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 each)

   A) Assign structure to the compound, based on the following data :

   Molecular formula : $C_5H_8O_2$

   I. R. : 1775, 1175 cm^{-1}

   M. S. (m/z) : 100, 85, 56

   P.M.R. (δ) : 1.35 (*d*, J = 6.5 Hz, 18 mm), 1.5 to 2.2 (*m*, 12 mm), 2.4 (*t*, 12 mm),

             4.5 (sextet, J = 6.5 Hz, 6mm).

   B) Deduce the structure of a compound based on the following data :   6

   Molecular formula : $C_{10}H_{11}NO_3$

   I.R. : 1630, 1600, 1530, 1500, 1350, 940, 850 cm^{-1}

   PMR (δ) :   1.35 (*t*, J = 6.5 Hz, 15 mm), 4.1 (*q*, J = 6.5 Hz, 10mm), 6.95 (*d*, J=8Hz, 10mm),

             7.58 (*d*, J = 8 Hz, 10 mm), 7.6 (*d*, J = 13 Hz, 5mm), 7.95 (*d*, J = 13Hz, 5mm).

   C) How many lines would be observed in the esr spectrum of methyl radical ? Comment on the intensities of these lines.

   D) The Mossbauer spectrum of a normal cubic spinel, $Fe^{2+}[Cr_2^{3+}]O_4$ shows a single resonance line. Explain the observed spectrum.

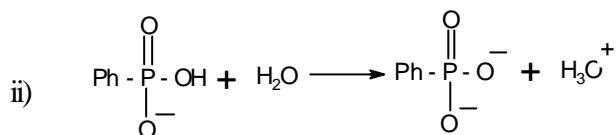   E) Calculate the force constant for $H^{35}Cl$ given that the fundamental vibration frequency is 8.67 x 10^{13} Hz.

   F) If the nmr frequency for ^1H and ^2H in a I T magnetic field are 42.57 and 6.54 MHz respectively and the nuclear g-factor of ^1H is 5.585, calculate the nuclear g-factor of ^2H.

2.   A) Match the Hammett sigma (σ) values with appropriate substituents.   4

	Substituent		σ
(i)	H	(a)	1.91
(ii)	m - O$^-$	(b)	0.54
(iii)	p-N$_2^+$	(c)	0.0
(iv)	p-CF$_3$	(d)	-0.70

   Ans.   (i) = ...   (iii)   = ...
   (ii) = ...   (iv)   = ...

B) Indicate for the following reaction series, whether the rho (p) value is positive or negative :   2
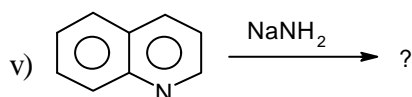
    i)   Ionization of benzoic acid in ethanol at 25^0.

    ii)

$$Ph - \overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}} - OH + H_2O \longrightarrow Ph - \overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}} - O^- + H_3O^+$$
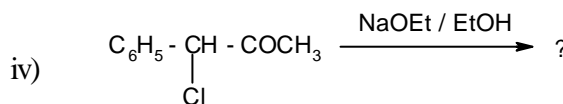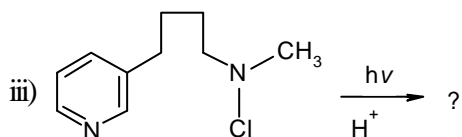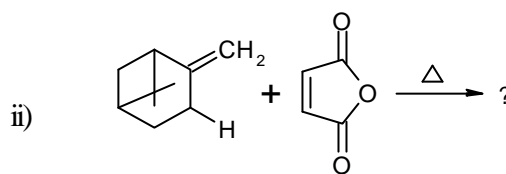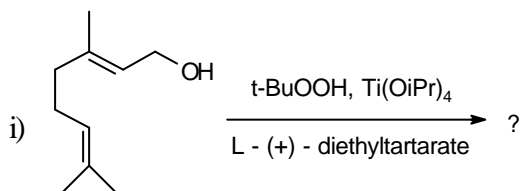
C) The nitrations of benzene and hexadeuterobenzene proceed at the same rate. Comment on the mechanism of the nitration.   3

