

2016

M.Sc. 4th Seme. Examination

CHEMISTRY

PAPER—CEM-402

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

(Physical Special)

Answer any *four* questions,
taking *two* questions from each group.

Group—A

Answer any *two* questions.

1. (a) State the basic principles of irreversible thermodynamics.

(Turn Over)

- (b) What do you mean by phenomenological co-efficients ?
Write down the expression for two-force and two-flux systems. State the Onsager reciprocity relation.
- (c) What is meant by entropy production in an irreversible process ?

$$(1\frac{1}{2}+1\frac{1}{2})+(2+2+1)+2$$

2. (a) Establish the interrelationship between two thermoelectric pressure in terms of the appropriate phenomenological co-efficients.
- (b) Define streaming potential and electroosmotic pressure in terms of the appropriate phenomenological co-efficients.

$$7+(1\frac{1}{2}+1\frac{1}{2})$$

3. (a) Establish the frequency shift of a ν -photon, $\Delta\nu = \frac{2E_R}{h}$.
- (b) Point out the conditions for which Mössbauer spectroscopy would be possible.
- (c) A free Mössbauer nucleus of mass 100.6 amu emits radiation of wavelength 0.1 nm. Calculate the recoil velocity and Doppler shift.

$$3+3+4$$

4. Potential energy of interaction between two parallelly oriented dipole is given by,

$$V = \frac{\mu_1 \mu_2}{4\pi \epsilon_0 r^3} (1 - 3 \cos^2 \theta)$$

θ is the angle between the two interacting dipoles. All other symbols have their usual significances.

Use the above expression to show that dipole-dipole interaction depends on temperature but dipole induced dipole interaction is independent of temperature. 5+5

Group—B

Answer any *two* questions.

5. (a) Define intrinsic viscosity. How is it determined ?
 (b) What is particle structure factor ?
 (c) How does diffusion method is helpful for determination of average molecular weight of a macromolecule ?
 (d) A solution of a protein was investigated in an ultracentrifugation velocity measurement at 20°C, the rotor speed being 50,000 rpm. The boundary receded as follows.

t (s)	0	300	600	900	1200	1500	1800
r (cm)	6.127	6.153	6.179	6.205	6.231	6.257	6.283

Calculate the sedimentation co-efficient and the molar mass of the protein.

Given $\bar{v} = 0.728 \text{ cm}^3 \text{ g}^{-1}$ and $D = 7.62 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$,
 $\rho = 0.9981 \text{ gcm}^{-3}$. (1+2)+2+2+3

6. (a) Why the \overline{M}_n is determined by osmometry method? Describe the thermodynamics involved in average molecular weight determination by osmosis?
- (b) Given the following composition molar mass data for a polydisperse polymer mixture.

mass (%)	25.0	50.0	25.0
M_i (kgmol^{-1})	1.00	1.20	1.40

Calculate the polydispersity index for the polymer mixture. (2+5)+3

7. (a) Write down the complete structure of oxytocin. What would be the net charge on this molecule at the average physiological pH of 7.3, at pH 4 and at pH 9? Indicate which atoms in oxytocin can potentially form hydrogen bonds with water molecules.
- (b) Define primary, secondary, tertiary and quaternary structure of proteins. (2+1+1+1+1)+4
8. (a) A ^{57}Fe nucleus has spins $3/2$ and $1/2$ in its excited and ground states, respectively. Into how many lines will the ν -ray spectrum split if (a) the nucleus is under the influence of only an internal electric field gradient and (b) only an external magnetic field is applied?

- (b) Predict the variation of isomer shift in Sn^{4+} , Sn^{2+} and Sn, covalently bonded to four groups. Explain the cause of this variation.
- (c) How can you differentiate between FeSO_4 and FeCl_3 with the help of Mössbauer spectra. 4+3+3
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(Organic Special)

Answer any *five* questions,
taking at least *two* from each group.

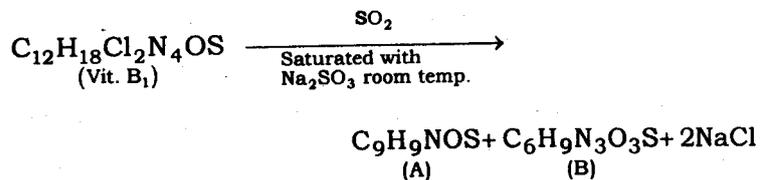
Group—A

1. (a) What is a 'supramolecular gel' and how is it formed ?
- (b) What are major the 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 ? 2+2+2+2
2. (a) Write the principles of green chemistry.
- (b) Give examples (i) a green synthesis of gold nanoparticles and (ii) a green organic synthesis.

