

B.Tech.

SECOND SEMESTER EXAMINATION, 2008-09

ENGG.CHEMISTRY

(EAS-102/EAS-202)

[Total Marks : 100]

Time : 3 Hours]

SECTION-A

Q. 1. Choose/Fill Correct answers :

20 × 1 = 20

(i) Conversion of an amide to a primary amine with one less carbon atom in presence of NaOH/Br₂ is known as :

- (a) Beckmann rearrangement
- (b) Cannizaro reaction
- (c) Diels-Alder reaction
- (d) Hoffmann rearrangement

(ii) According to the phase rule degree of freedom (F) =

(iii) Number of signals obtained in the ¹H NMR of CH₃CH₂OCH₂CH₃ shall be :

- (a) 10 (h) 1 (c) 2 (d) 4

(iv) The monomer in natural rubber is

(v) The half life period of a first order reaction is

(vi) S_N2 reaction is accompanied by of configuration.

(vii) For a strong acid-weak base neutralization titration the pH at the end point must be

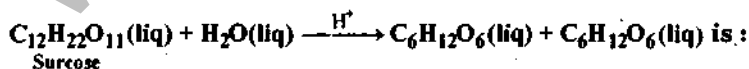
- (a) >7 (b) 7 (c) <7 (d) 10

(viii) The order of the bond length of O₂, O₂⁻, O₂⁺ is

(ix) conformer of n-butane has the highest potential energy.

(x) The finger print region in IR spectroscopy is in range.

(xi) The reaction :



- (a) zero order (b) first order (c) second order (d) fractional order

(xii) Optical isomerism in compounds due to restricted rotation around a single bond is called

(xiii) Coating of Sn over iron is an example of coating.

(xiv) The temporary hardness in water is due to the presence of

(xv) An example of electrically conducting polymer is

- (a) Poly vinylchloride (h) Poly styrene
- (c) Poly acetylene (d) Poly ethane

- (xvi) Net calorific value is than gross calorific value.
 (xvii) Corrosion is a process of of a metal.
 (xviii) o-nitrophenol has a melting point than p-nitrophenol.
 (xix) Diamond, graphite and are the allotropic forms of carbon.
 (xx) Wilkinson's catalyst is :

- (a) CH_3MgCl (h) $(\text{PhP})_3\text{RhCl}$
 (c) $\text{Et}_3\text{Al} / \text{TiCl}_4$ (d) n - BuLi

Ans. (i) Hoffmann rearrangement

- (ii) $F = C - P + 2$ (iii) 2 (iv) Isoprene (v) $\frac{0.693}{K}$ (vi) Inversion (vii) < 7 (viii) $\text{O}_2^+ < \text{O}_2 < \text{O}_2^-$
 (ix) Fully Eclipsed (x) $650-1450 \text{ cm}^{-1}$ (xi) First order (xii) Atrop isomerism
 (xiii) metallic coating/Tinning (xiv) bicarbonates of $\text{Ca}^{++}/\text{Mg}^{++}$ (xv) Polyacetylene
 (xvi) less (xvii) destruction (xviii) less (xix) fullerene (xx) $(\text{Ph P})_3\text{RhCl}$

SECTION B

2. Attempt any three of the following :

10 × 3 = 30

Q. (i). (a) Distinguish between thermoplastic and thermosetting polymers.

Ans.

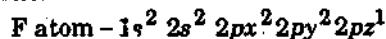
Thermoplastic

Thermosetting

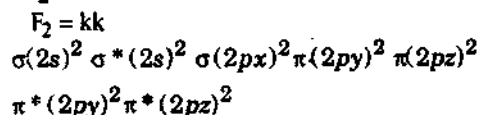
- | | |
|---|--|
| <p>(1) Polymers which are softened on heating and hardened on cooling are known as thermoplastics.</p> <p>(2) They can be moulded again and again.</p> <p>(3) These are generally formed by addition polymerisation.</p> <p>(4) They have linear structure and the different chains are held together by weak vander Wall's forces attraction.</p> <p>(5) On heating secondary bonds break; hence they get softened.</p> <p>(6) They are usually soft, weak and less brittle.</p> <p>(7) They are generally soluble in organic solvents.</p> <p>(8) Example PE, PVC, PMMA, Nylons, Polystyrene.</p> | <p>(1) Polymers which once hardened can't be softened again are known as thermosets.</p> <p>(2) They can't be remoulded.</p> <p>(3) Generally formed by condensation polymerisation.</p> <p>(4) They have cross linked three dimensional network type of structure.</p> <p>(5) On heating they undergo hardening because of taking place of any left over polymerisation on prolonged heating they undergo degradation. which is known as charring.</p> <p>(6) They are usually hard, strong and more brittle.</p> <p>(7) They are generally insoluble in organic solvents.</p> <p>(8) Ex. Phenolicresin, Epoxy resin, Bakelite etc.</p> |
|---|--|

Q. 2. (ii) (a) On the basis of molecular orbital theory explain why F_2 is diamagnetic while O_2 is paramagnetic? Calculate their bond orders.

Ans. F_2 molecule : The two participating F atoms contribute total 14 electrons.



There are eight molecular orbitals formed. In these MOs, 14 electrons are accommodated. The Electronic configuration of the F_2 molecule is



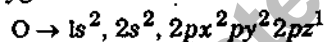
The bond order in

F_2 molecule is

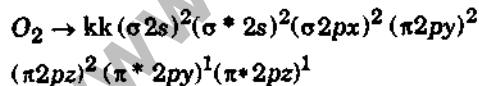
$$\frac{N_b - N_a}{2} = \frac{8 - 6}{2} = 1$$

Since the F_2 molecule has no unpaired electron. It is diamagnetic in nature.

O_2 molecule : The two participating oxygen atoms contribute a total of 12 valence electrons and $2 \times 4 = 8$ atomic orbitals towards the oxygen molecule.



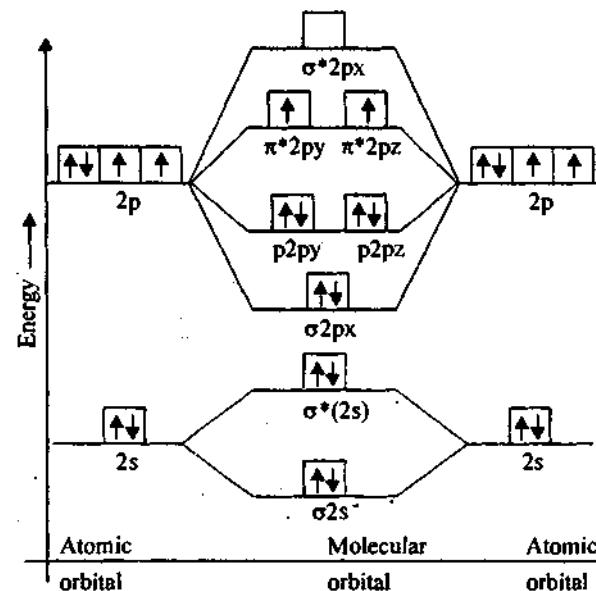
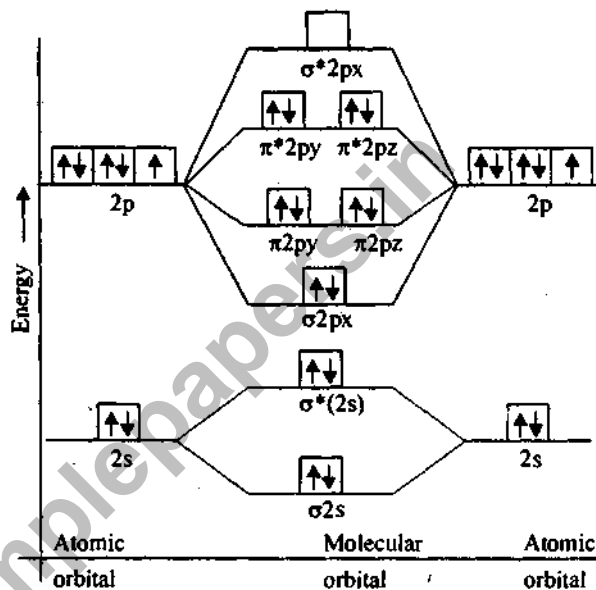
There are eight molecular orbitals and 12 electrons are accommodated.



The bond order = $\frac{8 - 4}{2} = 2$ It has two unpaired electron, So it is paramagnetic in nature.

Q. 2. (ii) (b) Calculate the number of atoms per unit cell in SC, BCC and FCC.

Ans. The number of atoms per unit cell can be calculated in solids as—



(a) **In simple cubic unit cell** : There are eight corners of the cube and at each corner there is an atom. Each corner atom is shared by eight adjoining cubes, therefore the share of the cube = $\frac{1}{8} \times 8 = 1$.

