

## CHEMISTRY SCIENCE PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

N.B. :- (i) Attempt Question No. 1 and Fourteen other questions.

## Q.1. Attempt any three of the following

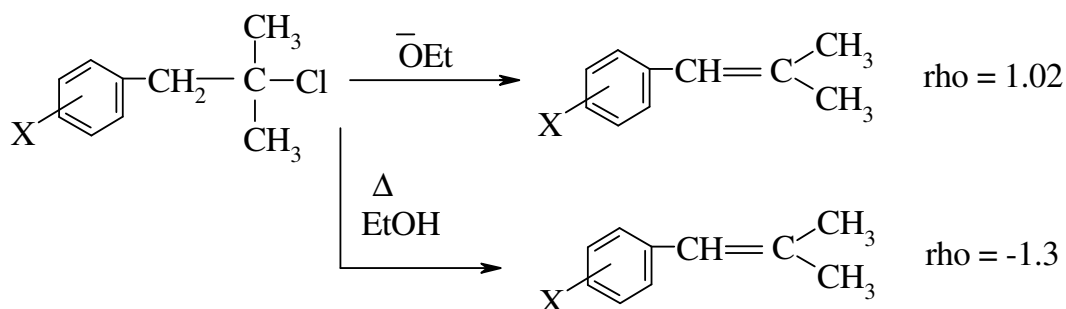
- A) Deduce the structure of a compound based on the following data : (6)
- Molecular formula :  $C_8H_9NO_2$
- U.V : 211 ( $\epsilon$  5550); 274 nm ( $\epsilon$  2450)
- I.R. : 1725, 1600, 830  $cm^{-1}$ .
- M.S. (m/z) : 151 ( $M^+$ ), 123, 106, 78, 29.
- P.M.R. ( ) : 1.35 (t, J = 7Hz, 3H), 4.2 (q, J = 7Hz, 2H), 7.75 (d, J = 8Hz, 2H)  
8.7 (d, J = 8Hz, 2H)
- B) Assign structure to the compound based on the following data : (6)
- Molecular formula :  $C_{10}H_{12}O_2$
- U.V : 211 ( $\epsilon$  1200)
- I.R. : 3250-2700 (broad), 1710, 1603, 758, 688  $cm^{-1}$ .
- M.S. (m/z) : 164 ( $M^+$ ), 105, 77, 60, 45.
- P.M.R. ( ) : 1.3 (d, J = 7Hz, 3H), 2.6 (d, J = 7Hz, 2H), 3.24  
(sextet, J = 7Hz, 1H) 7.20 (5H, m),  
10.8 (bs, exchangeable with  $D_2O$ , 1H)
- C) Photolysis of a solution of  $H_2O_2$  in isopropyl alcohol at 110 K leads to a free radical formation, the esr spectrum of which consists of seven lines with a hyperfine splitting of 20G, a line width of 10G and an intensity ratio of 1 : 6 : 15 : 20 : 15 : 6 : 1. Which radical is responsible for the esr spectrum ? Explain. (6)
- Given : i)  $I(^{12}C) = 0$   
ii)  $I(^{16}O) = 0$   
iii)  $I(1H) =$
- D) Explain the following Mossbauer observations : (6)
- | Sr.No. | Compound                 | $\delta$ , mm/s | $E_0$ , mm/s |
|--------|--------------------------|-----------------|--------------|
| i)     | $Fe(NO_3)_3 \cdot 9H_2O$ | 0.4             | 0.4          |
| ii)    | $Na_3[Fe(CN)_6]$         | -0.17           | 0.60         |
- E) The bond distance in  $^{79}Br_2$  is 228 pm. Calculate the principal moment of inertia ( $I_B$ ) of the molecule. (6)

F) Show that in the rotational spectrum the level having maximum population for a diatomic molecule is given by \_\_\_\_\_ with the symbols having their usual meanings.

(6)

Q.2 A) Answer the following.

