

**Chemical Science**  
**Paper III**

[Time Allowed :  $2\frac{1}{2}$  Hours ]

[Maximum Marks : 200]

- Note : (1) Attempt Question No. 1 and *Fourteen* other questions.  
(2) Log table is enclosed.

1. Attempt any *three* of the following :

6

A) Assign the structure to a compound which exhibits the given data :

Molecular formula :  $C_{10}H_{10}O_2$

U.V. : 230, 320 nm ( $\epsilon$  12000 and 24000 respectively). Bathochromic shift is observed on addition of alkali.

I.R. : 2.4 (s, 3H), 6.7 (d,  $J = 16$  Hz, 1-H), 6.9 (d,  $J = 8$  Hz, 2H),  
7.3 (d,  $J = 8$  Hz, 2H). 7.5 (d,  $J = 6$  Hz, 1 H),  
8.25 (bs, 1 H exchangeable with  $D_2O$ )

B) Deduce the structure of a compound based on the following data :

Molecular formula :  $C_{10}H_{11}NO_2$

U.V. : 222, 290 nm ( $\epsilon$  700 and 2500 respectively).

I.R. : 2245, 1600, 1480, 1220  $cm^{-1}$ .

PMR ( $\delta$ ) : 3.6 (s, 10 mm), 3.8 (s, 30 mm), 6.3 (t,  $J = 2$  Hz, 5 mm), 6.4 (d,  $J = 2$  Hz, 10 mm)

C) Quinone - hydroquinone redox system has been studied by esr wherein a semiquinone free radical exists as an intermediate. How many lines would be observed in the esr spectrum due to this free radical ? Comment on the intensities of these lines.

D) The observed Mossbauer spectrum of the compound  $Fe_3(CO)_{12}$  consists of three lines of equal intensity with the central line slightly broader than the other two. Elucidate the molecular structure of the compound.

E) The fundamental vibration frequency of  $H_2$  molecule is  $4395\text{ cm}^{-1}$ . Calculate corresponding zero point energy.

F) Sketch the ESR spectrum for an unpaired electron interacting with three protons in the following two cases :

Case :

- (i) the protons are not equivalent.  
(ii) the protons are equivalent.

2. A) Comment on the difference in the Hammett sigma ( $\sigma$ ) values of the following substituents. : 4

$$\sigma_p - F = 0.06$$

$$\sigma_m - F = 0.34$$

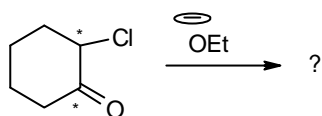
$$\sigma_p - \text{OMe} = -0.27$$

$$\sigma_m - \text{OMe} = -0.11$$

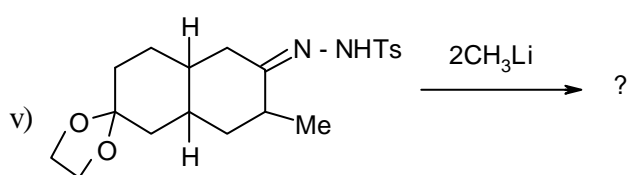
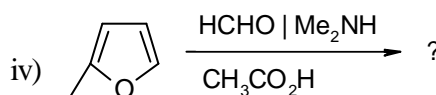
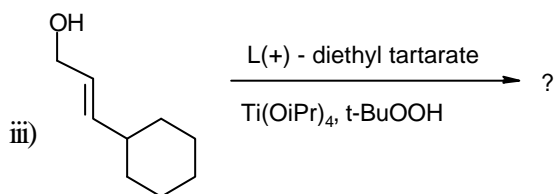
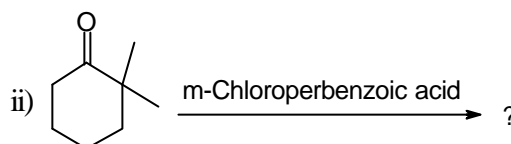
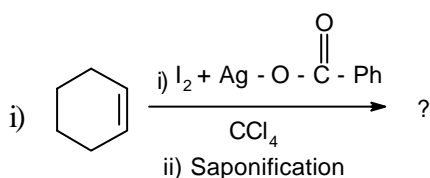
B) Explain why the rho ( $\rho$ ) value for a reaction series increases as the solvent polarity decreases. 2

