

CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

Note : Attempt question **one** and **fourteen** other questions.

1. Attempt any three of the following : 6
- A) Assign structure to the molecule having molecular formula C_8H_{10} . Assign the signals.
 IR : 3000 – 2900, 1900, 1500, 1430, 1400, 750, 690 cm^{-1} .
 NMR : 7.4 δ (m, 5H); 2.6 δ (q, J=7 Hz, 2H); 1.0 δ (t, J=7 Hz, 3H).
- B) Deduce the structure of the molecule having molecular formula C_3H_6O . Assign the signals. 6
 IR : 2720, 1720 cm^{-1} .
 NMR : 0.9 δ (t, J=6 Hz, 3H); 2.4 δ (dq, J=2 & 6 Hz, 2H); 9.7 δ (t, J=2 Hz, 1H).
- C) The fundamental vibrational frequency of A_2 is 4400 cm^{-1} . Assuming that the atomic mass of B is double that of A, estimate the fundamental vibration frequencies of AB and B_2 . 6
- D) State, with brief reasoning, which of the following molecules can show a pure rotational spectrum CO_2 , OCS, N_2 , ethylene, benzene, water.
 Which of the above molecules can show a vibrational spectrum ? 6
- E) The absorption spectrum of $[Co(NH_3)_6]^{3+}$ ion shows two bands which are assigned to the spin allowed transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. Comment on the changes in the absorption spectrum by the replacement of one of the ammonia molecules by Cl. 6
- F) The sulphate ion (T_d symmetry) shows two IR bands, one (ν_3) at 1104 cm^{-1} and the other (ν_4) at 613 cm^{-1} . How many bands will be observed in the IR spectrum of the complex $[Co(NH_3)_5OSO_3] Br_2$ (Symmetry Co_{3v}) containing co-ordinated sulphate ? Explain. 6
2. a) What are the $\langle \hat{L}^2 \rangle$ and $\langle \hat{L}_z \rangle$ values for 2p electron ? 5
- b) Calculate $\langle \hat{P}_x \rangle$ for a particle in a box $0 \leq x \leq 1$ in a state $\psi_1 = \sqrt{2} \sin(\pi x)$. 8
3. Explain briefly the following terms (with an equation and/or diagram, if required) 4
- i) First order perturbation theory.

- ii) Hermitian operator 2
- iii) Degeneracy 2
- iv) Variation theorem. 2
- v) Born-Oppenheimer approximation 2

4. a) Sketch the following bonding π MO's for benzene qualitatively. 6

$$\psi_1 = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_2 = \frac{1}{2\sqrt{3}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\psi_3 = \frac{1}{2} (\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

- b) Compute the MO energies corresponding to the MO's above 7

[Hint : $\epsilon_i = \int \psi_i^* \hat{H} \psi_i dt$. Use Huckel approximation]

5. Work out a table of microstates and term symbols for an atomic $s^1 p^1$ configuration. Identify the ground state term symbol. 13

6. a) How many degrees of freedom for vibrational motion are there for 6
- i) CO_2
 - ii) H_2O molecules ?

- b) The moment of inertia of a diatomic molecule is $1.44 \times 10^{-47} \text{ kg m}^2$. Its reduced mass is 10^{-27} kg . What is its bond length in picometers ? 7

7. Work out thermodynamic relationships. $s^1 p^1$ configuration. 13

$$\Delta G^\circ = \Delta H^\circ + \left(\frac{dE^\circ}{dT} \right)_p \quad \text{Where } E^\circ \text{ is standard e.m.f.}$$

