Chemical Science
Paper III

[Time Allowed : $2\frac{1}{2}$ Hours] [Maximum Marks : 200]

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

1. Attempt any *three* of the following : 6

A) Deduce the structure of the compound based on the following data :

Elemental analysis : C, 73.5; H, 10.2%

I.R. 1690, 1610, cm^{-1}

M.S. (m/z) : 98 (M^+), 83, 55, 43.

PMR (δ) : 1.9 (15 mm, *s*), 2.15 (30 mm, *bs*), 6.1 (5 mm, *bs*)

Upon hydrogenation, the product shows strong I.R. absorption at 1715 cm^{-1}.

B) Assign structure to the compound based on the following data : 6

Molecular formula : $C_6H_{12}O_3$

I.R. : 1715, 1350, 1070 cm^{-1}

M. S (m/z) : 132, 101, 75, 43

PMR (δ) : 2.1 (3H, *s*), 2.6 (2H, *d*, J = 6 Hz), 3.3 (6H, *s*), 4.7 (1H, *t*, J = 6 Hz)

C) How EPR spectra can be used to differentiate the following radicals ? 6

(i) o-benzosemiquinone.

(ii) p-benzosemiquinone.

D) Fe (o-phen)$_2$ (NCS)$_2$ compound shows high spin $\rightleftharpoons$ low spin equilibrium. How variable temperature Mossbauer spectra can be used to explain this phenomenon?

(o-phen = 1.10 phenanthroline) 6

E) The fine structure lines of CN band at 3883.4. A can be represented by :

$v = 25798 + 3.85\ m + 0.068\ m^2$ (in cm^{-1}).

Calculate the separation between the band origin and the band head. State direction of degradation of the band. 6

F) Sketch schematically the normal vibrations for the CO_2 molecule. Which of these are (a) infrared active and (b) Raman active ? 6

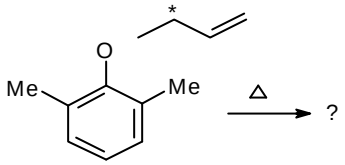
2. A) Explain the following observations : 4

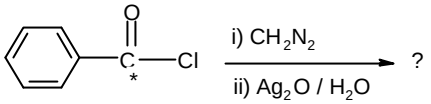
(i) The sign of value for basic hydrolysis of benzamide is positive but in case of acidic hydrolysis it is negative.

(ii) $\sigma_{p-F} = 0.06$, but $\sigma_{m-F} = 0.34$

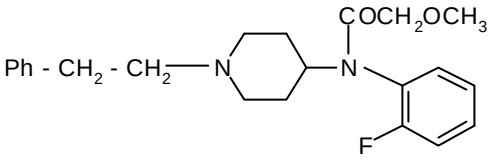
B) The e value for the alkaline hydrolysis of methyl benzoate is 2.39 and kH = 2.39 *l* mol^{-1}. Sec^{-1}. Calculate the rate of the hydrolysis of m-fluoro substituted ester $(\sigma_{m-F} = 0.34)$
(Use the relation $\log \frac{km-F}{KH} = e \cdot \sigma_{m.F}$) 3

C) Predict the product and trace the position of labelled atom in the following reactions. 6

i) 

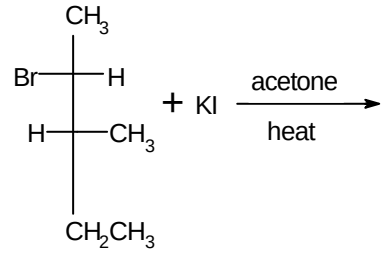
ii) 

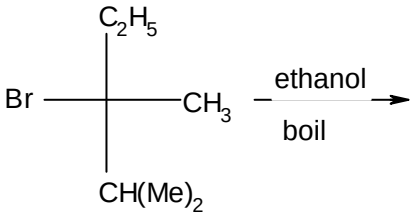
3. A) Propose a synthetic scheme for the preparation of I from2-fluoroaniline and 4-piperidinone. 6



