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.

(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,

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

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

(*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 ? $1\frac{1}{2}\times4+2$

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 B_1 as well as Lipomide, coenzyme $\underline{\underline{A}}$, FAD and NAD and restore their original state of reactivity. Show the different steps of the reaction. 4+4

Group—B

6. Vitamin 'B_1' on treating on treating 'SO_2' gives the following products :

$$\underset{\text{(Vit. } B_1)}{C_{12}H_{18}Cl_2N_4OS} \xrightarrow[\text{Saturated with } Na_2SO_3 \text{ room temp.}]{SO_2} \underset{(A)}{C_9H_9NOS} + \underset{(B)}{C_6H_9N_3O_3S} + 2NaCl$$

Identify 'A' and 'B' and deduce the structure of Vitamin 'B_1'. 4+4

7. (a) The following compound $(\underline{A})$ gives the products as follow :

$$\underset{(\underline{A})}{C_{13}H_{12}N_4O_2} \xrightarrow[\Delta]{Ba(OH)_2} \underset{(B)}{C_{12}H_{12}N_2O_3} + \begin{matrix} NH_2 \\ \diagdown \\ CO \\ \diagup \\ NH_2 \end{matrix}$$

$$\underset{(B)}{C_{12}H_{12}N_2O_3} \xrightarrow{\Delta,\ H_3O^{\oplus}} \underset{(D)}{C_9H_{14}N_2} + \begin{matrix} CHO \\ | \\ COOH \end{matrix}$$

$$\underset{(D)}{C_9H_{14}N_2} + \begin{matrix} CHO \\ | \\ COOH \end{matrix} \xrightarrow[\Delta]{NaOH \text{ soln}} \underset{(C)}{C_{11}H_{12}N_2O} + CO_2$$

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

(b) Synthesise Vitamin $\underline{B}_1$ 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 $\underline{B}_1$ 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 :

(i) $Os_5(CO)_{21}$ (ii) $[Os_8(CO)_{22}]^{2-}$ 2+2

(b) "Monocapped octahedral structure of $Os_7(CO)_{21}$ is in accordance with the nature of valence electrons available" — Justify. 2

(c) "The core structure of $O_5(CO)_{16}$ is trigonalbipyramidal" — Rationalise. 2

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

$$Ir_4(CO)_{12} \xrightarrow[\text{(ii) } [Et_4N]Cl]{\text{(i) Na, CO, THF}} \qquad 2$$

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

(i) $Fe(CO)_5 + Na^+[(MeO)_3BH]^- \longrightarrow (A)$

(ii) $Cr(CO)_6 \xrightarrow[\text{Reflux}]{CH_3CN} (B) \xrightarrow[25^\circ C]{C_6H_6} (C)$

(iii) $CrCl_3 + Na + CO \xrightarrow[0°–25°C/150\ atm.]{diglyme} (D)$

$(D) \xrightarrow[CO,\ H_2SO_4]{0°C,\ 50\ atm.} (E)$

(iv) $Fe(CO)_5 + NaOH \longrightarrow (F)$

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

(c) What will be the final product when

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

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

3. (a) How will you synthesize $[Fe_3(CO)_{11}]^{2-}$, starting from $Fe_3(CO)_{12}$? Discuss the structure of $[Fe_3(CO)_{11}]^{2-}$. 3

(b) Synthesize $[Co_3(CO)_{10}]^-$ from $Co_2(CO)_3$. Draw the structure of $[Co_3(CO)_{10}]^-$ and discuss. 3

(c) Explain the structural features in $[Fe_4(CO)_{13}]^{2-}$ complex. 2

(d) For $Co_3(CO)_9$ (μ_3 – CCl) cluster, confirm that the valence electron count is consistent with the metal framwork 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 disproportination. 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 sight structure of chlorophyll. 2
