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 μ =chemical potential; ϵ=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 $\bar{u}_\nu = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3\, d\nu}{e^{h\nu/k_B T}-1}$. Justify the Stefan's law giving the value for the Stefan-Boltzmann constant σ. $\left[Use\ \int_0^\infty \frac{x^3 dx}{e^x-1} = \frac{\pi^4}{15}\right]$. 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, μ_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, $\omega(\varepsilon) = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon^{1/2}$

(d) Consider the case of photons within a blackbody cavity, derive the number of stationary waves (ΔG) in the frequency interval ν to ν+Δν.

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

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

$u(r) = +\infty \quad for \quad 0 \leq r \leq \sigma$ and

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

show that n>3.

OR

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

4

UNIT - P - 3122

Answer ***any five*** questions from the following :

1. a) For a bimolecular reaction between the reactants A and B occuring 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 occuring via Laugmuir-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_2 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^{-8} M solution of catalase catalyses the decomposition of 0·5 M H_2O_2 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). $2\frac{1}{2}\times2$

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

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C$$

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

$$H^+(aq) + OH^-(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O(l) \text{ at } 25^oC \text{ is}$$

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

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