CHEMISTRY - II

If the questions attempted are in excess of the prescribed number, only the question attempted first up to the prescribed number shall be valued and the remaining ones ignored. Answer may be written either in English or in Bengali but all answers must be in one and the 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. Hemoglobin exhibits Bour effect, but myoglobin does not. Explain.

2. Compare the C-C lengths of the alkenes in $[Pt(C_2H_4)cl_3]$ and $[Pt(C_2F_2)Cl_3]$.

3. Predict the electronic transition spectra of a Mn^{2+} ion in an weak octahedral field.

4. $Cu(eu)_3^{2+}$ is less stable than $Ni(eu)_3^{2+}$. (en= ethslenecdiamine) Explain.

5. Co occupies the highest position of the spectrochemical series. Explain.

                                                              4x5

GROUP - B

6. Why a binary solution of two components cannot be completely separated if an azeotrope is formed ?

7. From the expression for energy levels in a rigid rotor, show how you can determine the bond length of a diatomic molecule ?

8. State Grothus Draper and Stark Einstein's laws of photochemistry.

9. Why is the life time of fluorescence much less than that of phosphorescence ?

10. For a second order reaction of the form A →pdts , show that the half life time is dependent on the initial concentration.

                                                              4x5

GROUP - C

11. Draw Fisher Projection formula of all the stereoisomers of 3-bromo - 2 - butanol. Assign R/S configuration to C-2 and -3 of one of the threo-isomers.

12. Predict the major diastereomer formed by reduction of n-BuCO CH(Et)cl with $NaBH_4$. Explain.

13. Explain atropisomerism with an example.

14. Outline a method of resolution of $(\pm) - CH_3CH(NH_2)CO_2H$

15. Explain the regioselectivity of addition of acrolein with 1-methoxybutadiene.

                                                              4x5

This section comprises 6 questions in three groups. Answer Any Four questions taking at least one question from each group.

GROUP - A

16. (a) State the ground state term symbols of a d^2 ion and predict the electronic spectra in an octahedral field.

    (b) Illustrate all the stereoisomers possible for $[Co(NH_3)_2 (H_2O)_2 Cl_2]^+$ ion.

    (c) Describe the active site of myoglobin and function of it.

    (d) Illustrate the structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Explain.

    (e) For which of the following species the experimentally determined magnatic moment should be higher ? Explain your answer.

    (i) $[N_iCl_4]^{2-}$ (ii) $[N_i(NH_3)_6]^{2+}$ 8x5
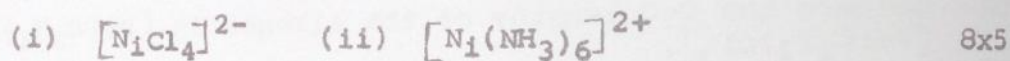
17. (a) Explain with examples the oxidative addition and insertion reactions. Give example of a fluxional organometallies.

    (b) What are ferredoxins ? Discuss the importance of ferredoxins in biology.

    (c) Calculate the CFSEs of $[Co(H_2O)_4 (NH_3)_2]^{3+}$, $[CoF_6]^{3-}$ and $[Co(CN)_6]^{3-}$ ions.

    (d) Explain with examples the chelate effect, trans effect and trans influence.

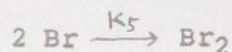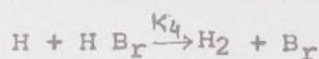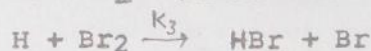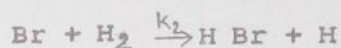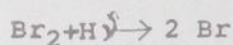   (e) Predict the geometries of $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$.   8x5

GROUP - B

18. (a) From first principles arrive at the expression for Gibbs Phase Rule, which connects the degree of freedom with number of components and phases.   10

    (b) Draw a labelled phase diagram of water, showing clearly the phase boundaries. Calculate the degree of freedom for each region in the diagram.   8

    (c) Write down the expression for Arrhenius' temperature dependence of reaction rate constant and explain the terms in it. In certain reactions it is seen that the rate constant decreases with rise in temperature. How do you account for this ?   2+2+3

    (d) Discuss two methods to experimentally determine the order of a reaction.   10

    (e) A first order reaction ($A \rightarrow B+C$) is 35 percent complete after 325 S. Calculate the rate constant. How long will it take for the reaction to be 70 percent complete ?   5

GROUP - B

19. (a) Draw a labelled Jablonski diagram with proper explanation
of the steps. 8

