

**M. Sc. 1st Semester Examination, 2018****CHEMISTRY****(Physical Chemistry)****Paper : CHEM 103C****Course ID : 11453****Time: 2 Hours****Full Marks: 40***The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words  
as far as practicable.*

1. Attempt *any five*: 2×5=10
- (a) What are the limitations of collision theory?
  - (b) What is primary solvation number?
  - (c) Explain the significance of volume of activation.
  - (d) 'Quantum Mechanics is a probabilistic approach'. Do you believe that?
  - (e) State the significance of de Broglie equation.
  - (f) Write down the time dependent Schrödinger equation for an electron moving in the coulombic field of a nucleus.
  - (g) What is the physical significance of commutation relation between two operators?
2. Attempt *any four*: 5×4=20
- (a) Derive the expression of rate constant following double layer activated complex. 5
  - (b) Deduce the rate law of a unimolecular gaseous molecule according to collision theory following Lindemann hypothesis. Comment on the situation at high pressure and low pressure conditions. 4+1=5
  - (c) Work out the expression of rate constant of a bimolecular like gaseous molecules. 5
  - (d) Make a connotative note on the point group of Ferrocene. 5
  - (e) State Bohr correspondence principle and illustrate it with an example of particle in a box. 5
  - (f) How does electron propagate in free space? Discuss it briefly. 5
  - (g) What is orthonormality? Show that wave function of particle in one-dimensional box maintaining orthogonality. 2+3=5

3. Attempt *any one*: 10×1=10

(a) (i) Deduce the expression of ion association constant following Bjerrum's treatment.

(ii) Derive the point group of  $[\text{Co}(\text{en})_3]^{3+}$  with proper pictorial representation. 5+5=10

(b) (i) A gas phase reaction  $2\text{A} \rightarrow \text{P}$  is bimolecular with an activation energy of  $24000 \text{ cal mole}^{-1}$ . The molecular weight and molecular diameter of A are 60 and  $35\text{\AA}$ , respectively. Calculate on the basis of collision theory the specific rate constant of the reaction at  $27^\circ\text{C}$ .

(ii) Write down Hammett equation giving the significance of each term.

(iii) What do you know about 'Abelian Group'?

(iv) 'An electron can not stay at nucleus'. — Comment. 3+2+2+3=10

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