MCHT 1.3

I Semester M.Sc. Examination, May 2014
CHEMISTRY
Physical Chemistry – I

Time : 3 Hours Max. Marks : 80

Instructions : *Question No.* ***1*** *and* ***any four*** *full questions from the remaining.*

1. Answer **any eight** questions : **(8×2=16)**

   a) State Wien's blackbody ration law.

   b) Define linear operator with one example.

   c) In the following reaction scheme, what is the total order the reaction,

   $A + B^{-1/2} \rightarrow$ product.

   d) Write integrated expression for the 1st and 2nd order rate constant.

   e) Define entropy; mention any two physical significance of entropy.

   f) Gibb's free energy decreases for all spontaneous process at constant temperature and volume. Give reasons.

   g) State :

      i) Lambert's law

      ii) Grothux-Draper law

   h) Molecularity of a reaction cannot be greater than 3. Give reasons.

   i) What is photosensitization ? In Photosynthesis process which material act as photosensitizer.

   j) Distinguish between Laser and Maser ?

2. a) Give brief account on particle duality of material.

   b) Write a note on Eigen values and Eigen functions with suitable examples.

   c) Show that f(x) = Sinx is commutative if $\alpha = \frac{d}{dx}$ and $\beta = \frac{d^2}{d^2x}$ where α and β are commutative operator. **(6+4+6=16)**

P.T.O.

3. a) Explain collision theory of reaction rate.

   b) For a first order reaction, if the initial concentration of the reactant is 0.005M and the rate constant is 4×10^{-4} sec^{-1} calculate the concentration at 4000 sec.

   c) How do you determine experimentally total order of a reaction ? Explain with suitable example. **(6+4+6=16)**

4. a) Show that $Cp = R + Cv$.

   b) Derive an equation for variation of free energy with temperature and pressure.

   c) How do you determine partial molar volume by apparent molar volume method (slope method) ? **(6+4+6=16)**

5. a) Distinguish between Fluorescence and phosphorescence.

   b) i) Write a note on Uranyloxalate chemical actinometer.

   ii) In the photochemical reaction $B \rightarrow C$, 1.0×10^{-5} moles of C is formed as a result of the absorption of 6.0×10^{7} ergs at 3600 Å. Calculate the quantum yield.

   c) Show that $A = \log \frac{I_0}{I_t}$ and explain the quantitative application of Beer's law.

   (4+6+6=16)

6. a) Write a note on effect of dielectric constant on the rate of a reaction.

   b) Mention any four postulates of quantum mechanics.

   c) Explain the effect of pressure change on the rate of reaction. **(6+4+6=16)**

7. a) Write any two limitations of Vant Hoff's equation and define chemical potential.

   b) Explain kinetics of decomposition of HI.

   c) Write a note on **any one** of the followings :

   i) Principles of Laser and its application in chemistry.

   ii) Determination of rate law for consecutive reaction. **(4+6+6=16)**
