

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

Molecular formula : C_8H_7N

IR (V_{max}) 2220, 1600, 1595, 745, 690 cm^{-1}

PMR (δ) : 3.6, 2H, S; 7.25, 5H, 5.

Mass (m/z) : 77, 90, 91, 117 (m^+)

B) Assign structure to a compound on the basis of the following data :

Molecular formula : $C_8H_{12}O$

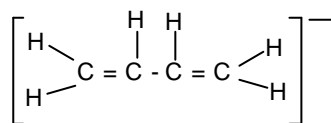
UV. : 288 nm (E 15000)

IR (V_{max}) : 1715, 1620, 856 cm^{-1} .

PMR (δ) : 1.22 (30 mm, S); 2.04 (15 mm, S); 2.30 (10 mm, S); 5.60 (5 mm, S)

Upon hydrogenation with Pd-C the compound yields a product, $C_8H_{14}O$, which strong IR absorption at 1744 cm^{-1} .

C) Determine the equivalent set of protons in the following butadiene anion radical and interpret its epr spectrum having fifteen lines.



$$\text{Given : } I (\text{for } ^1\text{H}) = \frac{1}{2}$$

$$I (\text{for } ^{12}\text{C}) = 0$$

D) Discuss the magnetic Mossbauer of ferromagnetic ^{57}Fe compound.

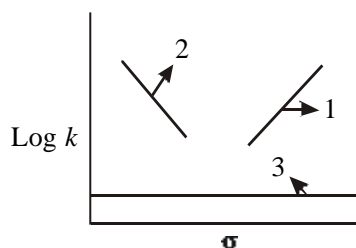
E) State, with reason, which of the following molecules can show a pure rotational microwave spectrum.

O_3 (Ozone), CS_2 , COS , CH_2Cl_2 , CH_4 and H_2O_2

F) Show schematically the process of electron transitions involved in PES.

2. A) What information is available about ρ (rho) from the given plots (1, 2 and 3) ?

3



B) Account for the following observations :

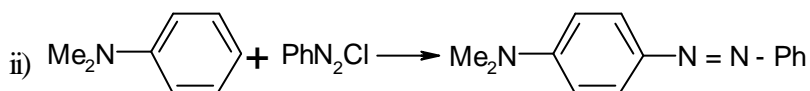
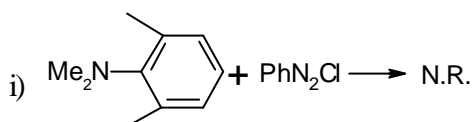
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(i) The e value for the decomposition of substituted benzoyl peroxides is small (0.374)

(ii) The m - N^+Me_3 group increases the acidity of benzoic acid, but m - SO_3 group decreases its acidity.

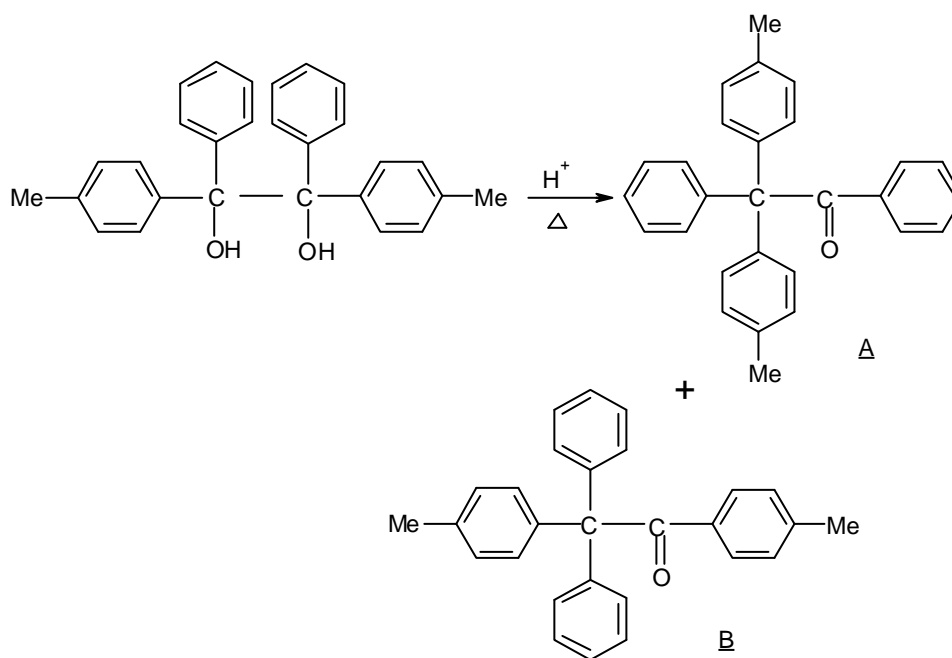
C) Comment on the following observations :

