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M – 7144

Reg. No. :

Name :

Third Semester M.Sc. Degree Examination, March 2022

Chemistry/Polymer Chemistry/Analytical Chemistry/Applied Chemistry

CH/CL/CA/PC 233 : PHYSICAL CHEMISTRY – III

(Common for Chemistry (2016 – 2019 Admission) and Polymer Chemistry
(2018 – 2019 Admission))

Time : 3 Hours

Max. Marks : 75

SECTION – A

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

- (a) Write the Hamiltonian for HeH^+ by considering Born-Oppenheimer approximation.

(b) Show that two molecular orbitals of H_2 are orthogonal.

(c) How does the bond order of central π -bond in butadiene differ from butadiene cation?
- (a) Calculate the number of contracted Gaussian functions and Gaussian primitive functions in C_5H_6 if the basis set is $6-31+G^*$.

(b) Construct a Z-matrix for H_2O_2 .

(c) Explain the Roothans concept of basis function.

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3. (a) What is meant by NQR?
- (b) How many lines will the ESR spectrum of the naphthalene negative have?
- (c) How does Doppler effect used in Mössbauer spectroscopy?
4. (a) Use the equipartition theorem to estimate the constant-volume molar heat capacity of C_6H_6 in the gas phase at $25^\circ C$.
- (b) The first electronically excited state of O_2 is $^1\Delta_g$ and lies 7918.1 cm^{-1} above the ground state, which is $^3\Sigma_g^-$. Calculate the electronic contribution to the molar Gibbs energy of O_2 at 400 K.
- (c) Calculate the temperature at which the population of I_2 at $v=1$ level have half the population as that of the ground state.
5. (a) What is meant by the controlled-potential electrolysis?
- (b) A constant current of 0.800 A is used to deposit copper at the cathode and oxygen at the anode of an electrolytic cell. Calculate the number of grams of each product formed in 15.2 min, assuming no other redox reaction occurs.
- (c) Calculate the pH of a solution that contains 0.225 M in H_3PO_4 and 0.414 M in NaH_2PO_4 .

(10 × 2 = 20 Marks)

SECTION – B

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

6. (a) Apply HMO method for π bonding in allyl cation. Find the energy of π molecular orbitals. Calculate the delocalization energy and the charge on each carbon atom in allylic anion.
- (b) A trial function for a particle in one dimensional box is given by

$$\Psi = c_1 x(a-x) + c_2 x^2(a-x)^2. \text{ Calculate } H_{11}, H_{12}, H_{22}, S_{11} \text{ and } S_{22} \text{ if } a = 1?$$



7. (a) What are the force field energy terms and their mathematical expressions involved in molecular mechanics method?
(b) How does the Hückel theory differ from the extended Hückel theory?
8. (a) Explain the basic principle of ENDOR.
(b) Explain the mechanism of spin-spin coupling in ^1H NMR.
9. (a) Explain how the internal energy and entropy of a system composed of two levels vary with temperature.
(b) Explain the origin of residual entropy.
10. (a) How do electrogravimetric and coulometric methods differ from potentiometric methods?
(b) How do you distinguish between a rotating disk electrode and a ring disk electrode?

(5 × 5 = 25 Marks)

SECTION – C

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

11. Derive expressions for first order correction to energy and wave function for nondegenerate level.
12. Explain the role of exchange correlation functional in density functional theory.
13. Explain the basic principle and its application of Mössbauer spectroscopy.
14. Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.
15. Explain the principle and application of polarography.

(3 × 10 = 30 Marks)