C) Devise suitable labelling experiments for determining whether the hydrolysis of ethylbenzoate occurs by the acyl-oxygen cleavage or by the alkyl-oxygen cleavage. 4

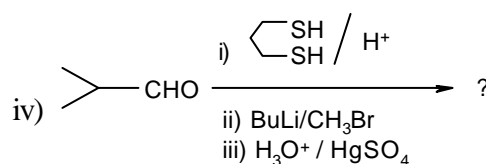
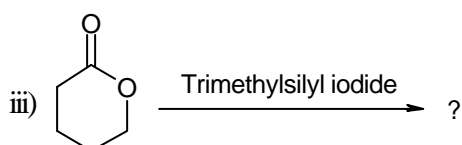
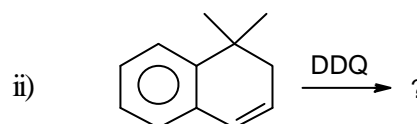
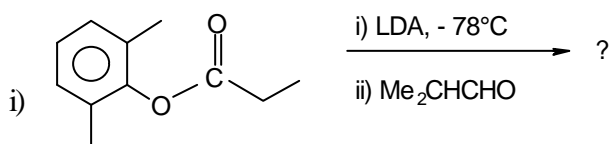
D) Predict the product and position of the label in the following reaction : 3

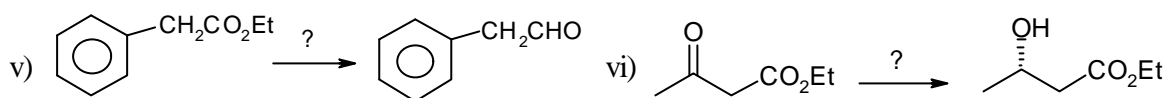


3. For each of the following predict the product, name the reaction and explain the mechanism involved. 13

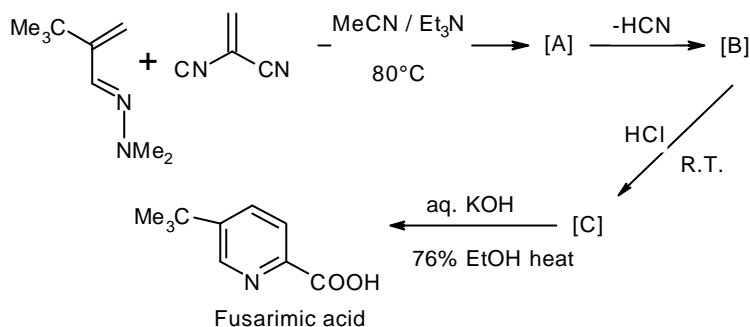


4. Complete the following sequences of reactions : 13





5. A) Fusarimic acid is a mould metabolite with antibiotic and antihypertensive activities. It can be prepared by the following sequence of reactions :



- (i) Identify A-C.
- (ii) Name the reaction involved in the formation of A.
- (iii) Draw the structure of fusarimic acid in its aqueous solution. 5

- B) 4-Methylpyridine on reaction with  $\text{NaNH}_2$  in xylene gives compound A.

Draw the structure of A. Why is an electrophilic reaction easily possible on A? 4

Draw the structure(s) of the product(s) formed when A is reacted with a mixture of conc.  $\text{H}_2\text{SO}_4$  and conc.  $\text{HNO}_3$ .

- C) A diketo compound A on heating with  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$  (p-TSA) in xylene forms 2-phenyl-5-methylfuran (I)

I can also be obtained when ethyl acetoacetate is treated with a 2-haloaldehyde B in the presence of a base.

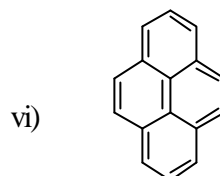
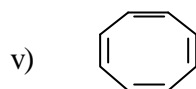
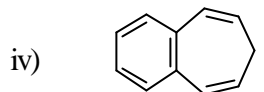
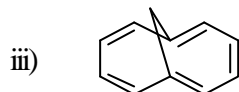
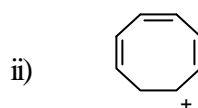
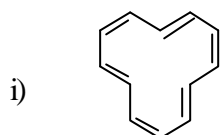
I on strongly heating with dimethyl fumarate gives C.

