FACULTY OF SCIENCE
M.Sc. I Semester Examination, May/June 2012

CHEMISTRY

Paper III

(Physical Chemistry)

Time : 3 Hours] [Max. Marks : 80

Answer all questions.

Section A

(Marks : 4 x 8 = 32)

1. (a) State and explain II law of thermodynamics.
   (b) Explain the entropy changes in reversible and irreversible processes.

2. (a) Write down IIKovic equation and explain the terms involved.
   (b) Derive Nernst equation.

3. (a) Define operator and explain Hermitian operator?
   (b) Explain the characteristics of well behaved function.

4. (a) Outline the significance of activated complex is the study of reaction rates.
   (b) Discuss Lintemann's theory of unimolecular reactions.

Section B

(Marks : 4 x 12 = 48)

5. (a) Derive Maxwell thermodynamic relations?
   (b) Deduce Van't Hoff reaction isotherms?

   Or

   [P.T.O.]
6. (a) Write the basic principle involved in cyclic voltammetry and explain cyclic Voltammogram of parathion.
(b) Explain the principles of amperometric titration. Draw the possible titration curves and explain the important features.

Or

(c) What are liquid junction potentials? Derive an expression for liquid junction potential in terms of the transport numbers of cation and anion of electrolyte.
(d) Explain the concentration cell without transference.

7. (a) Explain the terms:
(i) Linear operator
(ii) Eigen functions with suitable examples.
(b) Derive the time Independent Shrödinger equation from the postulates of quantum mechanics.

Or

(c) Show that the commuting operators, A & B have the same set of eigenfunctions.
(d) Explain the concept of wave-particle duality.

8. (a) Outline the collision theory of biomolecular reaction rates and comment on its applicability.
(b) Discuss the salient features of the photo chemical \( \text{H}_2 - \text{Br}_2 \) chain reaction and derive an expression for its quantum yield.

Or

(c) Write the Hammett and Taft equations and explain the terms and their significance.
(d) Discuss the reactivity - selectivity principle and the iso selectivity rule.