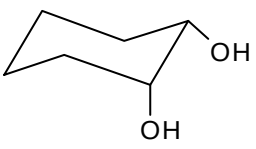
B) Draw the stereostructure of *cis-anti-trans* perhydrophenanthrene. 3

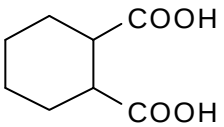
C) Draw the Fischer projections of the products and explain stereochemical changes involved in the reactions : 4

i) 

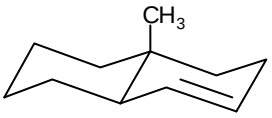
ii) 

4. A) Which products will be obtained when the following molecules react with Pb (OAc) Explain their formation. 4

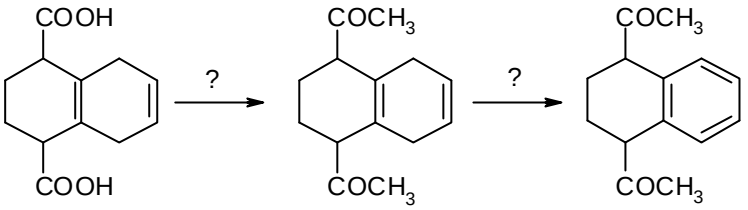




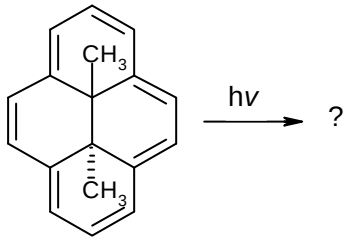
B) Give the products of (*i)* Prevost and *(ii)* Woodward hydroxylations of the following compounds. Indicate the appropriate conditions. 5

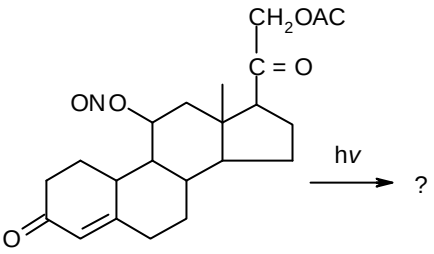


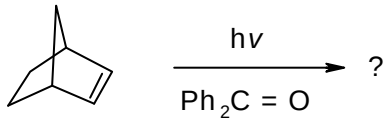
C) Complete the following reaction sequence, giving appropriate reagents. 4



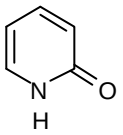
5. A) Predict the products, indicate the type of reaction and give the mechanism of each of the following reactions. 6

i) 

ii) 

iii) 

B) 2-Pyridone (I) is a stable compound.



I

1) Explain the stability of I. 3

2) State the explain the characteristic IR-Absorption of I 1

3) I shows four signals in the aromatic region in its PMR spectrum at 6.15, 6.57, 7.25 and 7.31. Assign them to the respective protons in I, with explanation. 3

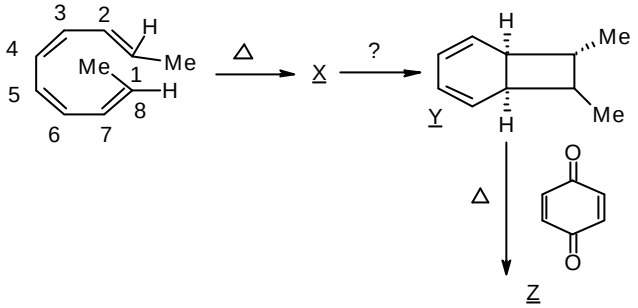
6. A) Cyclopentadiene reacts with maleic anhydride in a pericyclic reaction. 5

(i) What is the reaction called as ?

(ii) Show all the molecular orbitals of both the reactants.

(iii) Indicate the low energy HOMO and LUMO interactions.

(iv) Draw the structure of the product with the stereochemistry.