D) From the following observation regarding the Hofmann rearrangement what conclusion can be drawn about the mechanism?
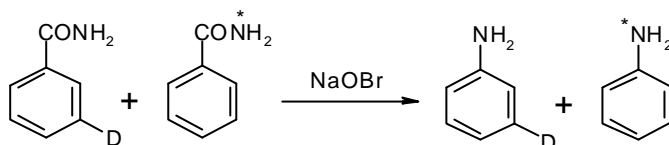
3.   For each of the following, predict the product, name the reaction and explain the mechanism involved: 13
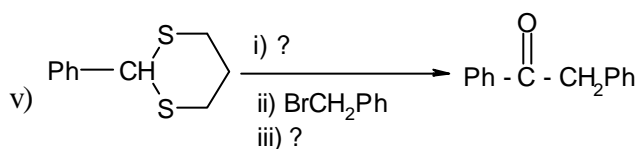

    i)   t-BuOOH, Ti(OiPr)$_4$ / L - (+) - diethyltartarate

    ii)

    iii)   hv / H$^+$

    iv) $C_6H_5 - \overset{\underset{|}{Cl}}{CH} - COCH_3$ NaOEt / EtOH
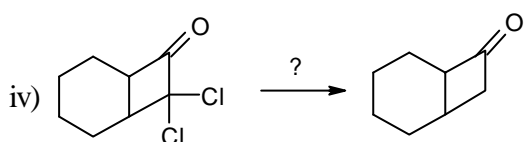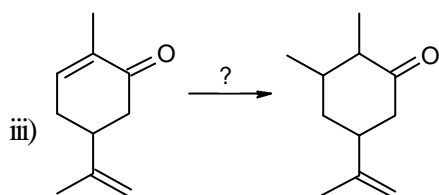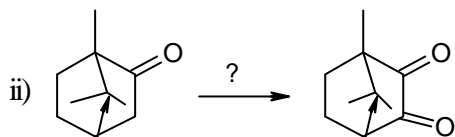
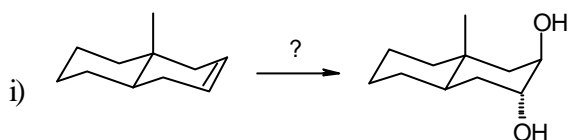   v)   NaNH$_2$

4.   A) Predict the products when the following compound reacts separately with each of the reagents: 8
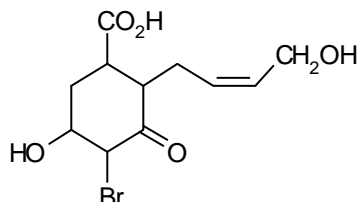
    (i)   TBTH

    (ii)   MnO$_2$

    (iii)   DCC

    (iv)   L(+) diethyltartarate, t-BuOOH, Ti(OiPr)$_4$

B) Indicate the reagents for the following conversions :   5

i)

ii)

iii)

iv)

v)

Ph—CH $\underset{S}{\overset{S}{\diagdown}}$ $\xrightarrow[\substack{\text{ii) BrCH}_2\text{Ph} \\ \text{iii) ?}}]{\text{i) ?}}$ Ph - C - CH$_2$Ph

5.   A) Draw the structures of the isomers of compound C$_9$H$_7$N.   3

B) One of the above isomers gives a dicarboxylic acid **A**(C$_7$H$_5$O$_4$N) on reaction with alkaline KMnO$_4$.
   A on heating forms a monocarboxylic acid **B**(C$_6$H$_5$NO$_2$). There are four monochloro derivatives of
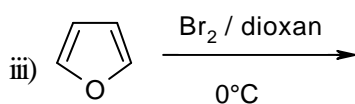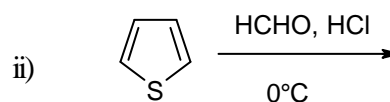   **B** possible.   7
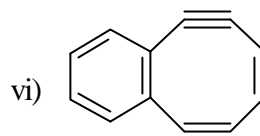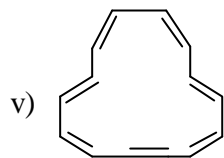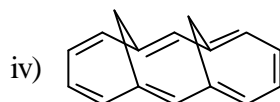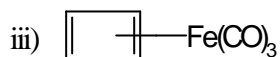
Structure Of **A** :