(a) Explain why the rho value is different in the following reactions. Comment on the mechanisms of the reaction. (7)

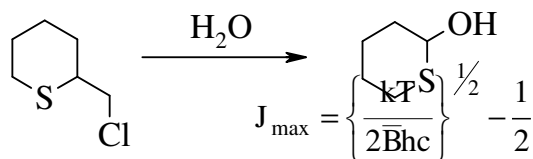


(b)  $\sigma_m - \text{COO}^- = -0.35$  but  $\sigma_p - \text{COO}^- = -0.20$

(c) The rho value is negative and high in electrophilic aromatic substitution reactions, Comment.

B) a) Explain why cyanide ion is more reactive, when KCN reacts with [18]-Crown-6. (3)

b) Explain the following reaction, identify the reaction. (3)

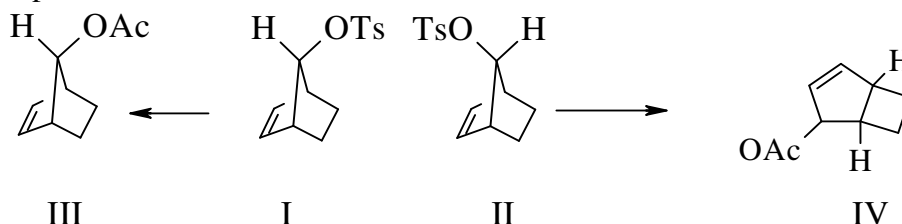


Q.3 Read the observations (1, 2 & 3) and answer the questions (A, B, C & D) given below : (13)

1) Acetolysis of the anti-tosylate I gives the anti-acetate III with retained configuration.

2) Acetolysis of the syn-tosylate, II gives rearranged acetate IV.

3) Compound I reacts  $10^7$  times faster than II.



(A) Select the most appropriate alternative. Compounds I and II are

a) enantiomers

b) diastereomers

c) conformational isomers

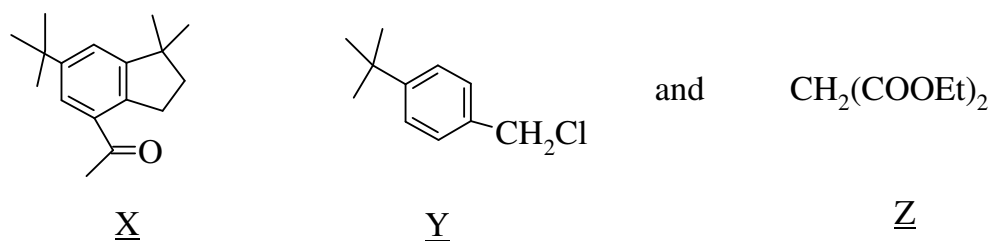
d) constitutional isomers

(B) Why I reacts faster than II ?

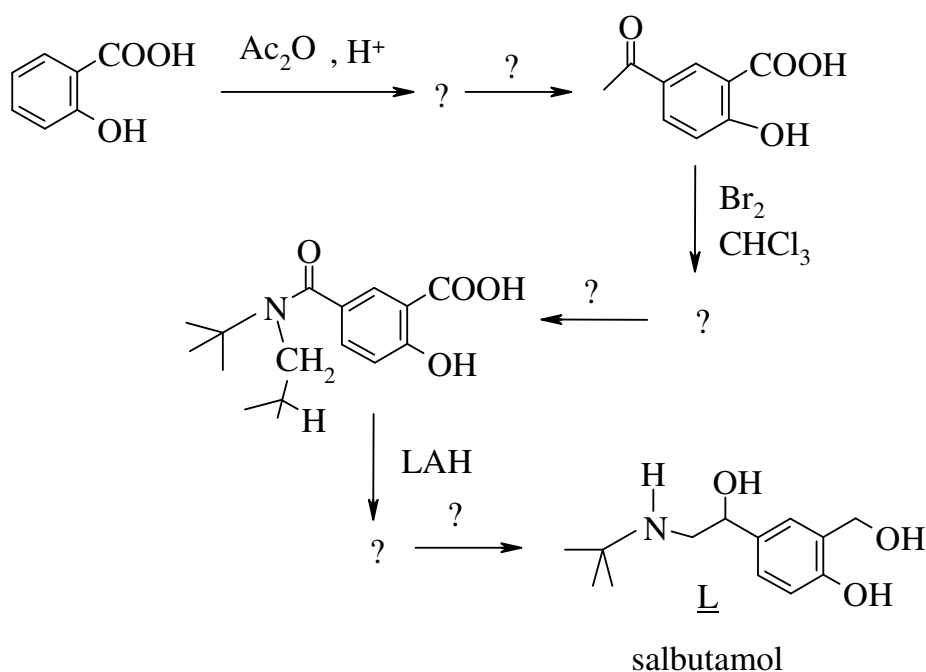
(C) Why I gives III with retained configuration ?

