

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 :

Elemental analysis : C, 55.8; H, 7.0%

I.R. 1765, 1635, 1380, 1220, 985, 950, 880 cm^{-1}

M.S. (m/z) : 86 (M^+), 43, 27.

PMR (δ) : 2.1 (3 H, s), 4.45 (1 H, dd, J = 9 and 3 Hz)

4.8 (1 H, dd, J = 16 and 3 Hz), 7.2 (1 H, dd, J = 16 and 9 Hz)

B) Assign the structure based on the following data :

Molecular formula : $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$

I.R. : 1605, 1530, 1350 cm^{-1}

M. SI (m/z) : 168 (M^+), 152, 122, 92, 76.

PMR (δ) : 7.90 (5 mm, t, J = 8.5 Hz.)

8.65 (10 mm, dd, J = 8.5 and 2 Hz),

9.00 (5 mm, t, J = 2 Hz)

C) Determine the number of EPR spectral lines that would be expected for each of the following ions.

Assume the unpaired electron is coupled only to the single nucleus.

(i) $^{63}\text{Cu}^{+2}$

(ii) $^{55}\text{Mn}^{+2}$

Given : I for $^{63}\text{Cu} = \frac{3}{2}$

I for $^{55}\text{Mn} = \frac{5}{2}$

D) Explain the following Mossbauer spectral observations :

	Compound	δ , mm/S	ΔE_Q , mm/S
(i)	FeF_3	0.489.....	0.0
(ii)	FeF_2	1.48	2.92

E) What is Stark effect ? Explain its importance.

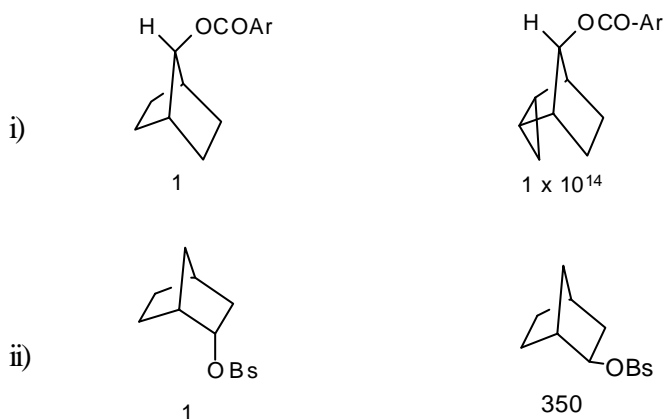
- F) C_2N_2 linear symmetric molecule, exhibits rotational Raman spectrum with alteration in line intensity
 2 : 1 for
 $C_2^{14}N_2$ and 3 : 1 for $C_2^{15}N_2$.
 Explain why ?

2. A) Account for the following observations : 4
- (i) Sigma (σ) ortho constants of general applicability are not available.
 (ii) The rho (ρ) value is influenced by changes in solvent polarity.

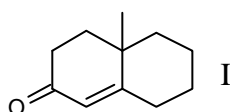
- B) The ρ value for the alkaline hydrolysis of methyl benzoate is 2.39 and $k_H = 2 \times 10^{-4} \text{ l mol}^{-1} \text{ sec}^{-1}$.
 Calculate the rate for the hydrolysis of m-Me substituted ester ($\sigma_{m-Me} = -0.07$)

(Use the relation $\log \frac{k_{m-Me}}{k_H} = \rho \cdot \sigma_{m-Me}$) 3

- C) Explain the difference in rates of solvolysis of the following molecules : 6