B) 

5

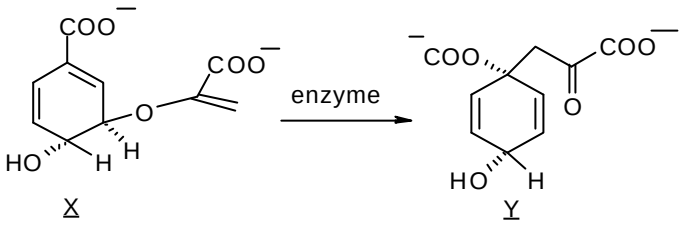
i) Write the configuration of the four double bonds in the starting material.

ii) Draw the structures of X and Z.

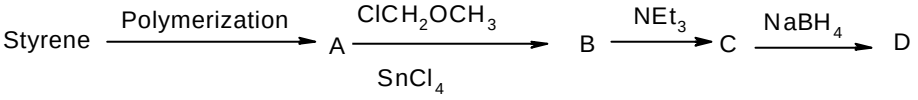
iii) Identify the reactions involved.

iv) Write the reaction condition for conversion of X to Y and process involved in first two conversions.

C) In the following enzyme-catalyzed conversion of X to Y, what kind of pericyclic reaction is involved. 3



7. A) i) Give the structures of the products (A - D) involved in the synthesis of the polymeric reagent (D). 4



ii) What applications do you expect for the above reagent (D) ? What advantages are expected for D over the corresponding classical reagent ? 3

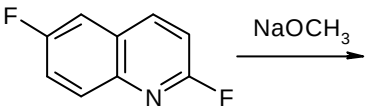
B) Match the following : 6

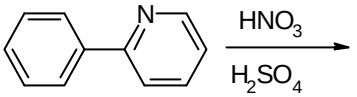
	Reagent		**Reaction**
(a)	DIBAL	(i)	Dehydrogenation
(b)	TBTH	(ii)	Umpolung
(c)	LDA	(iii)	Protection of enols
(d)	1, 3-Dithiane	(iv)	Reduction of halides
(e)	Trimethylsilyl iodide	(v)	Reduction of ester to aldehyde
(f)	DDQ	(vi)	Enolate formation

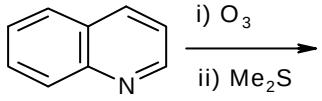
(a) ..... (b) ..... (c) .....

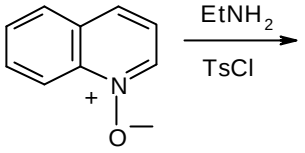
(d) ..... (e) ..... (f) .....

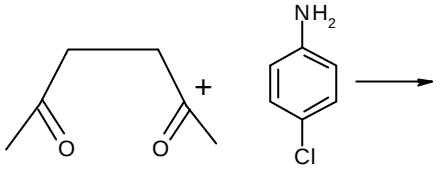
8. A) Draw the structures of the products of the following reactions : 6

i) 

ii) 

iii) 

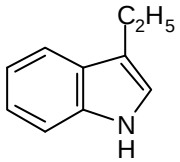
iv) 

v) 

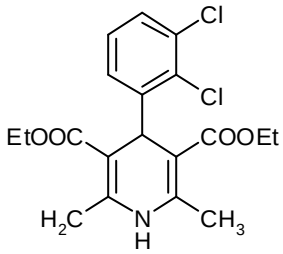
vi) $OHC - CH_2CH_2COCH_3 + NH_2NH_2 \longrightarrow$

B) Draw the structure of 4-(dimethylamino) pyridine. It is a stronger base than pyridine Explain its high basicity. 3

C) How will you prepare the following compounds ? 4

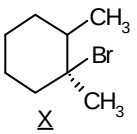
i) 

by Fischer indole synthesis.

ii) 

by Hantzsch synthesis

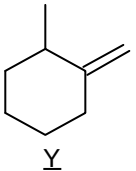
9. A) (i) Write the stereostrucure (chair form) of X. 5



X

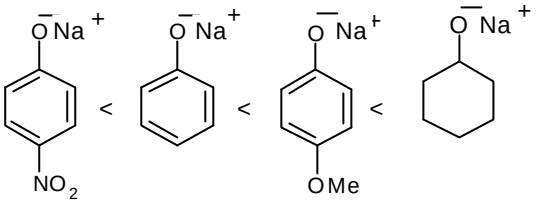
(ii) Does X undergo an E_2 reaction ? If yes, draw the major and minor products. Explain the formation of the products.