2



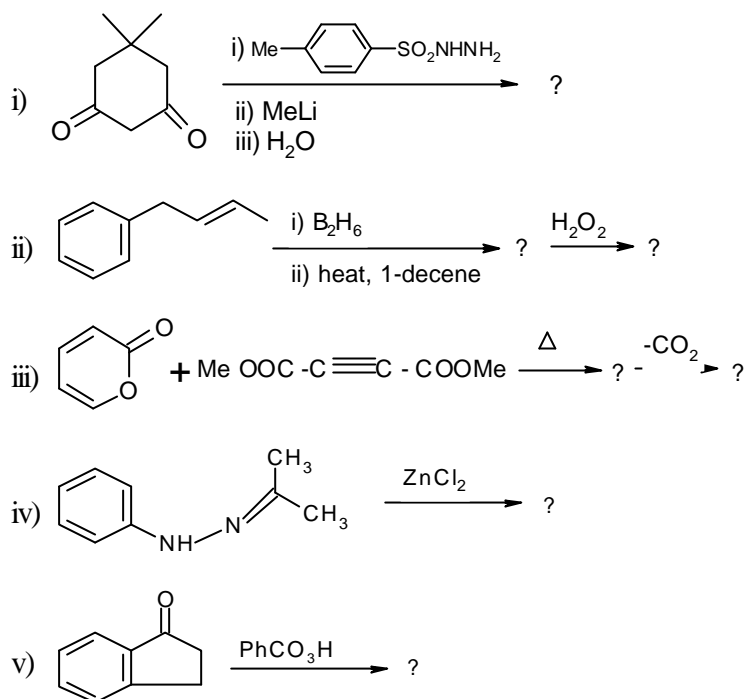
D) In the following transformation if migratory aptitude of p -tolyl group is 15.7 with respect to phenyl group, compute % composition of A and B.

4



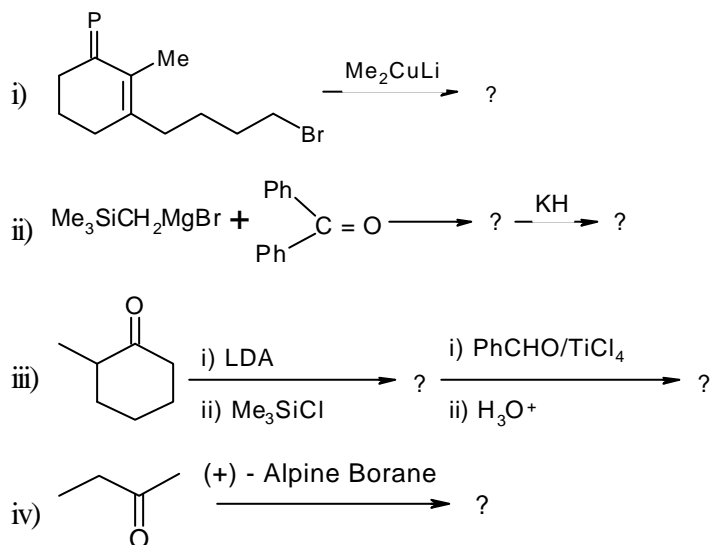
3. For the following, predict the products and name the reactions :

