2017

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.

(*Physical Special*)

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

Group—A

1. (a) Define grand partition function for fermions and hence derive Fermi-Dirac distribution law.

   (b) Can β (Lagrangian multiplier) be negative ? Explain your answer.   (2+5)+3

2. Derive the expression of ideal gas equation given by Einstein.

   10

3. (a) For a polarizable interface prove that

$$d\gamma = -q_M d\gamma - \frac{q_M}{Z_j F} d\mu_j - \sum_i \Gamma_i d\mu_i$$

where $d\nu$ is the infinitesimal change in surface tension and the other terms bear usual significance.

   (b) Define fuel cell. Write down the cathodic and anodic reaction of hydrogen-oxygen fuel cell.   7+(1+2)

4. (a) "The surface excess can have both positive and negative value." -- Justify. 2×5

   (b) What is 'ultraviolet catastrophe'?

   (c) Define solvent binding or electrostriction.

   (d) Define spectral energy density.

   (e) Write down the basic principle to study a high temperature fast gaseous reaction by shock wave method.

Group—B

5. Derive the rate equation between two uncharged species if the reaction is fully diffusion controlled. Discuss the effect of the sizes on the reaction rate. 8+2

6. (a) "In a reaction between two ions entropy of activation always decreases after formation of activated complex due to electrostriction." — Criticise the statement.

   (b) What do you mean by Potential Energy Surface (PES) and saddle point ? Explain with reference to the reaction

$$H^\alpha - H^\beta + H^\nu \rightarrow H^\alpha + H^\beta - H^\nu .$$ 4+6

7. Using appropriate expression for partition function find out the reaction rate according to absolute reaction rate theory. 10

8. (a) The energies of the first three energy levels of fluorine atom, determined from spectroscopy, are as follows —

Energy level	Energy, cm^{-1}
$^2P_{3/2}$	0.00
$^2P_{1/2}$	404.0
$^2D_{5/2}$	102,406.5

Calculate the electronic partition function.

(Turn Over)

(b) The fundamental vibrational frequency of F_2 is 2.676×10^{13} Hz. Calculate the vibrational partition function of F_2 at 25°C.

(c) The radii of two nonionic solutes A & B are 2.7 A° and 3.8 A° respectively. For a reaction between A and B in water at 25°C calculate the rate constant, if the reaction be diffusion controlled. Viscosity of the solvent is 0.9 CP. 4+3+3

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(Inorganic Special)

Group—A

(Answer any *two* questions)

1. (a) Discuss about the active site structure and the function of enzyme Xanthene oxidase. 4

(b) Draw the active site structure of super oxide dismutage. 3

(c) Explain the mechanism involves in the peroxidase catalized reaction. 3

2. (a) What is origin of colour centre ? Describe the mechanism of formation of F-centre.

(b) Derive the expression for dislocation and shear strength of a single crystal. 5+5

3. Write short notes on :

(a) Stimulated absorption ;

(b) Radiationless transitions ;

(c) Charge transfer excited states. 4+4+2

Group—B

(Answer any *two* questions)

4. (a) In presence of photon, the reaction between $[Mn_2(CO)_{10}]$ and PPh_3 generate two products, one is major and another is minor. Write the products of the reaction and explain the mechanism of products formation. 4

(b) When Photolysis of $[W_2(\eta^5 - C_5H_5)_2(CO)_6]$ is performed in presence of Ph_3Cl the radical $Ph_3C^{\cdot}$ is found in the reaction medium. Explain the formation of this radical.

3

(c) The parity selection rule for radiationless transition is precisely opposite of the selection rule for radiative transitions. Explain. 3

5. (a) Define "Actual lifetime" and "inherent lifetime" in photochemical reaction. 2

(b) State the conditions which must be satisfy for developing photochemical energy storage cycles. 4

(c) How can you distinguish between "static" and "dynamic" quenching of fluorescence ? 4

6. (a) Where carboxy peptidase is found ? Write down the active site structure and how it catalysis the hydrolysis of proteins. 4

(b) Write down the mechanism of nitrogen fixation by nitrogenase. 3

(c) Write short notes on photosynthetic electron transfer chain. 3

(*Organic Special*)

Answer any *five* questions.

1. (a) What is aromatic-aromatic (π-π) interaction ?

   (b) Show schematically the potential energy diagram for two interacting π-atoms as a function of their orientation.

   (c) Charge transfer transitions observed for EDA complexes are a consequence not a cause of the more general π-π interaction.

   (d) Give an example of Host-Guest complexation utilizing aromatic-aromatic interaction.   2×4

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

   (b) Design, synthesize and explain the mode of action of a protease enzyme mimic.   4+4

3. (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

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4. (a) What are cyclodextrins ?

   (b) p-chlorination of anisole is preferred in water in the presence of β-CD with rate acceleration. How do you explain this observation ?

   (c) Describe the use of a cyclodextrin derivative as a Ribonuclease enzyme mimic.   2+2+4

5. (a) Write the significance of multiple recognition sites in the selection of substrates during host-guest complexation.

   (b) Design a suitable *chiral* host for complexing *L-Trp* and show the mode of its complexation.

   (c) Design a receptor for the complexation of barbital.

   (d) Design and explain the mode of action of a protease enzyme mimic.   2×4

6. (a) What is the vertical distance of separation between adjacent base pairs in DNA double helix ?

   (b) What is the helical pitch in a DNA double helix ?

   (c) What is DNA melting ?

   (d) Write the mechanism of RNA cleavage by the enzyme Ribonuclease A.   1+1+3+3

7. (a) *Write the principles* of green chemistry.

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

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

   3+3+2

8. (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 ?

   2×4

9. (a) Define Ramachandran plot.

   (b) Locate the following secondary structural element of proteins in Ramachandran plot : β-helix, parallel β-pleated sheet, antiparallel β-pleated sheet, 3.10 helix.

   (c) What is protein quarternary structure ?

   2+3+3

(Turn Over)

10. (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. 2+2+4

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