(iii) Is it possible to get a Hofmann elimination product Y from X ? Why or Why not ?


Y

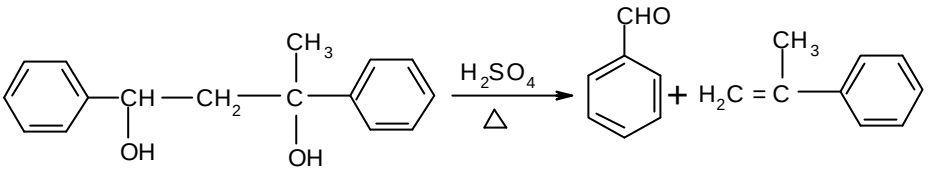
B) Answer the following :

1) Explain the given order of basicity of the following alkoxides. 2



2) 1-methylcyclohexene upon addition of HBr in the presence and absence of peroxide gives two different products. Write the structure of the products and explain the rules governing the additions. 4

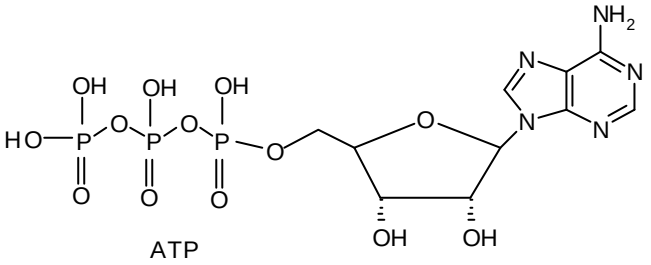
3) Propose mechanism and name the reaction, involved. 2



10. A) What are Ziegler-Natta catalysts ? Discuss with mechanisms, how these catalyse the polymerization of ethylene at low pressure and yield stereochemically regular polymers. 7

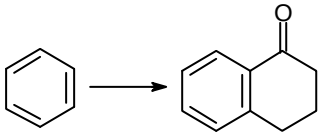
B) 1) Draw the structures of three pyrimidine bases in nucleic acids and name them. 2

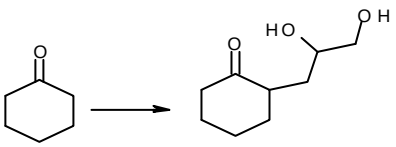
2) Identify various part of given ATP molecule. 2

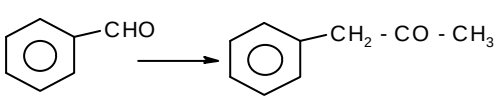


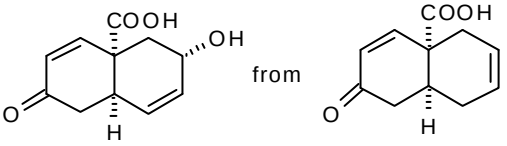
3) Write in brief about primary, secondary and tertiary structure of proteins. 2

11. How will you achieve the following transformations ? 13

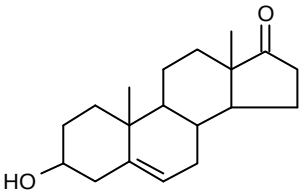
i) 

ii) 

iii) 

iv) 

12. Study the following structure (I) and answer the following :



(I)

1) Classify the above compound. 1

2) Propose biogenesis of (I). 3

3) What will be the structure of the product formed by the Oppenauer oxidation of (I)? 2

4) What will be the product formed when (I) is treated with an excess of *m*-chloroperbenzoic acid ? 2