Hence total number of atoms in a simple cubic unit cell = 1

(b) **In Body Centered Cube (BCC)** : B.C.C. unit cell has an atom at each corner of the cube and in addition, it has one atom in the centre of the cube. Since each corner atom is shared by eight adjoining cubes and the one center atom is not shared by an adjoining cube, the

B.C.C. unit cell contains :

8 atoms at the corner $\times \frac{1}{8}$, 1 atom

1 center atom = 1 atom

Total = 2 atoms.

(3) **In Face Centered Cube (F.C.C.)** :

A F.C.C. unit cell has an atom at each center of the face and an atom at each corner. Each atom present at the corner contributes $\frac{1}{8}$ to the unit cell whereas each atom at the face centered contributes $\frac{1}{2}$ to the unit cell since it is shared by two unit cells.

No of atoms per unit cell = 8 atoms at the corner $\times \frac{1}{8}$ + 8 face centered atom $\times \frac{1}{2}$

= 1 + 3 = 4 atoms.

Q. 2. (iii) (a) Write a short note on biogas as a source of energy.

Ans. Biogas : Biogas is a mixture of methane, CO_2 and other trace gases produced by the anaerobic decomposition of organic matter".

eg. Natural gas, Gobar gas etc.

Composition : The average composition of biogas is

CH_4 - 50 - 60%

CO_2 - 30 - 40%

H_2 - 5 - 10%

N_2 - 2.6%

H_2S , NH_3 etc. Traces.

Production : The production of biogas involves the following steps :

(1) **Solubilisation and hydrolysis** : The complex organic substances are solubilised by enzymatic hydrolysis.

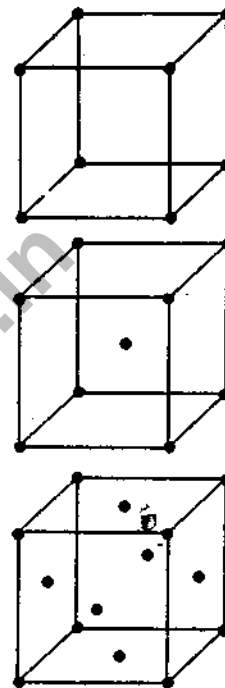
(2) **Acidogenesis** : Soluble organic compounds are converted into organic acids with gases like CC_2 , H_2 and H_2S .

Fermentative hydrolytic bacteria and Acetogenic bacteria are involved in this step.

(3) **Methanogenesis** : Acid and CO_2 act as substrate for this step and methanogenic bacteria like Methanococcus, Methanotheroxis etc. convert them into methane.

$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

$\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$



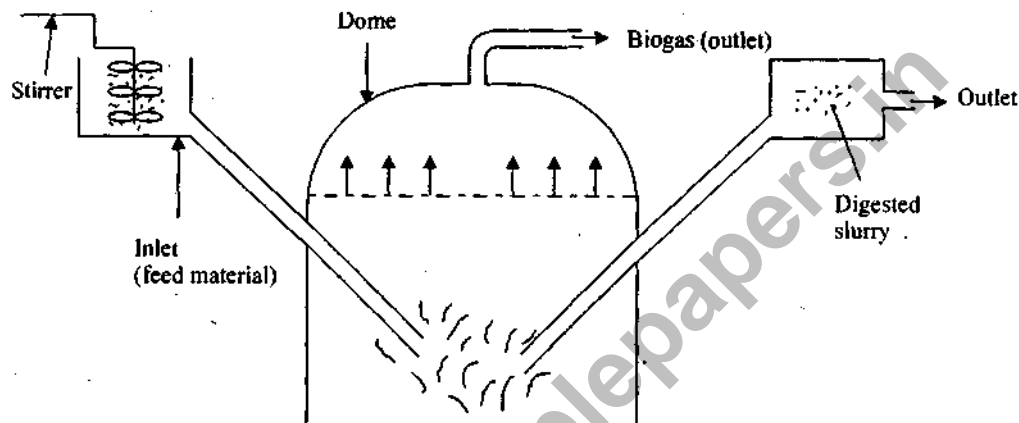
The production of biogas is carried out in biogas plant or digester made up of bricks or steel shown as :

Conditions for Optimum digestion :

pH = 6.0 – 8.0

Temperature = 30 – 40°C

Digestion period = 2.3 weeks for cow dung.



Characteristics : (1) It is odourless, smokeless and burns with a blue flame.

(2) It is lighter than air.

(3) Its ignition temperature is 750°C.

(4) Its Calorific value depends upon the CO₂ content (a non-combustible gas). The greater is the CO₂ content in biogas the lesser is its Calorific values. The average Calorific value of biogas is 6000 kcal/m³.

Applications : (1) Used for cooking and lighting.

(2) As a fuel to power stationary engines for generation of electricity.

(3) Compressed into Cylinders for use as a source of energy in automobiles.

(4) In the production of biogas, the manurial value of dung is not diminished.

Limitations – It is used in ten meters of the plant.

Q. 2. (iii) (b) Show that in case of a first order reaction, the time required for completion of 99.9% of the reaction is about ten times of that required for half the reaction.

Ans. For 1st order reaction

$$t_{1/2} = \frac{0.693}{k} \quad \dots(1)$$

k for 99.9%

$$t_{99.9} = \frac{2.303}{k} \log \frac{100}{100 - 99.9}$$

$$= \frac{2.303}{k} \log 10^3$$

$$= \frac{2.303 \times 3}{k} = \frac{6.909}{k}$$

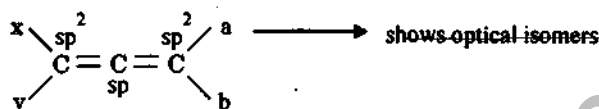
..... (ii)

from (i) & (ii)

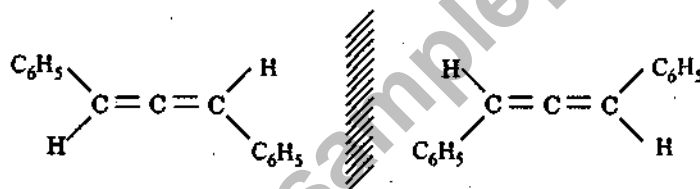
$$\frac{t_{99.9}}{t_{1/2}} = \frac{6.909/k}{0.693/k} = 9.98 \approx 10$$

Q. 2. (iv) Asymmetrically substituted compounds having even number of cumulative double bonds exhibit optical isomerism whereas those having odd number of cumulative double bonds show geometrical isomerism. Explain giving reasons.

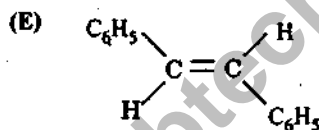
Ans. Compounds containing even no. of cumulative double bonds are called allenes.



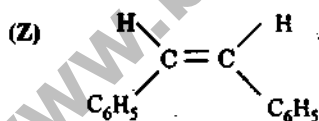
In the above compound central carbon is in sp hybrid state while remaining are sp^2 hybridised. Central carbon form two σ bonds due to $sp - sp^2$ overlap. Two mutually π electrons (p_y, p_z) are also at control central atom. The two carbon atoms are in plane perpendicular to each other. So the two forms of the compounds are non-superimposable mirror image of each other.



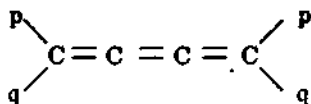
In case of odd no. of Double bonds (say one)



Both are in sp^2 hybrid state in one plane



So can show E/Z isomers (geometrical isomers)



Q. 2. (v) Define and Explain the terms involved in phase rule. Draw a net labelled phase diagram of water system and explain the areas and curves in it. What is the significance of the triple point and metastable curve in this system ?

Phase rule : This rule was put forward for heterogeneous systems and stated by American physicist willard Gibbs in 1874.

This rule may be stated as

$$F = C - P + 2$$

where F = number of degree of freedom.

C = number of component

P, phase of the system.

Phases : The homogeneous parts of a heterogeneous in equilibrium, which are physically distinct and mechanically separable and termed as phases.

eg. In the water system there are three phases —
ice (solid) water (liquid) vapour (gas) in equilibrium.

Component : The number of components of a system are the smallest number of independently variable constituents taking part in equilibrium by means of which the composition of each phase can be expressed either directly or in terms of chemical equations :

eg. (i) $\text{Ice (s)} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour (g)}$

This is one component system because the composition of each phase namely ice, water and vapour can be expressed in term of only one constituent H_2O . Therefore water system is a three phase and one component system.

