

CHEMICAL SCIENCES**Paper III****Time Allowed : 2½ Hours]****[Max. Marks : 200**

- Note :**
- (i) Question paper contains *Four* Sections.
 - (ii) Attempt questions from Sections I and II as per the instructions given therein.
 - (iii) *All* questions from Sections III and IV are compulsory.
 - (iv) Log table is enclosed.

SECTION I

Instructions : In this section you have to answer *all* questions (Q. No. 1 and Q. No. 2).

1. Answer either A or B or C or D :

- (A)
- (i) Define the units of the quantity of charge, Coulomb (C) and Faraday (F). [5]
 - (ii) A constant current 0.800 A is used to deposit copper at the cathode and oxygen at the anode of an electrolytic cell. Calculate the number of grams of copper formed in 15.2 mins., assuming no other reactions. (Given 1 F = 96485 C). [10]
 - (iii) Why spectrofluorometry is potentially more sensitive than spectrophotometry ? [5]

OR

- (B)
- (i) Draw the structure of the iron complex present in cytochrome *c* showing the axial ligands to the metal ion. [7]
 - (ii) Draw the structure of Fe₂S₂ and Fe₄S₄ centers. How are these Fe-S clusters bound to the respective iron-sulphur proteins ? [8]
 - (iii) The IR spectrum of [Fe₂(CO)₉] shows bands at 2090 (medium), 2020 (small) and 1830 (small) cm⁻¹. Predict its structure based on these data. [5]

[P.T.O.]

OR

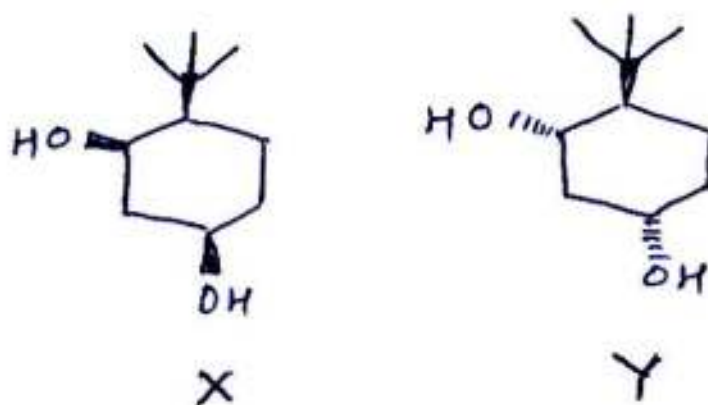
(C) (i) (a) Draw the stereostructures for compound X and Y. Indicate which forms intramolecular H-bonds and which gives intermolecular H-bonds. Explain your answer. Indicate whether X and Y are :

(1) Diastereomers

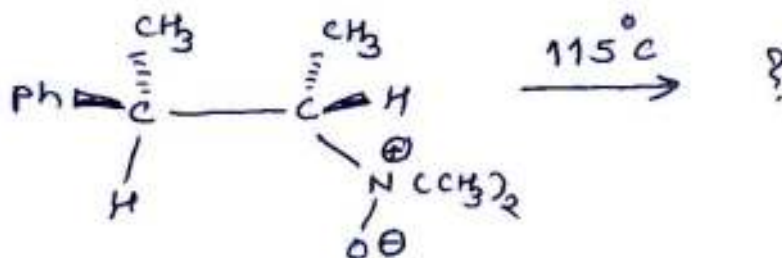
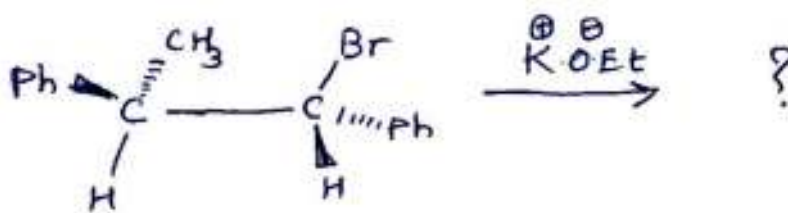
(2) Enantiomers

(3) Regioisomers.

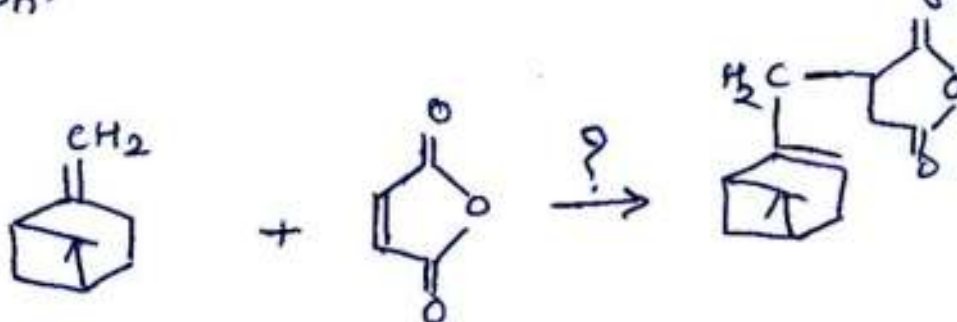
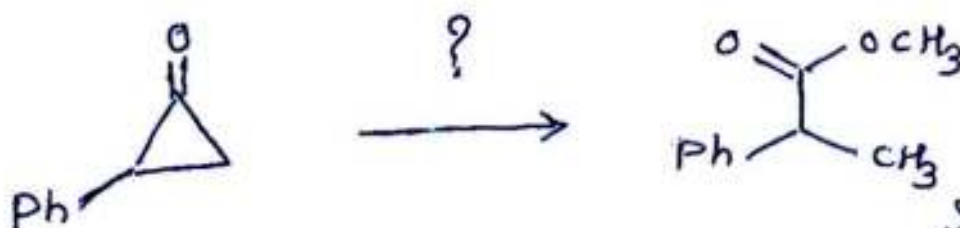
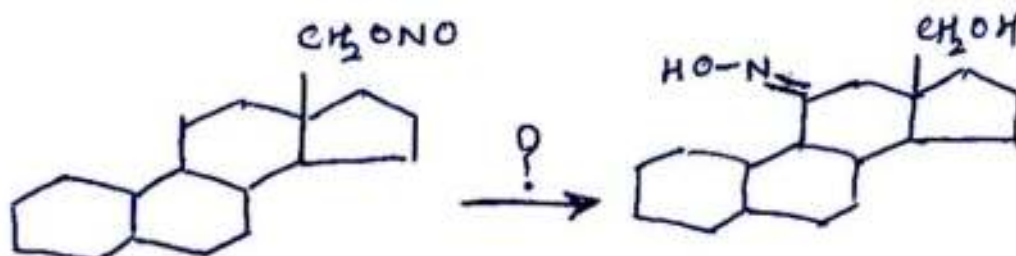
Both the compounds X and Y are rigid. Explain, why ? [5]