Structure Of **B** :

Structures of monochloro derivatives of **B** :

C) Draw the structures of the products :   3

i) $\xrightarrow[\text{R.T.}]{\text{DMF / POCL}_3}$

ii) $\xrightarrow[\text{0°C}]{\text{HCHO, HCl}}$
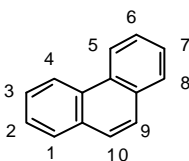
iii) $\xrightarrow[\text{0°C}]{\text{Br}_2 \text{ / dioxan}}$

6. A) Classify the following compounds into aromatic, antiaromatic, nonaromatic and homoaromatic : 6

i)

ii)

iii) [Fe(CO)$_3$ structure]

iv)

v)

vi)
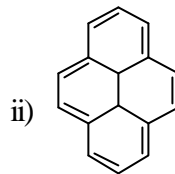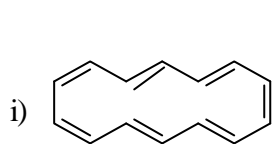
Ans.   (i) ....   (ii) ....

(iii) ....   (iv) ....

(v) ....   (vi) ....

B) The structure of phenanthrene is shown below :   5

i) Draw the resonance structures of phenanthrene.

ii) Predict which of the C - C bonds in phenanthrene is the shortest.

iii) Draw the structure of the compound (I) formed by fusing two benzene rings at C_3-C_4 and C_5-C_6 bonds in phenanthrene.

iv) In one sentence describe one of the characteristics of I.

C) When cyclopentadiene labelled with ^{14}C at one of the carbon atoms is treated with a base and subsequently regenerated shows all positions equally labelled. Explain.   2
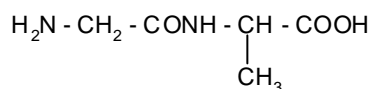
7. A) Match the following :   5

|			
(i)	Histidine	(a)	Digestive enzyme
(ii)	ATP	(b)	Peptide bond
(iii)	Sanger reagent	(c)	Energy source
(iv)	Chymotrypsin	(d)	Imidazole ring
(v)	Primary structure	(e)	N-Terminal analysis

Ans. i)   ii)   iii)   iv)   v)

B) How will you synthesize the following peptide using Merrifield resin?   4

$$H_2N - CH_2 - CONH - \underset{\underset{CH_3}{|}}{CH} - COOH$$

C) Draw the structure f 18-crown-6, Explain the role of 18-crown-6 in the following reaction :   4

$$CH_3(CH_2)_7Br + KF \xrightarrow[benzene]{18 - crown - 6} CH_3(CH_2)_7F$$
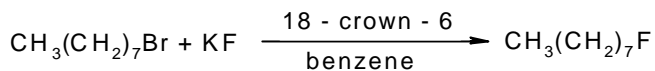
8.   A) Predict the major products of the following reactions with proper stereochemistry :   6

i)

i) LAH
ii) H_3O^+

ii)

RCOOOH

iii)

$NaBH_4$

iv)

$KMnO_4$, NaOH

v)

Br_2

vi)