(D) Show how IV is formed from II.

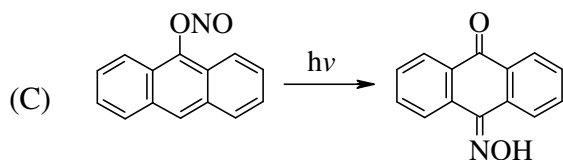
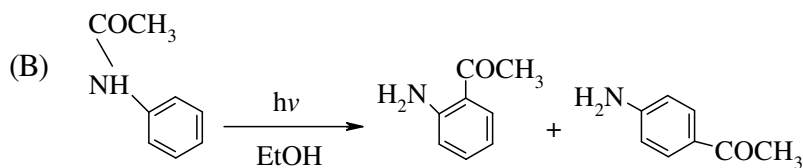
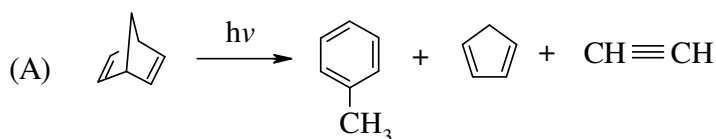
- Q.4** (A) Musks are compounds which retain and enhance the perfume of the other compounds. Celestolide X is a musk. How will you synthesise celestolide X from following starting materials Y and Z? (7)

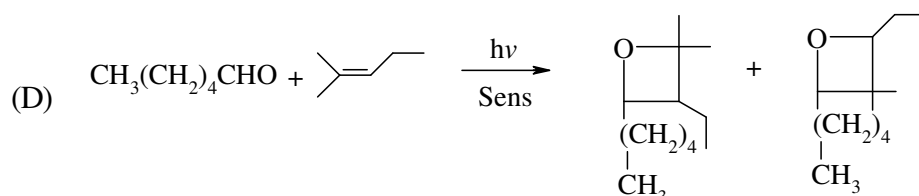


- (B) Complete the following synthetic scheme for the synthesis of salbutamol L an anti-asthma drug. (6)

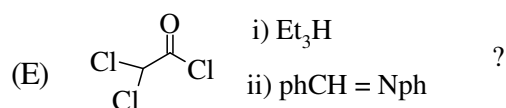
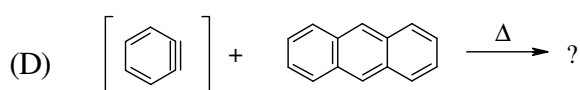
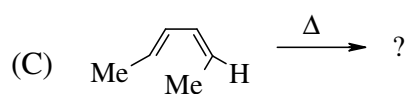
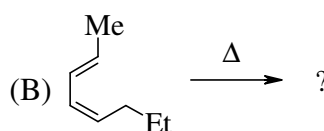
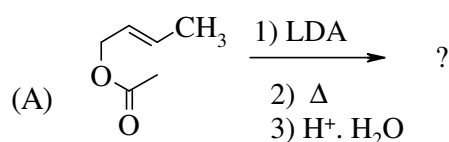


- Q.5** Indicate the type of reaction and mechanism involved in each step of the following transformations. (13)

