M. Sc. Chemistry Examination, 2025

(3rd Semester)

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** question.

(a) Describe and justify the classical limit conditions. Show that the Fermions under classical limit follow the distribution function associated with the classical particles.

(b) For a real gas, if the single particle partition function Q_1 and the number density ρ (=N/V) is known, then represent the pressure P of the system as an expansion in ρ determining the form of the coefficients for ρ^2 and ρ^3. When it is given:

(i) let $P = KT\sum_{j=1}^{\infty} b_j z^j$,

(ii) define $Z = \lambda Q_1 / V$,

(iii) use $\rho = \frac{N}{V} = \frac{z}{k_B T}\left(\frac{\partial P}{\partial z}\right)_{V,T}$,

(iv) $Z_1 = V$,

(v) $b_1 = (1!V)^{-1} Z_1$,

(vi) $b_2 = (2!V)^{-1}(Z_2 - Z_1^2)$,

(vii) $b_3 = (3!V)^{-1}(Z_3 - 3Z_2 Z_1 + 2Z_1^3)$,

(viii) $Z_N = N!\left(\frac{V}{Q_1}\right)^N Q_N$ 5

2. Answer *any* **one** question.

(a) Determine the form of the density of states for a 3-D particle in a box system. 4

(b) State how local density is related with the radial distribution function (RDF). Derive an expression for the internal energy of a thermodynamic system of monatomic fluid in terms of the RDF and comment on its use. 4

3. Answer *any* **one** question.

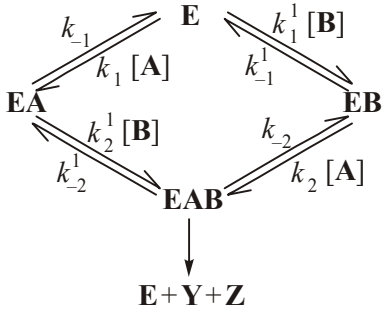
(a) Describe briefly the characteristics of boson particles. Show for an ideal Bose gas confined in a box, the number of molecules with the magnitude of wave vector in the range k to $k + dk$ is given by

$$\triangle N_k = \frac{\frac{V}{2\pi^2} k^2 dk}{\left(e^{-\frac{\mu}{KT}} e^{\frac{\hbar^2 k^2}{2mk_B T}}\right) - 1}.$$

9. *(a)* Discuss about the influence of the solvent on full microscopic diffusion controlled reaction where the basic equation is $k_D = 4\pi(D_A + D_B)d_{AB}$. The terms carry the usual meanings.

(b) The coefficient of viscosity of CCl_4 is $1{\cdot}04 \times 10^{-3}$ kg m^{-1}s^{-1} at 20 °C. Estimate the magnitude of diffusion-controlled reactions in this solvent, where $R = 8{\cdot}314$ J K^{-1} mol^{-1}. 3+2=5

10. Derive the rate equation for the random ternary-complex mechanism, taking the intermediates **EA**, **EB** and **EAB** to be in equilibrium with **E**, **A** and **B**.



where **Y** and **Z** are the reaction products. **A** and **B** are the substrates and **E** is an enzyme. 5

11. Briefly discuss about competitive and un-competitive inhibition with examples. 5

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Then show $\bar{N} = \frac{1}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{x^{\frac{1}{2}}}{(Z^{-1}e^x)-1}dx$, where Z = partition function $= e^{\mu/KT}$ and $\mu = -ve$.

(b) Describe how the second virial coefficient of an imperfect gas can be estimated experimentally. Derive the expression of second virial coefficient for a gas with inter-particle potential following square-well potential model and state significance of the result. 5

4. Describe the characteristic differences between the classical particles and fermions. For a classical monoatomic liquid of N particles, if the probability of finding the i^{th} molecule within dr_i at a distance r_i (for all $i = 1, ..., N$) is given by $P^{(N)}(r_1,...r_N)\,dr_1...dr_N = \frac{e^{-\beta U_N}}{Z_N}$, then write the form of the specific distribution function for $n(n \le N)$ particles, i.e. $P^{(n)}(r_1...r_n)dr_1...dr_n$, and the general distribution function as probability of finding 'any' one molecule within dr_i at a distance r_i (for all $i = 1, ..., n$) i.e. $\rho^{(n)}$. 1+2=3

5. Answer *any* **one** question.

(a) Prove that the expectation value of any observable $\hat{A}$ in a statistical ensemble represented by the density matrix $\hat{\rho}$ is given by $Tr[\hat{\rho}\,\hat{A}]$ (Use the form of $\hat{\rho}$ for a pure state i.e. $\hat{\rho} = |\psi\rangle\langle\psi|$).

(b) Define Fermi energy and provide qualitative explanation for the linear temperature dependence of the electronic contribution to the specific heat (C_v) for a simple metal. 3

UNIT—P-3122

Answer *any* **four** questions.

6. *(a)* Discuss the principle involved in the determination of the rate of a reaction using stirred flow method.

(b) The reaction $NO + Cl_2 = NOCl + Cl$ is second order with rate constant, $k = 8 \times 10^5$ L mole^{-1}s^{-1} at 1200 K. A stream of NO and Cl_2 in equimolecular amounts in an inert carrier gas is passed through tubular furnace of 1 cm in radius, 30 cm long at 1200 K, 1 atm pressure and a rate of 10 Ls^{-1}. If Cl_2 (in mole state) is 1% of gas stream at the entry to furnace, what will be the percentage of atomic Cl in the gas stream at exit? 2+3=5

7. *(a)* What possible effects can be observed during the collision of the beams in the study of fast reactions?

(b) Show a mechanism leading to a molecular collision when the potential energy surfaces are repulsive. Give an example. 2+3=5

8. What are the characteristics of the Shock-tube method in the study of fast reaction? Give the examples. 3+2=5