CSM(O)-CH-II/22

2022

CHEMISTRY

PAPER-II

Time Allowed — 3 Hours   *Full Marks — 200*

*If the questions attempted are in excess of the prescribed number, only the
questions attempted first up to the prescribed number shall be valued
and the remaining ones ignored.*

*Answers may be given either in **English** or in **Bengali**
but all answers must be in one and same language.*

Section-I

This Section comprises 15 questions in three Groups. Answer *any ten*
questions taking *at least three* questions from each Group.

Group-A

1. Write down the IUPAC name of Zeise's Salt. Do you expect any rotation in ethylene molecule of Zeise's Salt without hampering the stability of the complex? If possible explain it.   1+1+2=4

2. Metal deficiency and metal excess both may exert harmful effects — Explain with example.   2+2=4

3. $[CoF_6]^{3-}$ and $[NiF_6]^{2-}$ ions both have weak field F^- ion as ligand, yet $[CoF_6]^{3-}$ is paramagnetic and $[NiF_6]^{2-}$ is diamagnetic— Explain.   2+2=4

4. Draw all the optical and geometrical isomers of $[Co(en)_2Cl_2]^+$. (en = 1, 2-diaminoethane)   4

5. How ferrocene is prepared? What is the oxidation state of Fe in ferrocene?   3+1=4

Group-B

6. Derive Clausius-Clapeyron equation thermodynamically for liquid-vapour equilibrium.   4

7. For a 10°C rise in temperature the rate constant doubles for reaction I, trebles for reaction II. If the two reactions have comparable pre-exponential factors, what is the ratio of their activation energies?   4

8. Adsorption of gas on a solid surface is an exothermic process. Justify. Write down four differences between physisorption and chemisorption.   2+2=4

9. The number of the degrees of freedom for a system of a mixture of $H_2(g)$, $O_2(g)$ and $H_2O(g)$ may be either 4 or 2— Comment.   4

10. What is photostationary state? How does this differ from the equilibrium state?   4

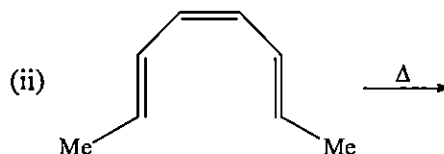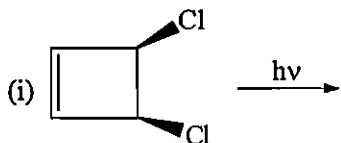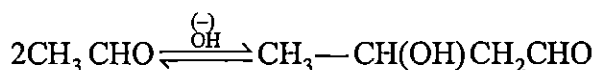28918   **Please Turn Over**

Group-C

11. Although the –OH group is not bulky, *cis* 1, 4-cyclohexane diol exist preferably in twist boat conformation — Explain. 4
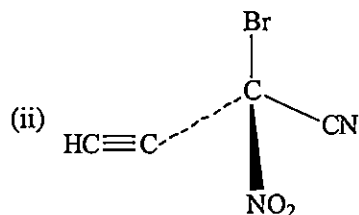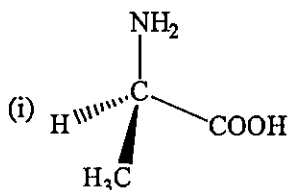
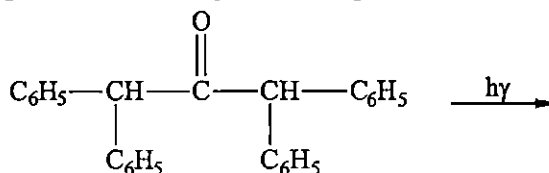12. Predict the product(s) of the following reactions and explain. 4

13. Carry out the mechanism of the following reaction: 4

$$2CH_3CHO \underset{\overset{(-)}{OH}}{\rightleftharpoons} CH_3—CH(OH)CH_2CHO$$

14. Assign description of the following molecules: 4

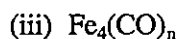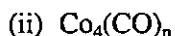15. Complete the following Norish Type I reaction with explanation (mechanism): 4

Section-II
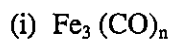
This Section comprises *six* questions in three Groups. Answer *any four* questions taking *at least one* question from each Group.