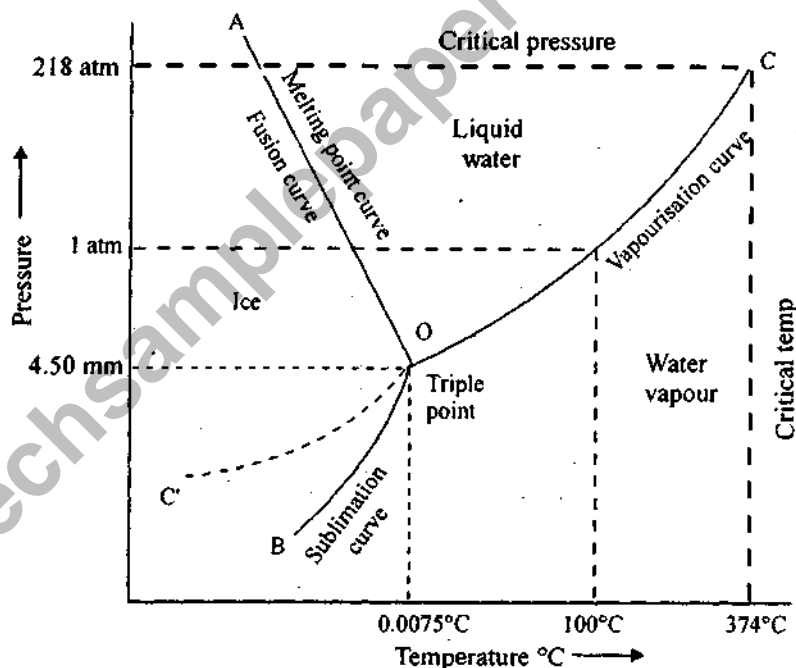
Degree freedom of Variance : The degree of freedom of a system at equilibrium is the minimum number of variables such as pressure, temperature and concentration which must be specified in order to define the system completely. It is also known as 'Variance of the system' and is denoted by 'F'.

Water system :

Water system is an important example of one

component system consisting of three phases namely Ice (solid) water (liquid), vapour (gaseous)

The salient features of water system are as follows : —



S.N.	Area/curve/point	Phase/equilibrium	$F = C - P + 2$	Remark
1.	Area OAB	Ice $P = 1$	$F = 2$	Bivariant P and T can be varied
2.	Area OAC	Water $P = 1$	$F = 2$	Bivariant P and T can be varied
3.	Area OBC	Vapour $P = 1$	$F = 2$	Bivariant P and T can be varied
4.	Curve OA	Ice \rightleftharpoons water $P = 2$	$F = 1$	Fusion curve, univariant P or T can be varied

5.	Curve OB	Ice \rightleftharpoons vapour	$P = 2$ $F = 1$	Sublimation curve univariant, P or T can be varied
6.	Curve OC	Water \rightleftharpoons vapour	$P = 2$ $F = 1$	Vapourisation curve, univariant, P or T can be varied
7.	Curve OC'	Water \rightleftharpoons vapour	$P = 1$ at metastable equilibrium	Metastable curve
8.	Point O	Ice \rightleftharpoons water vapour	$F = 0$	Triple point, invariant $P = 3$

Triple point 'O': At point 'O' all the three phases are in equilibrium.

Ice (s) \rightleftharpoons water \rightleftharpoons vapour

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Therefore triple point is invariant, i.e. all the three phases co-exist only at a particular temperature and particular pressure.

Temperature at triple point = 0.0075°C

Pressure at triple point = 4.58 mm of Hg

Metastable curve : OA' is metastable curve along which super cooled liquid is in equilibrium with vapour without separation of ice. As soon as the system is disturbed (by addition of ice, mechanical disturbance etc) entire supercooled liquid solidifies.

SECTION C

Q. 3. (a) What is electrochemical theory of corrosion ? Discuss the mechanism of electrochemical corrosion of iron with

(i) absorption of oxygen

(ii) evolution of hydrogen.

Ans. Electrochemical Theory or Wet Corrosion : It takes place mostly under wet or moist conditions through the formation of short circuited galvanic cells-wet corrosion is more common than dry corrosion.

Mechanism : Electrochemical corrosion involves—

(i) Separate 'anodic' and 'Cathodic' parts/areas between which current flows through the conducting medium.

(ii) Occurrence of oxidation (corrosion) at anodic areas which generates metallic ions.

(iii) Non-metallic ions like OH^- or O^{2-} are formed at cathodic areas.

(iv) Diffusion of metallic and non-metallic ions toward each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.

Rusting of iron in neutral aqueous solution of electrolyte in the presence of O_2 or in acidic environments with the evolution of hydrogen is electrochemically wet corrosion.

Fe^{2+} ions originated at anode and OH^- ions originate from cathode smaller Fe^{2+} ions diffuse more rapidly than the larger OH^- ions, so corrosion occurs at the anode, but rust is deposited near cathode.

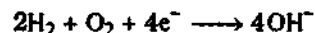
The electrons released at the anode are conducted to the cathode and are responsible various cathodic reactions such as :

(i) **Oxygen absorption** : In the presence of dissolved oxygen

(a) in acidic medium-



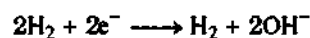
(b) in neutral weakly alkaline medium-



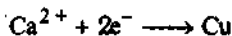
(ii) **Hydrogen Evolution** : In the absence of O_2

(a) in acidic medium $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$

(b) in neutral or alkaline medium



(iii) **Electroplating** : At the Cathode, metal ions collect the electrons and get deposited on the cathode surface.

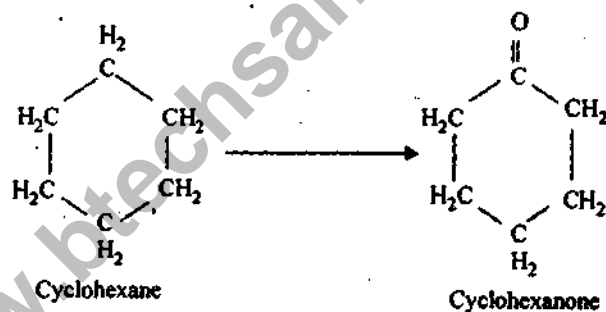


Q. 3 (b) Starting from cyclohexanone oxime, how can Nylon-6 be prepared ? Name the reaction and discuss its mechanism.

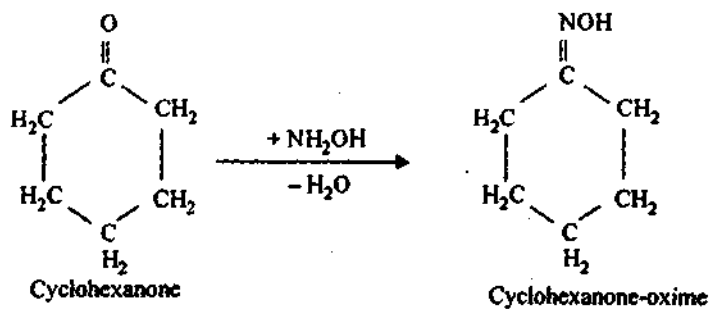
What are the important properties and used of Nylon-6 ?

Ans . Preparation :

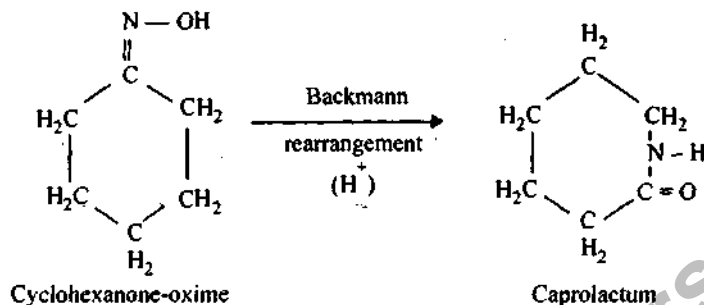
Step (i) Conversion of cyclohexane into cyclohexanone by oxidation :



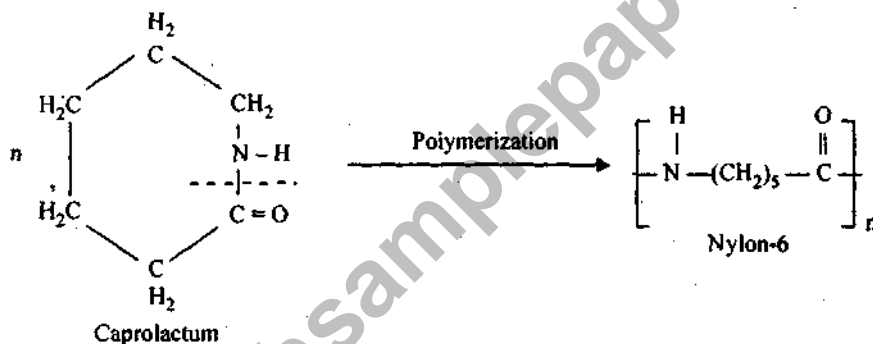
Step (ii) Conversion of cyclohexanone into cyclohexanone oxime by treatment with hydroxylamine NH_2OH



Step (iii) Conversion of cyclohexanone-oxime into caprolactum by Backmann-rearrangement in the presence of H_2SO_4



Step (iv) Ring opening polymerisation of caprolactum to give nylon -6



- Properties :** (1) Structure of nylon -6 is linear that permits side-by-side alignment.
 (2) It has high crystallinity which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties upto 125°C .
 (3) It is also sterilisable

Uses : It is mainly used for making tyre cords.