H_2, PtO_2
MeOH
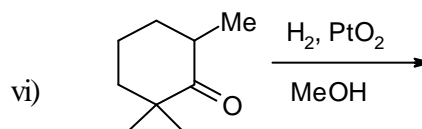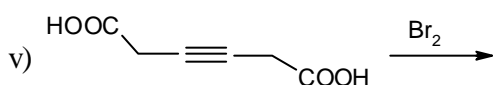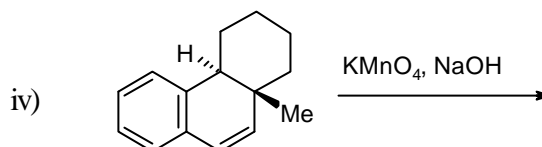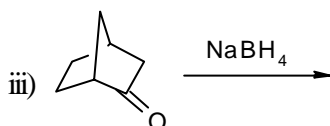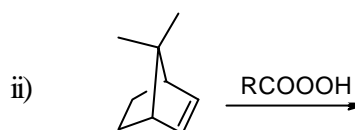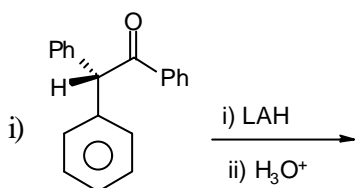
B) Trans, trans 2,6 - diethylbromo cyclohexane does not undergo elimination of HBr on treatment with a base. However, the corresponding trans, cis- or cis-, cis - isomers undergo the elimination.   4

C) In the pig liver esterase catalyzed selective hydrolysis of one ester group in compound I, the pro-R ester group undergoes the hydrolysis. Draw the Fischer projection of the product.   3

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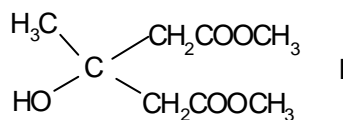
9.   A) Propose mechanisms for the following reactions :   9

i)

i) $AlCl_3$
ii) Ac_2O

ii)

I^-

iii)

HI
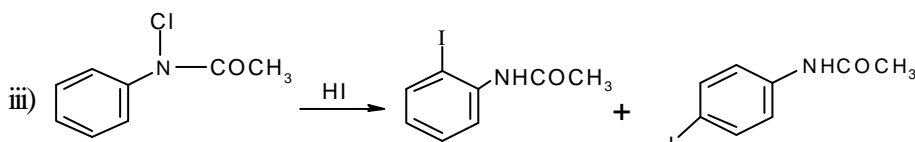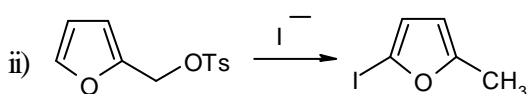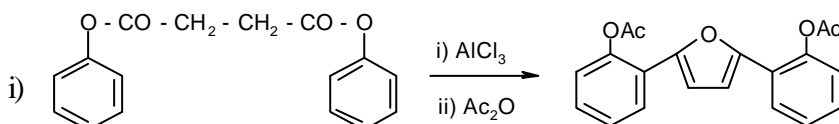
B) In the reaction given below both the products are optically active. Write the intermediate and mechanism of the reaction. 4
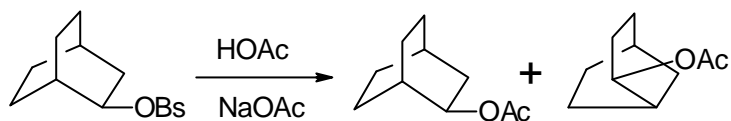
10. For each of the following predict the product(s), identify the reaction, and give the mechanism involved : 13

i)

ii)

iii)

iv)

v)