(b) Write the products in the following reactions : [5]



- (ii) Give appropriate reagents/reaction condition/s, name of the reaction and reaction mechanism of the following transformations : [10]



OR

- (D) (i) Define artificial transmutation. Which types of elementary particles are used in artificial transmutation ? [5]
- (ii) MX_3 , a trigonal planar molecule is distorted by lifting M atom out of the plane. What are the point groups of the ideal geometry and the distorted geometry ? List the symmetry operations for both the geometries. [5]

- (iii) A student designed an experiment to determine the electronic charge 'e'. A solution of I^- (aq.) was electrolyzed for period of 6.224 h using current of 0.0429 A to produce 1.259 g of I_2 . Based on this data, calculate the experimental value of e . (Given : molar mass of $I_2 = 253.81$ g). [5]
- (iv) The standard molar enthalpy of formation, $\Delta_f H^\circ$, of $NH_3(g)$ is -46.11 kJ mol^{-1} at 25°C . Using the following heat capacity data, calculate the standard molar heat of formation of $NH_3(g)$ at 1000 K.

$$C_p^0(H_2)/\text{J K}^{-1} \text{ mol}^{-1} = 29.07 - (0.837 \times 10^3 \text{ K}^{-1}) T + (2.012 \times 10^{-6} \text{ K}^{-2}) T^2$$
$$C_p^0(N_2)/\text{J K}^{-1} \text{ mol}^{-1} = 26.98 + (5.912 \times 10^{-3} \text{ K}^{-1}) T + (0.3376 \times 10^{-6} \text{ K}^{-2}) T^2$$

where $298 \text{ K} < T < 1500 \text{ K}$. [5]

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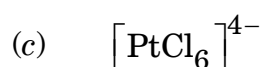
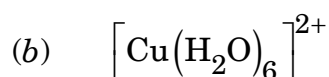
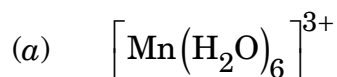
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2. Answer either A or B or C :

(A) (i) Which of the following complexes will undergo Jahn-Teller distortion ? Specify the type of distortion and calculate the stabilization energy :

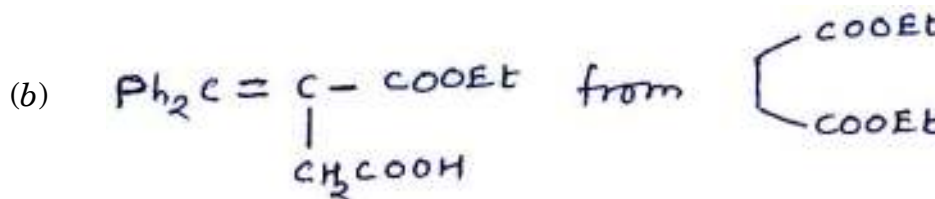


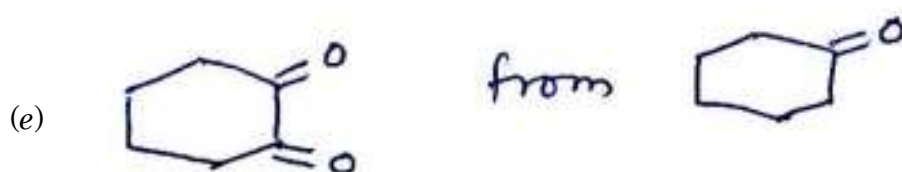
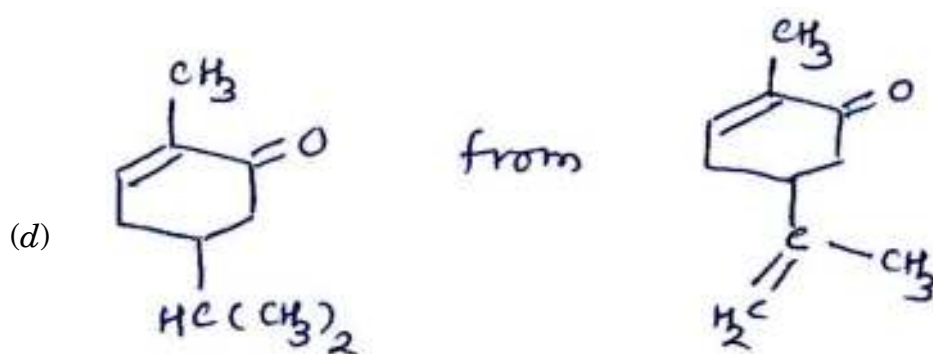
(ii) Suggest a suitable method for the synthesis of *cis* and *trans*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]$, starting from $\text{H}_2[\text{PtCl}_4]$. [6]