Group-A

1. (a) Find out 'n' in
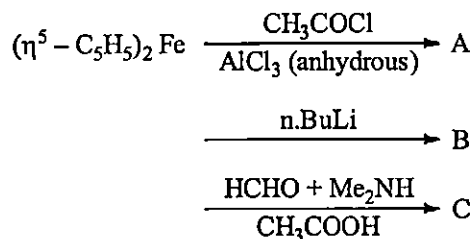
    (i) $Fe_3(CO)_n$

    (ii) $Co_4(CO)_n$

    (iii) $Fe_4(CO)_n$ 2+2+2=6

    (b) Using trans effect phenomenon prepare all possible stereoisomers of $Pt(Cl)(NH_3)(P_y)Br$ starting from $P + Cl_4^{2-}$ 2+2+2=6

(c) Identify the compounds A, B and C in the following reaction: 2+2+2=6

$$(\eta^5 - C_5H_5)_2\,Fe \xrightarrow[\text{AlCl}_3\text{ (anhydrous)}]{\text{CH}_3\text{COCl}} A$$

$$\xrightarrow{\text{n.BuLi}} B$$

$$\xrightarrow[\text{CH}_3\text{COOH}]{\text{HCHO + Me}_2\text{NH}} C$$

(d) Why is the change from deoxyhaemoglobin to oxy-form accompanied by a decrease in the observed magnetic moment? 3+3=6

(e) Evaluate the ground state term for Cr^{+3}. 4

(f) Account the carbonyl streching frequency (in cm^{-1}) of the following: 6

CO	$[V(CO)_6]^-$	$[Cr(CO)_6]$	$[Mn(CO)_6]^+$
2143	1860	2000	2090

(g) Using CFSE indicate whather $MnCr_2O_4$ is normal or inverted spined? 6

2. (a) What are fluxional molecules? Give one example. 3+1=4

(b) What are the different modes of finding in carbonyls? Describe with examples, also comment on the CO streching frequencies in those binding mode. 3+3+3=9

(c) Draw the active site structure of Ferrodoxins and comment on the magnetic property during electron transfer process. 2+4=6

(d) How can you incorporate –NH_2 group in Ferrocene? Explain why ferrocene is unreactive towards iodine where as cobaltocene is readily decolorizes the colour of iodine solution. 3+3=6

(e) Aqueous solution of Co (II) is pale pink in colour, but when excess conc HCl is added to it, solution become intensely blue — explain. 4

(f) Define hapticity of an organometallic ligand. Indicate various modes of binding of cyclopentadiene taking proper examples. 2+3=5

(g) Name any two of each major elements and trace elements. Name two biological function of Mg^{2+}. 2+2+2=6

Group-B

3. (a) Give a schematic plot of the energy profile diagrams for an exothermic reaction carried out in absence and presence of a catalyst. Hence explain how a catalyst takes part in the reaction.

    5

   (b) 100 g of a 1 : 1 (by weight) mixture of water and phenol is taken at 40°C. It shows two layers:

      (i) phenol (9.2%) in water and

      (ii) water (35%) in phenol. Find the amount of the two layers. Also mark the above three % values of phenol (w/w) in proper T-wt % of phenol diagram. Assume CST = 66°C, weight % of phenol at CST = 33%.

      7

   (c) For a simultaneous set of reactions $A \xrightarrow{k_1} B; \ A \xrightarrow{k_2} C$

   Show that:

   (i) $[B]/[C] = k_1/k_2$ at any time t, where $0 < t < t_{eqm}$

      (ii) If $k_1/k_2 = 2$, plot [A], [B], [C] on the same graph as functions of time, assuming that $[B]_0 = [C]_0 = 0$.

      4+4=8

   (d) Derive Langmuir adsorption isotherm, mentioning the assumptions involved. Suggest a suitable linear plot for its varification. In the Langmuir model of absorption of a gas on solid if rate constant of adsorption is equal to that of descorption at 1 atm pressure, the surface is 50% covered. Justify/criticise.

      5+5+5=15

   (e) The photochemical decomposition of HI proceeds by the following mechanism:

   $HI + h\nu \longrightarrow H + I$

   $H + HI \xrightarrow{k_2} H_2 + I$

   $I + I \xrightarrow{k_2} I_2$
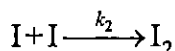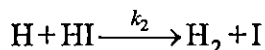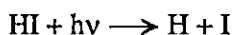
   Derive an expression for $-\dfrac{d[HI]}{dt}$ and hence calculate the quantum yield (φ).

      5

4. (a) Show that the following experimental observations follow the above kinetic features of the photochemical decomposition of gaseous HI. Absorption of 3.07×10^9 ergs of energy (light of wavelength 2537 Å) decomposes 1.30×10^{-3} moles of HI. One Einstein = $1.196 \times 10^8/\lambda$ ergs mole^{-1}.

      6

   (b) Establish how the frequency factor of a bimolecular reaction is related to $\Delta S^{\#}$. If the activation energy for the gaseous reaction $H_2 + I_2 \longrightarrow 2HI$ is 167 kJ and the ΔH for the reaction is $-8.2k$ What is the activation energy for the decomposition of HI?