(b) The photochemical reaction between H_2 and Br_2 follows
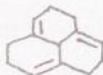the following steps

$$Br_2 + H\nu \xrightarrow{} 2 Br$$

$$Br + H_2 \xrightarrow{k_2} H Br + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + H Br \xrightarrow{k_4} H_2 + Br$$

$$2 Br \xrightarrow{k_5} Br_2$$

Find out an expression for $d[HBr]$ in terms of the rate
constants, absorbed intensity (Ia) and concentrations of
H_2, Br_2 and HBr. 12

(c) For the liquid - liquid phenol water system, draw the
phase diagram and label each region. Also find the degree
of freedom for each including the upper critical solution
temperature (UCST). 8

(d) Explain what do you understand by number and mass averaged
molecular weight giving expressions for both. 6

(e) State Raoult's law and derive the expression for partial
pressure P_i of pure liquid i at temperature T considering
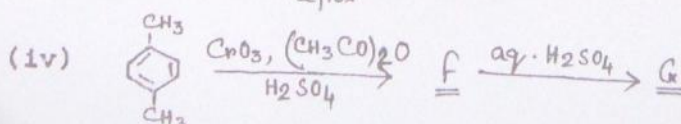an equilibrium between the pure liquid i and its vapour. 6
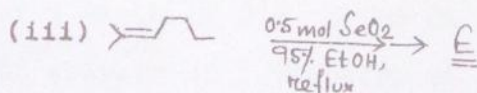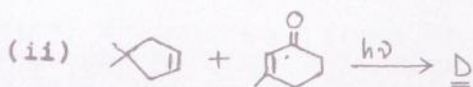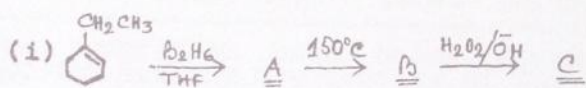
GROUP - C

20. (a) Draw Fischer projection formulae of the possible stereo-
isomers of 2,3,4 - trihydroxyglutaric acid. Comment on
their chirality, assigning R/S configuration to C-3 atom
in each case. 8

(b) Identify the symmetry elements present in the following
molecules. Assign point group and symmetry number to
each structures.

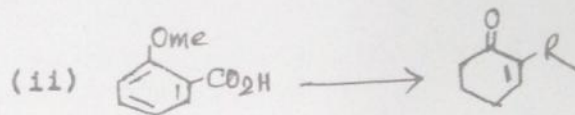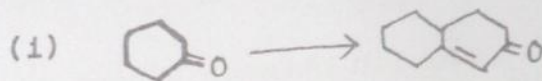1,3-Dichloroallene, cis-decalin, twist-boat conformer
of cyclo exane,

16

(c) Identify the products A - F of the following reactions.
(mechanism not required)

(i) $\xrightarrow[THF]{B_2H_6}$ A $\xrightarrow{150°C}$ B $\xrightarrow{H_2O_2/\bar{O}H}$ C

(ii) $\xrightarrow{h\nu}$ D

(iii) $\xrightarrow[\substack{95\% \, EtOH, \\ reflux}]{0.5 \, mol \, SeO_2}$ E

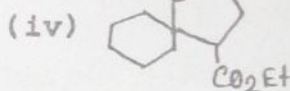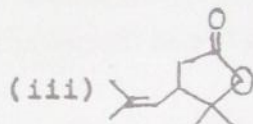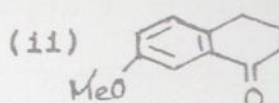(iv) $\xrightarrow[H_2SO_4]{CrO_3, (CH_3CO)_2O}$ F $\xrightarrow{aq. \, H_2SO_4}$ G 9

(d) Carry out the following conversions

(i)

(ii)

3+4

21. (a) Outline the synthetic route for each of the following compounds

(i)   (ii)

(iii)   (iv)

20

(b) What is meant by directed aldol condensation ? Explain it in case of aldol condensation of 2- pentanone and acetaldehyde.   6

(c) Depict the preferred conformer of trans-1,3 -di-tert-butylcyclohexane. Explain.   3

(d) Draw the conformations of the following cyclohexane derivatives. Comment on their energy difference, if any, on the basis of number of gauche butane interactions present. Also explain their chirality.

cis-1,2 - Dimethylcyclohexane, trans-1,2-Dimethylcyclo-hexane.   8

(e) How can you carry out cis-perhydroxylation of E-crotonic acid ? Depict the flying wedge projection formula of the product.   3