5) Propose a method to establish the nature of the double bond by degradation. Write the reactions involved. 3

6) Give characteristic IR frequencies, you expect for the compound (I). 2

13. A) Derive the structure of a compound based on the following data : 7

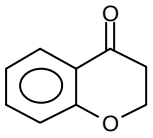
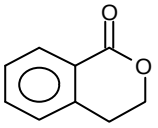
Elemental analysis : C, 63.2, H; 8.8%

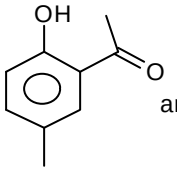
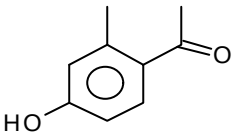
I.R. : 1720, 1650, 1185, 840, 700 cm^{-1}.

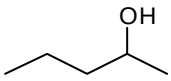
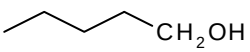
M.S. (m/z) : 114 (m^+), 99, 69, 41, 29.

P.M.R. (δ) : 1.25 (3 H, *t*, J = 6.5 Hz), 1.85 (3 H, *dd*, J = 6 and 1 Hz),
4.15 (2 H, *q*, J = 6.5 Hz), 5.85 (1 H, *dq*, J = 16 and 1 Hz), 6.95 (1 H, *dq*, J = 16 and 6 Hz)

B) How will you distinguish the following pairs by the indicated spectral method ? Explain. 6

a)  and  by I.R.

b)  and  by I.R. and PMR

c)  and  by M.S.

14. A) Match the entries in Column A from those given below : 8

	Column A	**Column B**
a)	Interpretation of wave function	.....
b)	3 s orbital	.....
c)	postulate of antisymmetry	.....

d) Spectrochemical series .....

e) Linear operator .....

f) Photoelectric effect .....

g) Huckel approximation .....

h) Free valence .....

Entries for column B :

π electron theory

Schrodinger

Fi = 4.732 - Ni

$\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau$

determinantal wave function

High or low spin complexes

Max Born

Pauli's exclusion principle

Kronecker delta

$(6 - 6p + p^2)\, e^{-p/2}$ $(p = 2\, Zr/a_0)$

$\hat{A}\{c_1 \phi_1 + c_2 \phi_2\} = c_1 \hat{A} \phi_1 + c_2 \hat{A} \phi_2$

B) To which symmetry operations for c_{3v} point group are the following combinations of operations equivalent ? 5

a) $\hat{c}_3^1 \hat{\sigma}_\upsilon(1)$

b) $\hat{\sigma}_\upsilon(1) \hat{\sigma}_\upsilon(2)$

c) $\hat{c}_3^2 \sigma_\upsilon(3)$

15. A) Evaluate the commutator $[\hat{x}, \hat{p}_x]$ State the significance of this result. 8

B) What is the degeneracy of the level having energy $\frac{75\, h^2}{8\, ma^2}$ for a cubic box of length a ? Write down the corresponding eigen functions in each case. 5

16. A) Deduce the expressions for the sp^2 hybrid orbitals from the appropriate combination of atomic orbitals. Sketch schematically sp^2 hybrid orbital. 8

B) Obtain the expression for electron density of H_2 molecule within simple MO framework. Sketch the bonding and antibonding orbitals. 5

17. A) For the thermal decomposition of ozone to oxygen the following mechanism has been proposed :

a) $O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ b) $O_3 + O \xrightarrow{k_2} 2O_2$

Deduce the rate law. 8

B) Calculate <x> and <p> for the ground state of a particle in 1D box of length a. 5

$(0 \le x \le a)$

18. A) Give the basic principle of photoelectron and auger spectroscopy. How one can utilize these methods for the determination of surface composition ? 6

B) The fundamental and first overtone transitions of ^{14}N, ^{16}O are centered at 1876.0 and 3724.20 cm^{-1} respectively. Evaluate equilibrium vibration frequency and the unharmonicity constant. 7

