2016

M.Sc.

3rd Semester Examination

CHEMISTRY

PAPER—CEM-302

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.

(*Organic Special*)

Answer any *five* questions.

1. (a) Define self-assembly ?

(b) What kind of interactions are involved in the self-assembly process ?

(c) Write the different types of supramolecular structures that can form by self-assembly.

(d) Write the structures of two triterpenoids that spontaneously self-assemble in liquids and the mode of their self-assembly. 2×4

2. (a) Write the principles of green chemistry.

(b) Give examples of (i) a green synthesis of gold nanoparticles and (ii) a green organic synthesis.

(c) How triterpenoids can be termed as "renewable nano"s ? 3+3+2

3. (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 ? 2×4

4. (a) Define the following secondary structural elements : α-helix, β-pleated sheet, β-turn, 3.10 helix ?

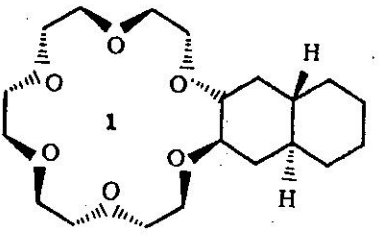
(b) Why proline is known as helix breaker ? $1\frac{1}{2}\times4+2$

5. (a) Design a receptor for the complexation of barbiturates, synthesize it and show the mode of its complexation.

(b) How the barbiturate receptors can be modified to design a protease enzyme mimic ? 2×4

6. (a) What is template effect ?

(b) How does macrocyclization work even through it is an entropically disfavorable process ?



(c) How does 18-crown-6 bind a monovalent cation ? Name a naturally occurring ionophore having similar selectivity ?

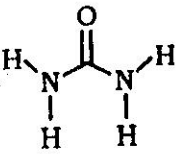
(d) Write the IUPAC name of compound **1** and propose a synthetic route. 2×4

7. (a) Define molecular recognition and write the principal forces involved in this process.

(b) How can one use 'U'-tube transport experiment for the separation of ions/molecules ?

(c) Design a suitable receptor for adepic acid, synthesize it and show the mode of its complexation. 2+2+4

8. (a) Design a receptor for urea **2**, synthesize it and show the mode of its complexation.



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(b) Design a suitable receptor for monopotassium salts of a dicarboxylic acid, synthesize it and show the mode of its complexation. 2×4

9. (a) What are cryptands ?

(b) How sodium sodide or potassium electride are formed ?

(c) How can one use cryptands as a Light Conversion Device ? 2+2+4

10. (a) Write the applications of crown ethers.

(b) What is the principle of preorganization ?

(c) How spherands can bind to metal ions more efficiently than the podands ? 2+2+4

(Inorganic Special)

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

Group—A

1. (a) What do you mean by DOSENCO state ? 2

(b) Describe the photochemical reduction and oxidation of H_2O molecules using $[Ru(bpy)_3]^{2+}$ as photosensitizer. 8

2. (a) What is the function of the enzyme alcohol dehydrogenase (ADH) ? Give the mechanism of action of the said enzyme. 1+3

(b) Draw the active site structure of ascarbic acid oxidase. Give mechanism of the oxidation of ascarbic acid by this enzyme. 2+2

(c) Draw the active site structure of cabalamine. 2

3. (a) Derive an expression of Hall coefficient for a metal. 3

(b) Find the expression for 'Frenkel defect' in solid. 3

(c) Write short note on edge dislocation. 4

Group—B

4. (a) How can you distinguish between static and dynamic quenching of theorescence ? 2

(b) Write down the criterias of a compound to function as a good photosensitizer. 3

(c) What are the thermodynamic and kinetic limitations on the photochemical conversion and storage of sunlight. 3

(d) Generally the photo-excitation of metal carbonyl compounds increase the weakness of metal-cobond. Explain. 2

5. (a) Discuss the active site structure of catalase and explain the dispropornation of H_2O_2 by the enzyme. 2+3

(b) Write down the mechanism of sulphite oxidase for the oxidation of sulphite. 3

(c) Draw the active site structure of cytochrome. 2

6. (a) Cite the differences between metal, insulator and semiconductor. 2

(b) Draw E–K diagram for direct and indirect lattice. 2

(c) Write short notes on : 3+3

(i) Resonance energy transfer ;

(ii) Spontaneous emission.

(*Physical Special*)

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

Group—A

1. Define grand partition function for bosons and hence derive Bose-Einstein distribution law. 10

2. What is meant by Bose-Einstein condensation ? Obtain the expression for the temperature at which the condensation phenomenone occurs. 2+8

3. (a) Derive Planck's law of radiation and hence show that both Wien's law and Rayleigh's law are simply particular cases of it.

   (b) Calculate the translational partition function for hydrogen atom at 3000K confined to move in a box of volume of 2.494×10^5 cm^3. Also determine the thermal de Broglie wavelength. 7+3

4. (a) Explain partition function and derive the expression relating entropy and molecular partition function.

   (b) What is 'spectral energy density'?

   (c) State Kirchoff's law of radiation. 6+2+2

Group—B

5. Derive the appropriate expression which show that the viscosity co-efficient (η) of a liquid can be determined from absolute reaction rate theory. 10

6. (a) What are microscopic diffusion controlled reactions ? Derive the expression for the rate of partially microscopic diffusion controlled reaction.

   (b) What is the dielectric contribution to the entropy of activation at constant ionic strength in solution of two ionic species ? (1+5)+4

7. (a) What is the utility of potential energy surface (PES) in a kinetic reaction ?

   (b) The following reaction occurs in aqueous solution

$$CH_2ClCOO^- + OH^- \longrightarrow CH_2OHCOO^- + Cl^-$$

   Deduce qualitatively the following :

   (i) The effect on the rate of decreasing dielectric constant.

   (ii) The effect on the rate of increasing ionic strength.

   (iii) The effect on the rate of increasing pressure.

   (iv) The sign of entropy of activation.

(c) The rate of a reaction in solution at 27°C is increased by 5 times when the pressure difference was made to 1000 atm. Calculate the volume of activation of the reaction. 1+6+3

8. (a) Starting from equation

$$d\nu = -q_M dV - \frac{q_M}{Z_j F} d\mu_j - \sum \Gamma_i d\mu_i$$

derive

$$\left(\frac{d\nu}{2RTd\ln a_{\pm}}\right)_{\text{const. } V_{-/+}} = -\Gamma_{+/-}$$

for 1 : 1 type of electrolyte, where ν = surface tension and Γ_i = surface excess for ith type of species at the interface and all other terms bear usual significance.

(b) Define surface excess (Γ). Write down the mathematical form of Gibb's adsorption equation.

(c) "The surface excess can have both positive and negative value" — Justify the statement. 6+2+2

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