

**M. Sc. CHEMISTRY EXAMINATION, 2017**

(3rd Semester)

**PAPER - XII-P****PHYSICAL CHEMISTRY SPECIAL**

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 boson particles and derive the distribution function associated with a thermodynamic system of bosons. 6

2. Derive an expression for the pressure of a thermodynamic system of monatomic fluid in terms of the radial distribution function. 6

OR

(a) Defining the grand partition function as,  $Y = \sum_{n=0}^H e^{n(\mu-\epsilon)/k_B T}$ , where  $\mu$  = chemical potential;  $\epsilon$  = energy of a level;  $T$  = temperature;  $k_B$  = Boltzmann constant, and also

$\langle n \rangle = \frac{1}{Y} \sum_{n=0}^H n e^{n(\mu-\epsilon)/k_B T}$ , show that for  $H=1$  one can get the Fermi-Dirac Distribution function.

(b) If the total energy density, for all frequencies, for a given blackbody is given by

$$\bar{u}_v = \frac{8\pi h}{c^3} \int_0^\infty \frac{v^3 dv}{e^{hv/k_B T} - 1}$$

Justify the Stefan's law giving the value for the Stefan-Boltzmann constant  $\sigma$ . [Use  $\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$ ]. 3+3

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

(a) Write short note on Percus-Yevick equation and its use.

(b) An ideal quantum gas has the same pressure, volume and internal energy relationship as that of an ideal classical gas – justify.

(c) Define Fermi Energy,  $\mu_0$ . For an ideal Fermi-gas of  $N$  particles in the ground state, its internal energy,  $E_0$  is given as,  $E_0 = (3/5)N \mu_0$ . Given, for a system (of volume,  $V$ ) of fermions of mass,  $m$ , the density of states is,  $\omega(\epsilon) = 4\pi \left(\frac{2m}{h^2}\right)^{3/2} V \epsilon^{1/2}$

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

(e) If the total energy density, for all frequencies, for a given blackbody is given by  $\bar{u}_v = \frac{8\pi h}{c^3} \int_0^\infty \frac{v^3 dv}{e^{hv/k_B T} - 1}$ . Justify the Stefan's law giving the value for the Stefan-Boltzmann constant  $\sigma$ . [Use  $\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$ ].

[ Turn over

4. For an imperfect gas with intermolecular interaction potential,  $u(r)$  as a function of intermolecular distance,  $r$  given as follows,

$$u(r) = +\infty \text{ for } 0 \leq r \leq \sigma \text{ and}$$

$$u(r) = -\alpha r^{-n} \text{ for } \sigma \leq r \leq \infty ,$$

show that  $n > 3$ .

OR

For free electrons in a metal conductor, the average number of electrons in a microlevel ( $\Delta N$ ) is given by  $\Delta N = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{\epsilon^{1/2}}{e^{(\epsilon-\mu)/k_B T} + 1} \Delta\epsilon$ , where  $\epsilon$ =energy of a microlevel,  $\mu$ =chemical potential= $\epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F}\right)^2 + \frac{\pi^4}{80} \left(\frac{k_B T}{\epsilon_F}\right)^4 + \dots\right]$ ,  $\epsilon_F$ =Fermi energy. (a) Depict the Distribution function at  $T=0$ . (b) What is the significance of  $\epsilon_F$  with respect to the occupation number at absolute zero. (c) Graphically depict  $\frac{\Delta N}{\Delta\epsilon}$  vs  $\epsilon$  at  $T = 0, T_1, T_2$  where  $0 < T_1 < T_2$ .

**UNIT - P - 3122**

Answer *any five* questions from the following :

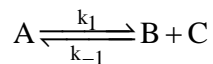
1. a) For a bimolecular reaction between the reactants A and B occurring on a catalyst surface, find out the expression for the fraction of surface covered by each of the reactants. Hence deduce the rate law for the reaction occurring via Langmuir-Rideal mechanism. Draw graphs to show how the rate (or the rate constant) varies with the concentration of either of the reactants. 5
- b) Find out the general expression for the rate of a free-radical initiated polymerisation reaction and show how the rate expression changes depending on the mechanism of initiation. 5
- c) In the presence of I<sub>2</sub> as chaperon, the recombination of I atoms does not become independent of chaperon concentration even at high pressures. Show that it can be explained in terms of the atom-molecule complex mechanism. Explain how the negative temperature coefficient of the rate can be explained qualitatively with its help. 5
- d) Two reactants A and B react with a single enzyme E to give the product following a random ternary complex mechanism. Illustrate the reaction steps and derive the rate equation. 5

OR

- i) What is meant by "Turnover number" in case of an enzyme catalysed reaction? What is its unit? A 10<sup>-8</sup> M solution of catalase catalyses the decomposition of 0.5 M H<sub>2</sub>O<sub>2</sub> per second. Find out the turnover number.
- ii) From mechanistic viewpoint what is the difference between non-competitive and uncompetitive inhibition? Also point out the difference in the Lineweaver-Burk plots for these two types of inhibition. (No deduction of rate law is required). 2½ × 2

[ Turn over

e) The dissociation of a weak acid,  $HA \rightleftharpoons H^+ + A^-$  may be represented by



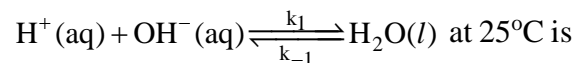
The rate constants  $k_1$  and  $k_{-1}$  can be measured by the T-jump technique. Prove that the relaxation time ( $\tau$ ) is given by

$$\tau = \frac{1}{k_1 + 2k_{-1}x_e}$$

where  $x_e$  is the concentration of each ion (B and C) at equilibrium. 5

OR

The equilibrium constant for the reaction



$$K_C = \frac{[H_2O]}{[H^+][OH^-]} = 5 \cdot 20 \times 10^{15} \text{ dm}^3 \text{ mol}^{-1}$$

The time dependent conductivity of the solution following a T-jump to a final temperature of  $25^\circ C$  shows on relaxation time ( $\tau$ ) of  $2 \cdot 0 \times 10^{-5}$  s. Determine  $k_1$  and  $k_{-1}$  at  $25^\circ C$ . 5

- f) Write a brief note on “Flash Photolysis” and its applications or, “Molecular Beam” method in the study of fast reactions. 5
- g) What do you mean by micellar catalysis? Describe Menger and Portnoy’s model for micellar catalysis and deduce the rate law.
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