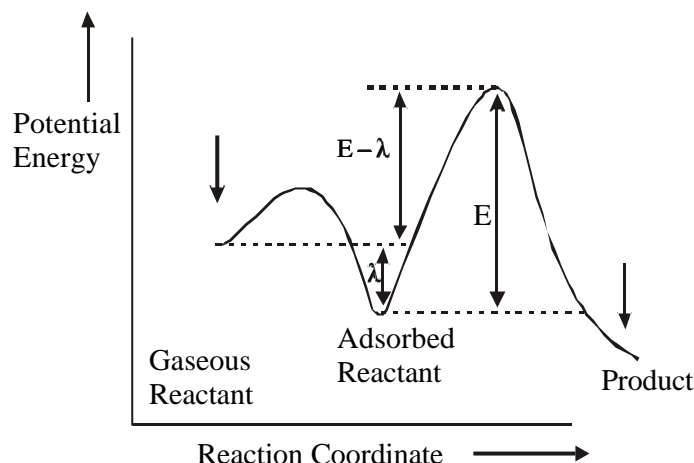
$$= \frac{\dots\dots\dots}{RT^2}$$

$$\left(\frac{d(\Delta G^\circ)}{dT} \right)_p = \dots\dots\dots$$

8. a) Show thermodynamically in which direction the reaction $\text{CO(g)} + \text{H}_2\text{O(g)} = \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ would proceed spontaneously at $T = 27^\circ\text{C}$ and $p = 1$ atm. The standard free energies of formation are : $\text{CO(g)} = -33$, $\text{CO}_2\text{(g)} = -94$, and $\text{H}_2\text{O} = -55$, all in Kcal mol^{-1} . 6
- b) Calculate the osmotic pressure in mm Hg for a 0.01 moles per litre solution of a compound at 27°C . $[R = 0.082 \text{ litre - atm}]$. 4
- c) Which quantities given below would become zero, when liquid water is vaporised at 100°C and 1 atm pressure. ΔH , ΔG , ΔS , ΔE . 3
9. a) State the number of phases, components and degrees of freedom for an aqueous (unsaturated) solution of sodium chloride. What are the variables represented by the degrees of freedom ? 6
- b) Describe the method of determination of solubility product of a sparingly soluble salt by the electrochemical cell emf method. 7
10. a) Write down the expression for the Freundlich adsorption isotherm. 2
- b) Illustrate graphically the variation in the volume of nitrogen gas adsorbed by charcoal at different pressures at two temperatures one very low (say -190°C) and other at 0°C . 5
- c) Calculate the vibrational partition function for Br_2 at 1000k given the vibrational frequency of bromine (ν_e) as 151.2 cm^{-1} . 6
- $$\frac{hc\nu_e}{k} = 218 \text{ K}$$
11. a) Eyring showed that the rate constant k_r of a chemical reaction is given by $k_R = \frac{kT}{h} K^\ddagger$ where K^\ddagger is the equilibrium constant of the reaction between the reactants and the activated complex. Formulate the rate constant k_r in terms of free energy of activation, entropy of activation and enthalpy of activation. 7
- b) Decomposition of phosphine on tungsten is first-order at low pressure and zeroth order at higher pressures. Account for these observation. 6
12. a) What relationship exists between Michaelis constant, K_M and substrate concentration $[S]$, when an enzyme catalysed reaction proceeds at 80% of maximum rate V_{max} ? 6

b) Given below is the activation energy profile for a unimolecular surface reaction involving inhibition :

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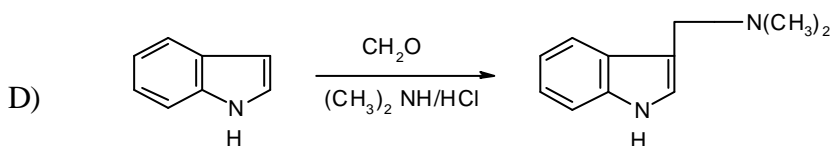
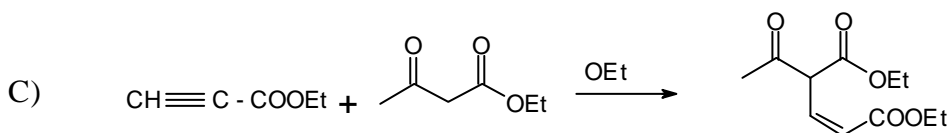
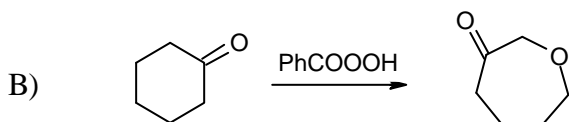
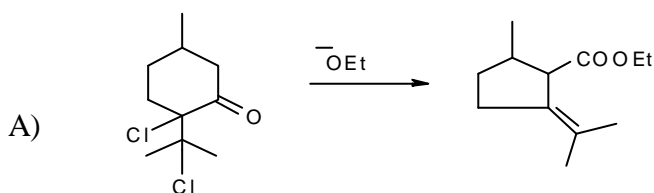


