

Ex/M.Sc/CH/3/U-P-3121/14/2018

M. Sc. CHEMISTRY EXAMINATION, 2018

(3rd Semester)

PHYSICAL CHEMISTRY SPECIAL

PAPER - XII-P

Time : Two hours

Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - P - 3121

1. Describe the basic features associated with the fermion particles and derive the distribution function associated with a thermodynamic system of fermions. 6
2. Derive an expression for the chemical potential of a thermodynamic system of monatomic fluid in terms of the radial distribution function. 6
3. Answer *any three* of the following : 3×3=9
 - a) Write a short note on Potential of Mean Force and comment on its usefulness.
 - b) Define direct correlation function and describe the HCN approximation with its use.

[Turn over

[2]

- c) For the Bose-Einstein condensation, comment very briefly on the ground state population near the critical point. The corresponding critical point being associated with $\rho \lambda^3 = 2.612$, estimate the critical temperature for the ^{87}Rb vapor with number density (ρ), $10^{11}/\text{cm}^3$. (λ is thermal de Broglie wave length).
- d) Define the Square-Well potential as a model intermolecular interaction potential and estimate the second virial coefficient of a gaseous system following this potential.
4. For a system of photon gas in thermal equilibrium with temperature, T , confined in volume, V , and having canonical partition function, Q , it is given $\ln Q = (8/45) \cdot [\pi^5 V / (ch\beta)^3]$. Evaluate the internal energy, pressure, entropy, Gibbs free energy of the system and comment on the chemical potential of the photon particles of such a system. (c = velocity of light, h = Planck's constant and $\beta = 1/kT$).

OR

The expression for pressure, P of a fluid at temperature, T and number density, ρ with two - particle interaction potential, $u(r)$ and radial distribution function, $g(r) (= g_0(r) + \rho g_1(r) + \rho^2 g_2(r) + \dots)$, is given by,

[5]

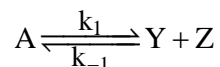
- where the rate constants k_1 & k_{-1} can be determined by following the reaction by T-jump relaxation method. Find out an expression for the relaxation time (τ) in terms of the rate constants.
- g) Discuss briefly about competitive and irreversible inhibitions with examples.

[4]

UNIT - P-3122

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

- a) Discuss the principles involved in the determination of rate constants using flow technique. What are the advantages and disadvantages of using flow technique ?
- b) Write a brief note on the Shock-tube method in the study of fast reactions.
- c) What is meant by ionic polymerization ? How many types are there ? Discuss the steps involved in the 'polar bond mechanism' for cationic polymerization and deduce the rate law.
- d) What is microscopic diffusion controlled reaction ? Discuss about full microscopic diffusion controlled reaction.
- e) Discuss the effect of temperature 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 mechanism.
- f) A fast reversible reaction occurs



[3]

$$\frac{P}{kT} = \frac{\rho^2}{6kT} \int_0^\infty r u'(r) g(r) 4\pi r^2 dr.$$

Justify that $g_o(r)$ may be approximated as, $e^{-u(r)/kT}$.
Comment on its utility. 4

[Turn over