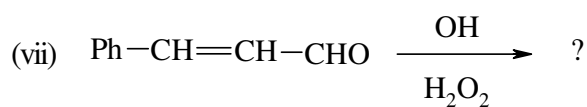
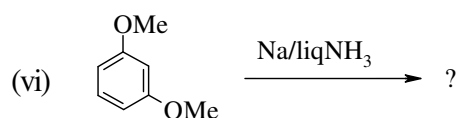
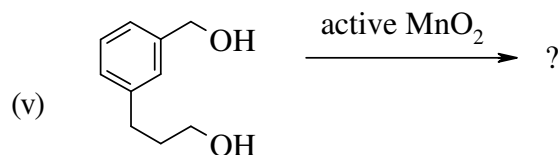
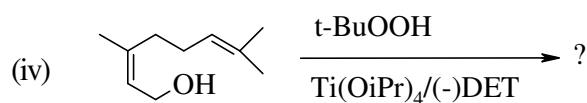
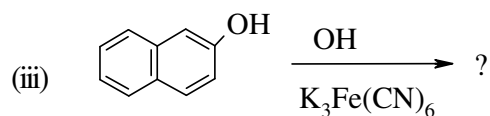
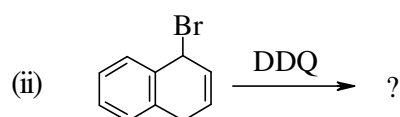
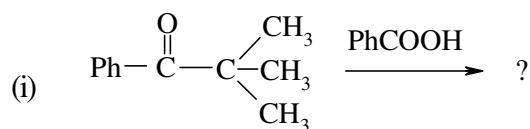




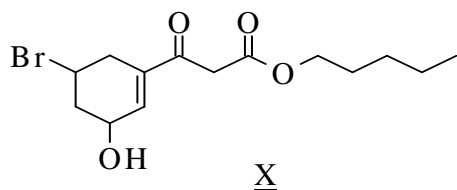
**Q.6** Predict the product/s and identify the reaction with mechanism. (13)



**Q.7** (A) Give product/s of the following reactions. (7)

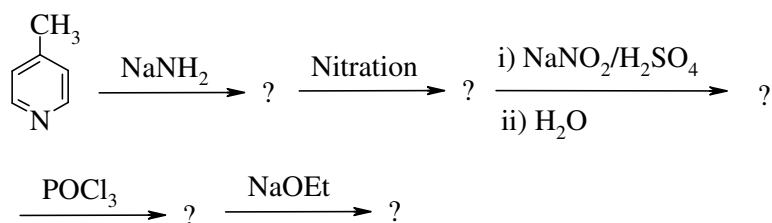


(B) Indicate products when molecule X reacts separately with the given reagents. (6)

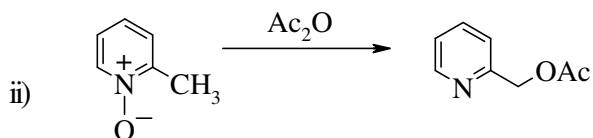
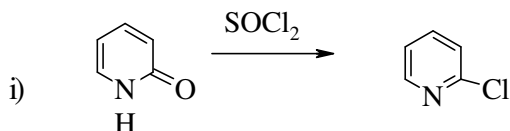


- |                      |                       |
|----------------------|-----------------------|
| (i) $\text{NaBH}_4$  | (ii) Baker's yeast    |
| (iii) $\text{MnO}_2$ | (iv) $\text{LiAlH}_4$ |
| (v) TBTH             | (vi) NBS              |

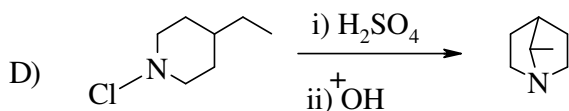
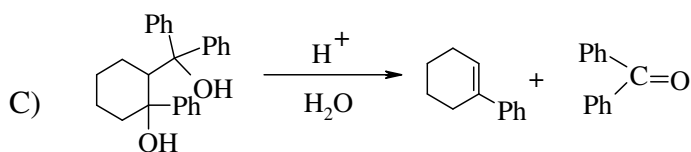
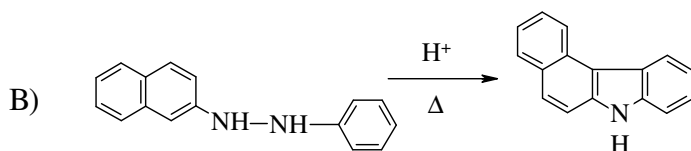
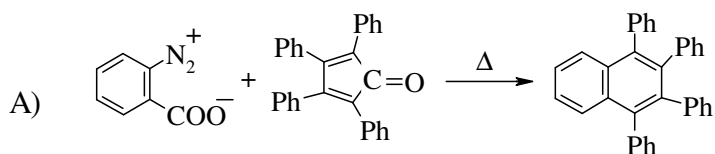
**Q.8** (A) Complete the following transformation by giving missing structures. (7)