(iii) The rates of self exchange reactions in two cobalt complexes $[\text{CoL}_6]^{2+/3+}$ and $[\text{CoA}_3]^{2+/3+}$ (L = neutral monodentate ligand and A = neutral bidentate ligand), are $9.0 \text{ mol}^{-1} \text{ s}^{-1}$ and $48.0 \text{ mol}^{-1} \text{ s}^{-1}$. Calculate the rate of outer sphere electron transfer between the two species (cross reaction), if the equilibrium constant between the two species is 3.57 under given temperature and pressure. [Consider $f = 1$]. [6]

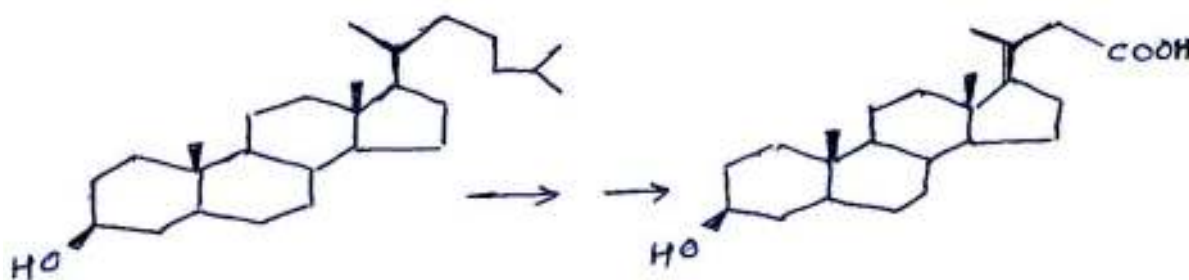
OR

(B) (i) Provide efficient synthetic route using appropriate reagents for the following compounds from the indicated starting material : [10]





- (ii) (a) Write down the steps involved in the following transformation with specific reference to the loss of two carbon atoms. [5]



- (b) State isoprene rule. Identify the isoprene units present in geraniol and farnesol. [5]

OR

- (C) (i) What are lyophilic and lyophobic sols ? Give *one* example of each type. [6]
- (ii) $\psi = N(27 - 18r + 2r^2) \exp(-r/3)$ is an eigenfunction, in atomic units, for the hydrogen atom eigenfunction :
- (a) What are the n , l and m quantum numbers for this state ?
- (b) How many radial nodes does this function possess ? What are the positions of the nodes ?
- (c) Give the orbital symbol of this state.
- (d) What is the energy of this state ? [8]
- (iii) Sketch the ESR spectrum for an unpaired electron in presence of three protons for the following cases :
- (a) The protons are not equivalent
- (b) The protons are equivalent
- (c) Two protons are equivalent and the third is different. [6]

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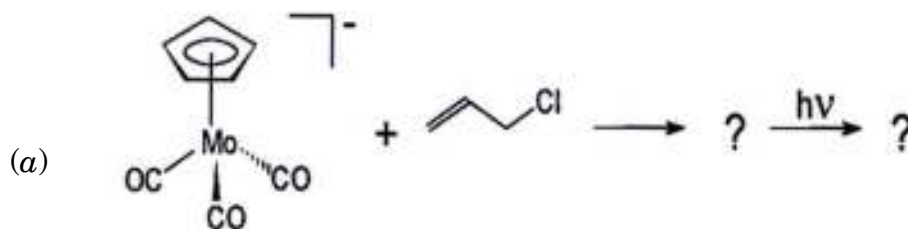
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SECTION II

Instructions : In this section you have to answer *all* questions (Q. No. 3 to Q. No. 5).

3. Answer either A or B or C :

- (A) (i) Explain the mechanism of hydroalumination reaction with a suitable example. Why is it usually anti-Markownikoff ? [4]
- (ii) Complete the following reaction. Draw the structure of the products formed in each step :



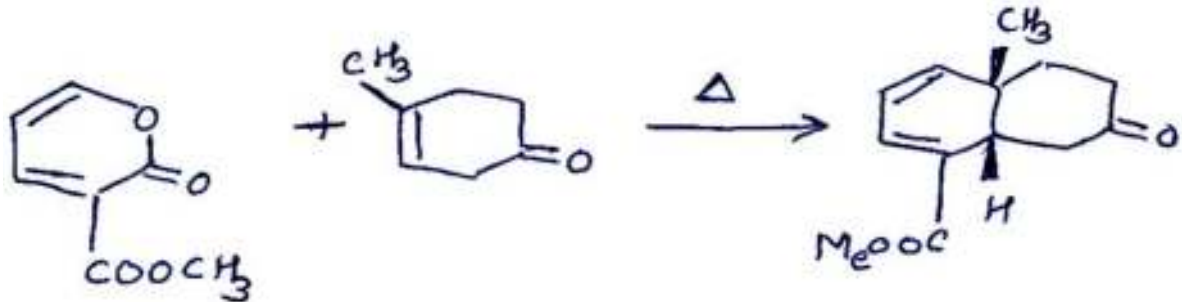
- (iii) Draw the catalytic cycle involving CH_3I for the synthesis of acetic acid by Monsanto process. [5]