- (i) Draw the structures of A and B.
- (ii) Write the reaction of formation of C from I. 4

6. A) Fullerene is a recently discovered allotrope of carbon. 7

- (i) Why is it called an allotrope of carbon ?
- (ii) What is the molecular weight of fullerene ?
- (iii) Does fullerene undergo any addition reaction with  $\text{Cl}_2$  ?
- (iv) What is the hybridization of carbon atoms in fullerene ?
- (v) Under which conditions is fullerene formed ?
- (vi) Name the other allotropes of carbon and the hybridization of carbon in them.

B) Classify the following compounds into aromatic, antiaromatic, non-aromatic and homoaromatic : 6



Ans. (i) .....

(ii) .....

(iii) .....

(iv) .....

(v) .....

(vi) .....

7. A) Match the following :

5

(i) Denaturation

(a) Polypeptide synthesis

(ii) Guanine

(b) Phase transfer catalyst

(iii) Merrifield resin

(c) DNA

(iv) 18-Crown-6

(d) Cytosine

(v)  $\alpha$ -helix

(e) Loss of biological activity

Ans. (i) .....

(ii) .....

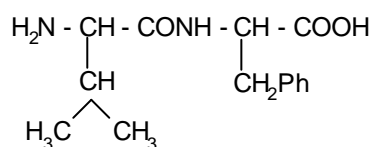
(iii) .....

(iv) .....

(v) .....

B) How will you synthesize the following peptide using solid phase method :

4

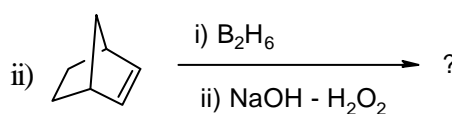
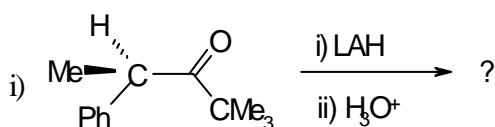


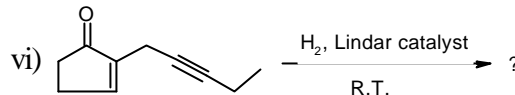
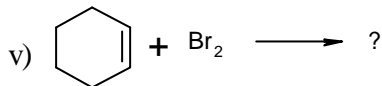
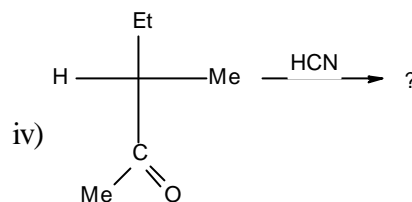
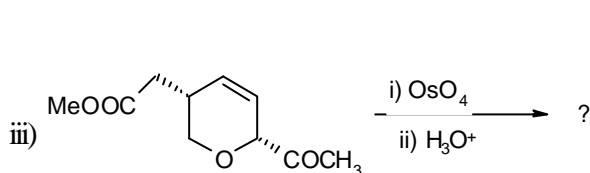
C) What is genetic code? Explain the role of m-RNA in transmission of genetic information?

4

8. A) Predict the major products of the following reactions with proper stereochemistry :

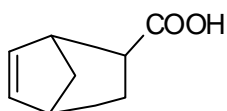
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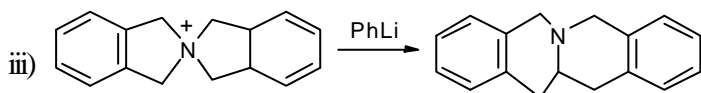
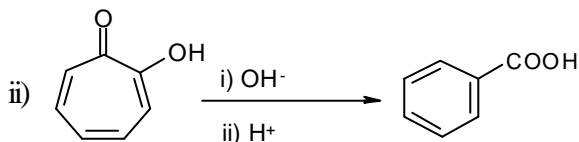
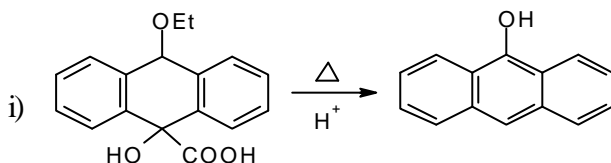


