M.Sc. 4th Semester Examination, 2015

CHEMISTRY

PAPER - CEM-402

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

(Inorganic Special)

Answer any five questions taking at least two from each Group

GROUP-A

1. (a) Calculate the bond valence in the following transition metal cluster compounds: 2 × 2

(i) \([\text{Nb}_6 (\mu_2 - \text{Cl})_{12} \text{Cl}_6]^{4-}\)

(ii) \([\text{Co}_2 (\mu_2 - \text{CH}_2)(\mu_2 - \text{Co}) (C_p^*)_2]^{4+}\)

(Turn Over)
(b) \([\text{Rh}_{11}(\text{CO})_{23}]^{3-}\) displays a structure with three face sharing octahedra \((g = 148, b = 25)\). Draw the metal core structure for this cluster.

(c) \([\text{Os}_2\text{Cl}_8]^{2-}\) displays staggered structure. Explain.

2. (a) Show the orbital overlap in 'tetragonal prismatic structure' in a metal-metal bonded species.

(b) What do you mean by 'Aurophilicity'? Explain with example.

(c) Give a brief account on 'quintuple bond'.

3. (a) What is the active site structure of the enzyme 'Xanthine Oxidase'?

(b) Give the mechanism involved in the oxidation of Xanthines to uric acids.

(c) Draw the active site structure of SOD. Explain the mechanism of oxidation of ascorbic acid to dehydro-ascorbic acid.
4. (a) What is 'nitrate reductase'. Write down the active site structure and discuss the mechanistic pathway of nitrate reduction. 

(b) Show the structure of 'Cobalamin' and explain its activity.

GROUP --B

5. (a) Justify the structure of the following Cluster compounds with respect to the number of valence electrons:

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Os₅(CO)₁₉</td>
<td>'Bow-tie'</td>
</tr>
<tr>
<td>(ii) Os₅(CO)₁₈</td>
<td>'Raft'</td>
</tr>
</tbody>
</table>

(b) How will you synthesize Rh₄(CO)₁₂ starting from Rh₂(μ-Cl)₂(CO)₄? Draw the structure of Rh₄(CO)₁₂.
(c) Predict the structure of Fe₄C(CO)₁₃.

6. (a) Draw the active site structure of cytochrome p-450 and write down the mechanistic pathway of hydroxylation activity.

(b) Write short notes on:

(i) Chlorophyll

(ii) PS-I and PS-II in Photosynthesis.

7. (a) Discuss the 'semibridging binding mode' of CO in Fe₂(CO)₇ (4, 4'-bipy).

(b) Cite one complex where CO acts as 6e⁻ donor. Show the binding mode of CO in the complex.

(c) 'Removal of all CO ligands in a transition metal carbonyl complex is rarely possible'—Justify.

(d) How will you synthesize Na₂[Fe(CO)₄]?
8. (a) Write down the basic principle involved in Mössbauer spectroscopy.

(b) Define self-assembly.

(c) What do you mean by ion-ion interaction and ion-dipole interaction.

(d) What is van der Waals interaction in supramolecular chemistry?

*(Organic Special)*

Answer any five questions taking at least two from each Group

**GROUP - A**

1. (a) Define self-assembly?

(b) What type of interaction are involved in the self-assembly process?

(c) Write the different types of supramolecular structures that can form by self-assembly.
(d) Write the applications of self-assembled structures (at least four).  

2. (a) What is a 'supramolecular gel' and how is it formed?  

(b) What are the major differences between a 'supramolecular' and a 'polymeric' gel?  

(c) Give some examples of Low Molecular Mass Organogelators.  

(d) How can one study the morphology of a supramolecular gel?  

3. (a) What is self-replication?  

(b) Write briefly the significance of such studies.  

(c) Propose a self-replicating scheme based on a model compound and explain how a simple template molecule can amplify.
4. The following compound, Vit. B₁, on treating gives the products as follows:

\[ \text{C}_{12}\text{H}_{18}\text{Cl}_{2}\text{N}_{4}\text{OS} \xrightarrow{\text{SO}_2} \text{Saturated with } \text{Na}_2\text{SO}_3, \text{room temp.} \text{C}_6\text{H}_9\text{NOS} + \text{C}_6\text{H}_9\text{N}_3\text{O}_3\text{S} \]

Identify the compound (A) and (B) and establish the structure of Vit. B₁.

5. (a) Write down the structures of (i) NAD and (ii) FAD and show their chemical mode of action in biological systems.

(b) Show how coenzyme of Vit. B₁ takes part in decarboxylation of pyruvic acid, the end product of carbohydrate metabolism and depict the chemical reactions involved therein.

GROUP - B

6. (a) Write the principles of green chemistry.
(b) "Nucleophilic substitution reactions are more common than electrophilic substitution in diazine system. The following reaction undergoes as shown:

\[
\begin{align*}
\text{Ph} & \quad \text{Br}_2 \\
\text{N} & \quad \text{N} \\
\text{Ph} & \quad \text{Br} \\
\end{align*}
\]

\[120^\circ C\]

Depict the mechanism of the reaction and state what kind of reaction path is followed during the transfunction.

