(34)

PG – 927

I Semester M.Sc. Examination, January 2016
(2010-11 Onwards) (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 de Broglie hypothesis.
   b) What are the requirements of a well behaved function ? Determine whether the following functions are well behaved over the indicated intervals :
   e^{-x} $(0, \infty)$, $\sin^{-1}x$ $(-1, 1)$.
   c) Define ladder operator and explain its function.
   d) Give a comparative account of spin and orbital angular momenta.
   e) Collision theory fails to explain reversible reactions. Explain.
   f) Explain the terms chain length and chain inhibition.
   g) Explain 'contact time' in study of fast reaction in flow method.
   h) Give the significance of Michaelis-Menten constant.
   i) Distinguish between enzyme and chemical catalysed reactions.
   j) State the variation theorem.
   k) Show graphically the different types of adsorption isotherms.
   l) Set up the HMO determinant for $H_3C - CH_2 - CH_2 - CH = CH_2$.

2. a) State the postulates of quantum mechanics.
   b) Obtain Schrodinger equation from the classical equation for a stationary wave and discuss the significance of eigen function and eigen value.
   c) Set up the Schrodinger equation for the particle in a 1-D box of length 'L' and without explicitly solving the equation, verify that $\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ are its eigen functions and $\frac{n^2h^2}{8mL^2}$ are its eigen values. **(3+4+5=12)**

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3. a) Solve the Schrodinger equation for a rigid rotator and obtain its normalized eigen functions and eigen values.

   b) Given the normalised wave function $\psi = N \sin(a\pi x)e^{-ibt}$ for $0 \le x \le 1/a$, evaluate the normalization constant 'N'.

   c) Explain the Pauli exclusion principle based on Paulis antisymmetry postulate for multielectron wave functions. **(5+3+4=12)**

4. a) Obtain the expression for the correction in energy of a non-degenerate system according to first order perturbation theory.

   b) Set up the HMO determinant for allyl radical and solve it to obtain π-electron energy levels and molecular orbitals.

   c) Explain slater type and self-consistent field orbitals. **(4+4+4=12)**

5. a) Enumerate the methods employed in the determination of the order of a reaction. Discuss any one method in detail.

   b) How does increasing ionic strength affect the rates of following reactions ?

      i) $S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$

      ii) $Co(NH_3)_5 Br^{2-} + OH^- \rightarrow Co(NH_3)_5 OH + Br^-$

   c) Calculate the activation energy of a reaction whose rate constant is tripled by a 10°C rise in the vicinity of 27°C. **(6+3+3=12)**

6. a) Discuss the kinetics of thermal chain reaction between H_2 and Br_2.

   b) Derive a general kinetic expression for the acid-base catalysis.

   c) Explain the effect of pH and temperature on enzyme activity. **(5+3+4=12)**

7. a) How is relaxation technique helpful in the study of fast reactions ?

   b) Derive the Gibbs adsorption isotherm.

   c) Discuss the Lindemann theory of unimolecular reaction rates. **(3+5+4=12)**