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' complexes. 2

(b) 

\[
\begin{align*}
\text{Cp} & \quad \text{Mo} \quad \text{R} \\
\text{P(oMe)}_3 & \quad \text{P} & \quad \text{CH}_3
\end{align*}
\]

\[\text{BH}_4^- \quad \rightarrow \quad \text{Cp} \quad \text{Mo} \quad \text{CH}_2 \quad \text{R}\]

\[
\begin{align*}
\text{P(oMe)}_3 & \quad \text{P} & \quad \text{CH} & \quad \text{C} \\
\text{C} & \quad \text{H}
\end{align*}
\]
In the above reaction, the attack of hydride ion at on \( \eta^2 \)-coordinated alkyne can lead to \( \eta^3 \)-allyl complex. Suggest the mechanism of this transformation.

(c) Complete the following reactions:

\( (i) \quad [\text{CpNi}(\text{CO})_2] + \text{RC} \equiv \text{CR} \rightarrow \)

\( (ii) \quad (\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3 + \text{PhC} \equiv \text{C} \rightarrow \text{Ph} \xrightarrow{\text{EtOH}} \text{Reflux} \)

\( (iii) \quad \text{CO}_2(\text{CO})_8 \xrightarrow{\text{t-Bu} \text{C} \equiv \text{P}} \text{THF} \quad \text{T} = < 25^\circ\text{C} \)

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

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

(c) Justify the 1, 2-migration mechanism in the "ring wizzing" of \( \eta^1 - \text{Cp} \) in [\( \text{Fe}(\eta^5 - \text{Cp})(\text{CO})_2(\eta^1 - \text{Cp}) \)] complex with respect to NMR-spectroscopy.
(d) Write down the complete reaction when molybdenum-hexacarbonyl is refluxed with norboranediene in octane media.

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

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

(c) Silver forms a 1:1 complex with ethylenediamine having a formation constant of $5.0 \times 10^4$. Calculate the concentration of silver ions in equilibrium in a solution containing 0.1 M each of the complex and the ligand.

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

(b) Calculate the concentration of free $Ca^{2+}$ ions
in a 0·10 M solution of CaY\(^{2-}\) at pH = 6·0 and at pH = 10·0. Use the data given below:

\[
\log K_f = 10·69
\]
\[
\alpha_y^{4-} = 2·3 \times 10^{-5} \text{ at pH = 6·0}
\]
\[
\alpha_y^{4-} = 0·36 \text{ at pH = 10·0.}
\]

(c) Complete the following reactions:

\[(i) \] \[
\text{Cp} \quad \text{Cl} \quad \text{Ti} \quad \text{Cl} \quad \text{Cp} \quad \text{2AlMe}_3 \quad \text{inert atm. Toluene}
\]

\[(ii) \] \[
\text{Cp} \quad \text{Fe} \quad \text{H} \quad \text{Cp} \quad \text{O} \quad \text{CO} \quad \text{[CPh}_3\text{]BF}_4
\]

GROUP – B

5. (a) Determine 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.

(b) The ground state of \(\text{NO}_2\) 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.

<table>
<thead>
<tr>
<th>(C_{2v})</th>
<th>(E)</th>
<th>(C_2(z))</th>
<th>(\sigma_v(xz))</th>
<th>(\sigma_v'(yz))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>(R_z)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_1)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>(x, R_y)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_2)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(y, R_x)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Using molecular orbital theory derive the expressions for the energy of symmetric and antisymmetric states of \(\text{H}_2^+\) ion. Deduce the expressions for symmetric function and antisymmetric function of \(\text{H}_2^+\) 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 $\text{H}_2\text{O}$ 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)

(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)

(c) Show that the representation of a direct product, $\Gamma_{AB}$ will contain the totally symmetric representation only if the irreducible $\Gamma_A = \Gamma_B$.

(d) Explain why the polarization effect is not observed in cubic or higher symmetry molecule.
8. (a) Predict the products

\[(i) \quad \text{CF}_3\text{SO}_3\text{H} \quad \text{Me} \quad \text{Re} \quad \text{ON} \quad \text{PPh}_3 \quad \rightarrow \]

\[(ii) \quad (\text{PPh}_3)_3\text{OsCl(NO)} \quad \text{CH}_2\text{N}_2 \quad \rightarrow \]

(b) Write basic principles of "Paper chromatography" and "ion-exchange chromatography".

(c) \ce{He^2+} and \ce{H^2+} both have same bond order but differ in their stability. Explain.