(c) What would be the product/s when treated as follows and indicate the reason with explanation:

\[\begin{align*}
\text{CH}_3 & \quad \text{Na/C}_2\text{H}_5\text{OH} \\
\text{H}_3\text{C} & \quad \Delta \\
\end{align*}\]
10. (a) Synthesise the sedative drug, pentothal starting from Ethyl isopentyl diethyl malonate and thiourea.

(b) Synthesis sulphapyrazine, an antibacterial drug from glyoxal and...
(c) Carry out the following transformation and indicate the product/s in each case with mechanism (any two):

\[2 \times 2\]

(i)

\[
\begin{align*}
\text{Ph} & \quad \text{KOH/THF} \quad \text{Room Temp.} & \quad \text{Ph} \\
\xrightarrow{\text{CH}_3-\text{CH}_2-\text{CHO}}
\end{align*}
\]

(ii)

\[
\begin{align*}
\text{H}_3\text{C} & \quad + \quad \text{NH}_2-\text{NH}_2 & \quad \Delta & \quad \text{Br}_2/\text{ACOH} (\Delta) & \quad \text{PCl}_5 & \quad [?] \\
\xrightarrow{\text{[?]}}
\end{align*}
\]

(iii)

\[
\begin{align*}
\text{CH}_2\text{ONa} & \quad \text{PCl}_3 & \quad \text{H}_2/\text{Pd-C} & \quad \text{BaSO}_4 \\
\xrightarrow{\Delta} & \quad \Delta & \quad \\
\end{align*}
\]

PG/IVS/CEM-402/15

(Turn Over)
(Physical Special)

Answer any four questions taking at least two from each Group

GROUP - A

Answer any two questions

1. (a) What type of molecular weight is determined by sedimentation equilibrium method and how? Why is it more advantageous than sedimentation velocity method?  

   (b) Calculate the molar mass of haemoglobin from the fact that in an equilibrium ultracentrifuge experiment at 20°C, \( c_2/c_1 = 9.40 \), \( r_1 = 5.5 \text{ cm} \) and \( r_2 = 6.5 \text{ cm} \). The ultracentrifuge rotor is operated at 120 rps. \( \bar{v} = 0.749 \text{ cm}^3 \text{ g}^{-1} \) and \( \rho = 0.9982 \text{ g cm}^{-3} \).

2. (a) Derive Flory-Huggins equation for the vapour pressure of a polymer solution.

   (b) The molar mass \( M_m \) of haemoglobin is 64,450 g mol\(^{-1}\). If it contains 0.35 mass percent of Fe, what is its minimum molar mass? Also, calculate the number of Fe atoms present in haemoglobin.
3. Write down the basic principle of chromatographic separation of the proteins. What is the basic difference in between the ion-exchange chromatography and affinity chromatography? What is HPLC (high pressure liquid chromatography) and why do this method give high resolution of protein components? 3 + 4 + 3

4. What is meant by entropy production is an irreversible process? Illustrate your answer with respect to heat flow. Establish Prigogene's principle of minimum entropy production. 2 + 3 + 5

GROUP - B

Answer any two questions

5. Derive the expression for the rate of entropy production for any electrokinetic process where an electric potential difference causes a pressure difference. Define any one such phenomenon in term of the phenomenological coefficients. 8 + 2
6. (a) Why in normal cases the frequency of \( \gamma \) emission of a excited radio nucleus is not equal to that of frequency of reabsorption of that nucleus?

(b) What do you mean by 'Doppler effect'? The half-life of \(^{67}\text{Zn}\) nucleus is 9400 ns. Calculate the line-width of \( \gamma \)-ray emission.

(c) Give an estimate of the valence state of an unknown tin compound using Mössbauer isotope \(^{119}\text{Sn}\).

(d) Explain why Mössbauer spectra of \([\text{Fe(CN)}_6]^{4-}\) and \([\text{Fe(CN)}_5\text{NO}]^{2-}\) are different although in both the cases the central atom is in same oxidation state?

7. State and prove Hellmann-Feynman theorem. Use this theorem to deduce the following expression of electrical polarizability (\(\alpha_{zz}\)).

\[
\alpha_{zz} = 2 \sum_{n \neq 0} \frac{(\mu_z)_{on}}{E_n^{(0)} - E_0^{(0)}}
\]

where symbols have their usual meaning.
8. Write the name (three letter code) and molecular structure of acidic, basic, polar but uncharged and non-polar amino acid residues (one from each group) found in the protein structure. What is the isoelectric point of a protein? Describe the acid-base titration curve of any acidic amino acid residue and show the different associated ionic forms of the residue.  \( 4 + 2 + 4 \)