vi)
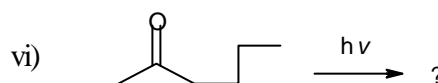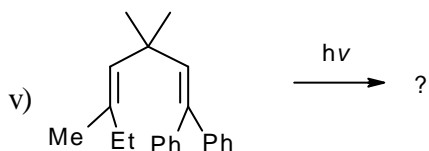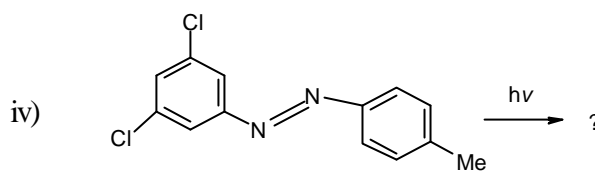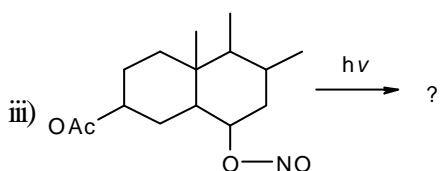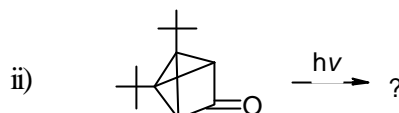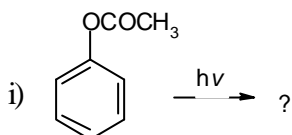
11. A) Complete the following sequence of pericyclic reactions giving stereochemistry of the products. Name the reaction types. 6
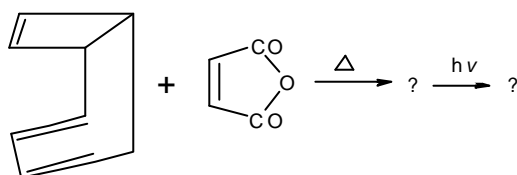
B) Predict the products and identify the types of the following pericyclic reactions : 7

i)

ii) $CH_3 - CH_2 - CH = CH - CH = CH_2$ $\xrightarrow{\triangle}$?

iii)
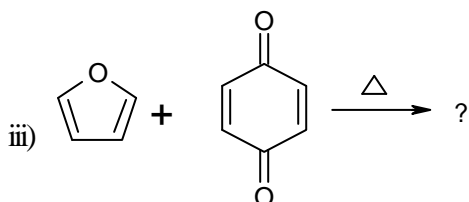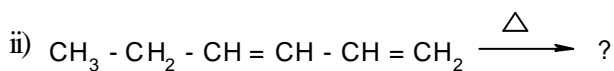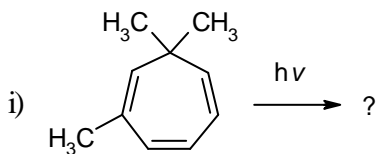
12. A) The following structure has been assigned to a steroid hormone. Answer the following related to the structural features of this compound : 8
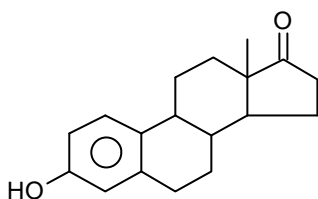
(i) How will you prove that it contains :

   (a)   Quaternar methyl group.

   (b)   Five membered ring ketone.

   (c)   Trisubstituted benzene with the indicated substitution pattern.

(ii) How will you bring about the following transformations on the above compound?

   (a)   Reduction of aromatic ring and the product obtained from it.

   (b)   Conversion to lactone and its structure.

B) Explain the biogenesis of the following : 5

i)   ii)
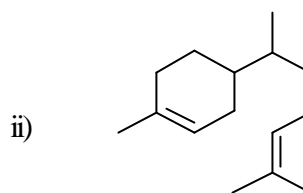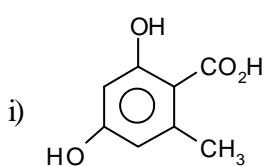
13. A) Assign structure to the compound which exhibits the following data : 6

   Molecular formula : C_5H_6O

   U.V. : 220 nm (ε 4000)

   I.R. : 1600, 1500, 780 cm^{-1}

   PMR (δ) : 2.3 (s, 15 mm), 5.85 (d. J = 2 Hz, 5 mm), 6.2 (dd, J = 1.5 and 2.0 Hz, 5 mm), 7.2 (d, J = 1.5 Hz, 5 mm).