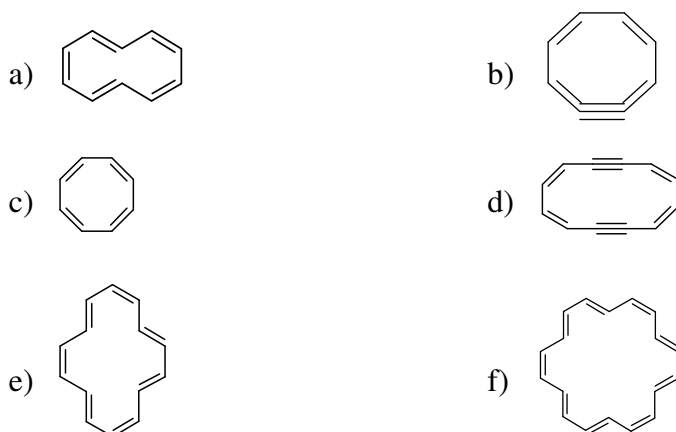
(B) Explain the formation of products in following reactions. (6)



**Q.9** Propose the mechanism for the following conversions and name the reaction involved. (13)



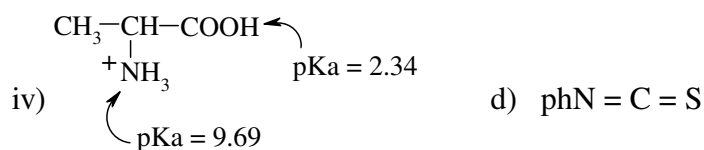
**Q.10 (A)** Which of the following compounds are aromatic and which are not aromatic ? (3)



(B) Cyclopentadiene has a pKa value of approximately 16.0 and is the most acidic hydrocarbon known. Explain. (3)

(C) Match the following. (4)

- | A              | B                   |
|----------------|---------------------|
| i) EDMN        | a) pH = 6.015       |
| ii) C-Terminal | b) thymine          |
| iii) adenine   | c) carboxypeptidase |



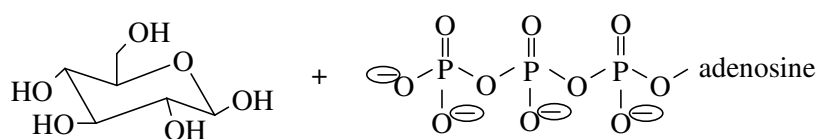
i) = .....

ii) = .....

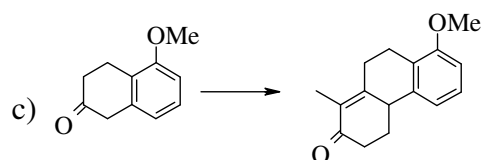
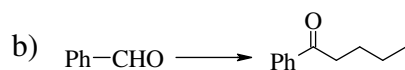
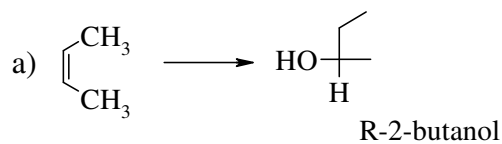
iii) = .....

iv) = .....