      5+5=10

   (c) Draw the phase diagram for water system and find the number of degrees of freedom at the triple point of water.

      4+2=6

   (d) Give examples of three model systems where the energy gap between successive levels (i) remains the same, (ii) decreases and (iii) increases.

      3

(e) The reaction $2A \leftrightarrow A_2$ occurs photochemically. The different steps in the reaction system are,

(i) $A \xrightarrow{h\nu} A^*$

(ii) $A^* + A \xrightarrow{k_2} A_2$

(iii) $A^* \xrightarrow{k_3} A + h\nu'$

(iv) $A_2 \xrightarrow{k_4} 2A$
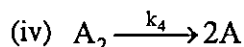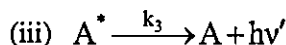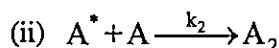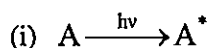
Applying the steady state concept of A^*, show that at photostationary equilibrium,

$$[A_2] = \frac{I_a}{K_4 \left\{ 1 + \dfrac{k_3}{k_2[A]} \right\}}$$

Also show that $[A_2]$ is independent of A when A is present in large excess. 6+2=8

(f) A heteronuclear diatomic molecule of reduced mass 1.63×10^{-24}g absorbs at 2880 cm^{-1}. Calculate the force constant assuming harmonic oscillator model. 4

(g) Methyl acetate was hydrolysed to acetic acid and methanol using 1 (N) HCl as catalyst. Aliquots of equal volume were removed at intervals and titrated with a solution of NaOH.

Time (min)	0	5	15	∞
NaOH (cm^3)	24.0	27.0	31.4	40.0

Show that it is a first order reaction and evaluate the average life period of the reaction, in minutes. 3

Group-C

5. (a) Draw the different conformers and their energy diagram of n-butane. 5

(b) Identify the product(s) of the following reaction and predict the major product with proper explanation. 5
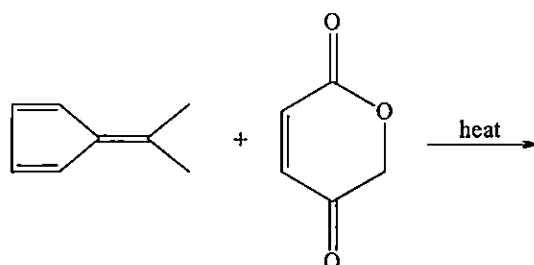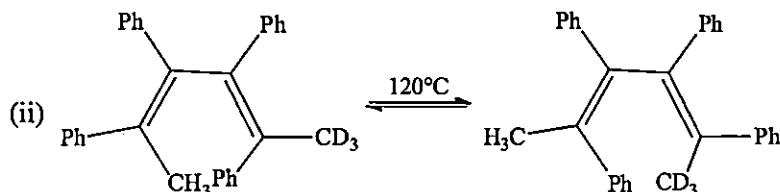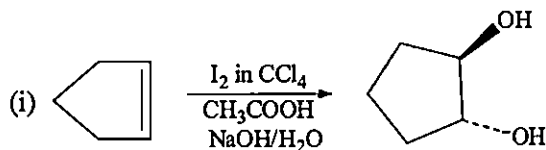

(c) LiAlH$_4$ reduction of R-Benzoin gives meso hydrobenzoin as the major product. Applying Cram's rule to rationalise the observation. 10

(d) Suggest the mechanism of the following transformation: 5×2=10

(i)

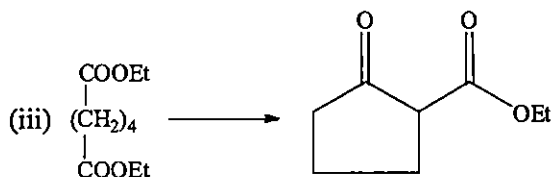$$\text{cyclopentene} \xrightarrow[\substack{CH_3COOH \\ NaOH/H_2O}]{I_2 \text{ in } CCl_4} \text{cyclopentane-1,2-diol (trans OH, OH)}$$

(ii)

$$\xrightleftharpoons{120°C}$$

(Ph-substituted diene with CD$_3$ and CH$_3$ groups transforming)

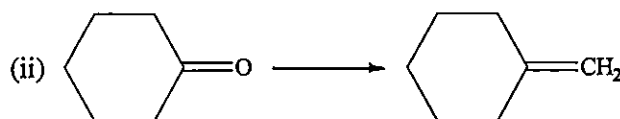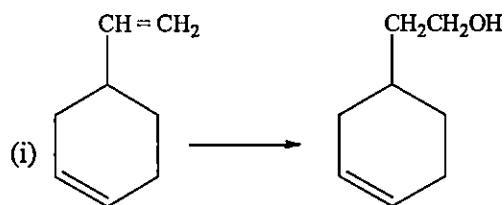(e) Synthesis   5×2=10