13



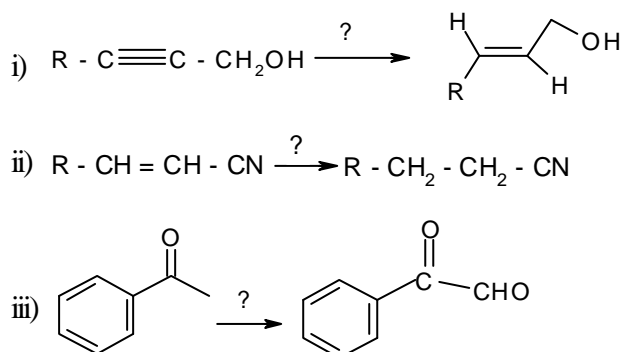
4. A) Predict the products in the following reactions :

8

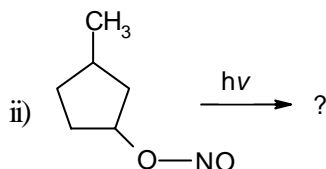
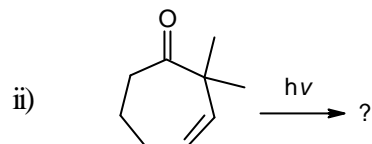
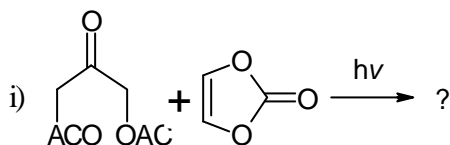


B) Indicate the appropriate reagents for the following conversions :

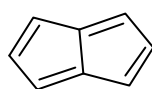
5



5. A) Predict the product and indicate the type of reaction for each of the following : 7

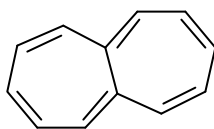


B) 1) Pentalene (I) is unstable even at -100°C . Explain. 2



I

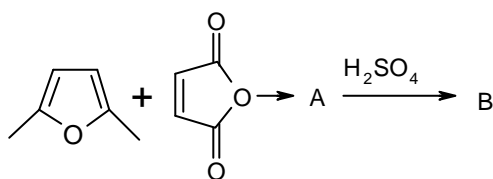
2) Heptalene (II) adds bromine and also reacts with acids. Explain. 2



II

3) Cyclooctatetraene reacts with potassium and forms a stable dianion. Draw the structure of the dianion and explain its stability. 2

6. A) Examine the following sequence of reactions :



1) Draw the structures of A and B. 2

2) Write the name of the first reaction. 1

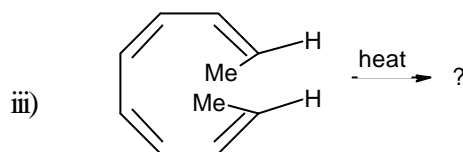
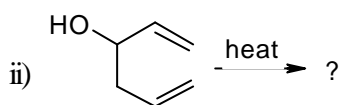
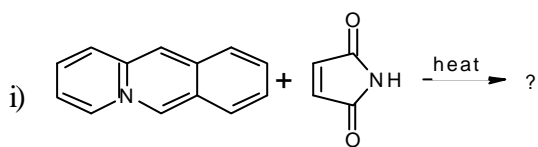
3) Indicate the preferred interaction (write 'Yes' after the selected interaction). 1

i) $\text{HOMO}_{\text{diene}} - \text{LUMO}_{\text{dienophile}}$:

ii) $\text{HOMO}_{\text{dienophile}} - \text{LUMO}_{\text{diene}}$:

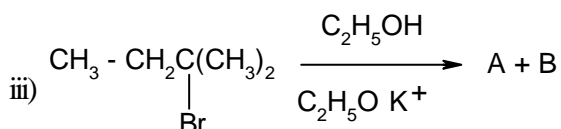
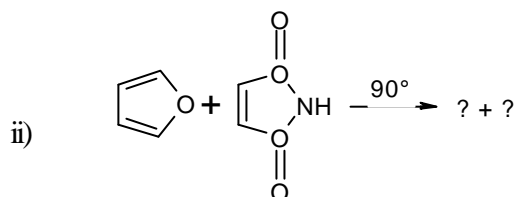
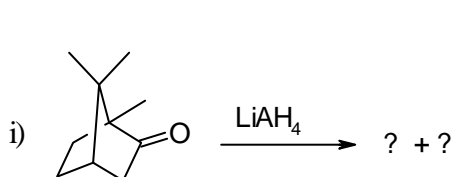
4) Show the preferred interaction using the FMO diagram.. 3

