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Reg. No. : .....

Name : .....

Third Semester M.Sc. Degree Examination, January 2023

Chemistry/Polymer Chemistry/Analytical Chemistry

CH/CL/PC 233 : PHYSICAL CHEMISTRY – III

(2020 Admission Onwards)

Time : 3 Hours Max. Marks : 75

SECTION – A

Answer **two** among (a), (b) and (c) from each. Each sub question carries **2** marks.

1. (a) Define free valence index. What is its significance?

   (b) State and explain the selection rule for molecular spectra.

   (c) Draw the MO energy level diagram for HF molecule. What is its bond order?

2. (a) Derive an expression for the most probable velocity of gas molecules.

   (b) What is Boyle temperature? Calculate its value for carbon dioxide if van der Waals constant *a* and *b* are respectively 3.59 dm^6 atm mol^{-1} and 0.0427 dm^3mol^{-1}.

   (c) Apply equipartition principle to find the heat capacity of *HCl* (in terms of gas constant) gas molecules.

3. (a) Mention the importance of population of states in NMR spectroscopy.

   (b) Explain the role of quadrupole transitions in Mossbauer spectroscopy.

   (c) Give the origin NQR transitions in some nuclei.

P.T.O.

4. (a) Explain the significance of principle of minimum entropy production.

(b) Sketch and explain the graphical representation of a three-component liquid-liquid system two pairs of partially miscible liquids.

(c) Mention the relevance of Onsager reciprocal relations.

5. (a) Compare RHF, ROHF and UHF.

(b) What are the characteristics of Force Field?

(c) Write a note on Pople type basis set.

(10 × 2 = 20 Marks)

SECTION – B

Answer either (a) or (b) from each question. Each sub question carries **5** marks.

6. (a) Discuss the Hartree - Fock self-consistent field (HFSCF) method in quantum mechanics.

(b) Define hybridization. Explain the quantum mechanics of sp^2 hybridization with an example.

7. (a) Write a short note on various types of intermolecular forces existing in gas molecules.

(b) Discuss the equation of states of real gases other than van der Waals equation.

8. (a) Explain the theory and applications of X-ray photoelectron spectroscopy.

(b) Explain the basic instrumentation of NMR spectroscopy.

9. (a) Apply irreversible thermodynamics in the context of thermal diffusion.

(b) Discuss the non - equilibrium thermodynamic studies of electrokinetic effects.

10. (a) Explain in detail the concept of semi empirical methods.

(b) Explain the relevance of constraints in MD Simulations.

(5 × 5 = 25 Marks)

SECTION – C

Answer any **three** questions. Each question carries **10** marks.

11. Write the basic principle of Huckel's molecular orbital theory (HMOT). Arrive at the expressions for calculating the pi electron energy and delocalization energy of 1,3 butadiene.

12. Discuss the properties of liquid state by mentioning vapour pressure, surface tension and viscosity.

13. Explain the basic principles and applications of ESR spectroscopy by mentioning the importance of electron *g* factor.

14. Discuss the thermodynamical aspects of various solid-liquid systems.

15. (a) What is z matrix? Write down the necessary steps in generating z matrix of a molecule. Compare the z matrices of eclipsed and staggered ethane.

    (b) Write a note on potential energy surfaces.

(3 × 10 = 30 Marks)

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