



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)

P.T.O.

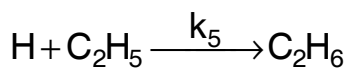
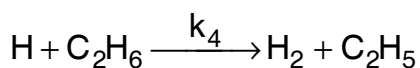
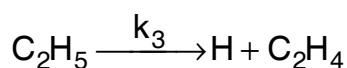
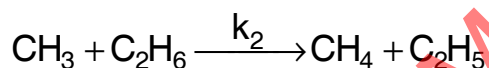
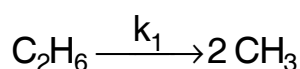


3. a) Find Eigen values and Eigen functions for a planar rotator (particle in a ring).
 b) The wave function for 1S atomic orbital of H atom is

$$\psi_{1S} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}. \text{ Show that the maximum probability of finding}$$

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



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 $\text{H}_2 - \text{Cl}_2$ is 10^6 , whereas it is almost unity for $\text{H}_2 - \text{Br}_2$ reaction.
- ii) $\text{H}_2 - \text{Br}_2$ and $\text{H}_2 - \text{Cl}_2$ reactions follow chain mechanism while $\text{H}_2 - \text{I}_2$ 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 $36 \mu\text{s}$ at 25°C . Calculate K_1 and K_{-1} in the reaction : $\text{H}^+ + \text{OH}^- \xrightleftharpoons[k_{-1}]{k_1} \text{H}_2\text{O}$. 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)**

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