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**Reg. No. : .....**

**Name : .....**

**Third Semester M.Sc. Degree Examination, June 2022**

**Chemistry With Specialization in Drug Design And Development**

**CHDD 533 : PHYSICAL CHEMISTRY III**

**(2020 Admission)**

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) Evaluate Bond Orders for $H_2^+$, H2, $He_2^+$ and $He_2$ - Discuss their relative bond energies?

   (b) Determine the molecular term symbols for the ground states of $He2^+$ and $He_2$?

   (c) The experimental ionization energies for a fluorine 1s electron from HF and $F_2$ are 66.981 and 67.217 $MJ.mol^{-1}$. Explain why these ionization energies are different even though the 1s electrons of the fluorine are not involved in the chemical bond.

2. (a) Calculate the root - mean - square velocity of an Oxygen molecule at $25^oC$?

   (b) A certain gas obeys the Vander Waals equation with $a=0.50m^6$ $Pa.mol^{-2}$ Its volume is found to be $5.00 \times 10^{-4}$ $m^3$ $mol^{-1}$ at 273 K and 3.0 MPa. From this information calculate the van der Waals constant *b.* What is the compression factor for this gas at the prevailing temperature and pressure?

   (c) How be the viscosity of a liquid can measured by using an Ostwald viscometer?

**P.T.O.**

3. (a) Discuss the origin of solvent contribution into shielding constant in NMR spectroscopy?

(b) Sketch the hyperfine structure of $XH_2$ radical (Given X nucleus has $l = \frac{5}{2}$)

(c) Discuss Doppler effect in Mossbauer spectroscopy?

4. (a) Briefly explain Phenomenological laws and Onsager's reciprocal relations?

(b) Define reversible and irreversible processes? - Provide simple examples for irreversible processes?

(c) Briefly explain transition point for double salt formation.

5. (a) What are the advantages of using GTOs over STOs?

(b) Write the Z-matrix of $BF_3$, molecule?

(c) How is non bonded interaction treated in molecular mechanics methods?

**(10 × 2 = 20 Marks)**

SECTION – B

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

6. (a) Use First order perturbation theory to calculate the energy of a particle in one-dimensional box from x = 0 to a x = a with a slanted bottom? ($V = V_x/a$) where a is the length of the box.

(b) Draw the $\prod$ molecular orbitals for benzene and represent the nodal planes?

7. (a) Give a brief account on various types of intermolecular forces

(b) Briefly explain Theory, Measurement and Equation of the viscosity of gases?

8. (a) Discuss theory and instrumentation of FT - NMR Spectroscopy?

(b) Give an account of principle and applications of Nuclear Quadrupole Resonance (NQR) Spectroscopy?

9. (a) Rationalize thermal osmosis using irreversible thermodynamics?

   (b) Derive relations for entropy production associated with heat flow and matter flow in simple irreversible system?

10. (a) What is the difference between ROHF and URHF?

   (b) Describe 6-311+g* basis set.

**(5 × 5 = 25 Marks)**

SECTION – C

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

11. Discuss the bonding in $H_2$ molecule by valence band theory (VBT)?

12. (a) Discuss degrees of freedom of gas molecules and law of equipartition of energy for linear and non-linear molecules? (7)

   (b) Write a short note on vacancy (hole) theory of liquids? (3)

13. (a) Discuss principle, instrumentation, and origin hyperfine structures of ESR spectroscopy? (7)

   (b) Sketch ESR spectrum of benzene radical anion ($C_6H_6$) (3)

14. (a) Draw and Explain the phase diagram of a three- component liquid system with the three pairs of partially immiscible liquids? (7)

   (b) Comment on far - from equilibrium thermodynamic systems with suitable examples? (3)

15. (a) How is electron correlation treated in DFT? (5)

   (b) What is exchange correlation functional? Explain with example? (5)

**(3 × 10 = 30 Marks)**

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