Q. 4. (a) Explain the method of proximate analysis of coal. 3.25 grams of coal was Kjeldahlized and NH_3 gas thus evolved was absorbed in 45 mL of 0.1 NH_4SO_4 . To neutralize excess acid, 11.5 mL of 0.1 N NaOH was required. Determine the percentage of Nitrogen in the coal sample.

Ans. Proximate Analysis : It involves the following determinations

(i) **Moisture content :**

$$\% \text{ of moisture} = \frac{\text{Loss in weight}}{\text{wt. of Coal taken}} \times 100$$

(ii) **Volatile matter :** The volatile matter present in the coal may be combustible gases (as H_2 , CO , CH_4 etc) or non-combustible gases (as CO_2 and N_2)

$$\% \text{ of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{wt. of coal sample taken}} \times 100$$

(iii) **Ash :** Ash is a non-combustible, useless matter which left behind when all the combustible substances have been burnt off from coal.

$$\% \text{ of ash} = \frac{\text{wt. of ash formed}}{\text{wt. of dry coal taken}} \times 100$$

(iv) **Fixed Carbon** : After the determination of moisture, volatile matter and ash contents, the remaining material is known as fixed carbon.

$$\% \text{ of fixed C} = 100 - \% \text{ of (moisture + volatile matter + ash)}$$

$$\% \text{ of N} = \frac{(\text{Vol. of H}_2\text{SO}_4 \text{ used to absorb NH}_3) \times \text{Normality of acid} \times 1.4}{\text{Mass of substance}}$$

volume of acid taken (.1N) = 45 ml (total)

(Remaining used for neutralisation with NaOH) = 11.5 ml (volume of NaOH)

Volume of acid left after absorption of NH₃

$$N_1 V_1 = N_2 V_2$$

$$.1N \times V_1 (\text{acid}) = .1N \times 11.5$$

$$V_1 = 11.5 \text{ ml}$$

Hence volume of acid used to absorb NH₃ =

$$= 45 - 11.5 = 33.5 \text{ ml}$$

$$\% \text{ N} = \frac{33.5 \times 0.1 \times 1.4}{3.25} = 1.44\%$$

or 1 ml 0.1 N acid (HCl / H₂SO₄) = 1.703 mg NH₃ = 1.40 mg N₂

Hence 33.5 ml = 1.4 × 33.5 mg N₂ = $\frac{1.4 \times 33.5}{1000}$ gm N₂

$$\% \text{ N} = \left[\frac{1.4 \times 33.5 \times 100}{1000 \times 3.25} \right] = 1.44\%$$

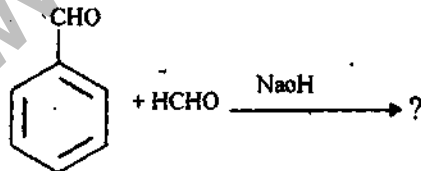
Q. 4. (h) Complete the following reactions and write their mechanism :

Write one application each of the above named reactions.

(i)



(ii)



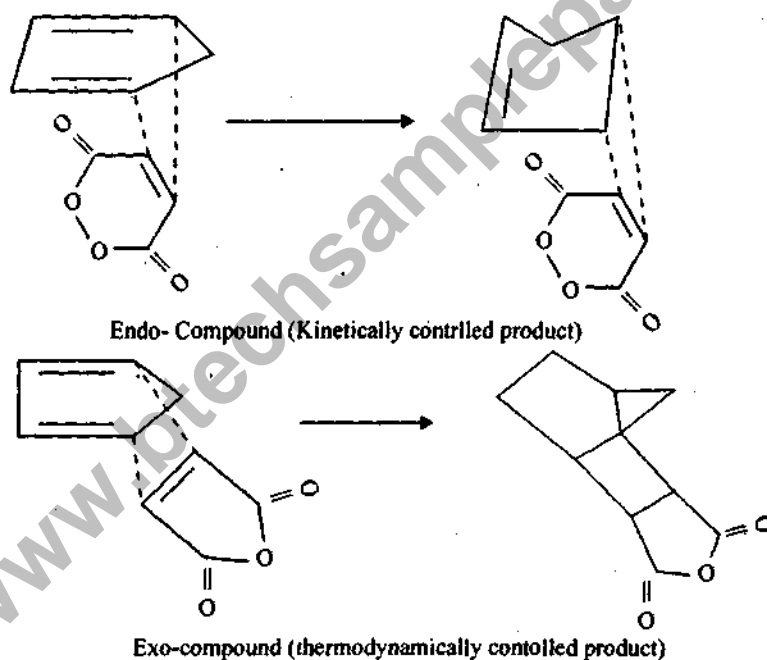
Ans.

(i) This is the Diels -Alder reaction. It is an example of cycloaddition. The product is cyclohexene.

In it when two unsaturated molecules combine to form a cyclic compound, with π electrons being used to form two new σ bonds. Specifically a conjugated diene and substituted alkene- the dienophile react to form a cyclohexene.



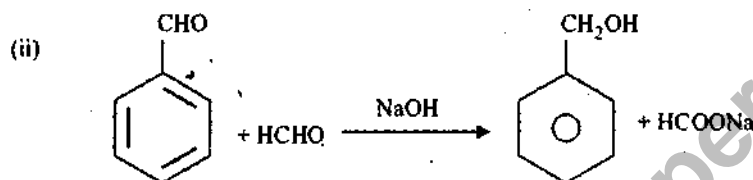
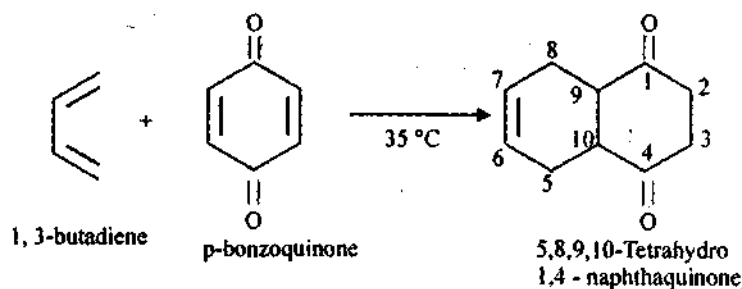
Mechanism : Diels alder reaction being cycloaddition reaction. So ring systems are formed without the elimination of any molecule. According to Wassermann (1950) ring formation occurs by both new bonds (of the addition) being formed simultaneously via the non-polar transition state. The β -orbitals of diene and dienophile overlap in an end wise fashion (instead of usual side ways overlap) leading to simultaneous bond formation).



This mechanism account for

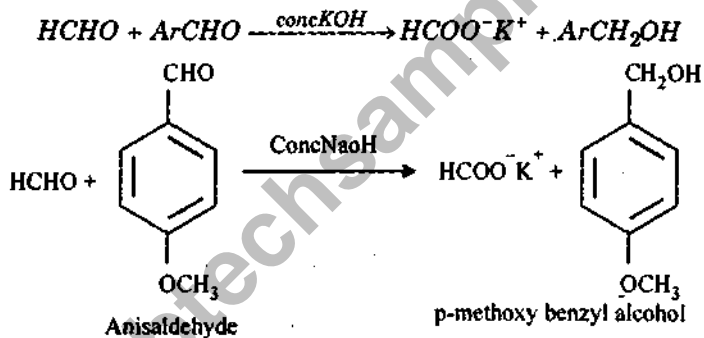
- (i) Stereo specific additions
- (ii) Steric effects

Application : It is used for the synthesis of many molecules. The importance of this reaction is two-fold. First a ring is generated and second, it takes very easily for a wide variety of reactions.