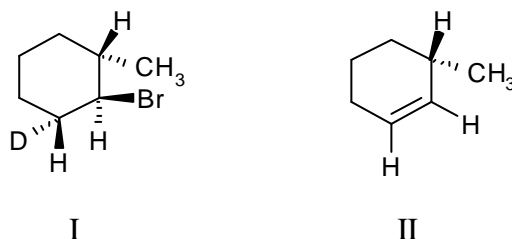


3. A) Propose a synthetic scheme for the preparation of I from cyclohexanone. 6

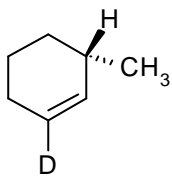


- B) Draw the stereostructure of cis-syn-trans perhydrophenanthrene. 3

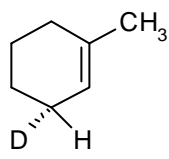
- C) 1) Compound I on treatment with sodium methoxide in methanol forms only II.
 Draw the chair form of I and explain the formation of II. 2



- 2) Explain the observation that III and IV are not formed in the above reaction. 2

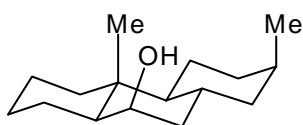


III

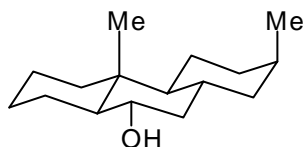


IV

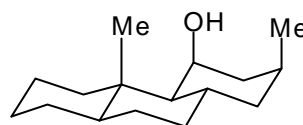
- 4 A) Arrange the following alcohols in decreasing order of reactivity towards chromic acid oxidation and justify the order. 4



1

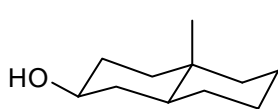


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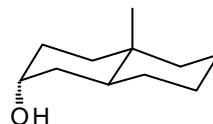


3

- B) In the conversion of I to II, reagents are, perbenzoic acid, heat (200°); LiAlH₄; AC₂O;



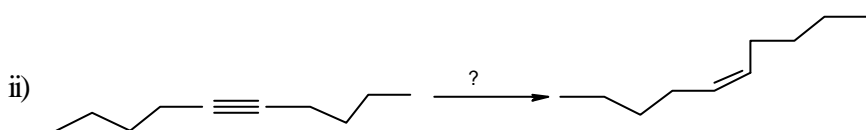
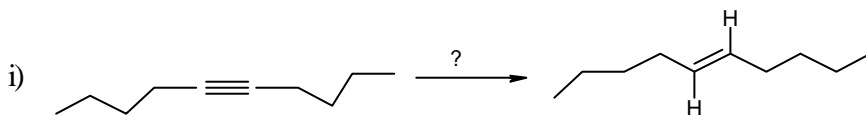
I



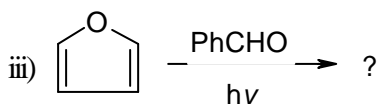
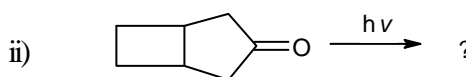
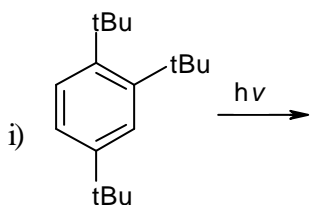
II

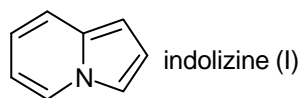
- Arrange the reagents in appropriate order and rewrite the reaction sequence. 6

- C) Write the proper reagents and name of the reaction for the following conversions : 3

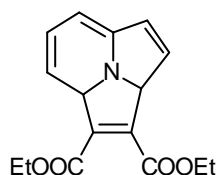


5. A) Predict the product/s and indicate the type of reaction and mechanism for each of the following : 6

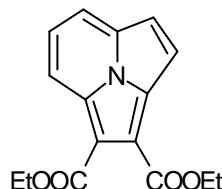




- 1) Explain the aromaticity of I.
- 2) I reacts with diethyl acetylene dicarboxylate(II) to give III, which on treatment with Pd/C gives IV.



