PG – 348

I Semester M.Sc. Degree Examination, Jan./Feb. 2014
(2010-2011 Scheme) (NS)
CHEMISTRY
C – 103 : Physical Chemistry – I

Time : 3 Hours Max. Marks : 80

***Instruction** : Answer question **1** and **any five** of the **remaining**.*

1. Answer **any ten** of the following : **(2×10=20)**

   a) State and explain Heisenberg uncertainty principle.

   b) Find out deBroglie wave length for a beam of electrons whose kinetic energy is 100 ev. (Given m = 9.1×10^{-28}g).

   c) What is J-J coupling ?

   d) Distinguish between a wave function and an eigen function with examples.

   e) Why the approximations are necessary in quantum mechanics ?

   f) Calculate the effective nuclear charge for 25 and 26 electrons of nitrogen using Slater's rules.

   g) Distinguish between macroscopic and microscopic kinetics.

   h) Write the reaction mechanism for pyrolysis of acetaldehyde.

   i) How do you account for the fact that an enzyme reaction has an optimum pH at which its activity is maximum ?

   j) What are the limitations of Lindemann theory of unimolecular reactions ?

   k) Give the Laplace equation and explain the terms involved in it.

   l) The rate of a second order reaction is 4.40×10^{-4} dm^3 $mol^{-1}s^{-1}$ at 30°C and 9.20×10^{-4} dm^3 mol^{-1} s^{-1} at 40°C. Calculate the activation energy of the reaction.

2. a) Formulate the time-independent Schrodinger equation.

   b) Pointout the concept of operators. Write the Hamiltonian operator for normal He atom and explain each term.

   c) Solve the Schrodinger equation for the particle in a ring. **(4+4+4=12)**

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3. a) Write the Schrodinger equation for hydrogen atom in spherical polar coordinates and separate it into R, ϕ and θ equations.

   b) What are the quantum numbers ? How many quantum numbers has an electron in the atom ?

   c) State the significance of radial and angular distribution functions. **(5+4+3=12)**

4. a) Apply variation method to obtain the ground state energy for a particle in a one dimensional box.

   b) Outline the HMO method for benzene.

   c) Obtain the expression for the correction in energy of a non-degenerate system according to first-order perturbation theory. **(4+4+4=12)**

5. a) Derive the relevant rate expression for the first order forward and backward reversible reaction.

   b) Compare collision theory with transition state theory of reaction rates.

   c) Predict, giving reasons the effect of an inert electrolyte concentration on the rate constant of the following reactions.

   i) $CH_2ICOOH + CNS^- \rightarrow$ Products

   ii) $S_2O_8^{2-} + I^- \rightarrow$ Products

   iii) $[CO(NH_3)_5\,Br]^{2+} + OH^- \rightarrow$ Products **(5+4+3=12)**

6. a) Derive the rate expression for the kinetics of photochemical reaction between H_2 and Br_2.

   b) Explain the lock and key mechanism for enzyme catalysed reactions.

   c) Depict Lineweaver-Burk plot using Michaelis-Menten equation and explain how it is useful to determine the value of K_m. **(5+3+4=12)**

7. a) Outline the relaxation technique for the study of fast reactions.

   b) Derive Gibbs adsorption isotherm equation and write its applications.

   c) Write a brief note on mechanical adsorption. **(4+5+3=12)**