B) Predict the product and name the type of each of the following reactions : 6

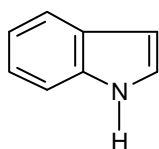


7. A) When the $^1\text{H NMR}$ spectrum of a compound is recorded on an instrument at 60 MHz a doublet ($J = 6\text{Hz}$) appeared at 2.5δ 6
- Calculate the shift of the signal from TMS in Hertz.
 - If the spectrum is recorded at 100 MHz, calculate the signal position in δ unit and in Hertz and line positions in Hertz.
 - The signal is due to a methylene group attached to an aromatic ring. If the methylene group is further substituted by a chlorine, will the peak shift to upfield or downfield ?

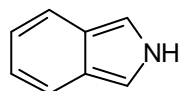
B) Give the products of the following reactions, indicating the major and minor isomers with proper stereochemistry : 7



8. Indole (I) and isoindole (II) are isomeric and have the following structures :



I

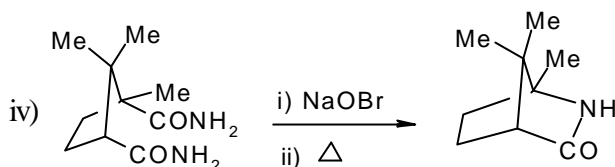
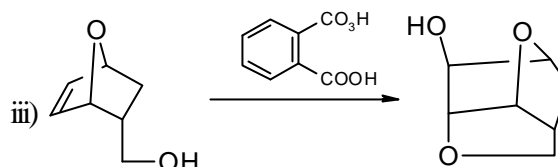
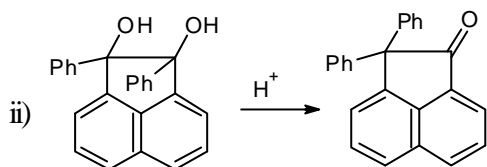
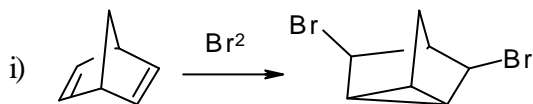


II

- Draw the resonance structures of both. 4
- Give the IUPAC names of both. 2
- One of these isomers is more stable. Which one is that isomer ? Why ? 2
- One of them undergoes Diels-Alder reaction. Which one is that isomer ? Why ? 2
- Indole-3-acetic is a plant growth regulator. Draw its structure and suggest its synthesis 3

9. Propose mechanisms for the following reactions :

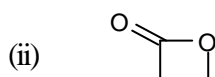
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10. A) 1) Draw the structures of the polymers of the following :

6

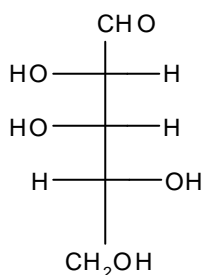
(i) Acrylonitrile



(iii) Ethylene + Propylene.

2) Draw the structures of the isotactic, syndiotactic and atactic forms of the polymer obtained from acrylonitrile.

B) 1) The structure of an aldopentose (I) is shown below :



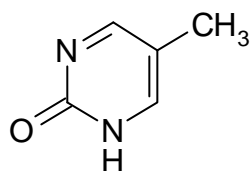
I

Draw the furanose forms of I.

2

2) In a nucleotide, a base is attached to the furanose sugar at C-1 through a β -Linkage, and a phosphate residues are attached to the C-3 and C-5 atoms. In a nucleotide of sugar I, base II is present. Draw the structure of such a nucleotide.

