M. Sc. Chemistry Examination, 2019

(3rd Semester)

Physical Chemistry Special

Paper - XII-P

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answer script for each unit.

UNIT - P - 3121

1. Derive an expression for the distribution function associated with a thermodynamic system of bosons ubder equilibrium, obtain its classical limit, and comment on the result. 6

2. Define radial distribution function (RDF) for a fluid ststem of spherically symmetric particles, comment on its value for an ideal gas and derive an expression for the internal energy of a thermodynamic system of monatomic fluid in terms of RDF.6

3. Answer ***any three*** of the following : 3×3=9

   a) For a system of ideal gas at pressure (P) volume (V) and internal energy (E), irrespective of nature of the gas particles being classical or quantum (Boson/Fermion), the relation, $PV = \frac{2}{3}E$, remains unchanged – justify.

b) Define direct correlation function and describe the Percus-Yevick approcimation with its usefulness.

c) Consider the case of photons within a blackbody cavity, derive the number of stationary waves (ΔG) in the frequency interval ν to $\nu+\Delta\nu$.

d) Define second virial cofficient of a gaseous system and state its usefulness. Estimate its value for a model thermodynamic systems of "Hard-Sphere" gas and comment on the result.

4. For a strongly degenerate ideal Boson gas, the λ has two solutions as follows,

$$\lambda = 1 - \frac{a}{\nu} \text{ for } \rho\Lambda^3 > g_{\frac{3}{2}}(1) \text{ ; with } a = \frac{\Lambda^3}{\rho\Lambda^3 - g_{\frac{3}{2}}(1)};$$

and $\lambda = \text{Root of, } \rho\Lambda^3 = g_{\frac{3}{2}}(1) \text{ for } \rho\Lambda^3 < g_{\frac{3}{2}}(1).$

Derive the temperature dependence of ground state population of the gas at a fixed density and comment. Given, μ =chemical protential, ρ=density, Λ= Thermal de-Broglie wavelength, $\lambda = e^{\beta\mu}$ and $\beta = 1/k_BT$.

OR

Express the canonical ensemble partition function in terms of the Hamiltonian operator and the complete set of eigen function assoctated with a closed thermodynamic system and show that it is independent of the set of functions used to calculate it.

UNIT - P-3122

5. Answer ***any five*** questions : 5×5

a) Write a short note on 'Stripping Machanism' of Molecular Beam method in the study of fast reactions.

b) What do you mean by flash photolysis ? Discuss. What are the advantages of flash photolysis ?

c) Discuss about the mechanisms of atom and radical combinations in terms of chemical kinetics.

d) Discuss the effect of pH on an enzyme catalyzed reaction and deduce an expression for the rate of reaction involving a single substrate and an enzyme following the Michaelis - Menten type of machanism.

e) Find out a general expression for the rate of a free-radical initiated polymerization reaction and show how the rate expression changes depending on the machanism of initiation.

f) What is enzyme inhibition ? Write a short note on non-competitive inhibition. Write an application of enzymatic analysis in medicine.

g) What do you mean by micellar catalysis ? Describe such catalysis in aqueous and non aqueous solvents.