

M.Sc. 2nd Semester Examination, 2013

CHEMISTRY

(Inorganic)

PAPER—CEM - 203

Full Marks : 40

Time : 2 hours

Answer any **five** questions taking at least
two from each Group

The figures in the right-hand margin indicate marks

GROUP – A

1. (a) Using group theoretical principle determine the characters of irreducible representations of C_{4v} point group. Write appropriate Mulliken symbols for these irreducible representations. 3
- (b) With the help of group theory justify that $\pi \rightarrow \pi^*$ electronic transition is electric-

(Turn Over)

dipole allowed but $n \rightarrow \pi^*$ electronic transition is not electric-dipole allowed for formaldehyde molecule. Given below the character table for C_{2v} point group. 5

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

2. Using molecular orbital theory derive the expression for the energy of symmetric and antisymmetric states of H_2^+ ion. Deduce the expression for symmetric and antisymmetric functions of H_2^+ ion. (Derivation of secular determinant is not required). 4 + 4
3. (a) What do you mean by conditional stability constant? 2

- (b) Calculate the concentrations of free Ca^{2+} ions in a 0.10 M solution of CaY^{2-} at pH 5.0 and 12.0. Use the data given below. 3

$$\text{Log}K_f = 10.69$$

$$\alpha_{\text{Y}^{4-}} = 3.7 \times 10^{-7} \text{ at pH} = 5.0$$

$$\alpha_{\text{Y}^{4-}} = 0.98 \text{ at pH} = 12.0$$

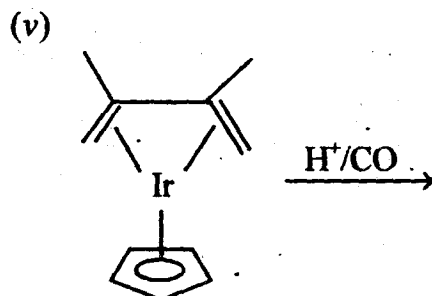
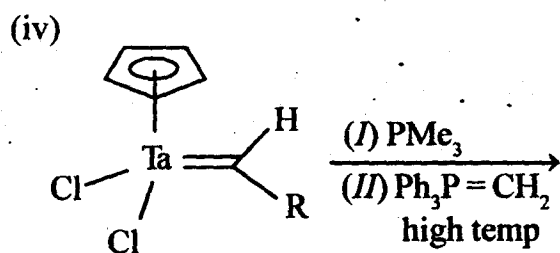
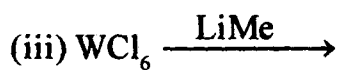
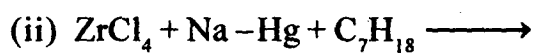
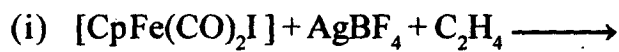
- (c) How EDTA selectivity can be increased for a metal ion? 3

4. (a) Use group theoretical principle to determine the symmetry of vibrational mode of $\text{Cis-N}_2\text{F}_2$ molecule using cartesian co-ordinate method. Identify the symmetry of IR and Raman active mode in this molecule. (Use the character table of C_{2v} point Group given in Q. No. 1) 3 + 1

- (b) What do you mean by representation of a direct product? Show that the representation of a direct product, Γ_{AB} , will contain the totally symmetric representation only if the irreducible $\Gamma_A =$ the irreducible Γ_B . 1 + 3

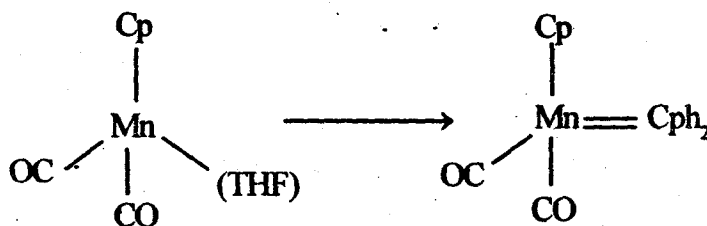
GROUP – B

5. (a) Complete the following reactions : 5



(b) "On forming $[\text{IrBr}(\text{CO})(\eta^2\text{-C}_2(\text{CN})_4)(\text{PPh}_3)_2]$, the C - C distance in $\text{C}_2(\text{CN})_2$ increases from 135 to 151 pm" - discuss. 2

(c) Put appropriate reagent for the following reaction. 1



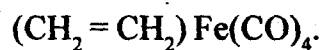
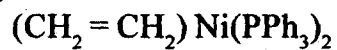
6. (a) What do you mean by ternary complex? Derive the expression for stability constant of ternary chelates. 1 + 4

(b) What are the differences between "chelating ligand" and "macrocyclic ligand"? 2

(c) Write the formula of Job's method used for the determination of composition of Metal-Ligand complexes. 1

7. (a) Discuss bonding in carbene complexes. 2

- (d) Which of the following M-alkene complex will look a most like metallacyclopropane and why? 1



8. (a) What is cyclic voltammetry ? Why it is so called ? What is its applications ? 2 + 1 + 1

- (b) Write down the relationship between excitation spectra and fluorescence spectra. 2

- (c) How does "flame photometry" differ from the "atomic absorption spectrophotometry" ? 2