III

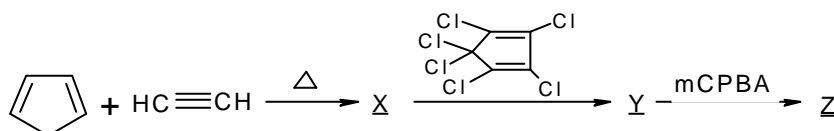


IV

Explain the reaction between indolizine and II.

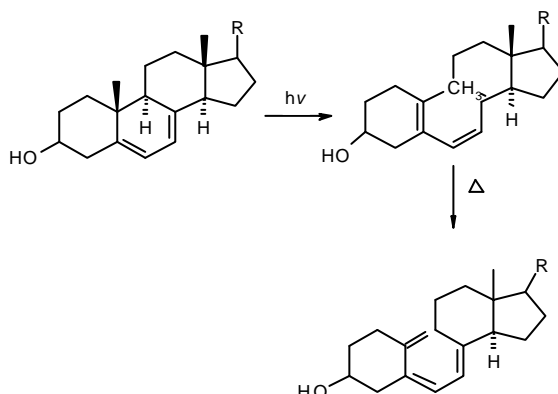
- 3) Are III and IV aromatic ?
 - 4) Explain the aromaticity of III/IV.
6. A) i) Draw the structure of 2E, 4Z, 6Z, 8E-decatetraene. 5
- ii) Will the thermal ring closure of the above compound be conrotatory or disrotatory?
 - iii) Give the structure of the product with proper stereochemistry.
 - iv) Under photochemical condition, will the ring closure of the above compound be con- or disrotatory?
 - v) Give the structure of the product with stereochemistry.

B) In the following reaction sequence, predict the structures of X, Y and Z. 5



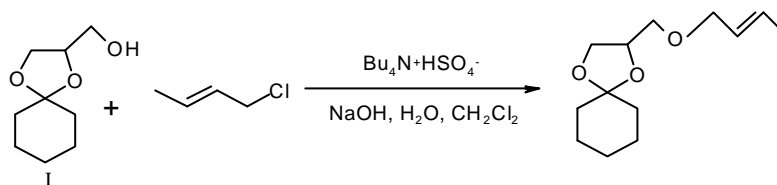
Identify the reactions involved in the above sequence.

C) Identify the pericyclic reactions involved in the following sequence with mechanism 3



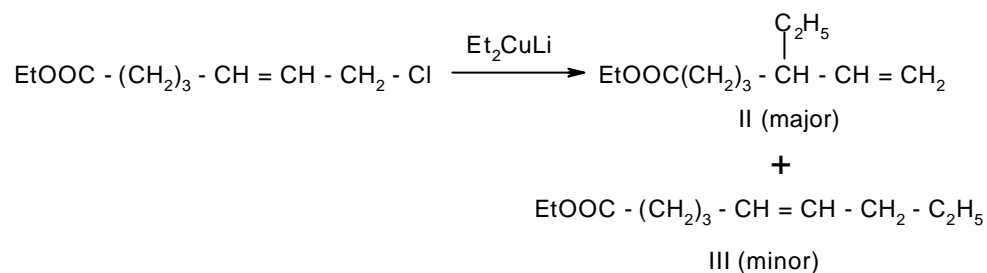
7. A) Study the following reaction and answer the following questions :

7

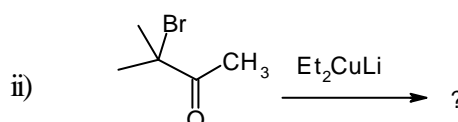
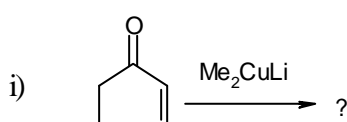


- 1) Under which conditions compound I is stable and under which unstable ?
- 2) Is the reaction homogeneous or heterogeneous ?
- 3) What kind of reagent $\text{Bu}_4\text{N}^+\text{HSO}_4^-$ is ?
- 4) Comment on the solubility of $\text{Bu}_4\text{N}^+\text{HSO}_4^-$ in organic solvents and in water.
- 5) What is the role of $\text{Bu}_4\text{N}^+\text{HSO}_4^-$ in the above reaction ?