- (c) How plant based chemicals are defined as 'renewable' chemicals ?
- (d) What is the significance of 'renewable chemicals' in society ? 3+2+1+2
3. (a) Define Ramachandran plot.
- (b) Locate the following secondary structural element of proteins in Ramachandran plot : α -helix, parallel β -pleated sheet, antiparallel β -pleated sheet, 3.10 helix.
- (c) What is protein quarternary structure ? 2+3+3
4. (a) Define the following secondary structural elements : α -helix, β -pleated sheet, β -turn, 3.10 helix ?
- (b) Why proline is known as helix breaker ? $1\frac{1}{2} \times 4 + 2$
5. (a) Draw the structures of FAD and NAD and state their mode of activity in biological reactions.
- (b) How pyruvic acid reacts with Vitamin B₁ as well as Lipomide, coenzyme A, FAD and NAD and restore their original state of reactivity. Show the different steps of the reaction. 4+4

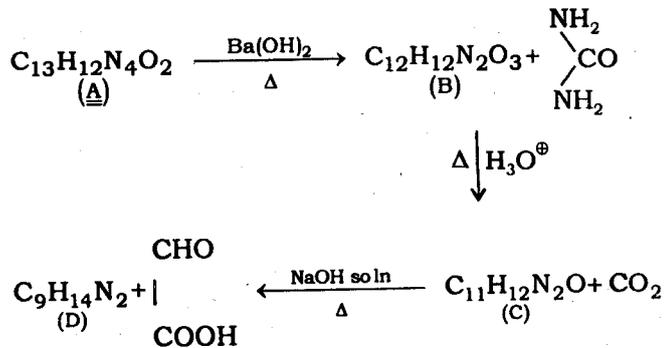
Group—B

6. Vitamin 'B₁' on treating on treating 'SO₂' gives the following products :



Identify 'A' and 'B' and deduce the structure of Vitamin 'B₁'.
4+4

7. (a) The following compound (A) gives the products as follow :



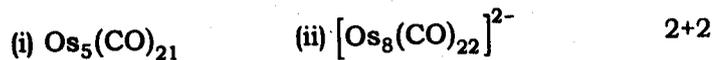
'D' was identified as 5N-methyl, 4, 5-diamino-O-Xylene, hence draw backwards and deduce the structure of 'A'.

- (b) Synthesise Vitamin B₁ starting from 3, 4-dimethyl aniline and ribose.

8. (a) Draw the reaction pathway of carbohydrate metabolism of glucose to pyruvic acid.
- (b) How Vitamin B_1 reacts with pyruvic acid to produce acetaldehyde as the end product. Give mechanism for each of the steps. 4+4
9. (a) Define self-assembly ?
- (b) What type of interactions 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*). 2×4
10. (a) What is protein tertiary structure ?
- (b) What types of bonds are involved in protein tertiary structure ?
- (c) What is protein denaturation ?
- (d) Protein 3D structure fall into two main groups. Elaborate with examples. 2×4
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(Inorganic Special)**Group—A**Answer any *two* questions.

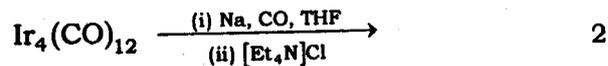
1. (a) Use Wade's rule to suggest the geometry of the cluster core of the following cluster molecules :



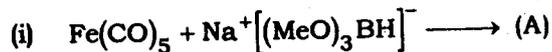
- (b) "Monocapped octahedral structure of $\text{Os}_7(\text{CO})_{21}$ is in accordance with the nature of valence electrons available" — Justify. 2

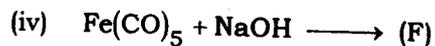
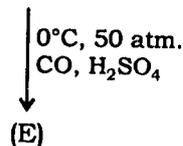
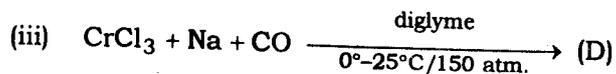
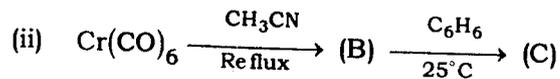
- (c) "The core structure of $\text{Os}_5(\text{CO})_{16}$ is trigonalbipyramidal" — Rationalise. 2

- (d) Complete the following reaction and predict the structure of the product —



2. (a) Predict the product of the following incomplete reactions :
1×6





(b) What do you mean by "Super reduced species"? 2

(c) What will be the final product when

(i) $[\text{Mn(CO)}_5]^-$ is reacted with Fe(CO)_5 .

(ii) Fe(CO)_5 is treated with $\text{Ph} - \overset{\text{O}}{\parallel} \text{C} - \text{Ph}$ and sodium metal in dioxane solvent. 1+1

3. (a) How will you synthesize $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, starting from $\text{Fe}_3(\text{CO})_{12}$? Discuss the structure of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$. 3

(b) Synthesize $[\text{Co}_3(\text{CO})_{10}]^-$ from $\text{Co}_2(\text{CO})_3$. Draw the structure of $[\text{Co}_3(\text{CO})_{10}]^-$ and discuss. 3

- (c) Explain the structural features in $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ complex. 2
- (d) For $\text{Co}_3(\text{CO})_9 (\mu_3 - \text{CCl})$ cluster, confirm that the valence electron count is consistent with the metal framework adopted. 2

Group—B

Answer any *two* questions.

4. (a) What is alcohol dehydrogenase (ADH)? Give the active site structure and mechanistic pathway for oxidation of alcohol? 1+2+2
- (b) Draw active site structure of Cytochrome c and mention its function in biological process. 3
- (c) Give the mechanistic action of SOD on super oxide. 2
5. (a) Write short notes on the structure of peroxidase and account for reduction of H_2O_2 by various organic molecules. 2+2
- (b) Draw the active site structure catalase and write down the mechanistic pathway of H_2O_2 disproportionation. 2+2

- (c) Give a mechanism of hydrolysis of peptides to proteins by carboxy peptidase. 2
6. (a) What is the function of sulphite reductase? Draw the active site structure and give the mechanism of the reduction of sulphite. 1+4
- (b) Give the mechanism of the nitrogen fixation by nitrogenase. 3
- (c) Draw the active site structure of chlorophyll. 2
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