PG Even Semester Examination, May 2025

CHEMISTRY

(4th Semester)

Course No.: CHM-653(C)

(Physical Chemistry-IV)

Full Marks: 70

Pass Marks: 28

Time: 3 hours

The figures in the right margin indicate full marks for the question.
Answer any five questions selecting one from each unit.

UNIT-I

1. (a) Define fluorescence quenching. Derive the kinetics of the fluorescence quenching for the following photophysical process

$M + h\nu \xrightarrow{I_{abs}} M^*$ [Photoactivation]

$M^* \xrightarrow{k_f} M + h\nu_f$ [Fluorescence]

$M^* \xrightarrow{k_{ISC}} M + heat$ [Internal Quenching]

$M^* + Q \xrightarrow{k_Q} M + Q$ [External Quenching]

2+3=5

(b) Difference between exciplex formation and excimer formation. 3

(c) Show the variation of the fluorescence intensity with quencher concentration for fractional quenching. 4

(d) Why does the triplet state typically have lower energy than the corresponding singlet excited state? 2

2. (a) Describe two radiative and two nonradiative photophysical pathways associated with the transitions of a molecule between different electronic and vibrational states. 6

(b) Write a short note on static and dynamic quenching. 3

(c) Define fluorescence lifetime. Show how the excited state population decays over time. 1+2=3

(d) How does Kasas' law explain the Stokes shift in fluorescence? 2

UNIT-II

3. (a) What is positive solvatochromism? Show that in the case of absorption, positive solvatochromism is observed on increasing the solvent polarity if the excited state dipole is higher. 1+4=5

(b) What is solvent relaxation? Explain the effect of temperature and viscosity on solvent relaxation. 1+4=5

(c) Calculate the spectral shift of a fluorophore in methanol with $\mu_E - \mu_G$ = 14D and a cavity radius of 4 Å. Dielectric constant of methanol = 33 and refractive

(c) What do you mean by thermodynamically and kinetically controlled reactions? Explain with a suitable example. 3

10. (a) Write the reaction mechanism of the decomposition of Ethane to Ethylene and find the rate expression for the formation of Ethylene. 2+2=4

(b) Considering Hinshelwood treatment, deduce the modified rate constant expression for an unimolecular reaction. What are the limitations that cannot be explained by Hinshelwood's treatment? 3+2=5

(c) Discuss in detail the RRK theory of unimolecular reaction. 5

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index = 1.33 (Note, esu = $g^{1/2}$ $cm^{3/2}/s$ and erg = g cm^2/s^2). 4

4. (a) Derive the Lipper-Mataga equation. Write two important significances of this equation. 7+1 =8

(b) How does the presence of a phenyl-methyl group in N-phenyl-N-methyl-6-aminonaphthalene-2-sulfonate affect its solvatochromic behaviour compared to 6-aminonaphthalene-2-sulfonate? 2

(c) Define fluorescence resonance energy transfer and fluorescence anisotropy. 4

UNIT-III

5. (a) What is the Thomson effect? Discuss the origin of the EMF based on classical and band theory. 1+4=5

(b) Define polarisation of the dielectric materials. Discuss the four possible components of the polarisation. 1+4=5

(c) Discuss the conduction mechanism of the charge transfer salt by taking a suitable example. 4

6. (a) What are the characteristic features of the ferroelectrics? How are ferroelectrics different from dielectrics? 3+2=5

(b) Why is $BaTiO_3$ ferroelectric? 3

(c) Write short notes on

(i) Pyroelectrics

(ii) Piezoelectrics 3+3 =6

UNIT-IV

7. (a) A liquid is characterized by short-range order and long-range disorder. Justify the statement. 2

(b) Write short notes on (i) Electrostatic energy, (ii) Induction energy, (iii) London dispersion energy. 6

(c) Discuss Clausius Virial Theorem. 6

8. (a) What are the assumptions of the simple cell model of liquid? 3

(b) Describe the intermolecular interactions between neutral atoms and molecules following the Lennard-Jones potential. 6

(c) Define the partition function for liquids. Write the expression of the canonical partition function in terms of Helmholtz free energy, internal energy, pressure, and entropy. 1+4=5

UNIT-V

9. (a) Write the mechanism of the Lindemann theory of unimolecular reaction. Obtain the rate expression of the Lindemann unimolecular reaction and discuss the effect of concentration or pressure on the order of the reaction. What are the limitations of the Lindemann theory of unimolecular reaction? 2+2+2+2=8

(b) Deduce the rate of the decomposition of ozone following an appropriate mechanism. 3