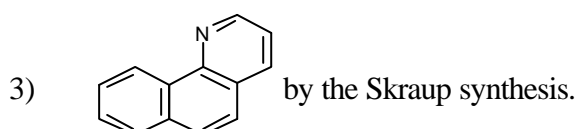
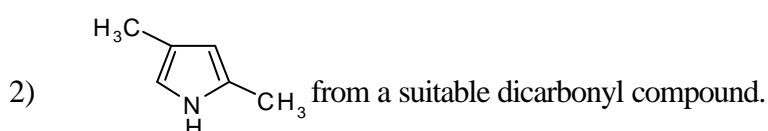
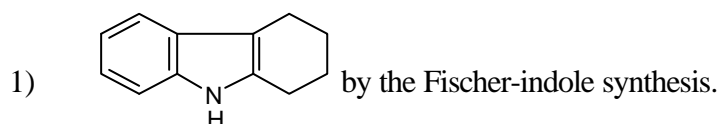
B) Lithium dialkyl cuprates (R_2CuLi) are called Gilman reagents. Study the following reaction and answer the following questions :



- 1) How is Et_2CuLi prepared ?
- 2) What is the mechanistic type to which the above reaction belongs ?
- 3) Why is II formed in more amount than III ?
- 4) Draw the structures of the products of the following reactions :

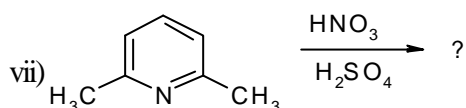
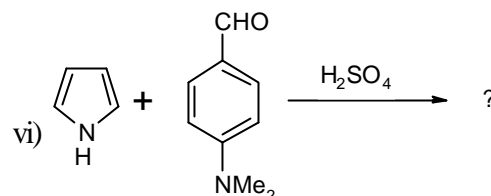
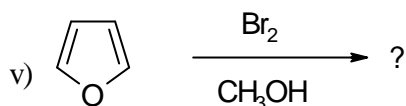
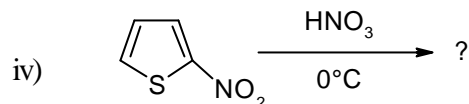
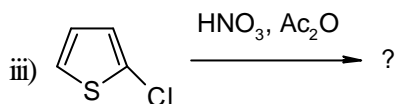
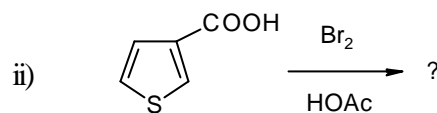
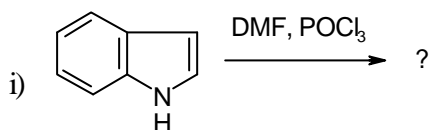


8. A) How will you prepare the following heterocycles ?

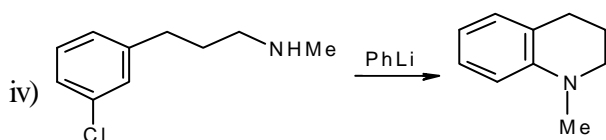
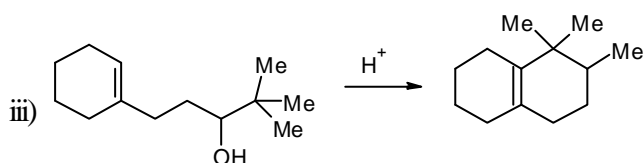
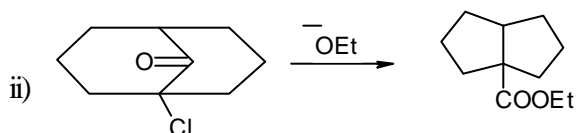
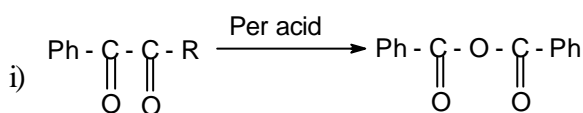