OR

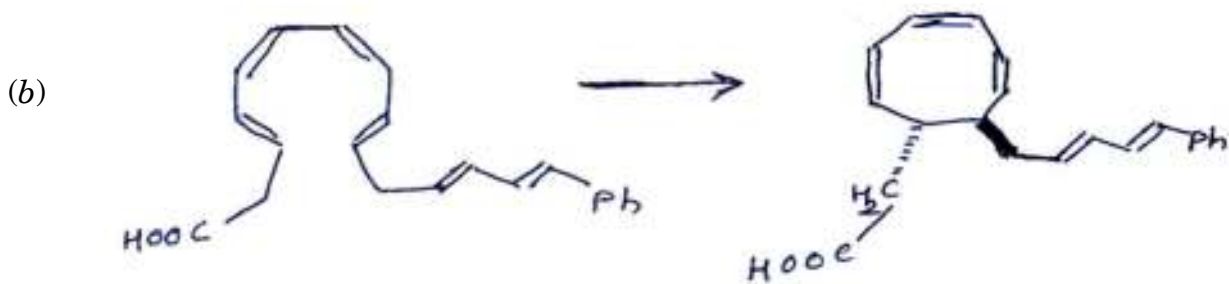
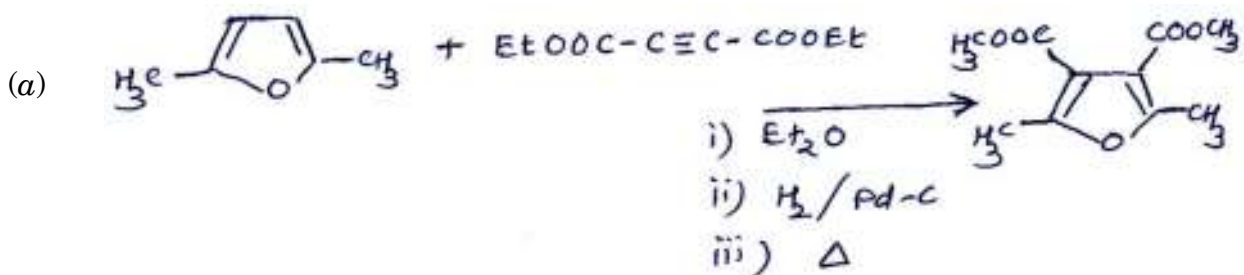
- (B) (i) Indicate the reaction involved in the following transformation. Explain the mechanism giving the intermediate involved. [4]



- (ii) Explain the mechanism, regiochemistry and stereochemistry involved in the following reaction. Indicate the pericyclic reaction and intermediate involved in the reaction. [4]



- (iii) Write the intermediates and mechanism for the following reactions. Name the reaction involved. [7]



OR

- (C) (i) Determine the possible term symbols for an excited state of the carbon atom having the electronic configuration $1s^2 2s^2 2p^1 3p^1$. [7]
- (ii) (a) Describe Schottky and Frenkel defects and their manifestations with suitable examples.
- (b) If the average energy required to create a vacancy in metal is 1 eV, calculate ratios of vacancies in the metal at 1000 and 500 K. (Given : $k_B = 8.625 \times 10^{-5} \text{ eV K}^{-1}$) [8]

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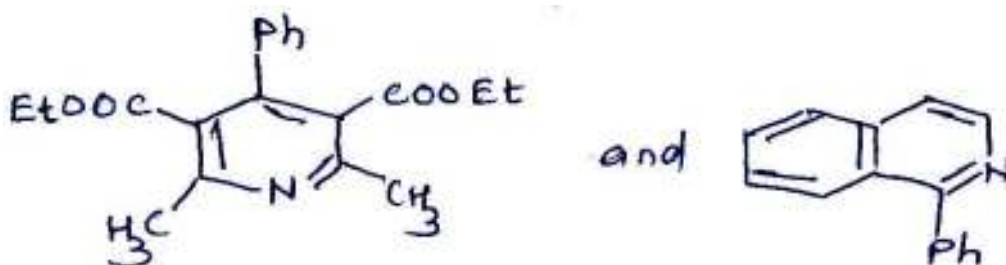
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4. Answer either A or B or C :

- (A) (i) What is semitopological description of structure and bonding in boranes. Using this draw the structures of B_4H_{10} and $B_{10}H_{14}$. [10]
- (ii) Why CCl_4 is unreactive in H_2O while $SiCl_4$ is rapidly hydrolysed? [5]

