2022 CHEMISTRY [HONOURS] Paper : IX

Full Marks : 80

Time : 4 Hours

The 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) Name two diamagnetic substances.
 - b) What is the dipole moment of tetrabutyl ammonium ion?
 - c) Give one example of bioluminescence.
 - d) How many degrees of freedom (vibrational) does CO₂ have?
- 2. Answer any **two** questions: $2 \times 2=4$
 - a) Write an expression for moment of inertia of CH₄ molecule. Assume C-H bond length to be r.
 - [Turn over]

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- b) What are the units of volume and molar magnetic susceptibility?
- c) What is thermodynamic probability?
- d) What is the relation between fundamental frequency and force constant?
- 3. Answer any **four** questions: $6 \times 4=24$
 - a) By drawing appropriate energy level diagrams, show the basis of Frank-Vondon principle. How does it affect the intensity of an electronic transition? 3+3
 - b) Write an expression for Morse potential, identifying all terms. What are overtones? What is the unit of anharmonicity constant? 2+2+2
 - c) Which non-radioactive alkali metal is expected to have the highest polarizability value in ground state? What is the difference between ferromagnetic and ferrimagnetic compounds? How is dipole moment of a molecule measured? 2+2+2
 - d) 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? 3+3

- e) The fundamental vibrational frequency of N_2 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
- f) Give one example each of diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic substance. What is the unit of electrical polarization?
- 4. Answer any **one** question: $10 \times 1=10$
 - a) Suppose in a photochemical reaction of type,

$A \xrightarrow{h\nu} B$

a container with compound A (1 mole) was irradiated for one hour with photons of 300nm wavelength. If the overall quantum yield was 0.3, how many molecules of B were produced? State your assumptions clearly. Which quantities remain constant in (i) microcanonical, (ii) canonical and (iii) grand canonical ensembles? 7+3 b) Write the Vlausius-Mosotti equation. Name an application of this equation. Name a compound with zero dipole moment but non- zero quadrupole moment. Name a compound with zero dipole and quadrupole moments but non zero octapole moment. Write the functional forms of dipole-dipole and dipole-quadrupole interactions.

2+2+2+2+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 weak chemical bonds.
 - b) Name an experiment showing particle nature of electron.
 - c) Give examples of two low-melting eutectics.
 - d) Write the time independent Schrodinger equation, explaining all terms.

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6. Answer any **two** questions:

- $2 \times 2 = 4$
- a) What is Aufbau principle?
- b) What is Zeeman effect?
- c) Give one example each of system with congruent and incongruent melting points.
- 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) Consider CO molecule and its frontier orbitals. Draw schematically a bonding, an antibonding and a non bonding MO of CO from among its frontier orbitals. 2+2+2
 - b) What conclusions were derived from Davisson-Gerner and Stem-Gerlach experiments? What are Rydberg states?

4 + 2

- c) Write the Planck distribution in terms of wavelength of radiation. Derive Wien's displacement law from this formula. 2+4
- d) Derive Nernst distribution law. Give an example where steam distillation is used.
 4+2

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- e) What are the differences between VB and MO wavefunctions? Briefly write why inclusion of VB terms is necessary to explain bonding in H_2 molecule. 3+3
- f) 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
- 8. Answer any **one** question: $10 \times 1=10$
 - a) Draw the phase diagrams of water and CO_2 . Can you write the functional forms of the various phase boundaries? How can such forms be derived? Explain using a solid-liquid phase boundary. How does this line differ between water and CO_2 ? Can you suggest a possible cause for such difference? 2+2+2+2+2
 - b) Is there any relation between deBroglie hypothesis and the uncertainty relation? What are the limitations of the Bohr model of H atom? What is meant by expectation value of an operator? Define radial distribution function. What is quantum defect? 2+2+2+2+2

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c) 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