M.Sc. 3rd Semester Examination, 2018

CHEMISTRY

PAPER – CEM-302

Full Marks : 40

Time : 2 hours

The figures in the right-hand margin indicate marks

(*Physical Special*)

GROUP – A

Answer any **four** questions : 2×4

1. Define grand partition function.
2. What is spectral emissive power ?
3. State Stefan-Boltzmann law of radiation.
4. What do you understand by full microscopic diffusion controlled reaction ?

5. Define saddle point.

6. How does the rate constant depend on hydrostatic pressure ?

7. Define 'surface excess' of solute.

8. What is a fuel cell ? Give one example.

GROUP – B

Answer any **four** questions : 4×4

9. Predict(with brief explanation) the sign of the entropy of activation for the following reactions :

   (*i*) $ClCH_2COO^- + HO^- \rightarrow HOCH_2COO^- + Cl^-$

   (*ii*) $CH_2BrCOOC_2H_5 + S_2O_3^{2-} \rightarrow CH_3(S_2O_3^-)COOC_2H_5 + Br^-$

   $2 + 2$

10. Write down, without derivation, Planck's equation for spectral distribution of Black Body radiation and comparing this with Wien's equation, establish the fundamental equation $E = h\nu$. $1 + 3$

(*Continued*)

11. Calculate the vibrational contribution to the molecular entropy of O_2 at 300 k. (Given the vibrational frequency = 15800 cm^{-1}). 4

12. (*a*) Define polarizable and nonpolarizable interface.

    (*b*) Find out the expression of efficiency of a fuel cell. (1 + 1) + 2

13. Calculate the rate constant between two non ionic solutes 'A' and 'B' with equal radii. Given viscosity of the solvent is 0.95 cP. What will be the effect on the rate if the radius of 'A' is doubled but 'B' remains same ? 2 + 2

14. The rate of a reaction at 300 K is doubled when the pressure is increased from 1 to 2000 atm. Calculate $\Delta^{\neq}V$(volume of activation), assuming it to be independent of pressure. 4

15. Considering exchange of energy and matter between two microcanonical ensembles

separately, define Lagrange's undetermined multipliers 'α' and 'β' and derive the relationship between α and β. 2 + 2

16. 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. 4

GROUP – C

Answer any **two** questions : 8 × 2

17. Derive a suitable relation to show that absolute reaction rate theory can be applicable in viscosity problems. 8

18. Derive the expression for the rate constant of a partial microscopic diffusion controlled reaction. 8

19. What is meant by Bose-Einstein condensation ? Obtain the expression for the temperature at which such a phenomenon occurs. 8

20. Starting from the equation :

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

derive

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

For 1 : 1 type electrolyte, where ν = surface tension and Γ_i = surface excess for i^{th} type of species at the interface and all other terms bear usual significance. 8

(*Inorganic Special*)

1. Answer any *two* of the following questions : 2 × 2

(*a*) Draw the active site structure of peroxidase enzyme.

(*b*) Discuss the mechanism of hydrolysis of the peptide bond by carboxy peptidase.

(*c*) Define Schottkey defect with at least one example.

(*d*) How could you distinguish between *F* center and *V* center in an impure solid ?

2. Answer any *two* of the following questions : 2 × 2

(*a*) How can you distinguish between static and dynamic quenching of fluorescence ?

(*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.

(*c*) Write the expression for calculating fluorescence quantum yield. Mention each term involved in this expression.

(*d*) Write down the mechanism of formation of color center in solid.

3. Answer any *two* of the following questions : 4 × 2

(*a*) Write the name of an enzyme which play major role for the detoxification of sulphur

compound. Draw active site structure and mechanism of action of this enzyme. 1 + 3

(*b*) Derive the expression for equilibrium concentration of Frenkel defect of an ionic crystal. 4

(*c*) Write the name of the enzyme which is involved in the reduction of nitrate anion. Draw the active site structure of this enzyme and discuss the mechanism of reduction of nitrate anion. 1 + 3

(*d*) Draw the active site structures of cytochrome P-450 and cobalamin. 2 + 2

4. Answer any *two* of the following questions : 4 × 2

(*a*) Derive the expression for Stern-Volmer equation.

(*b*) 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.

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

(*d*) Write short note on "edge dislocation" in solid.

5. Answer any *one* of the following questions : 8 × 1

(*a*) (*i*) Discuss the active site structure of superoxide dismutase.

(*ii*) Write the name of the protein enzyme which is responsible for the oxidation of ascorbic acid. Draw the active site structure of this protein enzyme and discuss the mechanism of oxidation of ascorbic acid. 3 + 5

(*b*) (*i*) Write the role of enzyme alcohol dehydrogenase. Briefly discuss about the active site structure and mechanism of action of this enzyme.

(*ii*) Why catalase is called a heme protein ?

Draw the active site structure of catalase and explain the mechanistic pathway of its action. (1 + 3) + (1 + 3)

6. Answer any *one* of the following questions : 8 × 1

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

(*b*) Write short notes : 4 + 4

(*i*) Spontaneous emission

(*ii*) PET and RET mechanisms of fluorescence quenching.

(*Organic Special*)

Answer **Q.Nos.1** & **2** and any **two** from **Q.Nos. 3, 4, 5, 6**

1. Answer any *four* questions : 2 × 4

(*a*) What are cryptands ?

(*b*) What is DNA melting ?

(*c*) Write the mechanism of RNA cleavage by the enzyme Ribonuclease A.

(*d*) Define self-assembly.

(*e*) What type of interactions are involved in the self-assembly process ?

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

(*g*) Give examples of two triterpenoids that spontaneously self-assemble in liquids.

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

2. Answer any *four* questions : 4 × 4

(*a*) How can one use cryptands as a Light Conversion Device ?

(*b*) Give an example of a green synthesis of metal nanoparticles with plausible mechanism.

(*c*) Give an example of a green synthesis of organic compounds.

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

(*e*) What is a 'supramolecular gel' and how is it formed ?

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

(*g*) Give a few examples of low Molecular Mass Organogelators.

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

3. (*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 ?

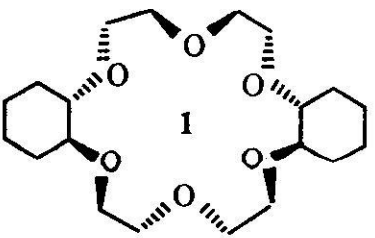
$\left(1\frac{1}{2}\times 4\right)+2$

4. (*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

5.



(*a*) What is template effect ?

(*b*) How does macrocyclization work even though 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

6. (*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