B) Draw the structures of the products of the following reactions :

7

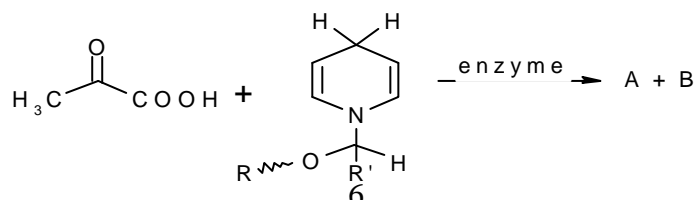


9. Propose the mechanisms for the following reactions and name the reactions involved in each case : 13



10. A) What is a chain polymerization reaction ? Give a suitable example and derive an expression for the degree of polymerization. 7

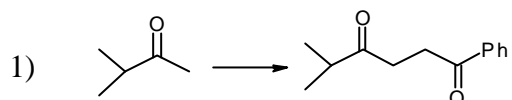
B) 1) NADH is nature's reducing agent. Explain the reduction of pyruvic acid. Write the structures of A and B. 2



- 2) Draw the structures of adenine (A), thymine (T), cytosine (C) and guanine (G). Show H-bonding in appropriate base pairs.

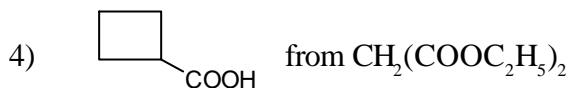
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11. How will you achieve the following transformations ?

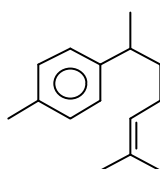


2) 2-Ethylhexanol from acetaldehyde.

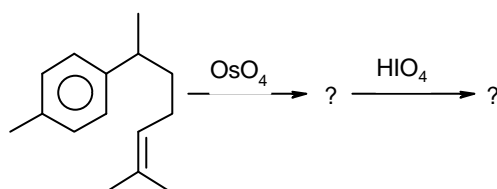
3) 3, 5-Dibromotoluene from 4-nitrotoluene.



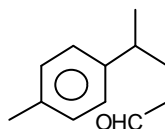
12. Study the structure of the natural product given below and answer the following :



- 1) To what class/subclass of natural products does it belong ? 2
- 2) Propose a biogenetic pathway for the same. 3
- 3) What will be the structure of the product formed when it is treated with anhydrous aluminium chloride ? 2
- 4) Give structures of the products in the following degradation sequence : 2



- 5) Propose a scheme for the synthesis of the same from the intermediate given below : 2

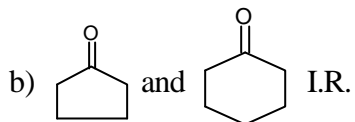
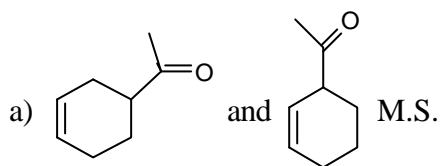


- 6) Give retrosynthetic analysis. 2

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

Elemental analysis	:	C, 80.0; H, 6.7%
I.R.	:	1605, 1250, 1200, 760, 695 cm^{-1} .
M.S. (m/z)	:	120 (M^+), 119, 91, 77, 65, 51
P.M.R. (δ)	:	2.65 (1H, <i>dd</i> , J = 8 and 2 Hz) 2.90 (1H, <i>dd</i> , J = 6 and 8 Hz) 3.70 (1H <i>dd</i> , J = 6 and 2 Hz) 7.22 (5H, S).

