PG/IIS/CEM/203/23(Old)

M.Sc. 2nd Semester Examination, 2023

CHEMISTRY

(*Inorganic*)

PAPER – CEM-203(Old)

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

Candidates are required to give their answers in their own words as far as practicable

GROUP – A

1. Answer any *four* of the following questions : 2×4

(*a*) Determine the characters of irreducible representation of D_4 point group.

(*b*) What do you mean by fluxional behaviour ? Explain with a proper example.

(*c*) Classify the following compounds with respect to closo, nido, arachno and hypo $[B_{12}H_{12}]^{2-}$, $[B_5H_{11}]$, B_6H_{10}, $C_4B_2H_6$.

(*d*) Write down the steps involved for the determination of symmetry of vibrational modes of non-linear molecule using 3N Cartesian coordinate as base vector.

(*e*) How will you synthesize Tebbe's reagent ?

(*f*) Draw the probable binding modes of allyl ligand.

GROUP – B

2. Answer any *two* of the following questions : 8×2

(*a*) Determine the characters of the irreducible representation of C_{3v} point group. Write the appropriate representation of C_{3v} point group. Write the appropriate Mulliken Symbols for these irreducible representations. Show that P_x and P_y orbitals, as a pair, provide basis for the E representation of C_{3v} point group. $2 + 2 + 4$

(*b*) (*i*) Calculate the styx number of $[B_4H_8]$, $[B_3H_8^-]$ and establish the most stable structure.

(*ii*) With the help of styx number 3100 draw the probable structure of boron hydride. 5 + 3

(*c*) (*i*) Schematically present the possible orbital interaction in Fischer's and Schrock's complexes. Discuss on the magnetic behavior in each case.

(*ii*) What is the fundamental difference between the alkene and alkyne complexes while binding to the transition metal ion ? Draw the possible binding modes of alkyne to transition metal ions. 4 + 4

(*d*) (*i*) Explain 'reversal of polarity' during the reaction of transition metal bound alkene complexes.

(*ii*) Which of the following metal alkene complex do you think will look most like a metalla cyclopropane ? Explain your answer.

(I) $(CH_2=CH_2)Ni(PPh_3)_2$

(II) $(CH_2=CH_2)Fe(CO)_4$

(*iii*) Write down the product(s) of treatment of $[Cr(CO)_6]$ with $LiCH_3$ followed by $[(CH_3)_3O]BF_4$. Propose the mechanism.

3 + 3 + 2

GROUP – C

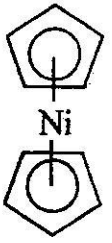
3. Answer any *four* of the following questions : 4 × 4

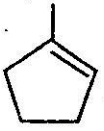
(*a*) What is the fundamental difference between the alkene and alkyne complexes while binding to the transition metal ion ? Draw the possible binding modes of alkyne to transition metal ions.

(*b*) Determine the characters of irreducible presentation of D_4 point group. Write the

appropriate Mulliken symbols for these irreducible representations.

(*c*) (*i*) Complete the following reactions

I. 

II. $Na_2[PdCl_4]$ +  $\xrightarrow{Na_2CO_3}$

(*ii*) 'NMR Spectroscopy is applied to detect/ monitor stereochemical non-rigidity'. Justify.

(*d*) (*i*) Write a short note on 'spectral transition probabilities'.

(*ii*) Use group theoretical principle to obtain the IR and Raman activity of the vibrational modes of H_2O.

(*e*) (*i*) Justify the 1, 2-migration mechanism in the 'ring wizzing' of η^1-Cp in [Fe(η^5-Cp)(η^1-Cp)$(CO)_2$] with respect to NMR spectroscopy.

(*ii*) Which among the following alkenes will bind most strongly to a metal ? Give reasons.

(I) Cyclooctadiene

(II) Ethylene

(III) Norborene

(IV) Cyclohexene

(*f*) (*i*) Explain why the polarization effect is not observed in cubic or higher symmetry molecule.

(*ii*) Discuss the NMR of $[Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$.