19. A) Classify the following nuclear reactions : 6

$^{236}_{92}U \rightarrow {}^{94}_{36}Kr + {}^{140}_{56}Be + 2\,{}^{1}_{0}n$

$^{9}Be\,(\gamma, n)\,{}^{8}Be$

$^{63}Na\,(n, \gamma)\,{}^{24}Na$

$^{63}Cu\,(p,\ p\ 3n\ 9\alpha)\,{}^{24}Na$

B) Complete the following : 7

$^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + ? + Q$

$^{22}_{11}Na \xrightarrow{?} + {}^{0}_{+1}\beta + \bar{\upsilon} + Q$

$^{63}Cu + \xrightarrow{?} {}^{64}Cu + {}^{1}_{1}H$

$^{27}Al + \xrightarrow{?} ? + {}^{35}Cl$

20. A) Derive : $C_p - C_v = \dfrac{TV\alpha^2}{\beta}$

Where α and β are coefficients of expansivity and compressibility. 7

B) At 300 K and 1 atm pressure, dinitrogen tetroxide is 20% dissociated into nitrogendioxide. Calculate the equilibrium constant and standard free energy change for the reaction : $N_2O_4 \rightleftharpoons 2NO_2$ at this temperature. 6

21. A) Using Kirchhoff's equation $\left(\dfrac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p$ and Maxwell's relations : 8

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V ; \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P ;$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V ; \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Show that :

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \text{ and } \left(\frac{\partial C_P}{\partial P}\right)_T = 0$$

B) 1 mole of an ideal gas undergoes isothermal reversible expansion from 10 to 1 atmosphere at 27^0C. Calculate ΔG for the expansion in Joules. 5

22. A) Show that in a binary ideal liquid solutions, the decrease in free energy of mixing is minimum when $X_1 = X_2 = 0.5$ (X_i are mole fractions) at a constant temperature. 5

B) Water exists in three phases : solid, liquid and vapour. Sketch the phase diagram for water and explain the significance of the diagram. 8

23. A) Consider a gas phase reaction : A $\rightleftharpoons$ B. The ground state energy level pattern of A and B differ by an energy term $\left(\Delta U_0^0\right)$ equal to 1200 J-mol^{-1}. The A and B molecules possess doubly and triply degenerated ground state levels. Calculate the equilibrium constant for the reaction at 1000^0C. 6

B) For two types of flows and fluxes, one can write :

$J_1 = L_{11} X_1 + L_{12} X_2$ and

$J_2 = L_{21} X_1 + L_{22} X_2$.

Prove on the basis of Onsager's theory, $L_{12} = L_{21}$. 7

24. A) Upon the action of the Bromine on fumaric acid, the following data were obtained : 6

Exp. I		Exp. II	
t/min	C	t/min.	C
0	8.87	0	3.81
95	7.87	1.3	3.51
$\overline{C} = 8.37$		$\overline{C} = 3.66$	
$\frac{-dc_1}{dt} = 0.0106$		$\frac{-dc_2}{dt} = 0.00227$	

Find the order of reaction.

B) Define the symbols in the equations 7

$$k_s = P\ Z\ e^{-E/RT}$$

$$k_s = \frac{KT}{h} e^{\Delta S^*/R} . e^{-\Delta H^*/RT}$$

Show that steric factor, P is related to the entropy of activation.

25. A) What is Equilibrium-Ultracentrifuge method ? Discuss in beief how its study leads to determination of molecular weight of a macromolecule. 8

B) Calculate the molar mass of a macromolecular substance from the following sedimentation-equilibrium data. Rotor-speed = 15000 r. m in^{-1}, temperature = 12.4^0C, buoyancy factor (1-vp) = 0.277. The concentration at equilibrium is 3.52 in arbitrary concentration units, at X = 6.827 cm and 13.52 in the same concentration units at X = 7.093 cm. 5

26. A) Discuss defects in non-stoichiometric compounds where metal is in excess. What are the consequences of these defects ? 5