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

i)   and   OH by PMR

ii) $CH_3CH = CH - CO_2Me$ and $CH_3 - CH = CH - O - \overset{O}{\overset{\|}{C}} - Me$ by I.R.
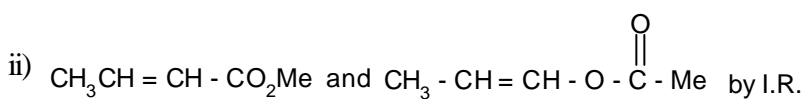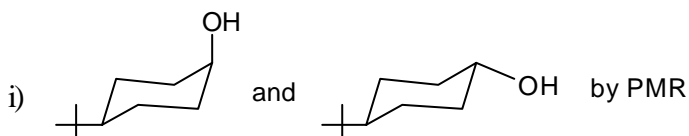
C) A hydrocarbon $C_{10}H_{14}$ exhibits the following M. S. data. Assign the structure giving proper explanation.

   m/z : 134, 105 (base peak), 77, 51. 3

14. The three (unnormalised) occupied Huckel molecular orbitals of benzene are given by :   13

$$\psi_1 = p_1 + p_2 + p_3 + p_4 + p_5 + p_6$$

$$\psi_2 = p_2 + p_3 - p_5 - p_6$$

$$\psi_3 = 2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6$$

a) Normalise these orbitals.

b) Show that ψ_1 and ψ_2 are orthogonal.

c) Sketch these MO's qualitatively.

d) Which of the MO's has the lowest energy?

e) Calculate the bond order p_{13}.

15. A) Consider a particle in a cubic box with sides of length ℓ. List the quantum numbers for the eigenstates with energy $\leq \dfrac{16h^2}{8m\ell^2}$. How many such eigenstates are there?   7

B) Identify the eigen functions of d^2/dx^2 from the following list. Which of them have positive eigenvalues?

(i) $\ell n\, 2x$ (iv) $\sin x + \cos x$

(ii) $5x^3$ (v) $\exp(-kx)$

(iii) $3x^2$ (vi) $x \cdot e^{-x^2}$ 6

16. Consider the internal coordinates for water molecule, the OH bonds q_1, and q_2 and the HOH bond angle θ. The character table for the C_{2v} point group is :   13

C_{2v}	E	C_2	σ	σ'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

a) Determine the reducible representation for the transformation of the internal coordinates of water under the symmetry operation in C_{2v}.

b) Decompose this reducible representation into the irreducible representation of C_{2v}.

c) Determine the symmetry of the vibration of water molecule.

17. The vibration-rotation spectrum of a diatomic molecule can be discussed in terms of the energy levels, $E_v, J = \left(v + \dfrac{1}{2}\right)\hbar\omega + hcBJ(j+1)$ Where v and J are the vibrational and rotational quantum numbers, ω is the vibrational frequency and B is the rotational constant. What are the energies or wave numbers at which the vibration - rotation transitions will be observed?   13

18.   One mol of an ideal monoatomic gas initially at STP is taken through the reversible steps shown below :
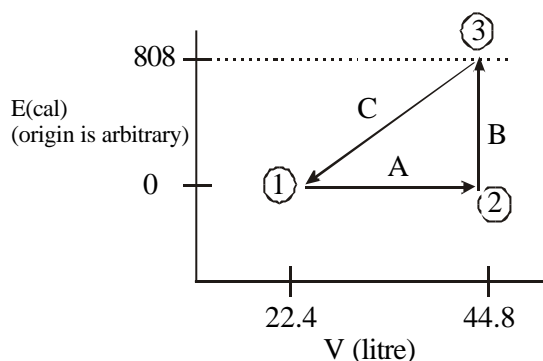
a) What is the pressure and temperature at point 2 ?   4

b) What is the pressure and temperature at point 3 ?   5

c) What is the work done in step C ?   4

19.   The following cooling curves were recorded for Sb-Cd system :

(At. wts. : Cd : 112, Sb : 122).