B) Distinguish the following pairs by the indicated spectral method.



c) A compound has the following important ions in its M. S. Assign structure if the I.R. spectrum shows carbonyl absorption. Explain formation of ions.

m/z : 120 (m^+), 105, 77

3

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

8

Column A

Column B

- a) Wave particle duality
- b) Correspondence principle
- c) 2p orbital
- d) Expectation value
- e) Lowering of symmetry
- f) Specific heats of solids
- g) Hermitian operator
- h) Slater' rules

Entries for column B :

$$\left\langle \frac{Zr}{a_0} \right\rangle e^{-Zr/2a_0} \cdot \cos\theta$$

$$\lambda = h / p$$

$$\int \psi^* \hat{A} \psi dt = \int \psi \hat{A}^* \psi^* dt$$

Einstein

effective nuclear charge

real eigenvalue

equivalence of quantum and classical mechanics

Jahn Teller distortion

Exclusion principle

perturbation theory

determinantal wave function

B) Fill the missing entries X, Y, Z, W in the character table of C_{4u} point group product below (partly)

5

C_{4u}	E	$2C_4$	C_2	$2\sigma_y$	σ_d
A_1	1	1	1	1	1
A_2	1	1	1	-1	X
B_1	1	-1	1	Y	-1
B_2	1	-1	Z	-1	1
E	W	0	-2	0	0

15. A) The radial part of 2s hydrogenic orbital is given by

$$R_{2s} = N \left(1 - \frac{Zr}{a_0} \right) e^{-Zr/a_0}$$

$$\text{With } N^1 = \frac{1}{\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2}$$

(in usual notations)

Calculate the most probable distance of an electron in the radial distribution of this orbital.

8

B) The multiplicity of every term of an atom with an odd number of electron must be an even number.

True or false ? Explain your answer. Give illustration.

5

16. A) Use $x(1-x)$ as a trial function for the particle in a 1D box with $0 \leq z \leq 1$. Estimate the ground state energy using the variational method (Assume $V = 0$ inside the box and $V = \infty$ outside the box).

8

B) Calculate the molar residual entropy of a crystal in which the molecule can adopt 6 orientations of equal energy at 0 K.

5

17. A) The HMO of butadiene are :

$$\psi_1 = 0.3755 (\phi_1 + \phi_4) + 0.6070 (\phi_2 + \phi_3)$$

$$\psi_2 = 0.6070 (\phi_1 - \phi_4) + 0.3755 (\phi_2 - \phi_3)$$

$$\psi_3 = 0.6070 (\phi_1 + \phi_4) - 0.3755 (\phi_2 + \phi_3)$$

$$\psi_4 = 0.3755 (\phi_1 - \phi_4) - 0.6070 (\phi_2 + \phi_3)$$

Sketch schematically the four π MO's in butadiene.

8

B) For SF_6 which of the following pairs of operators commute ?

5

(a) $C_4(z)$ and σ_h

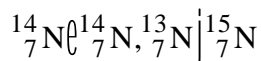
(b) σ_h and $\sigma(yz)$

Explain your answer.

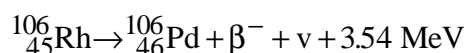
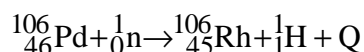
18. A) A substance has hydrophobic and hydrophilic moieties in the same molecule. How does its dissolution in water and in non-aqueous solvents differ from those of typical ionic substances ? 6

B) The rotational spectrum of HCl molecules shows the rotational lines are equally separated by 20.70 cm^{-1} . Calculate internuclear bond length. 7

19. A) Using Bethe's notation identify various isotopes of the following reaction : 6



B) Consider the following nuclear reactions :



Given the masses of neutron and proton are 1.008665 and 1.007825 amu, calculate Q value for the net reaction. 7

20. A) (i) Derive : $\left(\frac{\partial \epsilon}{\partial \sqrt{\lambda}} \right)_T = T \left(\frac{\partial P}{\partial T} \right) - P$

(ii) Derive : $\left(\frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left(\frac{\partial H}{\partial P} \right) - V$