B) Trans-ethyl 4-tertiary butyl cyclohexane carboxylate undergoes alkaline hydrolysis about 20 times faster than the corresponding *cis*-isomer. 4

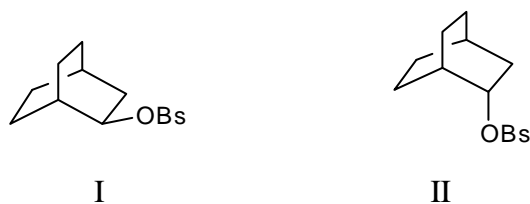
C) Suggest a method to achieve high enantioselectivity in the preparation of compound I using a chiral auxilliary. 3



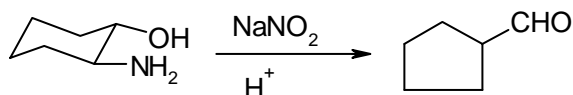
9. A) Propose mechanisms for the following reactions : 9



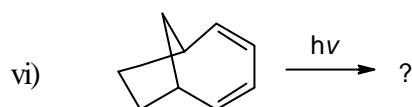
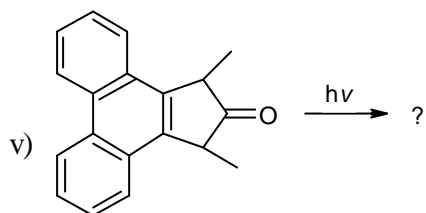
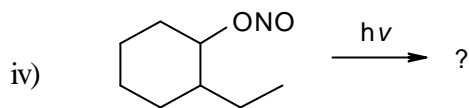
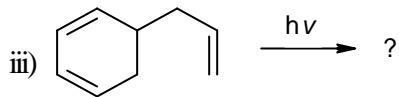
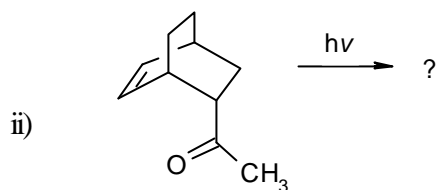
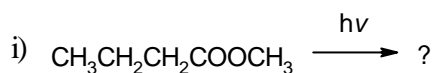
B) (i) Acetylsylation of exo-norboronyl brosylate (I) is 350 times faster than that of the endo-brosylate (II), Explain. 2



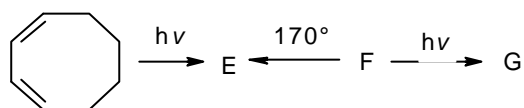
(ii) Explain the change in ring size in the following reaction : 2



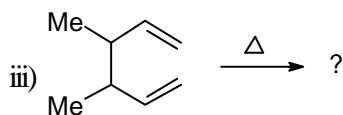
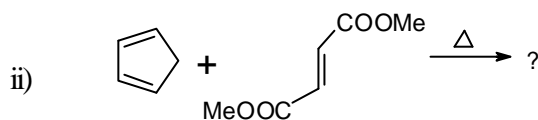
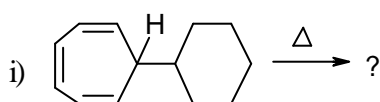
10. For each of the following predict the product(s), identify the reaction, and give the mechanism involved : 13



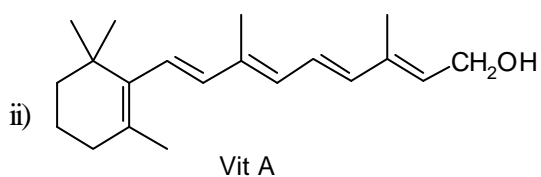
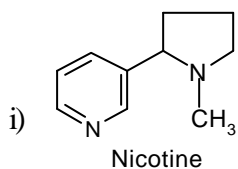
11. A) Predict the products of the following *three* electrocyclic reaction : 6



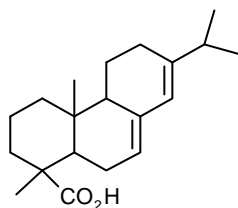
- B) Predict the products and identify the types of pericyclic reaction in the following : 7



12. A) Explain the biogenesis of the following : 6



B) The abietic acid has been assigned the following structure. What methods will you use to prove the following ? Explain the answer. 7



- (i) Presence of heteroannular diene system.
- (ii) Presence of isopropyl group.
- (iii) Presence of two quaternary methyl groups.
- (iv) Tricyclic ring system.