Cd	0	20	38	48	50	58	70	93	100
First break $^{\circ}$C	-	550	461	-	419	-	400	-	-
Constant temp. $^{\circ}$C	630	410	410	410	410	439	295	295	321

Construct a phase diagram, label it completely. Give the formula of any compound formed.

20.   Derive Debyenue-Huckel limiting law,   13

$$\log f_i = -Az_i^2 \sqrt{I}$$

Elaborate the corrections needed to make it applicable to concentrated solution and for electrolytes other than uni-univalent type.

21   A) How is the dissolution of amphiphilic molecules beyond a critical concentration different from that of simple solutes ?   7

B) Name the experimental methods that may be used to monitor the unique solution behaviour of amphiphilic molecules.   6

22.   A molecule can exist either in the ground energy state (taken to be zero) or an excited state of energy, ε ; there are no other excited states and both ground and excited states are nondegenerate.

a) Write the expression for the partition function.   4

b) Write the expression for the average energy.   5

c) Calculate the entropy for the case of infinite temperature.   4

23. A) Two possible structures for $S_2O_3^{2-}$ are : 7

i)

ii)
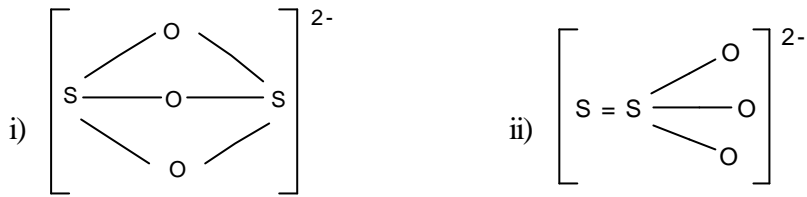
   Describe how tracer technique can be used to identify the correct one.

   B) Using the fractional change method show that the order of a reaction, n is :

   $$n = \frac{\log t_2 - \log t_1}{\log(a_o)_1 - \log(a_0)_2} + 1$$

   Where t and a_0 are the half-life and initial concentration respectively. 6

24. A) Photolytic flash and spectroscopic probe are simultaneously needed for studying fast reactions. Describe the role of the photolytic flash and the spectroscopic probe and comment on the time scales involved. 7

   B) Consider the equilibrium $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$. If the initial concentration of A is $[A]_0$ and that of B is zero, show that the equilibrium concentration of A, [A]eq is : 6

   $$[A]_{eq} = \left[\frac{k_2}{k_1 + k_2} \right][A]_0$$

25. A) Why are polymer molecules characterised by average molecular weights? Give the relations for the number and weight average molecular weights. 7

   B) The intrinsic viscosity of a polymer solution is $217 cm^3\ g^{-1}$. Calculate the approximate concentration of the polymer solution that would have a relative viscosity of 1.5. 6

26. A) The rate of sulphidization of copper metal to Cu_2S is faster than its rate of oxidation Explain on the basis of non-stoichiometrics in the sulphide and oxide. 4

   B) Show with the help of schematic band structure, position of Fermi energy level in the case of an intrinsic silicon at absolute zero temperature. Indicate how the position of Fermi energy level changes when the donors and acceptors are added to solid silicon. 5

   C) What are the colors of stoichiometric and non-stoichiometic nickel oxide? Explain the role of the non-stoichiometry on the electrical conductivity of nickel oxide. 4

27. A) Explain the following : 6
    (i)   Nitrogen is much less reactive than phosphorus.
    (ii)   In the carbon family, in general, tin compounds are used as reducing agents while those of lead are used as oxidizing agents.

    B) What are phosphazenes ? Give the structure of trimeric phosphazene. 4

    C) Draw the structure of ICl_2. Discuss its hybridization. 3

28. A) What are closo and nido carboranes ? Give their structures and also one method of preparation for each. 6

    B) Draw the structure of a sheet silicate. 4

    C) Explain why interhalogens are more reactive than the halogens. 3

29. A) What is the driving force that compells regular octahedral systems to undergo distortion? Explain this by taking the example of d^9 system. 7

    B) (i)   Account for the difference in the room temperature magentic moment of copper (II) acetate dihydrate (1.4 B.M.) and cupric acetylacetonate (1.84 B.M.). 3
    (ii)   Which one of the following is expected to have greater magnetic moment 3
        $[CoCl_4]^{2-}$ or $[CoI_4]^{2-}$? Why ?