    (i) Cinnamic acid through Perkin reaction.
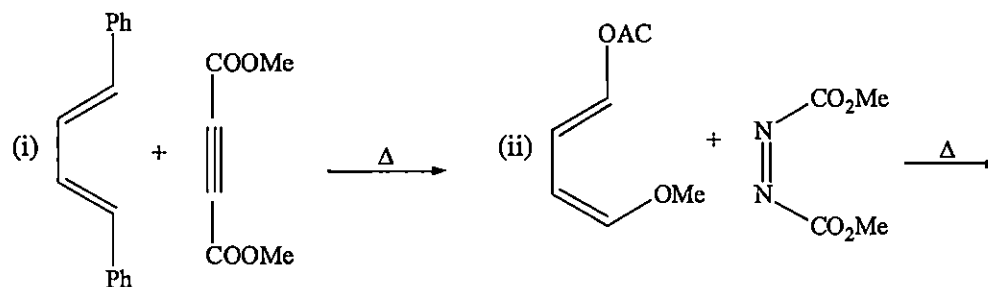
    (ii) 3-hydroxy-2-Butanone through acyloin condensation.

6. (a) How would you accomplish the following transformation?   5×3=15

(i)

$$\text{cyclohexene-CH=CH}_2 \longrightarrow \text{cyclohexene-CH}_2CH_2OH$$

(ii)

$$\text{cyclohexanone } (=O) \longrightarrow \text{cyclohexane} (=CH_2)$$

(iii)

$$\underset{\substack{| \\ (CH_2)_4 \\ | \\ COOEt}}{COOEt} \longrightarrow \text{cyclopentanone-2-carboxylic acid ethyl ester}$$

(b) Give the stereochemistry of the product of the given reactions.   5×2=10

(i)

$$\text{(Ph-diene)} + \underset{\substack{COOMe \\ \| \\ \| \\ COOMe}}{} \xrightarrow{\Delta}$$

(ii)

$$\text{(OAC, OMe diene)} + \underset{\substack{CO_2Me \\ N \\ \| \\ N \\ CO_2Me}}{} \xrightarrow{\Delta}$$
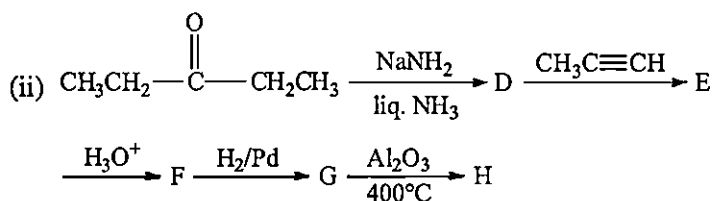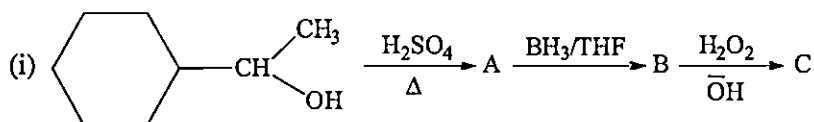
(c) Suggest the mechanism of the following Paternobuchi photo reaction.   6

(d) Identify A – H.   2×3=6

(i)

(ii)
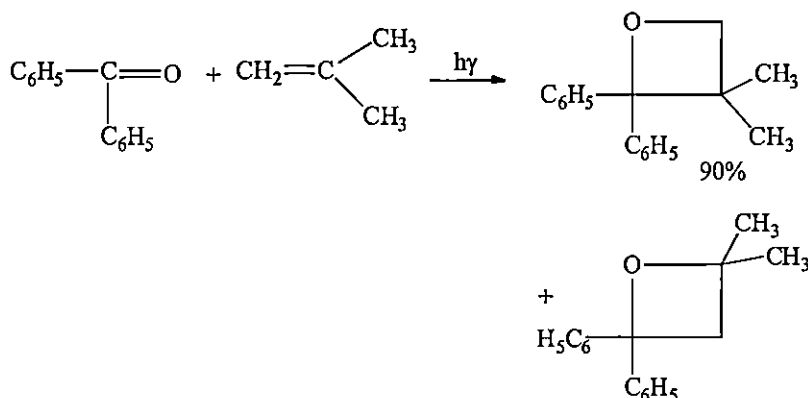
(e) Draw the Fischer Projection formula of the following molecules: 3

   (i) S–Lactic acid

   (ii) R–2-Butanol