2021 CHEMISTRY [HONOURS] Paper : IX

Full Marks : 80Time : 4 HoursThe figures in the right-hand margin indicate marks.Candidates are required to give their answers in
their own words as far as practicable.

GROUP-A

(Marks : 40)

- 1. Answer any **two** questions: $1 \times 2=2$
 - a) State the Grothus-Draper law.
 - b) Give one example of bioluminescence.
 - c) What is the dipole moment of benzene?
 - d) How many degrees of freedom (vibrational) does CO₂ have?
- 2. Answer any **two** questions: $2 \times 2=4$
 - a) Write the Stern-Volmer equation, explaining all terms.
 - b) What is thermodynamic probability?

- c) Name two intermolecular forces, with examples.
- d) What is the relation between fundamental frequency and force constant?
- 3. Answer any **four** questions: $6 \times 4 = 24$
 - a) Explain why in some cases absorption and fluorescence spectra appear as mirror images of each other. Give one example each of phosphorescence and chemiluminescence.
 - b) If acetone is irradiated with light of wavelength 280 nm, methyl radical and CO are produced. If irradiation is at the rate of 100 erg mol sec⁻¹ for 10 minutes, how many Einsteins of radiation was involved? If the quantum yield is 0.25, how many moles of CO were produced?
 - c) What is photostationary equilibrium? Give an example. Name two quenchers of fluorescence. 3+1+2
 - d) Give one example each of diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic substance. What is the unit

42(Sc)

of electrical polarization? 4+2

- e) Write an expression for energy of a rotational transition, explaining all terms. At a given temperature T, transition between which two levels show maximum intensity?
 2+4
- f) The fundamental vibrational frequency of N₂ is 2358 cm⁻¹. What is the force constant associated with $N \equiv N$ bond? Compare this value with force constant of 516 Nm⁻¹ for ¹H³⁵Cl molecule. 6
- 4. Answer any **one** question: $10 \times 1=10$
 - a) Write an expression for rotationalvibrational energy of a rigid rotor with harmonic vibration. Indicate the terms that must be included for a non-rigid rotor with anharmonic vibration. What is the anharmonic term for Morse potential? What are the selection rules for a rigid rotor with harmonic vibration? How do they change for a non-rigid rotor with anharmonic vibrations? 2+2+2+2+2
 - b) Describe photodimerization of anthracene.Write the relevant reactions and reaction conditions. What is a typical quantum yield

[3]

for this reaction? Name a possible sensitizer and a possible quencher for this reaction. 5+2+1+2

c) Write the Debye equation. How does it differ from Clausius-Mosotti equation? Name an application of Debye equation. What factors contribute to a molecule's orientation polarization? 2+2+2+4

GROUP-B

(Marks : 40)

- 5. Answer any **two** questions: $1 \times 2=2$
 - a) Give examples of two strong chemical bonds.
 - b) Give examples of two low-melting eutectics.
 - c) Name an experiment showing wave nature of electrons.
 - d) Write the time independent Schrodinger equation, explaining all terms.
- 6. Answer any **two** questions: $2 \times 2=4$
 - a) Give an example each of non-bonding and anti-bonding orbitals.
 - b) Give one example each of system with

42(Sc)

congruent and incongruent melting points.

- c) State two postulates of quantum mechanics.
- d) What is the no. of nodes (besides at r=0and at $r \rightarrow \infty$) for radial distribution of H atom wavefunction with quantum numbers n, *l*, m?
- 7. Answer any **four** questions: $6 \times 4 = 24$
 - a) Give an example each of aromatic, non-aromatic and anti-aromatic electronic systems. Draw corresponding orbitals or π electron configurations when applicable. 2×3
 - b) Derive Nernst distribution law. Give an example where steam distillation is used.
 4+2
 - c) Draw the phase diagram of water-triethyl amine system, identifying its fixed points. How does the diagram differ from that of water-phenol system?
 - d) State the limitations of the Bohr model. How can photo-electric effect be explained from quantum theory? Write the equation for observed frequency change in Compton effect. 2+2+2

- e) Draw the wavefunctions for 2s, 2p electrons in H-atom. 2×3
- f) What are the differences between VB and MO wavefunctions? Briefly write why inclusion of VB terms is necessary to explain bonding in H₂ molecule. 3+3
- 8. Answer any **one** question: $10 \times 1 = 10$
 - a) Name two models of spin-orbit coupling. Where are these applicable? Write an expression for charge transfer in terms of wavefunctions. Give an example where it can be realized. 2+2+4+2
 - b) Deduce phase rule for non-reactive systems. State your assumptions clearly. Give an example of Lever rule. What is an azeotrope? 6+2+2
 - c) Derive ground state energy of H atom from uncertainty principle. Can a particle (e.g. an electron) moving in a 2-D circular path have zero point energy? Explain. How can translational energy be quantized?

5+3+2