

OR

2. (a) What are partial molar quantities? Write the general expression for partial molar quantity of a component i in a mixture. $1\frac{1}{2} + \frac{1}{2} = 2$

- (b) Describe Nernst heat theorem. 2

- (c) Derive the following Maxwell relations starting from related thermodynamic equations : $2\frac{1}{2} + 2\frac{1}{2} = 5$.

$$(i) \left[\frac{\partial T}{\partial P} \right]_S = \left[\frac{\partial V}{\partial S} \right]_P$$

$$(ii) \left[\frac{\partial S}{\partial V} \right]_T = \left[\frac{\partial P}{\partial T} \right]_V$$

- (d) Derive an expression showing the variation of chemical potential with temperature and pressure. $2\frac{1}{2} + 2\frac{1}{2} = 5$

- (e) Derive Gibbs-Duhem equation for a mixture consisting of i number of components. 4

3. (a) What is black-body radiation? Describe the spectral distribution of black-body radiation. $1 + 4 = 5$

- (b) Write down any three postulates of quantum mechanics. 3

(c) What is Compton effect? X-rays with wavelength $1 \text{ \AA}$ are scattered from a carbon black. The scattered radiations are viewed at 90° to the incident beam. Calculate—

(i) Compton shift ($\Delta\lambda$);

(ii) wavelength of the scattered X-ray.

[Given : $m_e = 9.1 \times 10^{-31} \text{ kg}$,

$c = 3 \times 10^8 \text{ ms}^{-1}$, $h = 6.626 \times 10^{-34} \text{ Js}$]

$1 + 1\frac{1}{2} + 1\frac{1}{2} = 4$

(d) Solve the Schrödinger equation for a particle in one-dimensional box of length a and obtain the energy expression. 5

(e) What do you understand by quantization of energy? What will happen if the walls of a one-dimensional box are removed? $2 + 1 = 3$

OR

4. (a) What is photoelectric effect? Deduce Einstein's photoelectric effect equation.

$1 + 3 = 4$

(b) What do you understand by eigenfunctions and eigenvalues? Write down the eigenvalue equation. $1\frac{1}{2} + 1\frac{1}{2} + 1 = 4$

- (c) Show that if there are two eigenfunctions ψ_m and ψ_n corresponding to different values of m and n , then ψ_m and ψ_n will be orthogonal to each other. 3
- (d) Write notes on the following : $2 \times 2 = 4$
- (i) Zero point energy of a particle in one-dimensional box
 - (ii) Heisenberg's uncertainty principle
- (e) Derive Schrödinger wave equation using de-Broglie equation. 5
5. (a) What is an ensemble? Briefly explain the different types of ensembles. $2 + 3 = 5$
- (b) Define molecular partition function. Mention its significance. $2 + 2 = 4$
- (c) Derive the relation between molecular and molar partition function. 3
- (d) Write the expression for the following thermodynamic functions in terms of partition function : $2 \times 4 = 8$
- (i) Enthalpy
 - (ii) Entropy
 - (iii) Gibbs' free energy
 - (iv) Heat capacity (C_V)

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OR

6. (a) Define the following : $2 \times 2 = 4$

(i) Thermodynamic probability

(ii) Mathematical probability

(b) Derive the relationship between entropy and thermodynamic probability. 3

(c) Derive the Boltzmann distribution law assuming each energy level is degenerate. 4

(d) Prove that molecular partition function (Q) for a system is the product of translational, rotational, vibrational and electronic partition functions. 4

(e) Calculate the translational partition function of NO molecule at 300 K in a volume of 1000 m^3 , assuming the gas to behave ideally. 4

Given : $k = 1.38 \times 10^{-16} \text{ g cm}^2 \text{ s}^{-2}$

$h = 6.626 \times 10^{-27} \text{ g cm}^2 \text{ s}^{-1}$ 5

7. (a) What do you understand by flux and driving force in an irreversible process? 4

$1+1=2$

(b) Derive Onsager reciprocity relation. 5 5

(c) Derive Clausius inequality equation. 5

(d) Write a brief note on electrokinetic phenomena. 5 5

(6)

OR

8. (a) Define stationary non-equilibrium state. 2
- (b) Write down the four phenomenological equations. What is the significance of these equations? 4+1=5
- (c) Discuss Prigogine's principle of minimum entropy production. 5
- (d) Derive an expression for entropy production and entropy flow in an open system. 5
