

(2 1/2 Hours)

Total Marks : 60

**N.B. :** (1) All questions are compulsory.

- (2) **Figures** to the **right** indicate **full** marks.  
 (3) Draw **neat** diagrams wherever **necessary**.  
 (4) Symbols have usual meanings unless otherwise stated.  
 (5) Use of **non-programmable** calculator is allowed.

1. (a) Attempt any **one**:---

- (i) Show that the change in the entropy due to mixing of two ideal gases results in to the paradox. Explain how the paradox is resolved. **8**
- (ii) Consider two systems in contact with each other and isolated from surrounding. Using statistical concept of possible microstates accessible for the composite system, show that at equilibrium:  $T_1 = T_2$ ,  $P_1 = P_2$  and  $\mu_1 = \mu_2$  **8**

(b) Attempt any **one**:---

- (i) Describe the problem of one-dimensional simple harmonic oscillator. Hence show that the fundamental volume of the phase space is given by:  $\omega_o = h$ . **4**
- (ii) Let the entropy of the classical ideal gas is given by **4**
- $$S(N, V, E) = Nk \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} Nk$$
- Obtain equation for the specific heat at constant volume  $C_v$  and the specific heat at constant pressure  $C_p$ .

2. (a) Attempt any **one**:---

- (i) State and prove Equipartition theorem. **8**
- (ii) Consider a system of N quantum harmonic oscillators with frequency  $\omega$ . Derive the expression for N-particle partition function and prove that the Helmholtz free energy for the system is **8**

$$A = N \left[ kT \cdot \ln(1 - e^{-\beta \hbar \omega}) + \frac{1}{2} \hbar \omega \right]$$

(b) Attempt any **one**:---

(i) Show that the energy fluctuations  $\Delta E$  in canonical ensemble follows: 4

$$\langle (\Delta E)^2 \rangle = kT^2 C_v$$

(ii) Show that the N-particle partition function for a classical ideal gas is given 4

$$\text{by } Q_N(V, T) = \frac{1}{N!} \left[ \frac{V}{h^3} (2\pi m kT)^{3/2} \right]^N$$

$$\text{Use } \int_0^\infty dx \cdot x^2 \cdot e^{-ax^2} = \frac{1}{4a} \sqrt{\frac{\pi}{a}}.$$

3. (a) Attempt any **one**:---

(i) Derive the relation for density fluctuation in grand canonical ensemble given by 8

$$\frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{kT}{V} \kappa_T$$

where  $\kappa_T$  is isothermal compressibility of the system.

(ii) What do you mean by phase equilibrium? Show that Gibb's free energy is minimized at equilibrium. Hence derive the Clausius-Clapeyron equation. 8

(b) Attempt any **one**:---

(i) Sketch P-T phase diagram for Helium-4. State its properties in different phases. 4

(ii) Partition function of a system of independent localized particles is given by 4

$$Q_N(V, T) = [Q_1(V, T)]^N$$

Obtain the expression for pressure P and number of particles N.

4. (a) Attempt any **one**:---

(i) For a linear harmonic oscillator, show that 8

$$Tr(e^{-\beta \hat{H}}) = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}}$$

(ii) Derive an expression for antisymmetric wave function of indistinguishable particles. 8

(b) Attempt any **one**:---

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|--|----------|
| (i) Write a short note on wave functions of indistinguishable particles. | <b>4</b> |
| (ii) State and explain the postulate of equal a priori probabilities.    | <b>4</b> |

5. Attempt any **four**:---

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|---|----------|
| (a) Show that for micro-canonical ensemble:   | <b>3</b> |
| $P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} \quad \text{and} \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}$   |          |
| (b) Explain the phase space of a classical system. Hence discuss the concept of stationary ensemble.  | <b>3</b> |
| (c) For a system in canonical ensemble, show that $C_v = -T \left(\frac{\partial^2 A}{\partial T^2}\right)$ .   | <b>3</b> |
| (d) What is the 'virial' for a system? State virial theorem.  | <b>3</b> |
| (e) Define fugacity $z$ of the system. Show $q$ -potential is logarithm of the grand canonical partition function.  | <b>3</b> |
| (f) Calculate the slope of the solid-liquid transition line for water near the triple point $T = 273.16\text{K}$ , given that the latent heat of melting is $80\text{cal/g}$ , the density of the liquid phase is $1.00\text{g/cm}^3$ , and the density of the ice phase is $0.92\text{g/cm}^3$ . Estimate the melting temperature at $P = 100\text{atm}$ . | <b>3</b> |
| (g) What are the Hamiltonian and the wavefunction of a free particle in a three dimensional box of length $L$ ?   | <b>3</b> |
| (h) Write an expression for mean thermal wavelength. Explain each term.   | <b>3</b> |

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