B) Prove the relation for entropy change of mixing two ideal gases A and B at constant temperature :

$$\Delta S_{\text{mix}} = -nR [x_A \ln x_A + x_B \ln x_B] \quad 5$$

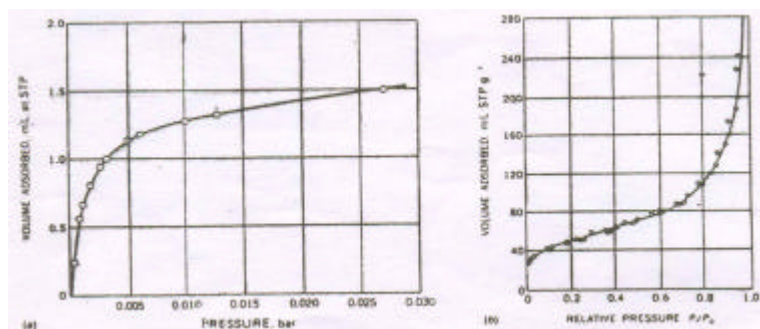
21. A) Explain how the entropy changes in the system and the surroundings occur in 8

- (i) reversible isothermal expansion
- (ii) irreversible isothermal expansion
- (iii) reversible adiabatic expansion
- (iv) irreversible adiabatic expansion

B) Calculate entropy change per mole of mono atomic gas, at constant pressure for a change in temperature from 27 to 127°C. (Assume that gas is ideal with a temperature independent C_p of 5 $\text{cal K}^{-1} \text{mol}^{-1}$). 5

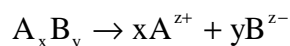
22. A) A system of 'C' components consisting of 'P' number of phases is at equilibrium. If 'f' are the degrees of freedom of such a system, derive a relationship between C, P and F. 5

- B) The data for adsorption isotherm for H₂ on Cu powder and for N₂ on silica at 25°C are shown in Figures (a) and (b) respectively below. How one tests the validity of Langmuir's adsorption to such data ? Which data correspond to Langmuir isotherm and how ? 8



23. A) The standard electrode potentials of the electrodes Cu²⁺/Cu and Ag⁺/Ag are 0.337 and 0.799 V. What would be the concentration of Ag⁺ in a solution containing 0.06 M Cu²⁺ ion when both the metals are deposited together. Assume that both silver and copper do not dissolve among themselves and activity coefficients are unity. 5

B) An electrolyte AB dissociates as



Relate the activities of respective ions, a_{\pm} to total activity, a and activity coefficients, γ_{\pm} to molality, m of KCl and CaCl₂ solutions. 8

24. What are unimolecular reactions ? Demonstrate that the order of unimolecular reaction changes from one to two when pressure is decreased. 13
25. A) Distinguish between chain polymerization and stepwise polymerization. Write in brief about kinetics of linear step reaction in condensation polymerization. How a chemist controls, the molecular weight of products in such reactions ? 8

B) 5.0 g of polymer of molecular weight 50.0 kg. mol⁻¹ is dissolved in 1 dm³ of water. If the density of this solution is 0.96 kg-dm⁻³, calculate the height of water that will represent the generated osmotic pressure. 5

26. A) Describe the thermodynamic defects that occur in stoichiometric compounds. 5
- B) Discuss the F-centres in non-stoichiometric compounds, citing a few examples. 4
- C) Calculate radius ratio $r_{A^{+}/r_{B^{-}}$ for A⁺ ion to fit in a simple cubic lattice of B⁻ ions. 4

