energy of the same reaction catalysed by an enzyme is 25.10 KJ mol^{-1}. Calculate the ratio of the rate constants of these reactions. 6

7. (a) Describe in detail double sphere model for ionic reactions in solutions. 8

   (b) Derive rate equation for opposing reactions of second order. 8

SECTION – D

8. (a) Show that charge on ionic cloud is equal and opposite to the control ion which is responsible for its formation. 8

   (b) Describe in detail Debye-Huckel limiting law of coefficients. Also comment on its limitations. 8

9. Write a note on the following : 8.8

   (a) Debye Huckel Bjessum equation

   (b) Huckel-Onsager treatment for aqueous solution and its limitations.

Roll No. .....

72052

M. Sc. Chemistry 1st Semester (for Other Affiliated Colleges Except UTD) Examination – December, 2015

PHYSICAL CHEMISTRY

Paper : Ch-402

Time : Three Hours] *[Maximum Marks : 80*

Before answering the question, candidates should ensure that they have been supplied the correct and complete question paper. No complaint in this regard, will be entertained after examination.

Note : Attempt ***five*** questions in all, selecting atleast ***one*** question from each Section. Question No. 1 is ***compulsory***. All questions carry equal marks.

1. (a) Can Every wave function be Eigen Function ? Explain. $2 \times 8 = 16$

   (b) Evaluate $\left(x, \frac{d}{dx}\right)$.

   (c) Why a small rise of temperature (10°C) doubles the rate of most of the reactions ?

   (d) Discuss the need of quantum mechanics.

(e) Activity coefficient of indivisual ion cannot be determined experimentally. Explain.

(f) Explain the term "Residual Entropy".

(g) Show quantitatively that entropy is a measure of disorder of the system.

(h) Calculate ionic strength of 0.3 molal $BaCl_2$ solution.

SECTION – A

2. (a) What are commutative operators ? Describe their utility giving suitable example. 5

(b) Derive Sehrodinger wave equation quantum mechanically. 5

(c) Define Hermitian operator. Show that operator for linear momentum is Hermitian. 6

3. (a) Determine average value of position, <x> for a particle moving in one dimensional box. 4

(b) Derive Debroglie equation using schrodinger wave equation for a particle in one dimensional box. 4

(c) Show that : 8

$$\hat{L}_z = -i\,\hbar.\frac{\partial}{\partial \phi}$$

Where $\hat{L}_z$ is operator for angular momentum.

SECTION – B

4. (a) Show that for an ideal gas, internal pressure $\left(\frac{\partial V}{\partial P}\right) = 0$. 4

(b) Describe the criteria for the spontaneity of a process interms of free energy and work function. Also discuss limitations of the criteria. 8

(c) Show that Adiabatic curve is steeper than isothermal curve. 4

5. (a) Comment on "Entropy as a measurable of Unavailable energy". 4

(b) Prove that $\Sigma n_i\, d\,\mu_i = 0$ where the symbols heve their usual meanings. 4

(c) Define partial molar quantities. Discuss their significance. Derive expression for the variation of Chemical potential with temperature. 8

SECTION – C

6. (a) Discuss in detail the Activated complex theory of Bimolecular reactions. Explain how this theory helps in the determination of standard enthalpy of activation and standard entropy of activation. **10**

(b) The activation energy of a non-catalyzed reaction at 310k is 83.68 KJ mol^{-1} and the activation