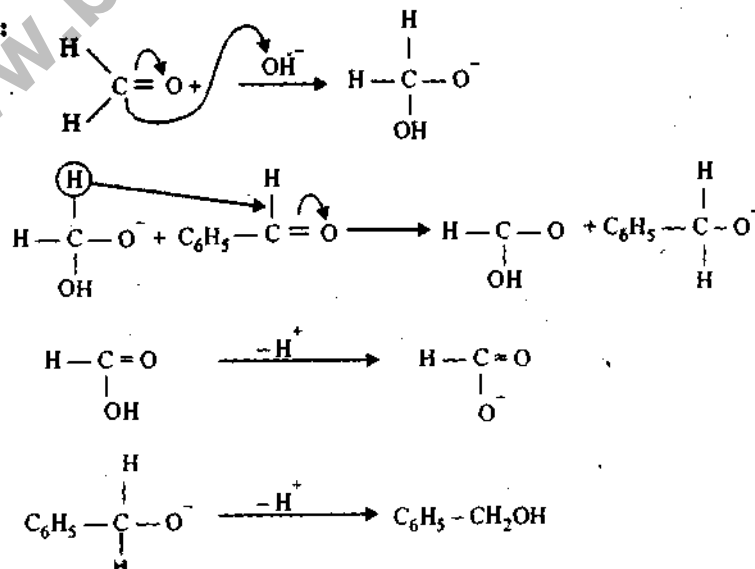


This reaction is cross cannizzaros reaction.

A mixture of two aldehydes undergo a cannizzaro reaction to yield all possible products. If one of the aldehydes is formaldehyde, potassium formate and the alcohol corresponding to the other aldehyde is exclusively formed, such a reaction is known as crossed cannizzaro reaction.



Mechanism :

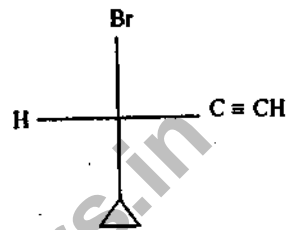
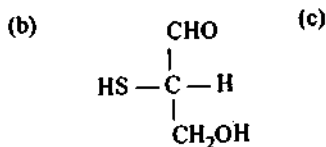
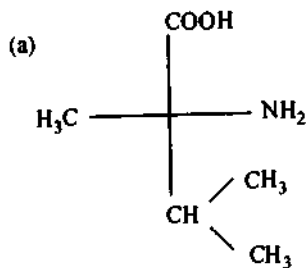


Applications : (1) Formation of cyclic adduct.

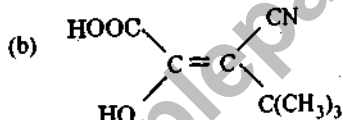
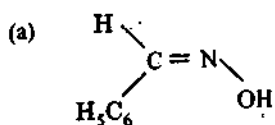
(2) Formation of alcohol and acid salts.

Q. 5. Attempt any one of the following :

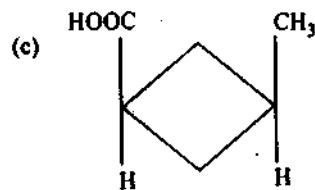
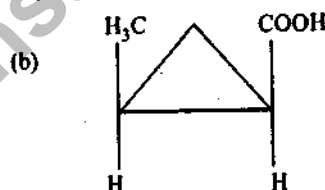
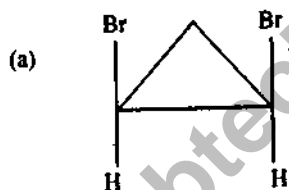
Q. 5. (a) (i) Assign R or S configuration of the following -



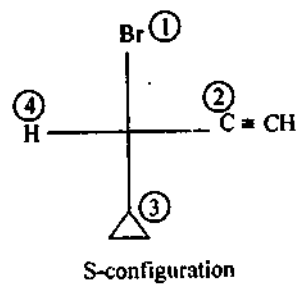
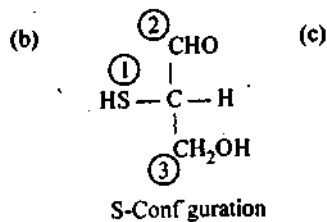
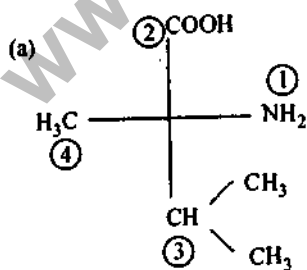
(ii) Assign E or Z configuration to the following :



(iii) Predict the number and draw all the possible stereoisomers for the following :

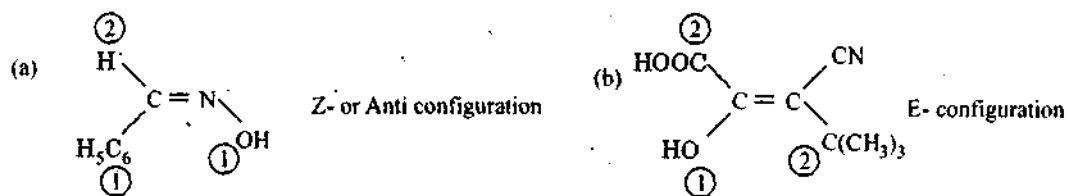


Ans. (i) Assign R or S configuration of the following -

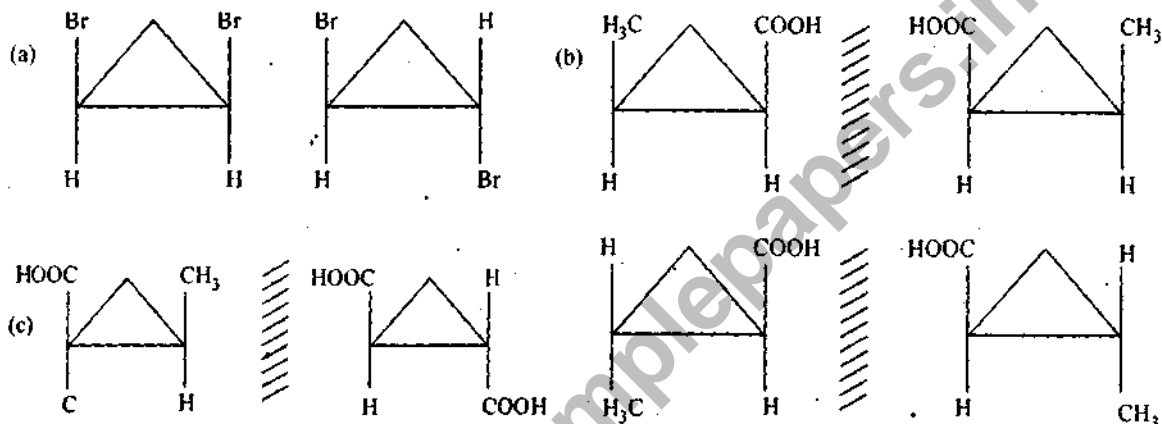


R-configuration

(ii) Assign E or Z configuration to the following :



(iii) Predict the number and draw all the possible stereoisomers for the following :



Q. 5. (b) Classify the types of reactions in titrimetric analysis. How is the completion of reaction indicated in titrations? Discuss the titrimetric analysis of:

(i) Strong base against weak acid.

(ii) $K_2Cr_2O_7$ (in acidic medium) against ferrous ammonium sulphate.

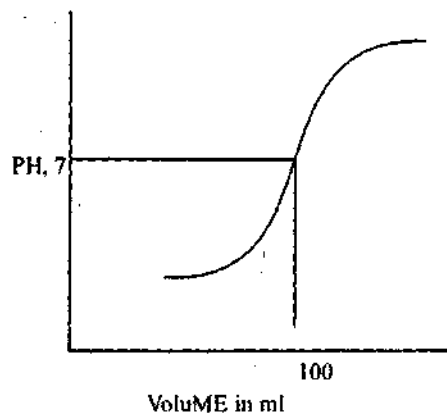
Ans. There are mainly four types of Titrimetric Analysis

(a) Acid-Base Titrations :

Selection of indicators in Acidimetry and Alkalimetry : In acidimetry and alkalimetry, a graph plotted between pH and volume of titrant shows a steep region near the equivalence point in a pH-titration curve. Thus, that indicator is selected which changes colour at approximately the pH at the equivalence point of the titration.

For titrating a weak acid against a strong base. The pH at the equivalence point is above 7, thus phenolphthalein can be used.

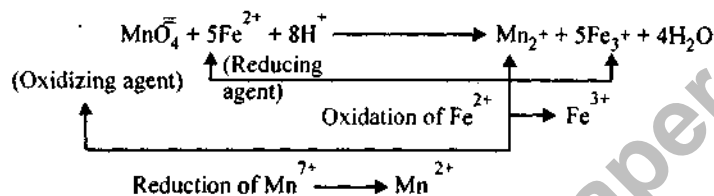
But for titrating a weak base against a strong alkali, the pH at the equivalence point is below 7, so phenolphthalein can not be used. However, methyl red or methyl orange can be used.



