PG/IIS/CEM-203/15

M.Sc. 2nd Semester Examination, 2015

CHEMISTRY

(*Inorganic*)

PAPER – CEM - 203

Full Marks : 40

Time : 2 hours

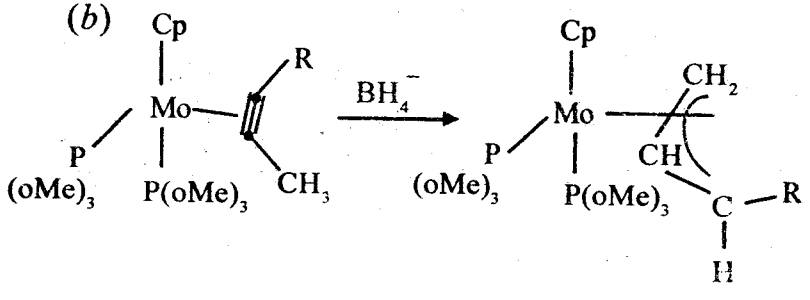
Answer any **five** questions taking at least **two** from each Group-A and Group-B

The figures in the right-hand margin indicate marks

GROUP – A

1. (*a*) Discuss the binding modes of 'alkene' ligand in 'transition metal alkene' compleres. 2

(*b*)



"In the above reaction, the attack of hydride ion at on η^2-coordinated alkyne can lead to η^3-allyl complex". Suggest the mechanism of this transformation. 3

(*c*) Complete the following reactions : 3

(*i*) $[CpNi(CO)_2] + RC \equiv CR \longrightarrow$

(*ii*)
$$(CH_3CN)_3W(CO)_3 + PhC \equiv C - Ph \xrightarrow[\text{Reflux}]{\text{EtOH}}$$

(*iii*)
$$CO_2(CO)_8 \xrightarrow[\substack{\text{THF} \\ T = < 25^\circ C}]{\text{t-Bu } C \equiv P}$$

2. (*a*) Discuss the possible orbital interaction in 'Fischer's Carbene' Complex. 2

(*b*) Why NMR Spectroscopy is used to detect flxional behaviour ? 2

(*c*) Justify the 1, 2-migration mechanism in the "ring wizzing" of $\eta^1 - Cp$ in $[Fe(\eta^5 - Cp)(CO)_2(\eta^1 - Cp)]$ complex with respect to NMR-spectroscopy. 3

(*d*) Write down the complete reaction when molybdenum-hexacarbonyl is refluxed with norborancdiene in octane media. 1

3. (*a*) Write short note on the "Irving Williams" order of stability constant for metals ion. 2

(*b*) Describe the determination of stability constant by Job's method. 3

(*c*) Silver forms a 1 : 1 complex with ethylenediamine having a formation constant of $5{\cdot}0 \times 10^4$. Calculate the concentration of silver ions in equilibrium in a solution containing 0·1 M each of the complex and the ligand. 3

4. (*a*) How can you derive the stability constant of ternary complexes by simultaneous equilibria method ? 2

(*b*) Calculate the concentration of free Ca^{2+} ions

in a 0·10 M solution of CaY^{2-} at a pH = 6·0 and at pH = 10·0. Use the data given below :

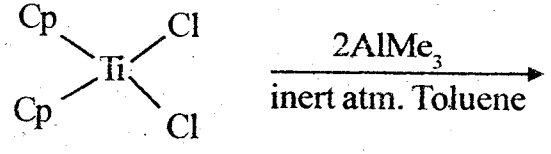
$\log K_f = 10{\cdot}69$

$\alpha.y^{4-} = 2{\cdot}3 \times 10^{-5}$ at pH = 6·0

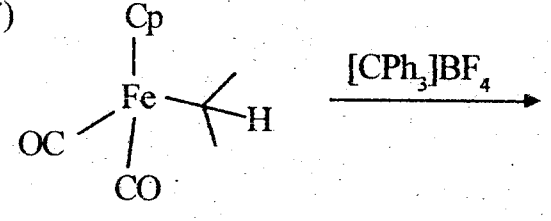
$\alpha.y^{4-} = 0{\cdot}36$ at pH = 10·0. 3

(*c*) Complete the following reactions :

(*i*)



(*ii*)



3

GROUP– B

5. (*a*) Dtermine the characters of the irreducible representations of C_{4v} point group. Write the appropriate Mulliken Symbols for these irreducible representations. Transformation

matrices for x and y give an E symmetry species, and z transforms as the A_1 species in C_{4v} point group. Find out how xy and $x^2 - y^2$ functions individually transform in C_{4v} point group. 3 + 3

(*b*) The ground state of NO_2 is A_1. To what excited states may it be excited by electric dipole transitions, and what polarization of light is it necessary to use ? Given below the character table for C_{2v} point group. 2

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
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

6. Using molecular orbital theory derive the expressions for the energy of symmetric and antisymmetric states of H_2^+ ion. Deduce the expressions for symmetric fuction and antisymmetric function of H^+_2 ion. Show electron

distribution of symmetric and antisymmetric states of this ion. (Derivation of secular determinant is not required). 4 + 3 + 1

7. (*a*) Investigate whether an A_1 electron in H_2O can make an electric dipole transition to a B_1 orbital. What polarized radiation will emitted or absorbed during this transition (Use the character table of C_{2v} point group given in **Q. No.5**) 2

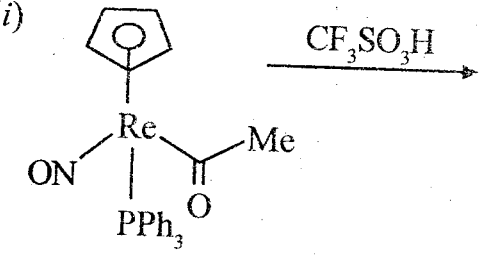
(*b*) Show that p_x and p_y orbitals provide basis for B_1 and B_2 representation for C_{2v} point group. (Use character table of C_{2v} point group given in **Q.No.5**) 2

(*c*) Show that the representation of a direct product, Γ_{AB}, will contain the totally symmetric representation only if the irreducible Γ_A = the irreducible Γ_B. 2

(*d*) Explain why the polarization effect is not observed in cubic or higher symmetry molecule. 2

8. (*a*) Predict the products $1\frac{1}{2} \times 2$

(*i*)



(*ii*)

$$(PPh_3)_3OsCl(NO) \xrightarrow{CH_2N_2}$$

(*b*) Write basic principles of "Paper chromatography" and "ion-exchange chromatography". $1\frac{1}{2} \times 2$

(*c*) He_2^+ and H_2^+ both have same bond order but differ in their stability. Explain. 2