. at δ position	= 18 nm
3 r.r. at higher position	= 54 nm
4 extended double bond in Conjugation	= 120 nm
1 homoannular diene	= 39 nm

Total = 463 nm

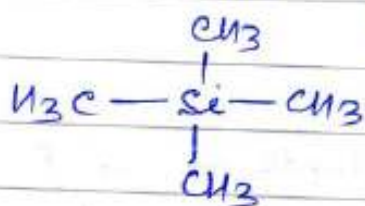
Structure II:

Base value	= 215 nm
07 exocyclic double bonds	= 35 nm
1 r.r. at β position	= 12 nm
1 r.r. at γ position	= 18 nm
1 r.r. at δ position	= 18 nm
5 r.r. at higher position	= 90 nm
4 extended double bond in Conjugation	= 120 nm
1 homoannular diene	= 39 nm

Total = 547 nm

Ans:

TMS is tetramethylsilane having structure and



it has 12 equivalent hydrogens. It is most commonly used as reference compound because —

1. It is chemically inert, hence do not react with compounds under analysis.
2. It is volatile and has b.p. 27°C . Due to this reason precious sample may be easily recovered.
3. It gives a single, sharp and intense absorption peak because all its twelve protons are equal.
4. It is soluble in most of the organic solvents.
5. Its proton absorbs at higher field than that of almost all organic compounds, hence overlapping of signals does not occur.

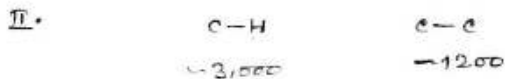
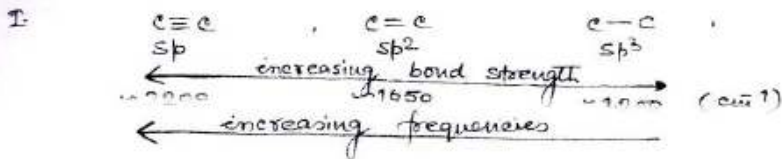
Answer (6c)

Various Effects on Vibrational Frequencies :-

Bond Strength :-

Vibration frequency of a bond increases, when the bond strength increases.

Example :



C-H bond is stronger than C-C bond.

2. Mass :- frequency increases when the reduced mass decrease & vice versa.

O-H bond has higher frequency than O-D because D has higher mass no. than H.

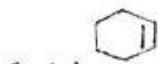
3. Hydrogen Bonding :- Hydrogen bonding lowers the vibrational frequency. Stronger the H-bonding, greater is the absorption shift towards lower wave number than normal value. Two types of H-bonding can be distinguished by IR spectrum -

- Intermolecular H-bonds give a broad bands, while
- Intramolecular H-bonds give a sharp & well defined peak.

In very dilute solution formation of intermolecular H-bonding does not takes place because molecules are widely separated i.e. in dilute solution sharp band is obtained due to intramolecular H-bonding. When the concentration (of the alcohol & phenols) is increasing the sharp band is replaced by broad band due to intermolecular H-bonding takes place.

4. Resonance :- Resonance lowers the vibrational frequency. Resonance results in partial π -bond character between the two double bonds with decrease in the strength of double bonds. Conjugated db's therefore vibrate at lower frequencies than ~~to~~ similar isolated double bonds.

For. eg.



Cyclohexene (isolated db)

$\nu(C=C)$ $\approx 1645 \text{ cm}^{-1}$



Conjugated

1620 cm^{-1}



Aromatic

1600

It is clear from this example that due to conjugation, vibrational frequency decreases.

5. Inductive Effect:

(A) Group having + I effect lowers the vibrational frequency

Example = CH_3 is a + I group and on this basis we can give the relative vibrational frequency of the following. From formaldehyde to acetone, number of methyl group is increasing and therefore the vibrational frequency is decreasing.



(B) Group having - I effect lowers the vibrational frequency

Example = F is a - I group and on this basis we can give the relative vibrational frequency of the following. As the number of F group is increasing, vibrational frequency is also increasing.