Step (iv) Determination of Temporary hardness :

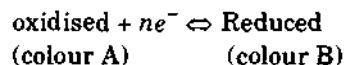
$$\text{Temporary hardness} = \frac{1000 \times (V_2 - V_3)}{V_1} \text{ ppm}$$

(c) Redox Titrations : In the process of reduction oxidation or redox titration, the transfer of electrons takes place from reducing agent (which itself gets oxidized) to an oxidizing agent (which itself gets reduced).



Indicators employed in Oxidation-titrations :

(a) Redox indicator : In this colour of oxidised form is different than the colour of the reduced form



ex. Diphenylamine, Ferrion and Nitroferroin.

(b) Self indicator : The most commonly used self indicator is potassium permagnate. It is intensely coloured but when added to a reducing agent in solution becomes colourless. As soon as all the reducing substances have been removed, the next drop of permagnate colour the solution pink. This is taken as the end point or equivalence point.

(c) Adsorption indicator : ex. Starch-iodine indicator. Iodine forms an intensely blue coloured complex with starch solution. When iodine is used as a titrant a starch solution remain colourless as long as it is being used in the reaction. The first drop of excess iodine causes the starch to acquire intense blue colour. The change is reversible and this indicator is very widely used.

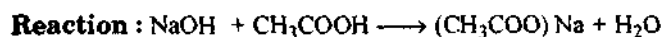
(d) Precipitation Titrations : The titrations accompanied by the formation of insoluble precipitates when the solutions of two reacting substances are brought into contact with each other are called precipitation titrations.

The titrations involving soluble silver salt as titrant are known as argentometric titrations.

The requirements of precipitation titrations are

- (a) formation of practically insoluble precipitate
- (b) Rapid formation of precipitate
- (c) Ease in the detection of end point.

Titrametric Analysis of strong base/weak acid : It explain let us take the example of NaOH (strong base) and CH₃COOH (weak acid).



Since the product is Na(CH₃COO) which hydrolyse to give pH in range more than 7 (8.7). So suitable indicator will be phenolphthalein.

Procedure : 10 ml of acid is taken in a flask and added to it, 2 drops of phenolphthalein. At the end point light pink colour will appear. Take two concordant reading and calculate.

$$N_1 V_1 = N_2 V_2$$

N_1 & N_2 = Normality acid (known) & Normality of base (standard solution) respectively.

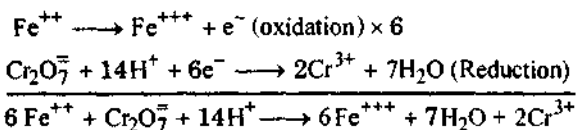
V_1 & V_2 = Volume of acid (known) & reading with the help of burette respectively.

Result : [Normality & equivalent] gm/lit

Titrimetric analysis of $K_2Cr_2O_7$ against ferrous ammonium sulphate Redox titration :

This is type of Redox titration.

Reaction :



Procedure : Standard solution of $K_2Cr_2O_7$ is taken in burette. Acidified solⁿ (known volume) of unknown ferrous ammonium sulphate is taken in titrating flask. External indicator is $K_3Fe(CN)_6$ which gives blue colour $Fe_3[Fe(CN)_6]_2$ initially and blue colour disappear at the end point. All Fe^{2+} ions are changed to Fe^{3+} .

Calculation : $N_1 V_1 = N_2 V_2$

Result : [Normality \times Equivalent] gm/litre

Q. 6. Attempt any one of the following :

Q. 6. (a) (1) What is an electrochemical series ? Give its applications with suitable examples.

Ans. Electrochemical series : The standard reduction potential of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These electrodes can be arranged in order of increasing or decreasing order of their reduction potentials. The arrangement of element in order of increasing reduction potential value is called Electrochemical series.

The electrochemical series also called activity series. The standard reduction potential of hydrogen electrode is zero. The electrodes above hydrogen have negative reduction potential while those placed below have positive reduction potential.

	Electrode	Electrode reaction (reduction)	E° (volts)
	Li	$Li^+ + e^- \rightarrow Li(s)$	-3.05
	K	$K^+ + e^- \rightarrow K^+(s)$	-2.93
Increasing tendency for oxidation	Ca	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87
	Na	$Na^+ + e^- \rightarrow Na(s)$	-2.71
	Mg	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.37
	Al	$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66

	Zn	$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
	Cr	$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74
	Fe	$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.44
	Co	$Co^{2+} + 2e^- \rightarrow Co(s)$	-0.28
	Ni	$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.25
	Sn	$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14
	Pb	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13
	H	$2H^+ + 2e^- \rightarrow H_2(g)$	0.00
	Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.34
	Hg	$Hg_2^{2+} + 2e^- \rightarrow Hg(l)$	+0.79
Increasing tendency for reduction	Ag	$Ag^+ + e^- \rightarrow Ag$	+0.80
	Br ₂	$Br_2(l) + 2e^- \rightarrow Br^-(aq)$	+1.80
	Cl	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	+1.36
	Au	$Au^{3+} + 3e^- \rightarrow Au(s)$	+1.42
	F ₂	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Application of electrochemical series :

(1) **To predict the relative oxidising and reducing power :** The species which has negative reduction potential are difficult to reduce. ex. Li is the strongest reducing agent. The species below hydrogen or have positive reduction potential are easily reduced and these are strong oxidising agents.

(2) **To predict whether a metal will react with acid to give H₂ gas :** Metals above hydrogen in Electrochemical series have great tendency for oxidation so they displace hydrogen from acids.

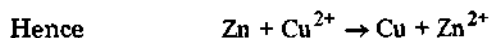
(3) **To predict the spontaneity of any redox reactions :** For any spontaneous reactions free energy change (ΔG) should be negative.

$$\Delta G = -nFE_{cell}, E_{cell} = +ve \text{ for spontaneous reaction}$$

$$E_{cell} = E_{cathode} - E_{anode}$$

(4) **To predict the replacement tendency (Relative) :** If a metal has lower value of reduction potential it shows a great tendency to assume the oxidised form and it will displace another metal (with higher value of reduction potential) from the solution of latter.

For ex : $E^\circ(Cu^{2+} / Cu) \geq E^\circ(Zn^{2+} / Zn)$



Zinc will displace copper from its solution spontaneously.

(5) To predict correct metallurgical methods : E° value of Cu, H_2O and Al are +0.34, -0.83 and -1.66 V. It means Cu get more easily reduced than water and water gets more easily reduced than aluminium. Hence, copper can be produced by the electrolysis of aqueous copper sulphate but not aluminium. This is due to the fact that when $Al^{3+}(aq)$ is electrolysed, the H_2O will be electrolysed but not $Al^{3+}(aq)$.

(6) For Calculation of equilibrium constants As : $\Delta G^\circ = -RT/n K \text{ eq.}$

and $\Delta G^\circ = -nFE^\circ$ hence $E^\circ = \frac{RT}{nF} \ln E_{eq} = \ln k_{eq} \frac{nFE^\circ}{RT}$

Q. 6. (a) (ii) Discuss the applications of Liquid crystal.

Ans.

- (1) Liquid crystals consume very little electricity. As such they have been used in digital displays like pocket calculators digital wrist watches, etc.
- (2) Liquid crystals due to their mechanical and electrical properties lying between crystalline solids and isotropic liquids have been used in gas-liquid chromatography.
- (3) The cholesteric type of crystals are employed for detecting tumours in the body by a method called thermography.
- (4) They are used as solvent for the study of structure of anisotropic molecules spectroscopically.

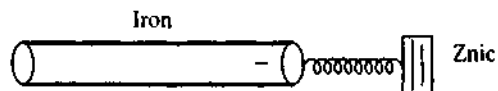
OR

Q. 6. (a) (1) Explain giving reasons, what will happen if :

(i) an underground iron pipe is connected through an insulated wire to a block of zinc metal ?

Ans. Underground iron pipe connected to insulated Zinc will be protected from corrosion. This is called cathodic protection.

Zinc is more positive than Iron. Zn/Fe will act as a galvanic system when Zn will act as anode and iron as cathode. So, instead of iron Zn will be rusted

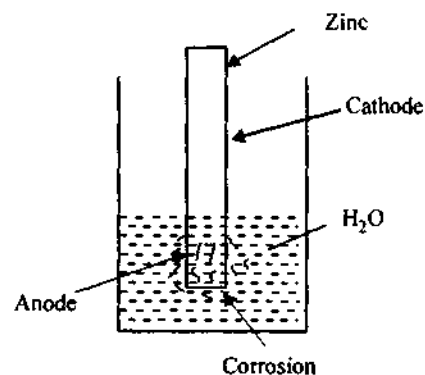
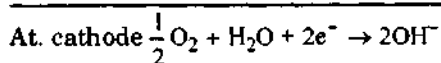
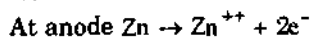


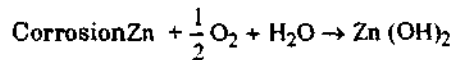
(ii) a metallic rod is vertically half submerged under water.