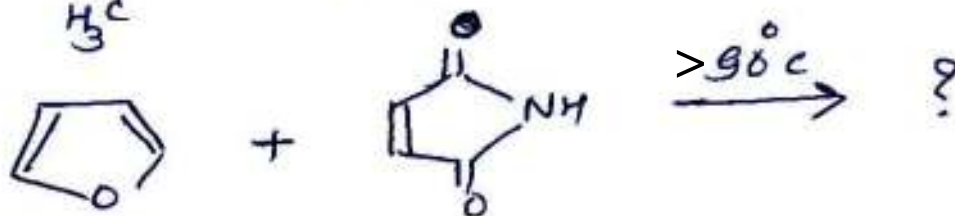
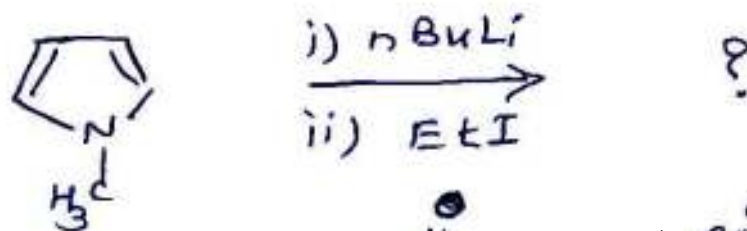
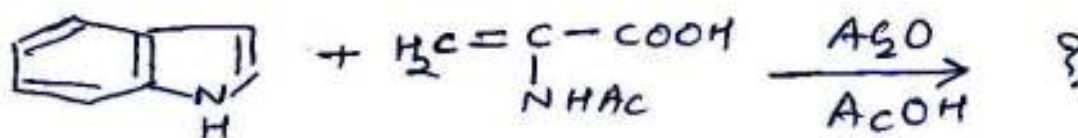
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- (B) (i) (a) Derive the synthesis of the following heterocycles. [4]

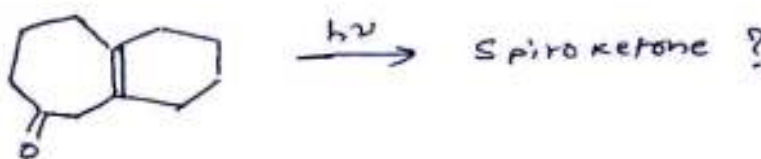
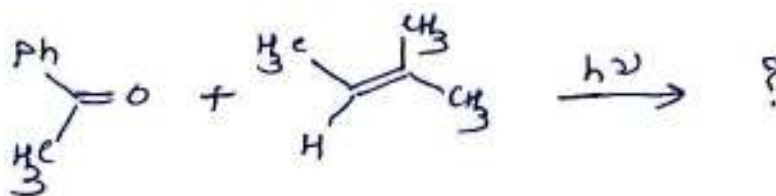


[Hantzsch syn.]

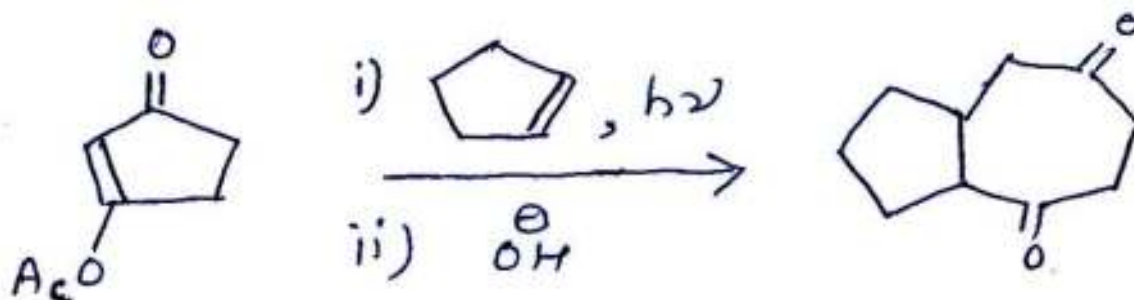
- (b) Give the product/s of the following reactions : [3]



- (ii) (a) Predict the product in the following conversions and suggest mechanism : [5]



- (b) Give the mechanism for the following conversion : [3]



OR

- (C) (i) Define a new thermodynamic function $\psi = U - TS + RT$, where R, S, T and U have their usual meanings. Show that $\Delta\psi(V, T)$ can be used as a criterion for spontaneity of physical processes and chemical reactions. [5]
- (ii) What is ideal solution ? Prove that the change in free energy of mixing of A and B for the ideal solution is :

$$\Delta G_{\text{mixing}} = RT(x_A \ln x_A + x_B \ln x_B) \quad [10]$$

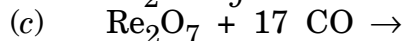
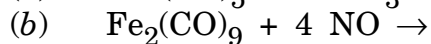
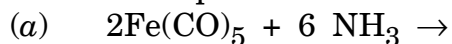
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5. Answer either A or B or C :

(A) (i) Predict the products of the following reactions : [5]



(ii) Calculate the number of cluster valence electrons in $[\text{Ir}_4(\text{CO})_{12}]$. Draw the structure based on cluster valence electrons ($Z = 77$ for Ir). [5]

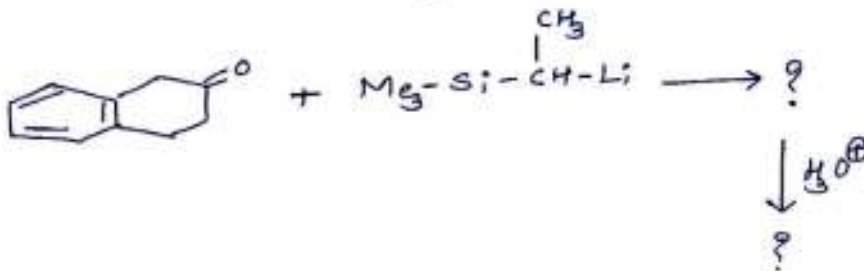
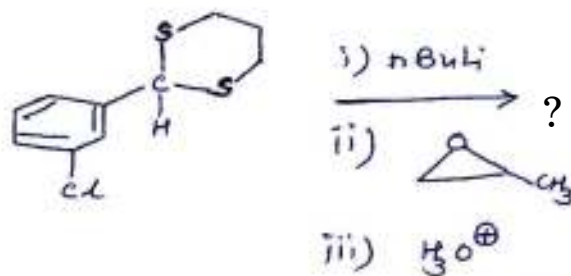
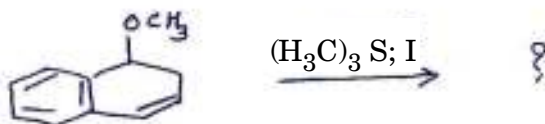
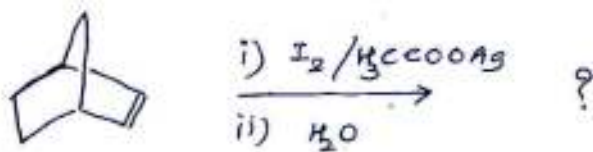
(iii) CoCl_2 dissolves in water to give a pale pink solution. Addition of conc. HCl to this results in the formation of bright blue coloured solution. Explain. [5]

