



I Semester M.Sc. in Chemistry Degree Examination, September 2016
PHYSICAL CHEMISTRY – I

Time : 3 Hours

Max. Marks : 80

Instruction : Answer **any eight** questions from Part – I and **any four full** questions from Part – II.

PART – I

- i. What are nodes and anti nodes ?
- ii. Define linear operator with one example.
- iii. In the following reaction scheme, what is the total order of the reaction,
$$A + B^{-1/2} \rightarrow \text{product.}$$
- iv. Write an integrated expression for the 1st and 2nd order rate constant.
- v. What is meant by absolute entropy ?
- vi. What are reversible and parallel reactions ? Give an example.
- vii. State Lambert's law and Grothss-Draper law.
- viii. What is meant by chemiluminescence ? Give an example.
- ix. What is meant by photosensitization ? In photosynthesis process which material act as photosensitizer.
- x. Distinguish between Laser and Maser.

PART – II

1. a) Give brief account on particle duality of material.
b) Derive the mathematical expression for the Heisenberg's uncertainty principle.
c) Show that $f(x) = \sin x$ 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)
2. d) For a first order reaction, if the initial concentration of the reactant is 0.005M and the rate constant is $4 \times 10^{-4} \text{ sec}^{-1}$ calculate the concentration at 4000 sec.
e) Derive the rate expression for parallel reaction.
f) How do you determine experimentally total order of a reaction ? Explain with suitable example. (6+4+6=16)

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3. g) Show that entropy is a measure of unavailable energy.
h) Derive an equation for variation of free energy with temperature and pressure.
i) Discuss briefly Nernst heat theorem. (4+6+6=16)
4. j) 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 \AA . Calculate the quantum yield.
k) Derive the rate expression for photochemical combination of hydrogen and bromide.
l) Show that $A = \log \frac{I_0}{I_1}$ and explain the quantitative application of Beer's law. (6+4+6=16)
5. m) Write a note on effect of dielectric constant on the rate of a reaction.
n) What are the plank's assumptions about radiation ?
o) Explain the effect of pressure change on the rate of reaction. (4+6+6=16)
6. p) Write any two limitations of Vant Hoff's equation and define chemical potential.
q) Explain kinetics of decomposition of HI.
r) Discuss activated complex theory for the calculation of the energy of activation. (4+6+6=16)
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