PG – 848

M.Sc. I Semester Examination, January 2017
CHEMISTRY
(2010-11 Scheme) (NS)
C-103 : Physical Chemistry – I

Time : 3 Hours | Max. Marks : 80

***Instruction** : Answer question No. **1** and **any five** from the remaining.*

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

   a) Find the commutator of x and $\frac{d}{dx}$.

   b) Write time dependent Schrödinger wave equation and mention its importance.

   c) Write spectroscopic term symbols for the ground states of P and Ne.

   d) Formulate slater determinantal wave function for Li atom.

   e) Does a free particle have zero point energy ? Explain.

   f) Find STO's (Slater Type Orbitals) for the 2S and $2P_z$ orbitals of N atom.

   g) Distinguish between collision cross section and reaction cross section.

   h) State and explain steady state approximation.

   i) Define Michaelis Menton constant and explain its significance.

   j) Justify the observation that unimolecular gas phase reactions follow first order kinetics at high pressures and second order kinetics at low pressures.

   k) Explain the significance of a ladder operator.

   l) Define isosteric heat of adsorption. How is it measured ?

2. a) Define a Hermitian operator and show that it has real Eigen values.

   b) State the postulates of quantum mechanics.

   c) Find the average value of the position of a particle confined to a one dimensional box of length 'a'. **(4+4+4)**

3. a) Find Eigen values and Eigen functions for a planar rotator (particle in a ring).

   b) The wave function for 1S atomic orbital of H atom is

   $\psi_{1S} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\left(r/a_0\right)}$. Show that the maximum probability of finding the electron in this orbital is at $r = a_0$ where r = radial distance and a_0 = Bohr radius.

   c) Explain Pauli exclusion principle based on antisymmetry concept. **(4+4+4)**

4. a) State and prove variation theorem.

   b) Find the ground state energy of He atom by Perturbation method.

   c) Obtain the π-electron energy levels of benzene using HMO method. **(4+5+3)**

5. a) Decomposition of ethane takes place according to the following mechanism

   $C_2H_6 \xrightarrow{k_1} 2\,CH_3$

   $CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$

   $C_2H_5 \xrightarrow{k_3} H + C_2H_4$

   $H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5$

   $H + C_2H_5 \xrightarrow{k_5} C_2H_6$

   Assuming steady state concentration for CH_3, H and C_2H_5, derive the rate law for decomposition of C_2H_6.

   b) Account for the following :

   i) The quantum yield for the photochemical reaction between $H_2 - Cl_2$ is 10^6, whereas it is almost unity for $H_2 - Br_2$ reaction.

   ii) $H_2 - Br_2$ and $H_2 - Cl_2$ reactions follow chain mechanism while $H_2 - I_2$ reaction follows molecular mechanism. **(6+6)**

6. a) Explain briefly temperature jump method for the study of fast reactions.

   b) When a sample of water is heated with a beam of microwave radiation, the equilibrium in the water dissociation reaction is disturbed. It was found that the relaxation time for returning to the new equilibrium is 36 μs at 25°C. Calculate K_1 and K_{-1} in the reaction : $H^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O$. Ionic product of water is 10^{-14} at 25°C.

   c) Represent Linweaker-Burk plot and explain its significance. **(4+5+3)**

7. a) Write BET adsorption isotherm. What limiting condition it approximates to Langmuir adsorption isotherm.

   b) Explain electrokinetic phenomena with an example.

   c) Spontaneous adsorption is always exothermic. Justify the statement. **(4+5+3)**