13. A) Assign structure to the compound based on the following data. Explain your answer.

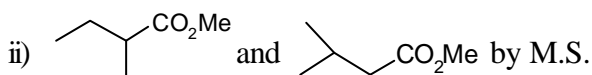
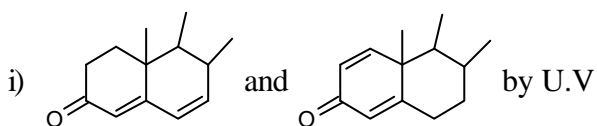
Molecular formula : C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>

I.R. 1720, 1290 cm<sup>-1</sup>.

M.S. (m/z) : 126, 95

PMR (δ) : 3.85 (s, 12 mm), 6.5 (dd, J = 4 and 2 Hz, 4 mm), 7.1 (dd, J = 4 and 1 Hz, 4 mm), 7.55 (dd, J = 2 and 1 Hz, 4 mm).

B) How will you distinguish the following pairs, by the indicated spectral method ? 4



C) Explain the following : 3

- (i) The PMR spectrum of 2, 2, 3, 3-tetrachlorobutane shows a singlet at r.t. whereas two singlets of unequal intensity are observed at -45°.
- (ii) The PMR spectrum of t-butylfluoride shows a doublet at 1.4 ppm with J = 20 Hz.

14. Show that  $y_{1,0}(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$  and  $y_{2,0}(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$  are orthogonal and normalised. Identify the corresponding hydrogenic orbitals (e.g. s, 2p<sub>x</sub>,..... etc.) 13

15. Work out the table of microstates and term symbols for 3d<sup>1</sup> 4s<sup>1</sup> electronic configuration. Identify the ground state. What are the degeneracies of the states ? 13

16. Supply the missing entries X, Y, Z, U and V in the character table for  $T_d$  point group. Give a brief justification. 13

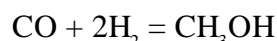
$T_d$	E	$8C_3$	$6C_4$	$3C_2$	$6\sigma_d$
$A_1$	1	1	1	1	1
(X)	1	1	-1	1	(U)
E	(Y)	-1	0	2	0
$T_1$	3	0	1	-1	-1
(Z)	3	0	-1	-1	(V)

17. Given that  $\frac{N_\alpha}{N_\beta} = e^{-g_1 \mu_N B/kT}$  and assuming that the exponential factor is small, obtain an expression

for the relative population difference  $\frac{\delta N}{N} = \frac{N_A - N_B}{N_\alpha + N_\beta}$ . Calculate  $\delta N/N$  for a proton in a magnetic field of 0.3T at 4K. ( $g_1 = 5.586$ ,  $\mu_N = 5.05 \times 10^{-27} \text{ JT}^{-1}$  and  $K_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ ). 13

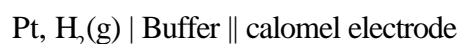
18. An isolated system consists of 1 mol of an ideal gas, a heat reservoir at temperature, T and a machine for compressing the gas. The gas at temperature, T, expands freely to twice its initial volume. It is then compressed back to the initial volume by the machine at temperature T. The gas again expands freely to twice the initial volume. What is the minimum  $\Delta S$  for the whole system (including the gas, the machine and the reservoir) at the end of the three steps? 13

19. An equilibrium mixture for the reaction



at 700 K consists of 2 atm of  $\text{CH}_3\text{OH}$ , 1 atm of CO and 0.1 atm of  $\text{H}_2$ . The mixture is allowed to expand to twice its original volume at 700 K. Calculate the new equilibrium pressures for CO,  $\text{H}_2$  and  $\text{CH}_3\text{OH}$ . 13

20. A) The e.m.f. of the cell,



is 0.5164 V at 25°C. Given that the reduction potential of normal calomel electrode is 0.280 V and the pressure of  $\text{H}_2(\text{g})$  is 1 atm. Calculate the pH of the buffer. 6