Ans. When a metal is half dipped under water, there will be formation of differential aeration corrosion. The position of metal above, water will be acting as cathode and inside acts as anode. It is anode where corrosion will take place

ex. Zinc.

Reaction



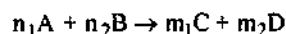


Q. 6. (2) (i) Giving appropriate examples distinguish between order and molecularity of reaction.

Ans. Order of reaction : No of atoms/molecules/ions which determine the rate of reaction is called order of reaction.

OR

Sum of the powers of concentration terms in rate equation of the reaction is called order of reaction.

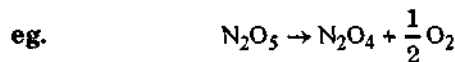


$$\text{if } \frac{dx}{dt} = k [\text{A}]^{n_1} [\text{B}]^{n_2}$$

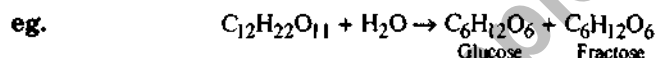
$$n_1 + n_2 = \text{order}$$

order may be 0, 1, 2, - - - even in fraction.

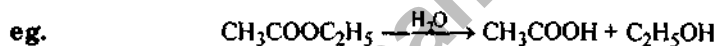
Molecularity : Total no. of atoms/ions/molecules which are involved in the leading step of the reaction. It has value 1, 2, 3 - - - - -.



molecularity = 1 (unimolecular)



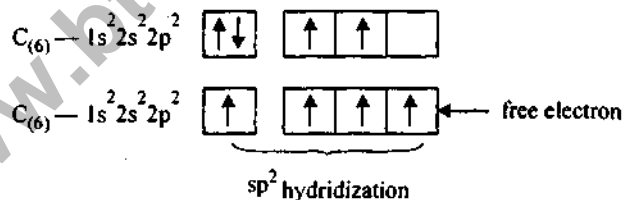
order = 1 Molecularity = 2



They are called pseudounimolecular

(iii) Describe the structure of Graphite. How it acts as conductor of electricity ?

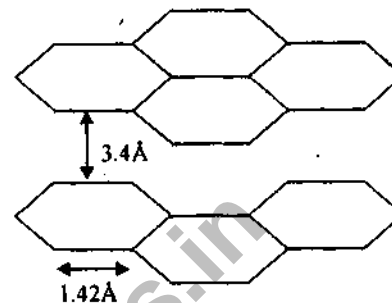
Ans. It has planer two dimensional structure. Several layers are held together by weak Vander Wall forces. Each carbon atom is in sp^2 hybridization



In some crystals belonging to this type, the continuous network of covalent bond is two dimensional. Graphite offers a very good example. Its structure is represented in figure.

Each C-atom is covalently bonded to three others, instead of four as in diamond. Thus, all atoms in a single plane are linked to give flat hexagons as in benzene, naphthalene, anthracene etc. The hexagons are held together. In sheet like structure, parallel to one another. The C—C covalent bond distance is 1.42 Å.

The distance between the sheet of layers, however, is comparatively larger being about 3.4\AA . This rules out the possibility of covalent bonding between the layers. Such crystals in which the various sheets of atoms are separated from one another by a distance larger than the maximum permissible for the formation of a chemical bond are said to be layer lattice.



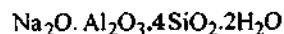
A chemical bond is not possible between carbon atoms in different layers of graphite, the fourth valency remains unsatisfied, i.e. some electrons remain free or unpaired. This permits the passage of electricity through graphite and makes it a good conductor of electricity. Graphite is a good conductor of electricity due to the mobility of the π -electron. Graphite is a good lubricant due to the weak Vander waals forces which permit layers to slide easily over one another.

Q. 6. (h) Explain the zeolite process for water softening and the regeneration of zeolite. What are the limitations of this process ?

The hardness of 1000 litres of a water sample was completely removed by passing it through a zeolite softener. The softener then required 30 litres of NaCl solution containing 1.5 g/L of NaCl for regeneration. Calculate the hardness of the sample of water.

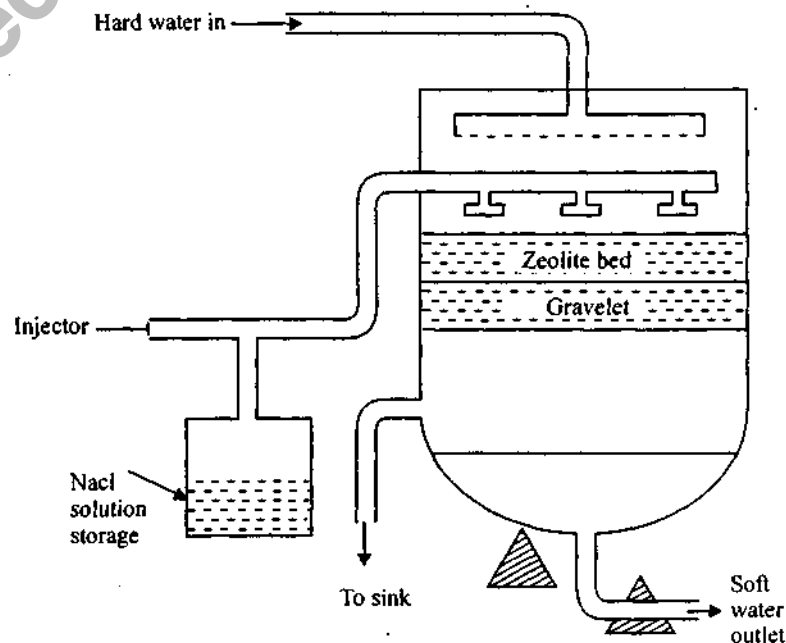
Ans. Zeolite or Permutit Process : Chemical structure of sodium zeolite may be represented as : $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x, 2 - 10$ and $y = 2 - 6$. Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness producing ions in water. Zeolites are also known as permutits. Zeolites are of two types :

(i) Natural Zeolites are non-porous. For example, natrolite.

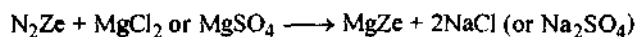
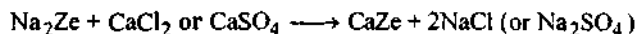
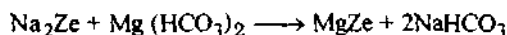


(ii) Synthetic Zeolites are porous and possess gel structure.

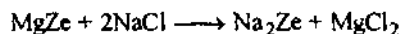
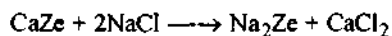
They are prepared by heating together china clay, felspar and soda ash. Such Zeolites possess higher exchange capacity per unit weight than natural zeolites.



Process : For softening of water by this process, hard water is fuded at a specified rate through a bed of zeolite, in a column. The hardness-causing ions (Ca^{2+} , Mg^{2+} etc.) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts. Reaction taking place during the softening process are :



Regeneration : After some time, the zeolite is completely converted into calcium and magnesium zeolite and it gets exhausted. Now, the supply of hard water is stopped and the exhausted zeolite is treated with a concentrated brine (10% NaCl) solution.



The washing containing CaCl_2 and MgCl_2 are led to drain and the regenerated zeolite bed is ready to use again for the softening purpose.

Limitations :

- (1) If supplied water is turbid, the turbidity will clog the pores of zeolite bed, thereby making it inactive. Therefore, suspended matter must be removed the water is used in zeolite bed.
- (2) Water containing excess of acidity or alkalinity, may attack the zeolite. It is preferable to have the pH of the water passing through the zeolite softener around 7.0.
- (3) Hot water should not be used as the zeolite tend to dissolve in it.
- (4) Water containing large quantities of Fe^{2+} and Mn^{2+} when passed through the zeolite bed are converted to their respective zeolites which can be easily regenerated.