Answer the following questions :

- i) How many activated complexes are formed ?
 - ii) What do the energies E , λ and $(E - \lambda)$ correspond to ?
 - iii) State giving reasons, whether the overall reaction is exothermic or endothermic ?
13. a) What is meant by monodisperse and polydisperse polymer ? Define number average and mass average molar mass of a polymer. Mention one method of determination of molar mass of a polymer and indicate whether it gives the number average or mass average molar mass. 8
- b) A sample of polymer consists of two components present in equal masses, one having $M_r = 30,000$ and the other $M_r = 12,000$. What are the values of mass average and number average molar mass ? 5
14. a) What are Frenkel defects ? Draw a suitable diagram and explain. 5
- b) Which of the following elements when introduced substitutionally in pure silicon will produce n-type silicon? Sb, Cu, Pb, Al, Mg, B, In, Mn, Ga, P, O, As
- c) Explain the mechanism of oxidation of copper metal to Cu(I) oxide. 5
15. a) Give IUPAC nomenclature for the following 8
- i) $[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]$
 - ii) K_2NiF_6
 - iii) $[\text{Co}(\text{en})\text{Cl}_3\text{H}_2\text{O}]$
 - iv) $\left[(\text{en})_2 \begin{array}{c} \diagup \text{NH} \diagdown \\ \text{Co} \quad \quad \text{Co} \\ \diagdown \text{NH} \diagup \end{array} (\text{en})_2 \right]^{4+}$

- b) The complex ion $[\text{FeF}_6]^{3-}$ is in high state. Calculate its spin - only magnetic moment and crystal field stabilisation energy (CFSE) in terms of Dq . 5
16. a) State the factors that determine the magnitude of crystal field splitting parameters. 5
- b) Account for the following 8
- i) $[\text{Ni}(\text{CO})_4]$ shows tetrahedral geometry
- ii) $[\text{Ni}(\text{CN})_4]^{2-}$ shows square - planar geometry.
17. a) Draw molecular orbital diagram of $[\text{FeF}_6]^{3-}$ 8
- b) Write possible isomers of the complex $[\text{Co}(\text{NH}_3)_4(\text{CO})_3 \text{I}]$. How will you distinguish between these coordination isomers ? 7
18. a) Draw and explain the structure of $\text{Fe}_2(\text{CO})_9$. 7
- b) Explain the structure of ferrocene on the basis of valence bond theory. 6
19. a) Give one method for the synthesis of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and explain the nature of bonding in $\text{M}-\text{N}_2$ groups. 7
- b) Explain the steps involved in the synthesis of acetaldehyde using palladium (II)-copper (II) chloride. 6
20. a) Explain why absorption bands of the lanthanides are weak but sharp. State the colours of the following ions. 7
- Ce^{3+} , Nd^{3+} , Sm^{3+} , Tm^{3+} , Lu^{3+}
- b) The Mossbauer spectrum of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ shows a quadrupole doublet, while that of $\text{K}_4\text{Fe}(\text{CN})_6$ shows a single line. Explain. 6
21. a) Give a brief account of phosphate esters. 7
- b) With the help of flow chart, explain the principles underlying the extraction of germanium from germanite. 6
22. a) Define 6
- i) Controlled-cathode-potential electrolysis
- ii) Working electrode
- iii) Cathode depolarizer