B) Discuss the structure of K_2 $[PtCl_6]$. Why is it known as an antifluorite structure ? 4

C) Show that in a cubic close packed structure, the volume of space occupied by the lattice is 74%. 4

27. A) Discuss the structure and bonding in "Inorganic Graphite" $(BN)_x$ and compare it with that of graphite. 6

B) Explain "Polyhydroxy compounds are added in the titration of boric acid aganist NaOH". 3

C) Compare the structure and bonding in BF_3 and BrF_3. 4

28. A) Draw the structures of pyrosilicate and chain silicate. 5

B) Discuss the structure of Mica. 4

C) What are Fullerenes ? Why are they so called ? 4

29. A) Discuss structure and bonding in sulphurous acid and dithionic acid. 4

B) What is Phospham ? Hos is it prepared? 4

C) Discuss the structure and bonding in IF_5 and IF_7. 5

30. A) Why are magnetic properties of Lanthanide complexes not much affected by nature of the ligands ? 5

B) Discuss the use of Lanthanide complexes as NMR shift reagents. 5

C) What are the main differences in spectral behaviours amongst the elements of 4*f* and 5*f* series ? 3

31. A) Work out the ground state spectral terms for the following ions : 6

(a) Ni^{2+} (b) Ti^{3+} (c) Co^{2+}.

B) The four coordinated complexes of Ni(II) with weak field ligands are tetrahedral and paramagnetic while those with strong field ligands are square planar and diamagnetic Explain. 4

C) The orbital contribution to magnetic moment is quenched on octahedral complexation of d^1 ion. Explain. 3

32. A) Account for the following :

(i) Co^{3+} ions tend to form low spin octahedral complexes even with comparatively weak field ligands.

(ii) $[NiCl_4]^{2-}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is dimagnetic. 6

B) What are Racah parameters ? How are they related to each other ? Explain how these parameters can be employed for interpreting the metal ligand bonding. 4

C) Draw the structures of cis and trans isomers of bis (glycinato) Cu(II) 3

33. A) Draw the structures of cis and transfer reaction involving transition metal complexes. Explain the conditions necessary for the occurrence of such reactions. 6

B) Explain "The magnetic moment of $[Fe(dtc)_3]$ (dtc = diethyl dithiocarbamate ion) is close to that of a low spin species at 4K. However, at 300K, the value is as high as 5.00 BM". 3

C) What are metal clusters ? Give a broad classification of cluster compounds. 4

34. A) Assuming 18 electron rule to be valid, find out the number of Fe-Fe bonds in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. 4

B) What are organometallic compounds ? Give a broad classification of organometallic compounds. 4

C) How are sigma bonded organometallic compounds of transition metals prepared ? 5

35. A) Define the following terms used in quantitative analysis by AAS. 6

i) Ionization suppressor

ii) Releasing agent

iii) Protective agent

B) i) What do you mean by aerosol in AAS ? 2

ii) Calculate the average number of plates and plate height for a 40 cm column of GLC using the following data. 5

Given

Compound	t_R, min	$W_{1/2}$, min
Air	1.9	------
Methylcyclohexane	10	0.79
Methylcyclohexene	10.9	0.82
Toluene	13.4	1.06

36. A) Give the significance of various terms in Van Deemter equation. 4

B) What is the advantage of multiple batch extractions over a single extraction ? 4

C) The potassium ions in 300 ml of a solution containing 1% KCl are to be removed by passing through cation exchange resin column in the H^+ form. Calculate the minimum weight of dry resin required for removal. 5

Given : i) Ion exchange capacity of resin = 5.1 meq/g of dry resin.

ii) At wt. of K = 39.098, Cl = 35.45.

37. A) Give only the names of metalloproteins/metalloenzymes that involve the following : high spin Fe(II), low spin Fe(II), an organometallic compound, a cubic architecture, a d metal ion and a tetrameric protein. 7

B) Identify *two* significant biological roles for iron and copper, providing examples of the corresponding proteins/enzymes. 6