OR

(B) (i) Write the structure of GC pair indicating the hydrogen bonds present. [4]

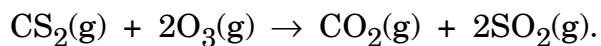
(ii) Write the structure of NADH. [3]

(iii) Predict the products/intermediates in the following chemical conversions : [8]



OR

- (C) (i) The following reaction was studied using a large excess of CS₂ : [10]

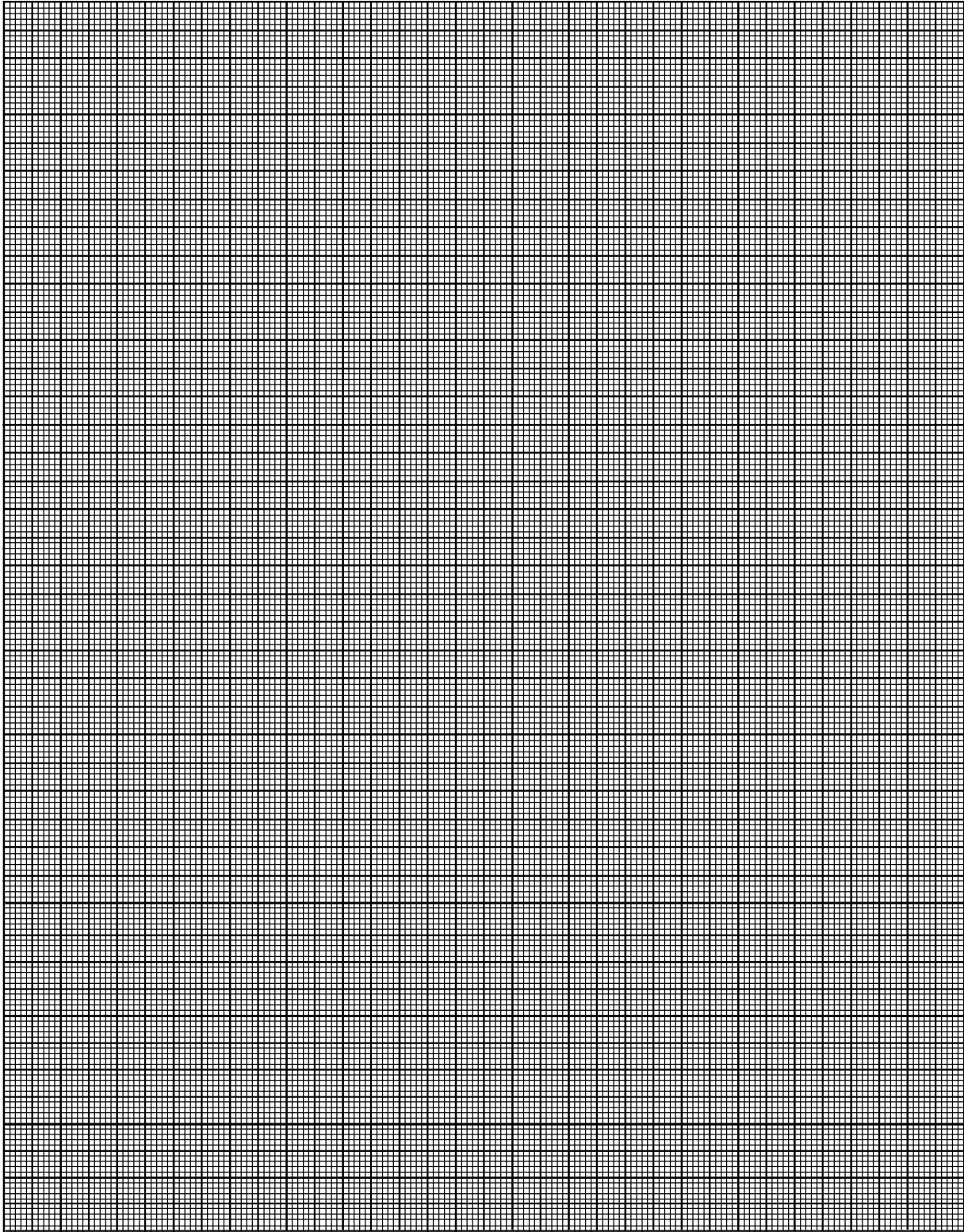


The pressure of ozone as a function of time is as follows :

Find the order of the reaction.

Time/s	Ozone pressure/Torr
0	1.76
30	1.04
60	0.79
120	0.52
180	0.37
240	0.29

- (ii) Which are *three* important steps involved in the formation of addition polymers. [5]



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SECTION III

Instructions : In this section you have to answer *all* questions (Q. No. 6 to Q. No. 14).