(D) Explain the phosphorylation of D-glucose by ATP. Give structure of products. (3)

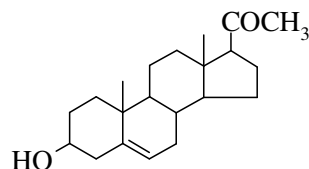


**Q.11 (A)** How the following transformations can be effected ? Identify the steps invoked. (10)

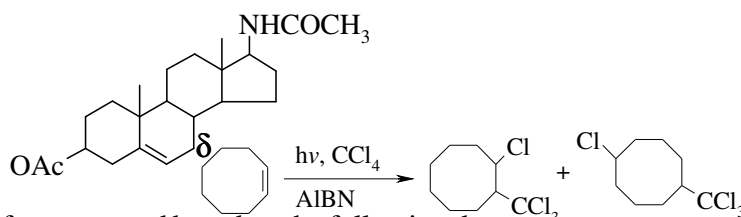


(B) Explain the following reaction. (3)

**Q.12** Study the following structure and answer the following questions. (13)



- (A) Classify the compound.  
 (B) Give characteristic I.R. frequencies for the above compound.  
 (C) How many signals will be observed for the methyl groups in PMR ? Give their chemical shifts.  
 (D) What will be the product formed on treatment with excess of m-chloroperbenzoic acid ?  
 (E) Write the structure of the product formed on Oppenauer oxidation.  
 (F) How would you convert it into ?



**Q.13** (A) Derive the structure of a compound based on the following data : (8)

Molecular formula : C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>

U.V. : 275 nm (ε 21000)

I.R. : 1720, 1626, 1605, 1150, 850, 820 cm<sup>-1</sup>

M.S. (m/z) : 232 (M<sup>+</sup>), 176

P.M.R. ( ) : 1.0 (d, J = 7 Hz, 6H), 2.0 (m, 1H), 2.38 (s, 3H),  
 3.95 (d, J = 7 Hz, 2H), 6.16 (d, J = 16 Hz, 1H),  
 7.20 (d, J = 8 Hz, 2H), 7.41 (d, J = 8 Hz, 2H),  
 7.75 (d, J = 16Hz, 1H).

(B) Deduce the structure based on the following Carbon - 13 N.M.R. data :

Molecular formula : C<sub>8</sub>H<sub>10</sub>O

C-13 NMR ( ) : 38(t), 63(t), 126(d), 128(d), 129(d), 139(s)

**Q.14** (A) Match the entries in column A from those given below. (7)

Column A	Column B
i) Slater rule	Centrosymmetric molecules
ii) Space group	Dirac
iii) Neutrino	Pauli
iv) Well-behaved function	Schrodinger equation

- v) Ensemble light scattering
- vi) Spin of the photon -decay
- vii) Rule of mutual exclusion Effective nuclear charge  
Shoenflies  
Hermann - Mauguin  
Gibbs

(B) The  $C_{2h}$  group has symmetry elements : E,  $C_2$ , and  $i$ . Write down the multiplication table. (6)

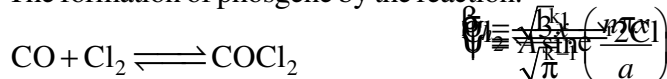
**Q.15** (A) For a particle in a box do the wavefunction and the linear momentum,  $p_x$ , operator obey eigen value equation ? Explain the significance of this result. (7)

(B) What is linear variation ? State and explain the variational theorem. If one uses for the particle in 1D box the ground state energy is zero which seems to violate the variational principle. Is it true ? Explain your answer. (6)

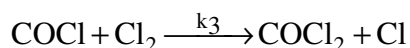
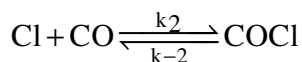
**Q.16** (A) Obtain the expression for the sp hybrid orbitals. Show that they are orthogonal. (7)

(B) What is LCAO ? Sketch the simple MO diagram for the  $N_2$  molecule. Whether the system is stabilized by addition of an electron or removal of an electron. Explain your answer. What do you understand by suffixes 'u' and 'g'. (6)

**Q.17** (A) The formation of phosgene by the reaction. (7)



appears to follow the mechanism



Assuming the intermediate Cl and COCl are in steady state, what is the rate law for this reaction ?

(B) Obtain the expectation values for the kinetic and potential energies for the hydrogen atom in its ground state. The ground state wavefunction is (in atomic units).

