

(CBCS Scheme) CHEMISTRY

Paper C - 103 : Physical Chemistry - I

Time: 3 Hours

Max. Marks: 70

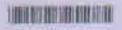
Instruction: Answer Question No. 1 and any five of the remaining questions

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 d²/dx². 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 x³ in the interval 0 ≤ x ≤ a.
- d) Estimate in terms of 'h' 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.
- 1) 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.
- Express the velocity constant in terms of thermodynamic parameters AG and AH.
- The relaxation time for a fast reaction is 6 micro seconds and the value of equilibrium constant is 4 x 10°. Calculate the rate constant of forward reaction.
- i) How does the catalyst enhance the rate of reaction ?
- k) Represent Linweaker-Burk plot and explain its significance.
- I) 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 x 10⁻²⁸g). (4+3+3=10)

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- 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,O, -> Products
 - II) S,O, 2 + 21 → 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)
- 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 unimotecular reactions.
 - b) Write BET adsorption isotherm. What limiting condition it approximates to Langmuir adsorption isotherm?
 - e) Explain the effect of temperature on an enzyme catalyzed reactions.

(4+3+3=10)