6. (i) Cesium bromide crystallizes in a cubic lattice and has a density of 4.49 g cm^{-3} . Calculate the unit cell parameter ' a ' of CsBr. (Given : molar mass of CsBr = 212.8; Avogadro number is 6.023×10^{23}). [4]

- (ii) Predict the shapes of the following molecules using VSEPR model :
- (a) BF_3
 - (b) PCl_5
 - (c) $[\text{PCl}_6]^-$. [6]

7. (i) Explain the splitting of d orbitals in $\text{Fe}(\text{CO})_5$ with proper illustration. [5]

- (ii) For each of the following two metal ions, predict which of the given ligands would give the more stable complex and explain your choice. Identify the geometry and calculate the crystal field stabilization energy in the more stable complex formed by each metal ion :
- (a) Hg^{2+} with $\text{C}_2\text{H}_5\text{S}^-$ or $\text{C}_2\text{H}_5\text{O}^-$
- (b) Zn^{2+} with $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. [5]

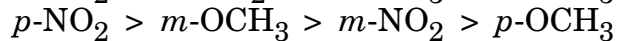
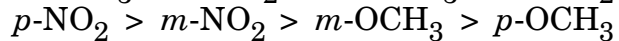
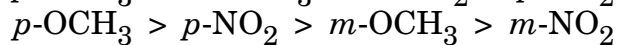
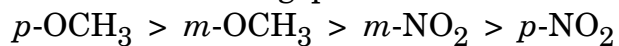
8. (i) What magnetic field is required to satisfy the resonance condition in an ESR instrument, which uses an 8 mm microwave radiation ? Assume $g = 2$ for your calculation. ($h = 6.626 \times 10^{-34}$ Js.; $\mu_B = 9.274 \times 10^{-24}$ JT⁻¹) [5]

- (ii) A photon of wavelength λ has an equivalent momentum of h/λ . Calculate the recoil velocity of a free ⁵⁷Co nucleus when emitting a gamma ray of 0.1 nm wavelength. What is the Doppler shift of the gamma ray to an outside observer ? (1 atomic mass unit = 1.66×10^{-27} kg) [5]

9. (i) Cycloheptatriene is 10^{20} times weaker in acid strength than cyclopentadiene ($pK_a = 16$). Explain the fact. [5]

- (ii) On treatment of 2-aminocyclohexanol with nitrous acid, *trans* isomer gives product A and *cis* isomer gives products A and B. Write structures of A and B and explain their formation giving reasons. [5]

10. (i) Benzoylation of anilines has ρ value of -2.64 and base catalysed hydrolysis of methyl benzoate has ρ value of $+2.38$. Select the proper order for relative rates of the reaction for each of the above reaction from the following possibilities for substituents on benzene.



Justify your selection with suitable explanation.

(Given : $\sigma_{p\text{-OCH}_3} = 0.23$, $\sigma_{m\text{-OCH}_3} = 0.17$, $\sigma_{p\text{-NO}_2} = 0.78$,
 $\sigma_{m\text{-NO}_2} = 0.71$) [5]

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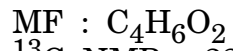
- (ii) What are the characteristics for neighbouring group participation reaction ? Which type of functional groups are capable of causing NGP ? Give evidence for stereochemical outcome of the reaction. [5]

11. (i) Deduce the structure of a compound based on given spectral data :
- MF : C_6H_6O
IR : 2720 (w), 2100, 1685, 1610 cm^{-1}
 1H NMR : 2.0 (s, 9 mm)
 3.5 (s, 3 mm)
 6.2 (d, J = 3 Hz, 3 mm)
 9.9 (d, J = 3 Hz, 3 mm)
 ^{13}C NMR : 24.0 (q) 81.0 (s) 88.0 (d)
 135.0 (d) 142.0 (s) 192.0 (d)
Mass (m/z) : 94(M^+), 66 (100%).

[6]

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(ii) Deduce the structure of a compound based on given spectral data :



^{13}C NMR : 22.3 (t)

27.9 (t)

68.9 (t)

178.2 (s)

[4]