**Q.18** (A) Deduce the "term symbols" for  $d^8$  configuration. (7)

(B) Explain in brief, how one determines the spectroscopic dissociation energy ( $D_0$ ) using the Birge - Sponer extrapolation. How  $D_0$  differs from the equilibrium dissociation energy. (6)

**Q.19** (A) Obtain the ratio of population of hydrogen nuclei at two nuclear spin energy levels corresponding to  $M_1 = \pm \frac{1}{2}$  in an applied field of 14,000 gauss at 300°K. (7)



(B) The rotational partition function for a certain gas may be written as  $Q = aT^{3/2}$  where  $a$  is a constant. Show that the rotational heat capacity is per mole. (6)

**Q.20** (A) Calculate the activity of water and its activity coefficient from the data given below for the vapour pressure of water at different sucrose molalities (at 298 K). (7)

$m$ (sucrose)/mol.kg <sup>-1</sup>	0	0.2	0.5	1.00
$P$ /Torr	23.75	23.66	23.52	23.28

(B) Calculate the change in entropy when 10.0 g of tin are heated from 20°C to 300°C. Given Latent heat of fusion 14 cal g<sup>-1</sup>.

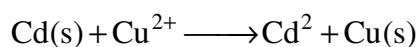
Sp. heats of solid and liquid tin are 0.055 and 0.064 respectively. Melting point of tin is 232°C. (6)

**Q.21** (A) Prove that (7)

(B) State Nernst heat theorem. How does it differ from third law of thermodynamics? Write in brief on the unattainability of absolute zero of temperature. (6)

**Q.22** (A) Write the expression for activities of NaCl, CaCl<sub>2</sub>, CuSO<sub>4</sub> and LaCl<sub>3</sub> in terms of their molalities and mean ionic activity coefficients. (7)

(B) Assume that the following reaction occurs in our electrochemical Cell : (6)



- What is the representation for the cell for this reaction?  $\left(\frac{\partial G}{\partial v}\right)_T, \left(\frac{\partial P}{\partial T}\right)_v - P$
- What is the standard emf ( $E^\circ$ ) for this cell at 298°K?
- What is  $\Delta G^\circ$  for this cell at 298°K?

Given :  $\left(\frac{\partial G}{\partial v}\right)_T, \left(\frac{\partial P}{\partial T}\right)_v = 0.3394 \text{ V}$

and  $E_{\text{Cd}^{2+}, \text{Cd}}^0 = -0.402 \text{ V}$ .

**Q.23** (A) Starch is broken down to maltose by “amylase”. What type of catalytic reaction is this? What will happen to rate of such reactions when the temperature is raised to a very high value? (6)

(B) The adsorption of a gas is described by the Langmuir isotherm with  $K = 0.85 \text{ kPa}^{-1}$  at 25°C. Find the pressure at which the surface coverage is 15%. (7)

**Q.24** (A) What is electro-osmosis? How the concept can be clarified by studying the electrical double layer? (7)

(B) State Onsager’s reciprocity theorem. Explain how one can study production of entropy in chemical reactions. (6)

**Q.25** (A) Explain nuclear fission and fusion with suitable examples. (7)

(B) A nonionic surfactant forms microheterogeneous system both in water and in hexane. What are the differences between them? Explain. (6)





B) Match the entries in column X from those given below in column Y. (5)

Column X	Column Y
i) Gas solid chromatography	1. current measurement
ii) Paper chromatography	2. measurement of electricity
iii) Coulometry	3. adsorption
iv) Amperometry	4. partition
v) Polarogram	5. current Vs Potential curve

Answer : (i) ..... (ii) ..... (iii) ..... (iv) ..... (v).....

C) What is distribution coefficient,  $K_D$  and distribution ratio, D in solvent extraction technique ? How D is correlated to  $K_D$  ?

**Q.37** A) Explain, why simple iron porphyrins do not functions as  $O_2$  carriers ?

B) Match the entries in column X with those given in column Y. (5)

Column X	Column Y
i) thiolate ligands	1) ionophores
ii) cation transport across biological membranes	2) Fe-S cluster synthesis
iii) $Mn^{n+}$	3) Probe by $Co^{2+}$
iv) bonding interactions	4) redox functions
v) $Zn^{2+}$	5) HSAB concept

Answer : (i) ..... (ii) ..... (iii)..... (iv) ..... (v).....

C) Write in brief about  $Na^+ - K^+$  ion pumps. (5)

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