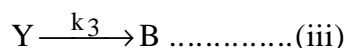
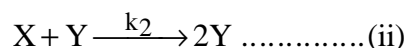
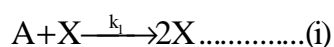
- B) Compressibility and electrostriction effects in solution are of different origin even though both result in volume decrease. Explain the difference between the two effects. 7



21. A) Consider the adsorption of gas molecules on a solid surface. If the pressure of the gas is  $p$  and the fraction of the surface covered by the adsorbed gas molecules is  $\theta$ , write down the expressions for the rates of adsorption and desorption. Derive the Langmuir adsorption isotherm using these expressions. 6

B) In crystal, CO molecules can orient with the C = O axis pointing in one direction or the exactly opposite direction. The two situations have the same energy. If under an external electric field, all the CO molecules are forced to orient along one direction alone, what is the change in entropy? 7

22. A) Taking the following general example, explain the oscillating or periodic variation of the concentration of X and Y following the Lotka - Vottera mechanism :



Note that steps (i) and (ii) are autocatalytic in nature. 6

B) Match the following : 7

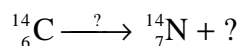
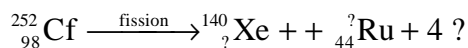
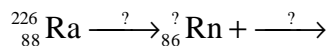
<b>Group A</b>	<b>Group B</b>
(i) $CH_3CHO \rightarrow CH_4 + CO$	(1) Molecularity
(ii) $H_2O \rightleftharpoons H^+ + OH^-$	(2) Photochemical reaction
(iii) Number of molecules participating in the rate - determining step of a reaction	(3) Second order reaction
(iv) $H_2 + Br_2 \rightarrow$ products	(4) Third order reaction
(v) $t_{1/2} \propto \frac{1}{a_0^2 k_1}$	(5) Fast reaction
(vi) $E + S \xrightleftharpoons[k_{-1}]{} ES$	(6) Chain reaction
(vii) $n CH_2 = CH_2 \rightarrow -(CH_2 - CH_2)_n-$	(7) Michaelis - Menten mechanism

23. Draw schematic diagram of the potential energy surface for (A) an endothermic reaction and (B) an exothermic reaction. Indicate clearly that relative energies of reactants, products and activated complex and the energy of activation. 13

24. A) 10 mol each of polymer molecules with molecular weights of  $10^4$  and  $10^5$  g mol<sup>-1</sup> are mixed. Calculate the  $\bar{M}_w$  and  $\bar{M}_n$  and polydispersity index. 7

B) Draw the possible stereospecific forms of the polymer  $\left( \begin{array}{c} \text{CH}_2 - \text{CH} \\ | \\ \text{R} \end{array} \right)_n$  6

25. A) Fill up the following : 7



B) One  $\text{cm}^3$  of blood withdrawn from the patient's body, labelled with  $^{32}\text{P}$  and reinjected into his body. After homogenisation, one  $\text{cm}^3$  of blood was withdrawn again and the sample showed a total activity of 250 net counts in 10 min. Find the volume of the blood in the patient's body, given that  $0.1 \text{ cm}^3$  of the labelled blood before injection showed an activity of 14000 counts per min. 6

26. A) Show that the rate of oxidation of Nickel metal is proportional to the sixth root of the partial pressure of oxygen. 4

B) The electronic configuration of magnesium is  $1s^2 2s^2 2p^6 3s^2$ . Give reasons to explain the fact that magnesium metal is a conductor, despite the fact that its 3s shell is filled. 4

C) Electrical conductivity of a pure metal decreases, with an increase in temperature while that of a semiconductor increases, Explain. 5

27. A) Explain the following : 6

(i) The trend in Lewis acid character is :  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ .

(ii) Silicon dioxide is a solid while  $\text{CO}_2$  is a gas.