Numerical :



NaCl will be required = $30 \times 1.5 = 45$ gm NaCl equivalent to Ca^{2+}

Equivalent wt of $\text{NaCl} = 58.5$ eq wt of $\text{CaCO}_3 = 50$

so 58.5 g of $\text{NaCl} = 50$ g CaCO_3

$$\therefore 45 \text{ g } \text{NaCl} = \frac{50 \times 45}{58.5} = 38.46 \text{ g } \text{CaCO}_3 / 10^3 \text{ lit}$$

$$= 38.46 \times 10^3 \text{ mg}/10^3 \text{ lit}$$

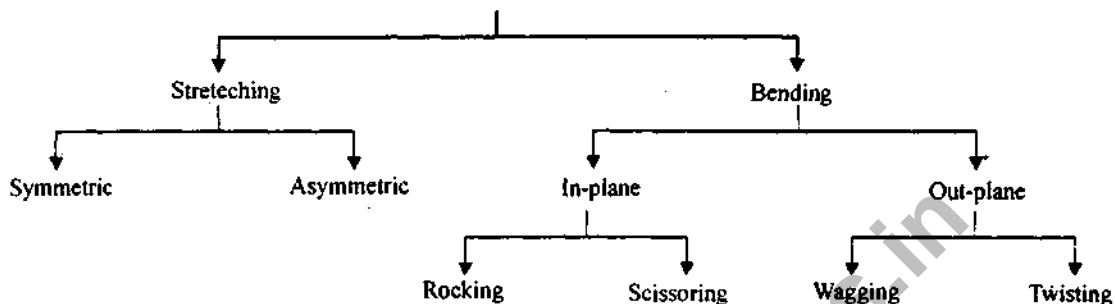
$$= 38.46 \text{ ppm.}$$

Q.7. Attempt any one of the following :

7. (a) (i) Describe the different molecular vibrations encountered in IR Spectroscopy. How would you distinguish between the compounds in each of the following pair by IR spectral studies :

- (i) Phenol and cyclohexanol
- (ii) cis- and trans-2-butene
- (iii) acetaldehyde and acetone

Ans. Different Molecular vibrations are (Normal modes in AX_2 groups)



Examples of AX_2 groups

(i) Methylene groups ($-CH_2$)

(ii) $-NO_2$ groups

(iii) $-NH_2$ groups

Stretching Vibrations : In it bond angle remains constant, but the bond length changes.

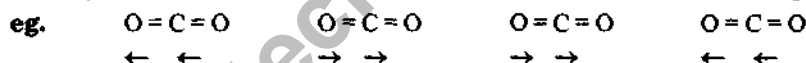
It is of following two types :

(a) **Symmetric** : It involves alternate stretching and compression of bonds in symmetrical manner.



In case of CO_2 molecule two oxygen atoms move away from or towards the central carbon without change in the bond angle.

(b) **Asymmetric** : In it one bond is stretched and the other is compressed and vice-versa.



(ii) **Bending vibrations** : In it bond angle changes but bond length remains constant.

Bending vibrations can either take place with in the same plane or out of plane

Both are of two types :

In plane bending vibrations : (i) **Rocking** : Involves the movement of atoms in same direction and (ii) **Scissoring** in it two atoms joined to a central atom move towards and away from each other with the change in bond angle.

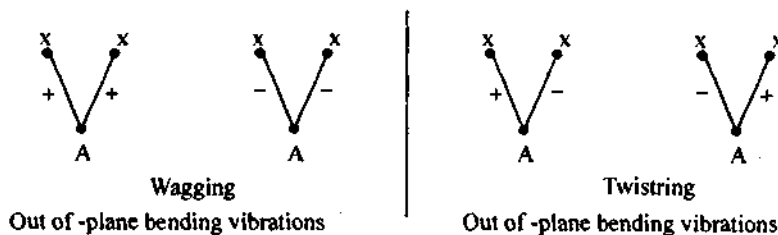


Inplane bending vibrations rocking

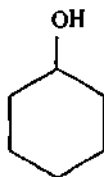
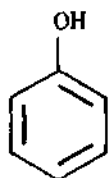
Inplane bending vibrations scissoring

Out of plane bending vibrations : (I) **Wagging** : In it both the atoms move up and below the plane with respect to the central atom. (II)

Twisting, it involves the movement of one atom up and the other atom down the plane w.r.t. the central atom.



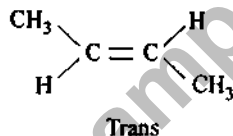
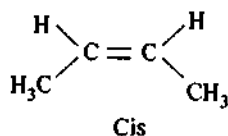
Phenol C_6H_5OH & **Cyclohexanol**



In phenol Ar—H stretching about 3000 cm^{-1} .

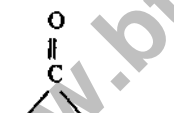
In case of cyclohexanol the cis stretching is below 3000 cm^{-1}

(ii) Cis and trans 2-butene

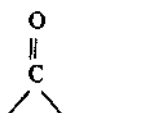


bending frequencies of cis-2 butene absorb is in the region 690 cm^{-1} while the trans isomers absorb 970 cm^{-1}

(iii) Acetaldehyde and Acetone



Frequency at 1745 cm^{-1}



Frequency at 1710 cm^{-1}

Q. 7. (a) (ii) Explain shielding and deshielding of a nuclens in NMR spectroscopy.

A compound having the molecular formula $C_{10}H_{14}$ gave the following 1H NMR data :

δ 0.88 (6H, doublet)

δ 1.86 (1H, multiplet)

δ 2.45 (2H, doublet)

δ 7.12 (5H singlet)

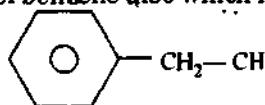
Identify the compound based on proper explanation.

Ans. Shielding : Circulation of electrons about the proton itself generate a field aligned in such a way that at the proton it opposes the applied field. The field felt by the proton is thus diminished and the proton is said to be shielded.

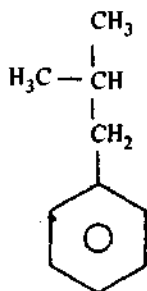
Deshielding : circulation of e^- generate a field that can either oppose or reinforce the applied field at the proton. If induced field reinforces the applied field felt by the proton is said to be deshielded.

→ Hence 4 signals are observed in $C_{10}H_{14}$ it means four types of protons are there

- (i) 5H signals (singlet) at 7.12 δ value confirms presence of benzene ring.
- (ii) 2H doublet means it is attached near by carbon having one proton and 2H is attached to carbon of benzene also which has not effect for splitting.



- (iii) 1H (CH) is showing multiplet splitting means it is attached to CH_2OH one side and on other side with two remaining carbon atoms.
- (iv) 6H doublet are attached to carbon having one H.



So the structure is

Q. 7. (b) What are organo-metallic compounds ? Discuss the mechanism of the reaction for the preparation of polypropylene for the preparation of polypropylene using Ziegler-Natta catalyst. Give the structures of stereo regular polypropylene thus obtained.

The compounds in which the carbon atoms of organic group are bound to metal atoms are known as organo metallic compounds.

Eg. Alkoxide such as $RM(OR')$ is considered to be an organo metallic compound because the organic group (R) is bound to metal (M) and metal-to-carbon bond is present, whereas $(RO)_xM$ is not an organometallic compound. This is because the organic group (R) is bound to Metal (M) by oxygen (O).

Types of organometallic Compounds

(1) **Simple organometallic compounds** - have only hydrocarbon radical or hydrogen atom attached to the metal atom ex. $(C_2H_5)_4Pb$, $(CH_3)_3SnH$ etc. These are of two types --

(a) **Symmetrical** : If both hydrocarbon radical are same $(C_2H_5)_2Hg$, $(C_2H_5)_2Pb$ etc.

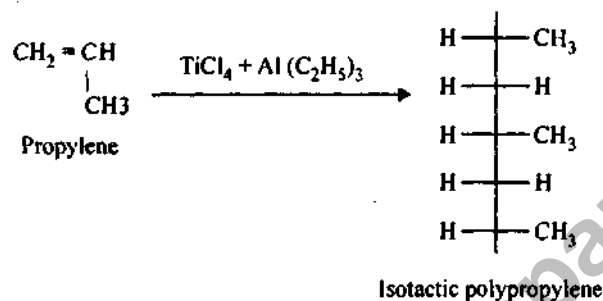
(b) **Unsymmetrical** : If both attached hydrocarbon radical are different. $(C_2H_5HgC_4H_9)$ etc.

(2) **Mixed organometallic compound** : Such compounds have groups other than hydrocarbon radicals or hydrogen atom attached directly to the metal atom.

eg. C_2H_5MgBr , $(C_4H_9)_2SnCl_2$ etc.

Ziegler Natta Catalyst : It is an organometallic catalyst $[Et_3Al : TiCl_4]$. It is used in the polymerisation of propylene.

When propylene is polymerised using $[TiCl_4 + (C_2H_5)_3Al]$ in heptane at 323 K, it preferentially forms isotactic polymer. In isotactic polypropylene all the methyl groups are on the same side, this stereo regular arrangement results in higher melting point, hardness and superior properties.



Preparation of Polypropylene