3



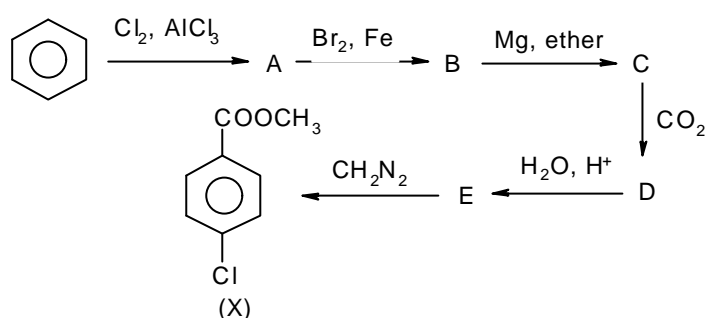
II

3) Name the bases present in DNA and RNA.

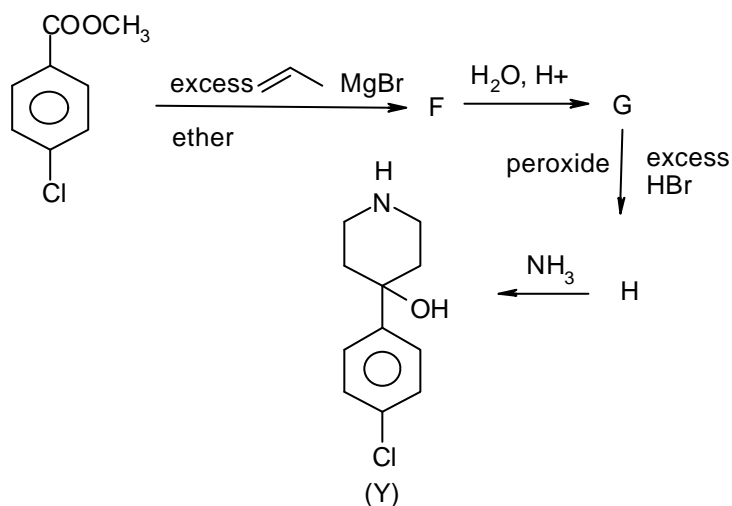
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11. Compound M is a powerful neuroleptic. The intermediates required for its preparation are prepared through the following sequences of reactions. Identify all the unknown compounds in these sequences. Compound M is prepared by condensing Y with Z. Identify the structure of M. 13

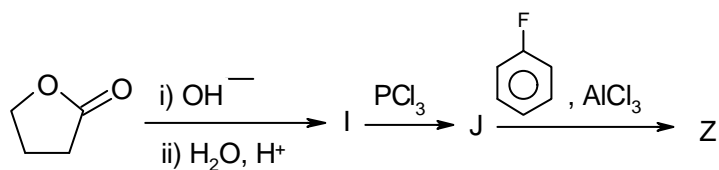
Sequence 1



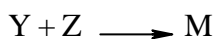
Sequence 2



Sequence 3

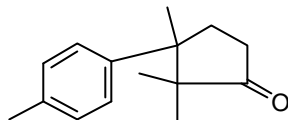


Preparation of M



12. A sesquiterpene has been assigned the following structure

13



Answer the following :

- i) How will you prove that it contains a cyclopentanone ring?
- ii) How many methyl signals will be observed in its PMR ?
- iii) How will you reduce it to the corresponding hydrocarbon ? Give the reaction involved.
- iv) What will be the product of base catalysed deuteration with an excess of D_2O ?
- v) Indicate the diastereotopic protons in the compound.
- vi) Give the structure of the product when the compound is treated with m- chloroperbenzoic acid.
- vii) Suggest a biogenetic pathway.

13. A) Assign structure to a compound based on the following data :

6

Molecular formula : $C_{10}H_{10}O_3$

U.V. : 275 nm (ϵ 20,000)

I.R. : 3250, 1660, 1605 cm^{-1}

P.M.R. (δ) : 1.49 (3H, *d*, $J = 6.5$ Hz),

2.60 (2H, *d*, $J = 6.5$ Hz), 4.57 (1H, sextet, 6.5 Hz)