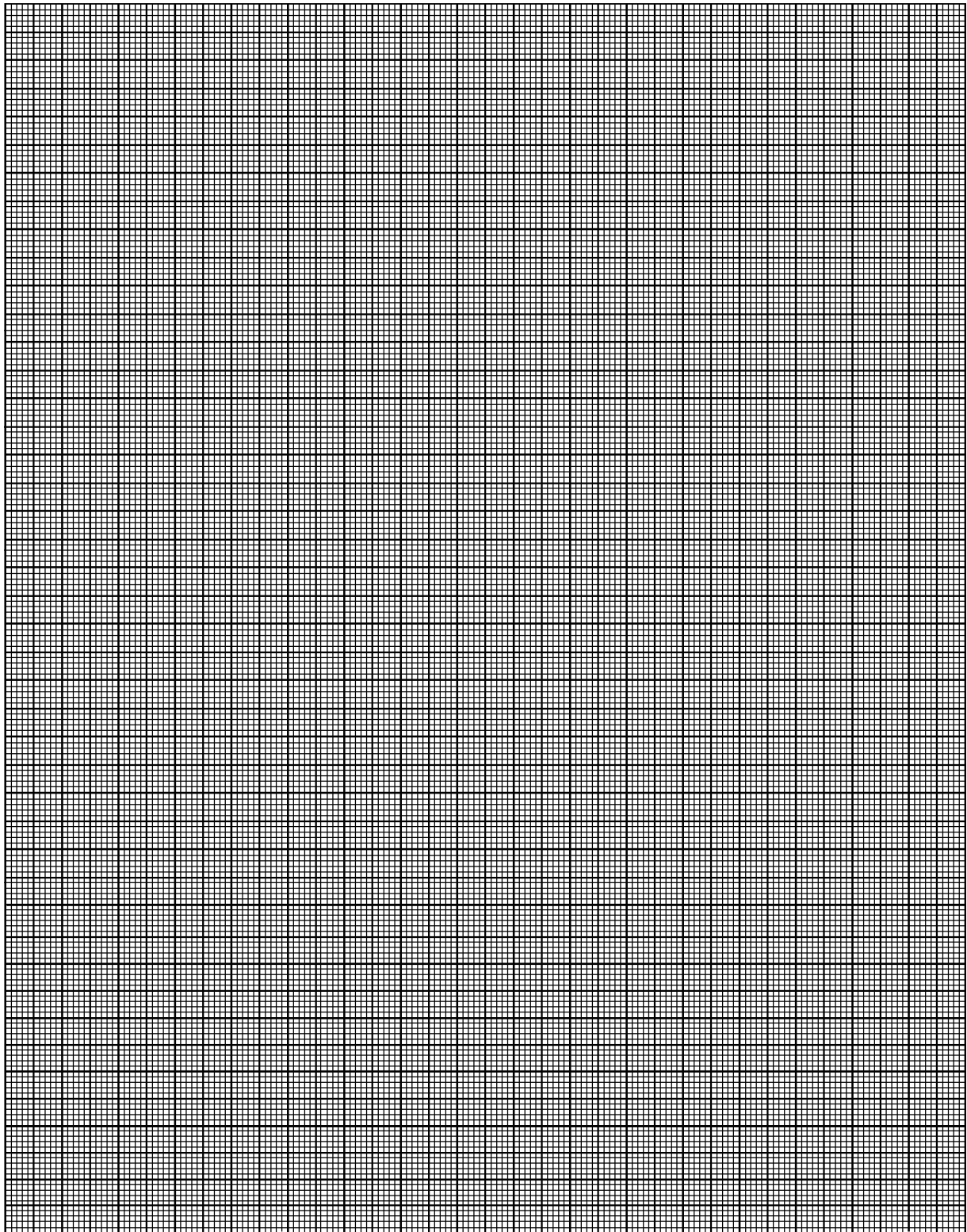
12. Consider a real system. Assume that a real wavefunction is a combination of two orthonormal functions such that $H_{11} = -15$, $H_{22} = -4$ and $H_{12} = H_{21} = -1$ (in arbitrary units). Evaluate the approximate energies of the real system. [10]

13. Refer following values of mean activity coefficient (γ_{\pm}) of potassium chloride solution : [10]

No.	Concentration (mol kg ⁻¹)	γ_{\pm}
1	0.005	0.9274
2	0.010	0.9024
3	0.020	0.8702
4	0.030	0.8492
5	0.040	0.8320
6	0.060	0.8070
7	0.080	0.7872
8	0.100	0.7718

Evaluate the constant "A" in Debye-Hückel limiting law.

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14. The mechanism for the action of enzymes (E) on substrates (S) is as follows :



where ES is the enzyme-substrate complex and P is the product. Knowing this, derive Michaelis-Menten equation :

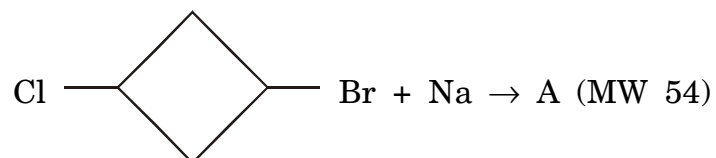
$$-\frac{d[s]}{dt} = \frac{k_b [s]}{k_m + [s]} \quad [10]$$

SECTION IV

Instructions : In this section you have to answer *all* questions (Q. No. 15 to Q. No. 19).

15. The reagent 1, 10 phenanthroline (Phen) forms a chelate $[\text{Fe}(\text{Phen})_3]^{2+}$ with Fe^{2+} . The absorbance of a 10.0 mL standard iron solution containing 20.0 μg of iron at 510 nm in a 1 cm cell was found to be 0.397. Calculate the molar absorptivity of $[\text{Fe}(\text{Phen})_3]^{2+}$. (Given : At. Wt. of Fe = 56). [5]
16. Arrange the following ions in the increasing order of the acidity of their hydrated ions :
 Pr^{3+} , Ce^{3+} , Nd^{3+} , Dy^{3+} , Ho^{3+} . [5]

17. Deduce the structure of a product A in the following conversion based on data. Suggest possible mechanism.



^1H NMR of A : δ 0.45 (s, 2H)
1.34 (m, 2H)
1.44 (m, 2H)

Hint : A is converted to butadiene at 225°C.

[5]

18. The density of Schottky defects in certain samples of NaCl is 5×10^{11} per m^3 . If the observed interionic ($\text{Na}^+ - \text{Cl}^-$) distance is 2.82 \AA , what is average activation energy required to create the Schottky defect ? [5]

19. Derive the formula for the Raman shifts of pure rotational Raman lines for a diatomic molecule. What is the spacing between adjacent lines ? What is the spacing between the unshifted line and each of the lines close to the unshifted line ? [5]

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