- b) Differentiate between amperostatic coulometry and potentiostatic coulometry. 7
23. a) List the variables which affect the physical properties of electrolytic deposits. Why is an auxiliary reagent always required in a coulometric titration? 7
- b) How many steps are involved in the thermogram of calcium oxalate dihydrate when it is heated from ambient to 900°C. Explain each step on the basis of thermal decomposition reaction of the compound. 6
24. a) Define (i) elution (ii) stationary phase (iii) retention time (iv) selectivity factor as applied to chromatographic analysis. 8
- b) Explain the exhaustive and counter current extractions. 5
25. a) In extraction of cerium (IV) with 2-thionyltrifluoroacetone in benzene, the distribution ratio was 999.0. If the volume of the organic phase was 10.0 mL and that of the aqueous phase was 25.0 mL. Calculate the percentage of extraction. 6
- b) A freshly-cut piece of wood gives 16,000 counts of β -ray emission per min per kg. An archaeological sample of wood gives a corresponding count rate of 13,000 per min per kg. Calculate the age of the wood sample. ($t_{1/2}$ for ^{14}C = 5,500 years) 7
26. Suggest mechanisms for the following. Identify the reaction involved. 13

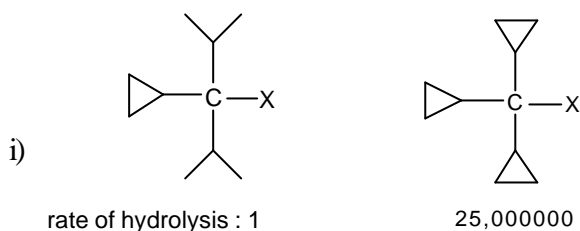


27. a) The ρ value for ionization of benzoic acid in H_2O is 1 but in ethanol the ρ value is 2.3. Why ?

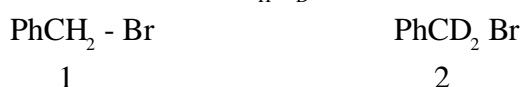
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b) Explain the following

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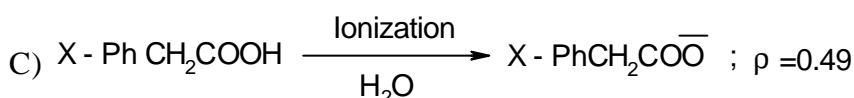
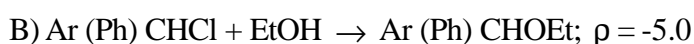
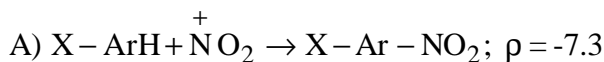


ii) For hydrolysis of 1 and 2 $k_H/k_D = 0.94$. Explain



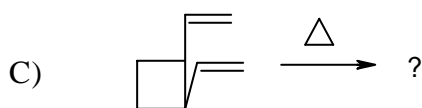
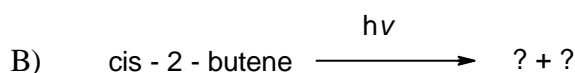
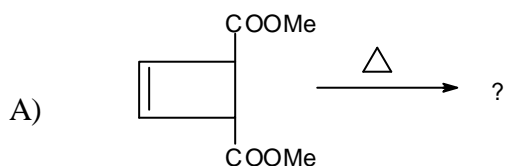
c) Account for sign and magnitude of ρ values observed for the following reactions.

6



28. Predict the product and its stereochemistry for the following reactions. Indicate for each reaction (i) type of pericyclic reaction (ii) necessary selection rule.

13



29. A) Draw two chair and one boat conformation of cis-4-methyl cyclohexanol. Evaluate the energies of the chair conformers given that ΔF for methyl = 1.7 and for hydroxyl = 0.7 K cal/mol.

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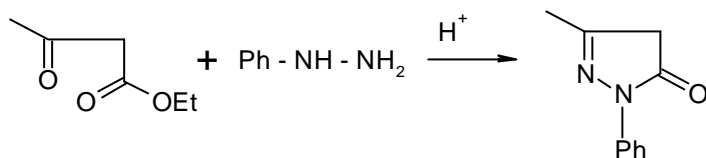
B) On treatment with $KMnO_4$ cis - 2 - butene yields a diol of m.p. 34° and trans - 2-butene yields a diol of m.p. 19° . Both diols are optically inactive. Resolution converts diol of m.p. 19° (but not the one of the m.p. 34°) into two optically active fractions of equal and opposite rotations.

a) What are the configurations of the diol m.p. 19° and that of m.p. 34° ? Why is only one of them resolvable ?

