M.Sc.—Chem-IIS (408)

2019

Time : 3 hours

Full Marks : 80

Answer from both the Section as per direction

The figures in the right-hand margin indicate marks

Candidates are required to answer in their own words as far as practicable

(PHYSICAL CHEMISTRY-II)

SECTION—A

1. Answer any *four* questions : 4 × 4

(*a*) Find out the relation between Gibbs Free energy and Helmholtz free energy.

(*b*) Derive an expression for molecular partition function of an ideal gas. (only for translational partition function)

(*c*) What is phenomenological law and write the Onsager's reciprocity relations.

(*d*) Explain the steady state approximation using kinetic equation.

(*e*) Discuss the relaxation method for studying the fast reaction.

(*f*) Write IIIrd law of thermodynamics and its ony one consequences.

Or

2. Answer *all* questions from the following : 2 × 8

(*a*) Define chemical potential.

(*b*) Write Ist and IInd law of Thermodynamics.

(*c*) What is thermodynamic probability ?

(*d*) Write brief on the irreversible thermodynamics for biological systems.

(*e*) What is activated complex theory ?

(*f*) Define kinetic salt effect.

(*g*) Write the mechanism of hydrogen-Bromine photochemical reactions.

(*h*) What is Nernst's heat theorem ?

SECTION–B

Answer **all** questions : 16 × 4

3. Define partial molal properties. How partial molal volume is determined ? Explain. 4 + 12

Or

(*a*) Define fugacity.

(*b*) Write consequences and application of Nernst heat theorem. 4 + 12

4. Derive the following expressions :

(*a*) $$U = -nRT^2\left(\frac{\partial \ln q}{\partial T}\right)_V$$

where U is the internal energy and q is partition function.

(*b*) $A = -kT \ln Q$

where, A is the Helmholtz function or work function and Q is the molar partition function. 8 + 8

Or

Explain Fermi-Dirac statistics. 16

5. Derive an expression for entropy production and entropy flow in an open system. 8 + 8

Or

Write short notes on the following topic in brief : 8 + 8

(*i*) Microscopic reversibility

(*ii*) Electrokinetic phenomena.

6. Discuss the stopped flow and quenched flow method for studying the fast reaction and also give kinetics involved in plug flow and stirred flow reaction. 8 + 8

Or

(*a*) Explain Lindemann theory of unimolecular reaction and also give its shortcomings. 10

(*b*) Write the suggestions of Hinshelwood regarding unimolecular reaction kinetics. 6