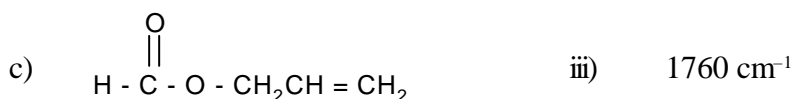
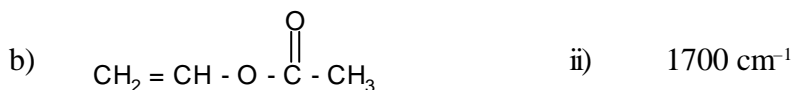
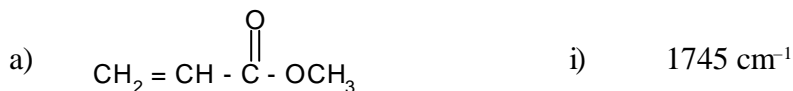
6.40 (1H, *d*, $J = 2$ Hz), 6.51 (1H, *dd*, $J = 8$ and 2Hz),

7.81 (1H, *d*, $J = 8$ Hz), 8.51 (1H, *s*, exchangeable with D_2O).

Compound gives violet colouration with $FeCl_3$ and forms oxime.

B) Match the I.R. carbonyl frequencies with the respective structures.

3

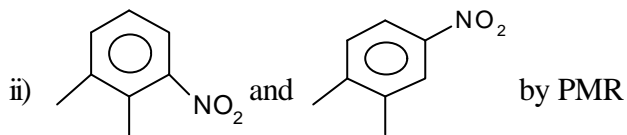
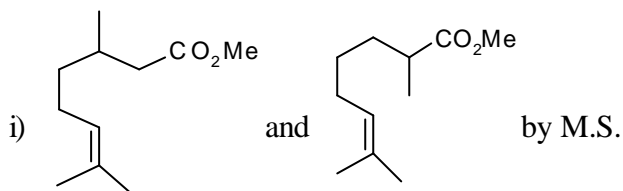


Ans. (a) (b)

(c)

C) Distinguish between the following pairs by the indicated spectral method :

4



14. A) Match the entries in column 'A' from those given below :

8

Column 'A'

Column 'B'

Secular equations

Zero point energy

Uncertainty principle

Commutator of $\hat{\alpha}$ and $\hat{\beta}$

Mulliken electronegativity

Hartree-Fock equation

2s orbital

Heitler-London covalent function

Entries for Column 'B'

$$\frac{[\phi_a(1)\phi_b(2)] + [\phi_a(2)\phi_b(1)]}{\sqrt{1+A}}$$

$$\frac{1}{2}h\nu_0$$

e^{-r}

$$\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}$$

$$\sum (H_{ij} - ES_{ij})C_j = 0$$

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{eff}} \right\} \phi_i = \epsilon_i \phi_i$$

$$\Delta x \Delta p_x \geq h/2$$

$$\hat{\alpha}\hat{\beta} + \hat{\beta}\hat{\alpha}$$

$$(I-2)/2$$

$$[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

$$(r-2)e^{-r/2}$$

B) The Maxwell distribution of speeds is given by

$$F(V)dv = 4\pi V^2 [m/(2\pi kT)]^{3/2} \exp[-mV^2/(2kT)].dV$$

Show that the most probable speed equals $(2kT/m)^{1/2}$. 5

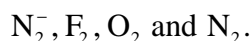
15. A) Which of the following are eigen functions of the operator $\frac{d^2}{dx^2}$? Give your reasons. 8

(i) e^{ikx} (iii) $\cos(kx)$

(ii) e^{-x^2} (iv) $kx - \frac{kx^2}{2}$

B) Make a qualitative sketch of ψ_3 and ψ_3^2 for a particle in a one-dimensional box $|0 \leq x \leq 1|$. 5

16. A) Arrange the following molecules in order of decreasing bond energy.



Give your reasoning briefly. 8

B) The HMO energies of butadiene are $\alpha \pm 1.618\beta$ and $\alpha \pm 0.618\beta$. Calculate the delocalization energy of butadiene. 5

17. A) The vibrational contribution to the internal energy is given by

$$E_v = RT \frac{x}{e^x - 1}$$

Where $x = hcw/kT$ (usual notations used). Show that the corresponding contribution to heat capacity

is $R \cdot \frac{e^x \cdot x^2}{(e^x - 1)^2}$ 8

B) Find the missing entries in the character table of C_{2v} group produced below (partly). 5