27. A) What makes borax a useful primary standard in quantitative analysis? Give a balanced equation, representing the reaction involved in the titration of borax. What indicator will you use in such a titration ? 6
- B) Explain :
- (i) BF_3 has no net dipole moment whereas NF_3 has. 7
- (ii) Borazine is more reactive than benzene towards addition of HX. 7
28. A) Draw the structures of the ring silicates $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$. 5
- B) Discuss the structure of Talc. 4
- C) Why are zeolites used as molecular sieves ? 4
29. Discuss the structure and bonding in :
- a) Sulphuric acid and thiosulphuric acid. 4
- b) Tetrasulphur tetranitride (S_4N_4). 4
- c) Chlorine trifluoride (ClF_3) and triiodide ion (I_3^-). 5
30. A) Compare and contrast the electronic spectra of the complexes of lanthanides and 3d-transition metal ions. 7
- B) Work out the spin-only magnetic moment for the following ions :
- (i) La^{3+} (ii) Ce^{3+} (iii) Eu^{3+}
- Given : At. no., La = 57, Ce = 58, Eu = 63. 6
31. A) Draw the Orgel diagram for d^2 configuration in both octahedral and tetrahedral environments. On the basis of these diagrams, predict electronic transitions in corresponding complexes. 5
- B) Explain with the help of suitable examples how you would differentiate between the tetrahedral, square planar and octahedral geometries of Ni^{2+} complexes on the basis of their magnetic properties. 5
- C) Amongst the octahedral complexes of the following ions, which ones do not show Jahn-Teller distortion in the ground state ? 3
- (i) Cu^{2+} (ii) Ti^{3+} (iii) $\text{Mn}^{3+}(\text{h.s.})$
32. A) Rationalize the fact that Δ_0 (or $10 Dq$) increases in order : 5
- hexaquo cobalt (II) < hexaquo cobalt (III) < hexaquo rhodium, (III).

- B) Construct the *d*-orbital splitting diagram and write *d* electron configuration (as t_{2g}^m, e_g^n , where *m* and *n* are integers) for the following :
- (i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ 4
- C) Draw the structures of all possible isomers of $[\text{O}_s(\text{b}_{\text{py}})_2\text{Cl}_2]$, where $\text{b}_{\text{py}} = 2$, 2-bipyridine. 4
33. A) Provide the mechanism involved in the base catalyzed hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. 6
- B) Give an example for each of the following reactions : 4
- (i) Oxidative addition (ii) Reductive elimination.
- C) What are fluxional molecules ? Give two examples of fluxional molecules. 3
34. A) Explain why Mn does not form a mononuclear carbonyl. What is the structure of $\text{Mn}_2(\text{CO})_{10}$? Suggest a method to confirm its structure. 6
- B) Eventhough N_2 is isoelectronic with CO fewer examples of compounds of N_2 are known as compared to the number of metal carbonyls. Explain. 4
- C) What is the formula for a Grignard reagent ? How are Grignard reagents synthesized? 4
35. A) Differentiate between the following :
(with reference to chromatography)
- (i) Capacity factor and selectivity factor. 2
- (ii) Retention time and dead time. 2
- B) How do gas-liquid and gas-solid chromatography differ ? 3
- C) (i) Define : Ion exchange capacity of a resin. 2
- (ii) In partition chromatographic analysis of an organic compound, the solvent front was 18 cm while the front due to compounds X, Y, Z and W were 16.6, 14.3, 10.2 and 5.7 cm respectively. If the R_f value of unknown compound was 0.79, identify the compound. 4
36. A) Differentiate between the following :
- (i) DTA and DSC 4
- (ii) Voltammetry and amperometry. 4

B) A thermal curve of a 125.70 mg sample that contained a mixture of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (mol. wt. 146.12) and a thermally stable salt had a mass loss Δm of 6.98 mg at an onset temperature of about 140°C corresponding to vaporization of water. Determine the percentage (W/W) of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in the sample. (Given : mol. wt. of $\text{H}_2\text{O} = 18$) 5

37. A) Explain : "It is the ligand that is involved in the electron transfer in chlorophyll whereas it is the metal that is involved in oxygen transfer in Haemoglobin/Myoglobin." 7

B) Discuss the differences between $2\text{S}, 2\text{Fe}$ and $4\text{S}, 4\text{Fe}$ cubanes. 6