30. A) Experimentally, how would you distinguish between the following pairs of isomers ? 6
    (i) $[Cr(NH_3)_5\ BrSO_4]$ and $[Cr(NH_3)_5\ Br]SO_4$
    (ii) $[Co(NH_3)_5\ (ONO)]^{2+}$ and $[Co(NH_3)_5\ (NO_2)]^{2+}$

    B) (a)   How can you perform the following transformations ? 3
    (i) $[Co(NH_3)_5\ (NO_2)]Cl_2\ \rightarrow\ [Co(NH_3)_5\ (ONO)]Cl_2$
    (ii) $[Co(NH_3)_5\ (ONO]Cl_2\ \rightarrow\ [Co(NH_3)_5\ (NO_2]Cl_2$

    (b)   The magnetic susceptibility of hydroxo binuclear Cu(II) complexes depends on the Cu-O-Cu angle. Explain. 4

31. A) What information do you get regarding the nature of metal - ligand bonding in complexes from the "nephelauxetic effect"? 5

B) a) Define, with the help of appropriate equations, step-wise and overall stability constants for a four-coordinate complex. 5

b) Predict the spin state of the following complexes : 3
   (i) $[Co(NH_3)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ iii) $[Fe(CN)_6]^{4-}$

32. A) Provide the mechanism involved in the base catalyzed hydrolysis of $[Co(NH_3)_5Cl]^{2+}$. 7

B) Predict the product of substitution by :
   (i) Two NH_3 molecules in $[PtCl_4]^{2-}$
   (ii) Two Cl^- ions in $[Pt(NH_3)_4]^{2+}$
   On the basis of relative trans directing incfluence of Cl^- and NH_3. 6

33. A) What do you understand by the term "Cluster valence electron count" ? Provide the cluster electron valence count for $Rh_4(CO)_{12}$ and $[Re_4(Co)_{16}]^{2-}$. 5

B) The lanthanide complexes are less stable and show greater flexibility in geometry and coordination number as compared to the complexes of d-block elements. Comment. 4

C) What are iso- and hetero-poly acids? Give one example each of 6- and 12- poly acids. 4

34. A) What is Wilkinson's catalyst ? Discuss its role in the bydrogenation of olefins. 6

B) Rationalise the fact that $(C_6H_6)_2$ Cr is quite susceptible to air oxidation whereas $(C_6H_5F)_2$ Cr is relatively stable. 4

C) Although CO is a weak Lewis base, it acts as a strong ligand. Explain. 3

35. A) Draw a schematic DTA curve for the decomposition of $CaC_2O_4 . H_2O$ in air and in CO_2 atmospheres and explain the nature of the curves. 5

B) Sketch a photometric titration curve for Fe (III) with SCN^- ion when a photometer with a green filter is used to collect data. Why is a green filter used ? 4

C) (i) Between the two compounds-phenolphthalene and fluorescein which one shows greater quantum yield of fluorescence ? Why ? 2
   (ii) Why is helium or hydrogen used as the carrier gas when a thermal conductivity detector is used in GLC ? 2

36. A) Name various types of ion-selective electrodes and draw a labelled diagram of solid state ion-selective electrode. 5

   B) Explain the basic principle involved in anodic stripping voltammetry. Mention its advantages over other techniques. 4

   C) Briefly describe reversed phase HPLC. Name at least three stationary phases used in reversed phase chromatography. 4

37. A) Define ionophores. Explain how they help in ion transport across the membrane. 5

   B) With reference to oxygen uptake in hemoglobin, explain what is the "Cooperative effect"? 4

   C) Give a brief account of coffer containing enzymes. 4