C_{2v}	E	C_2	σ_v	U
A_1	1	1	1	X
A_2	1	1	-1	Y
B_1	1	-1	Z	-1
B_2	1	W	-1	1

18. A) State the conditions under which Clausius-Clapeyron equation is valid.

Explain how this equation can be utilised for determination of heat of vaporisation of a liquid [No derivation is required]. 8

B) 1.80% solution of glucose was found to be isotonic with 5.96% solution of raffinose. Calculate the molecular weight of raffinose (Mol. wt. of glucose = 180). 5

19. A) Write down the expression for Langmuir's monolayer adsorption isotherm stating the significance of the terms. [No derivation is required]. Show that at low pressures the expression leads to the result

- that adsorption is directly proportional to pressure. 8
- B) Why is heat of adsorption always negative ?
- C) Explain how charcoal in vacuum line cooled with liquid nitrogen helps in achieving high vacuum. 5
20. A) State with reason which one of the following pair of isotopes is more stable 4
 ^{15}O , ^{16}O
- B) List isotopes, isobars and isotones in the following nuclides. 6
- C) What is the mean deviation when the counts of a radioactive sample registered is 10,000 counts per minute ? 3
21. A) Mention any *three* methods of determining molecular weights of polymers. State in each of the methods whether weight average or number average molecular weight is determined. 6
- B) Define turbidity. What happens to turbidity with increasing polymer concentration? 7
22. A) The partial molar volume of an aqueous solution of NaCl is given by :

$$V_{(\text{ml})} = 1001.38 + 16.6253 n^2 + 1.7738 n_2^{1.5} + 0.1194 n_2^2$$
 Where n^2 is the molarity of NaCl. Calculate the partial molar volume of NaCl when its molarity $n_2 = 0.04$. 7
- B) CaCO_3 is heated in a closed vessel so that it partially decomposes to give CaO and CO_2 . State the number of components present in the system and calculate the number of degrees of freedom. 6
23. A) The rate constant of a reaction was measured as a function of temperature with the following results:
- | | | |
|---------------------------------|-------|------|
| T/k | 500 | 550 |
| k/ $\text{M}^{-1}\text{s}^{-1}$ | 0.035 | 0.35 |
- Estimate the energy of activation, E_a . Assume $R = 8.0 \text{ JK}^{-1} \text{ mol}^{-1}$. 7
- B) 1.6 g of oxygen undergoes free expansion from 1l to 10ℓ at 298 K. Calculate ΔS_{sys} and ΔS_{univ} . Assume $R = 8.0 \text{ Jk}^{-1} \text{ mol}^{-1}$. 6
24. One electrode of the Weston standard cell is a 12.5% cadmium amalgam in a saturated solution of cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) and the other electrode consists of mercury and solid mercurous sulfate in the same solution. Represent the cell in the usual notation, write the cell reaction and estimate its EMF. $E^0(\text{Hg}_2\text{SO}_{4(\text{s})}|\text{Hg}) = +0.6141 \text{ V}$ and $E^0(\text{Cd SO}_{4(\text{s})}|\text{Cd-Hg}) = -0.4042 \text{ V}$. 13
25. Reflections from a cubic crystal are recorded on a diffractometer using CuK_α X – rays (wavelength

154 pm). The first order reflection from (111) planes occurs at $10^\circ 59'$. Calculate the cell dimension.
 $\sin(10^\circ 59') = 0.191$. 13

