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I Semester M.Sc. Examination, February 2019
(CBCS Scheme)
CHEMISTRY
Paper C – 103 : Physical Chemistry – I

Time : 3 Hours Max. Marks : 70

Instruction : *Answer Question No.* ***1*** *and* ***any five*** *of the remaining questions*

1. Answer **any ten** of the following : **(10×2=20)**
   a) Show that sin 2x is not an eigenfunction of the operator d/dx, but of d^2/dx^2. What is its eigenvalue ?
   b) Give the degeneracy of the states of the hydrogen atom for which n = 3. Designate all states.
   c) What is normalisation of a wave function ? Normalize the function x^2 in the interval $0 \leq x \leq a$.
   d) Estimate in terms of '$\hbar$' values of spin and orbital angular momenta for an electron occupying a 'd' orbital.
   e) For a trial wave function $\psi = c_1\phi_1 + c_2\phi_2$, write the secular determinant.
   f) Write spectroscopic term symbols for the ground state of P and Ne.
   g) Define steric factor and mention its importance in the study of reaction kinetics.
   h) Express the velocity constant in terms of thermodynamic parameters ΔG and ΔH.
   i) The relaxation time for a fast reaction is 6 micro seconds and the value of equilibrium constant is 4×10^4. Calculate the rate constant of forward reaction.
   j) How does the catalyst enhance the rate of reaction ?
   k) Represent Linweaker-Burk plot and explain its significance.
   l) Spontaneous adsorption is always exothermic. Justify the statement.

2. a) Setup the Hamiltonian operator for helium atom. Express its atomic units.
   b) Write brief notes on commutative and non-commutative operators.
   c) Calculate the energy of an electron in the ground state confined to a box of 2 Å width and moving in one direction (Me = 9.1×10^{-28}g). **(4+3+3=10)**

P.T.O.

3. a) Solve the Schrödinger equation for a harmonic oscillator and find its asymptotic solution.

   b) Write the Schrödinger wave equation for H-atom in spherical polar coordinates and separate its radial part. **(5+5=10)**

4. a) Give quantum mechanical interpretation of Pauli's exclusion principle.

   b) Write the essential steps for evaluating the ground state energy of He atom using perturbation method. **(5+5=10)**

5. a) Apply variation method for a particle in a one-dimensional box.

   b) Obtain the expression for relaxation time and explain temperature jump method for the study of kinetics of fast reactions. **(5+5=10)**

6. a) Predict the effect of ionic strength on the following reactions :

      i) $2H^+ + 2Br^- + H_2O_2 \rightarrow$ Products

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

      iii) $Fe^{2+} + Co(C_2O_4)_3^{3-} \rightarrow$ Products

      iv) Inversion of sucrose

   b) Discuss in detail the activated complex theory of reaction rates. In what way this theory superior to Collision theory ? **(4+6=10)**

7. a) The half life of a first-order reaction is 30 min at 30°C and 45 min at 20°C, respectively, calculate the energy of activation of the reaction.

   b) Obtain Michaelis-Menten equation for an enzyme catalyzed reaction and give the different ways in which it can be graphically represented. Highlight the significance of its constants. **(4+6=10)**

8. a) Explain how the Hinshelwood theory is an improvement over the Lindemann theory of unimolecular reactions.

   b) Write BET adsorption isotherm. What limiting condition it approximates to Langmuir adsorption isotherm ?

   c) Explain the effect of temperature on an enzyme catalyzed reactions. **(4+3+3=10)**