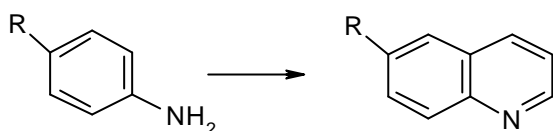
b) What is the stereochemistry of hydroxylation with $KMnO_4$?

33. a) Suggest mechanism for the following.

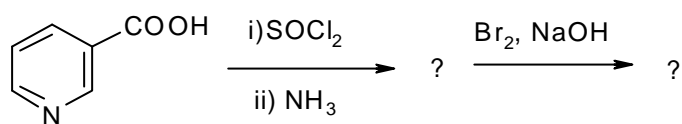
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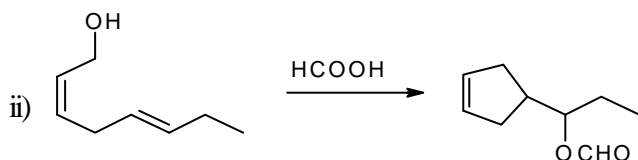
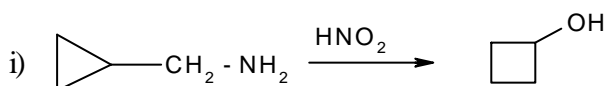
b) How is the following transformation accomplished ?



c) Write the structure for the intermediate and the final product.



34. A) Propose mechanisms for the following.



B) i) For principal bases found in DNA are

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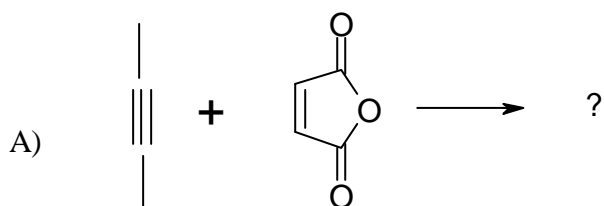
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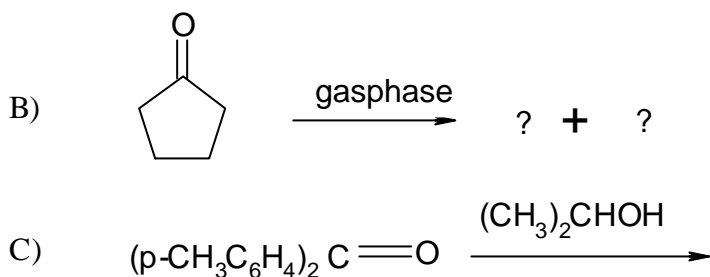
ii) The carbon - nitrogen bond in peptides is 1.32 \AA as compared to 1.47 \AA for the usual carbon-nitrogen bond. What does it indicate. 2

iii) Give the structure of adenosine triphosphate 2

35. Predict the major products of the following photochemical reactions. Explain briefly the process involved.

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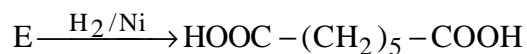
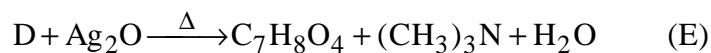
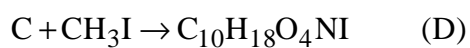
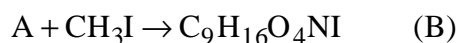




36. a) Compound A, $\text{C}_8\text{H}_{13}\text{O}_4$ is obtained by oxidation of tropinone

10

- i) A has a neutralization equivalent (using NaOH) of 94 ± 1 .
- ii) A does not react with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, cold KMnO_4 or Br_2/CCl_4
- iii) Exhaustive methylation gives the following results



Based on the above data answer the following questions.

- a) What is the nature of oxygen functions ?
- b) What is the nature of nitrogen ?
- c) Indicate the number of rings.
- d) How many double bonds are there in compound E ?
- e) What is the nature of oxygens present in E ?
- f) Write a probable structure for compound A.