26. A) Discuss the following : 5
- (i) Thermodynamic defects in stoichiometric compounds. 4
 - (ii) Structure of perovskite. 4
- B) Why does AgBr predominantly exhibit Frenkel defect ? 4
27. A) Discuss in brief the use of lanthanides as shift reagents in NMR spectroscopy. 5
- B) Of the trivalent lanthanide ions only Gd^{3+} shows magnetic moment in agreement with that calculated from spin only formula. Explain. 4
- C) Explain why both Sm^{3+} (f^5) and Dy^{3+} (f^9) exhibit yellow colour. 4
28. A) What are Silicones ? Give preparation and properties of silicones. 7
- B) What are Ultramarines ? 4
- C) Why is borazine called as “Inorganic Benzene”? 2
29. A) Give reasons : 8
- (i) Trisilylamine is less basic than trimethylamine.
 - (ii) Thallium, a group IIIA element of the periodic table, exhibits properties similar to alkali metals.
- B) Write a note on “Fluorocarbons”. 5
30. A) What is superphosphate ? Give its preparation and use. 4
- B) Describe the synthesis and explain the structure of phosphazene. 5
- C) Give the structures of elemental sulphur and phosphorous. 4
31. A) Which of the following statement is/are correct ? Give reasons for your answers : 6
- i) The values of molar extinction coefficients of d-d bands are the same for $CS_2[CoCl_4]$ and $[Co(H_2O)_6]SO_4$.
 - ii) The electronic spectral bands of transition metal compound are broader than those of lanthanide compounds.

- iii) The complex $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2$ has a pale pink colour attributed to the spin forbidden transitions.
- B) How are cis- and trans - isomers of $[\text{PtCl}_2(\text{NH}_3)_2]$ complex synthesized from $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{PtCl}_4]^{2-}$? 4
- C) A single absorption peak is observed at 9000 cm^{-1} for CCl_4 complex. What will be your estimate of Δ for a V(IV) complex in an octahedral symmetry ? 3
32. A) How will you distinguish between the following isomers ? 5
- $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{CoSO}_4(\text{NH}_3)_5]\text{Br}$
 - Cis and trans $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
- B) The complex ion $[\text{CuCl}_4]^{2-}$ exists but $[\text{CuI}_4]^{2-}$ does not. Explain 2
- C) Draw all the isomers of a complex of the type $\text{M}(\text{abcd e e})$ where e e is a bidentate ligand. 6
33. A) Orbital angular moment is quenched when $3d$ metal ions are complexed. Explain. 4
- B) Discuss the electronic spectrum of square pyramidal $[\text{VO}(\text{EDTA})]^{2-}$ complex, which exhibits three bands at 12800 cm^{-1} ($\epsilon = 23.2\text{ mol}^{-1}\text{ cm}^{-1}$); 17200 cm^{-1} ($\epsilon = 19\text{ mol}^{-1}\text{ cm}^{-1}$) and 29800 cm^{-1} ($\epsilon = 22\text{ mol}^{-1}\text{ cm}^{-1}$). 5
- C) Which d^1 configurations in octahedral symmetry show spin crossover behavior in coordination compounds ? Why ? 4
34. A) What is ferrocene ? Give structure and discuss the bonding in ferrocene on the basis of molecular orbital treatment. 6
- B) What is hapticity ? Explain the classification of organometallics based on hapticity system. 3
- C) Assuming the 18-electron rule to be valid, predict the number of metal-metal bonds in $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ on the basis of valence electron count. 4
35. A) i) Define the terms “exclusion limit” and “permeation limit” in size exclusion chromatography (SEC). 3
- The retention volume of naphthalene (mol. wt. 128) on SEC column was 124 mL. A gel column had an exclusion limit of 80,000, while a protein of molecular weight 1,20,000 had a retention volume of 15 mL on the same column. Assuming that naphthalene has molecular weight less than permeation limit of the gel, calculate the total pore volume and distribution coefficient of a sample which has a retention volume of 52 mL. 5

- B) Discuss the role of chelating agent in solvent extraction technique. 5
36. A) Discuss the characteristics of cyclic voltammogram of $K_3[Fe(CN)_6]$. 4
- B) Differentiate between the following :
- i) Specific conductance and equivalent conductance. 3
 - ii) TGA and DTA. 3
- C) What are the WCOT and FSOT columns in GLC ? 3
37. A) Identify one significant role for the following elements in the biological processes : 10
- i) Fe; ii) Mn;
 - iii) Cu; iv) Zn, v) Mg.
- B) Why is iron used as its EDTA complex, rather than in the form of a simple salt, for supplying iron to plants in basic soils ? 3