(d) Derive the rate equation for the following special case of the ping-pong bi-bi mechanism :

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EA$$

$$EA \xrightarrow{k_2} EA' + Y$$

$$EA' + B \xrightarrow{k_3} E + Z$$

Where Y and Z are the reaction products. A and B are the substrates and E is an enzyme.

(e) Write a short note on irreversible inhibition with examples. Discuss briefly about applications of enzymatic analysis in industry.

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

M. Sc. Chemistry Examination, 2023

(3rd Semester, CBCS)

Paper: XII P

[Physical Chemistry Special]

Time : Two Hours Full Marks : 40

(20 Marks for each unit)

Use a separate answer script for each unit.

UNIT - P - 3121

1. Answer any ***one*** of the following :

(a) Describe the Classical Limit condition and show that under that condition both the quantum statistics becomes classical Boltzmann satistics.

(b) Starting from the definition of a microstate and a macrostate and suitable constrains: derive the form of the thermodynamic probability of a macrostate for an isolated system following Fermi-Dirac statistics, in terms of the total number of particles (N), the degeneracy of a particular "i^{th}" energy level (g_i) and the number of particles in a particular "ith" energy level (n_i). 5

2. Answer any ***one*** of the following :

   (a) Describe briefly the pair correlation function, g(r) and derive an expression for internal energy of a monatomic liquid involving g(r). 5

   (b) (i) For a system composed of electrons in a metallic conductor, determine the number of electron waves between energy range of E and E+dE. 3

   (ii) Graphically depict the variation of the ratio of occupancy of a particular energy level and degeneracy of that level i.e. $\left(\frac{n_i}{g_i}\right)$ versus $\frac{(\epsilon_i - \mu)}{k_B T}$ (where the symbols used have their usual meaning), for a system obeying Maxwell-Boltzmann, Bose-Einstein. Fermi-Dirac and Classical statistics. 2

3. Answer any ***one*** of the following : 4

   (a) Describe how second virial coefficient, $B_2(T)$ for an imperfect gas can be determined experimentally and obtain its theoretical expression for a gas with intermolecular interactions following Square-Well potential.

   (b) Derive the form of the Bose-Einstein transition temperature T_c starting from a suitable from a suitable form for the number density of an ideal Bose gas $\left(\rho = \frac{N}{V}\right)$.

4. Answer any ***two*** questions : 2x3=6

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

   (b) Using the form of the spectral radiancy of a black body as $\rho\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{1}{e^{hc/\lambda k_B T} - 1} d\lambda.$, justify the Wien's Displacement Law and determine the Wien's displacement constant.

   (c) Use a suitable form of the density matrix to represent the statistical average of an observable and show that it is basis independent.

UNIT - P - 3122

5. Answer any ***four*** questions : 4x5

   (a) Write a brief note on the Shock-tube method in the study of fast reactions.

   (b) 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.

   (c) What is microscopic diffusion controlled reaction? Discuss about full microscopic diffusion controlled reaction.