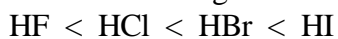
B) What is inorganic benzene ? Write down the structure and compare its reactivity with benzene. 4

C) Draw the structure of  $\text{PCl}_5$  and mention its hybridisation. 3

28. A) What are silicones ? Give general method of preparation and mention the uses. 6

B) Draw the structure of  $\text{B}_4\text{H}_{10}$  and indicate the number of bridging hydrogens. 6

C) The trend in acidic character of the halogen acids is : 3



Explain.

29. A) Mention the factors affecting high spin-low spin crossover in complexes. Illustrate your answer with suitable examples. 7
- B) Explain the following : 6
- $[\text{Co}(\text{C}_2\text{O}_4)_3]^{2-}$  complex is intense blue, while  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is faint pink.
  - Calculate spin only magnetic moments of  $[\text{MnF}_6]^{4+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ .
30. A) How do entropy and enthalpy affect the stability constants of complexes in solution ? 6
- B) Explain how Racah parameters of free ions are affected due to complexation. What information could be obtained regarding the nature of Metal - Ligand bond? 7
31. A) Does the rate of electron transfer by sphere mechanism depend on the bridging ligand? 4
- B) The rate constant for the aquation of  $[\text{Pt}(\text{dien})\text{Cl}]^+$  ion in an aqueous solution is : 5  
 $K_{\text{obs}} = K_1 + K_2 [\text{Y}]$ , where Y is the entering ligand. Explain the two pathways (dien = diethylene triamine).
- C) Write the systematic names of the following : 4
- $\text{K}_2(\text{OsCl}_5 \cdot \text{N})$
  - $[(\text{NH}_3)_5\text{Co} - \text{O} - \text{O} - \text{Co}(\text{NH}_3)_5]^{5+}$
32. A) On the basis of outer sphere mechanism, explain why the electron transfer reaction between  $[\text{Fe}(\text{o-phen})_3]^{2+}$  and  $[\text{Fe}(\text{o-phen})_3]^{3+}$  is fast whereas the reaction between  $(\text{Co}(\text{NH}_3)_6)^{2+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is slow. (o-phen = ortho-phenanthroline) 5
- B) Draw all the possible isomers for : 4
- $[\text{Os}(\text{2-2'-bipyridyl})_2\text{Cl}_2]$
  - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$
  - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- C) Which of the ligands in each of the following pairs will cause greater crystal field splitting in octahedral field : 5
- $\text{NH}_3$  or  $\text{H}_2\text{O}$
  - $\text{Cl}^-$  or  $\text{CN}^-$
  - $\text{NH}_3$  or ethylene diamine
  - $\text{F}^-$  or  $\text{NH}_3$ .

33. A) Give classification of metal clusters citing one example in each case. 5
- B) Explain the role of  $[\text{Ru}(\text{bipyridyl})_3]^{2+}$  in solar energy conversion. 4
- C) Explain the use of Lanthanide complexes of fluorinated diketone ligands as shift reagents in NMR spectroscopy. 4
34. A) Name 2-electron, 3-electron, 4-electron and 6-electron donor ligands which form organo-metallic compounds with transition metals. Describe at least two methods of synthesis of ferrocene and draw its structure. 8
- B) Discuss the role of the catalyst  $\text{HCo}(\text{Co})_4$  in hydroformylation reactions. 5
35. A) Draw a schematic amperometric titration curve for  $\text{Pb}^{2+}$  by oxalate ion, at dropping mercury cathode at a potential of - 1.0 V Vs SCE using  $\text{KNO}_3$  as a supporting electrolyte. Explain the nature of the curve. 4
- B) Draw a schematic TGA curve for decomposition of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in air and in  $\text{CO}_2$  atmospheres. Explain the nature of the curves. 5
- C) (i) Mention the advantages of hyphenated chromatographic methods. 4  
(ii) Define controlled-cathode-potential electrolysis.
36. A) Define the terms : 6  
(i) Retention time  
(ii) Half - wave potential  
(iii) Ion-exchange capacity.
- B) With respect to basic principle, compare AAS with Flame photometric techniques. 4
- C) Differentiate between exhaustive extraction and a countercurrent extraction. 3
37. A) Explain why zinc is considered as an ideal biosite. 4
- B) Taking chlorophyll as an example, explain the role of magnesium in the transmission of energy. 5
- C) Explain the role of iron in oxygen transfer and storage in the human system. 6