

2024

CHEMISTRY — HONOURS

Paper : CC-9

(Physical Chemistry - 3)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question no. 1** and **any eight** questions from the rest.1. Answer **any ten** questions :

1×10

- (a) What is an Azeotropic mixture? Give one example.
- (b) What is the difference between ideal solution and ideally dilute solution?
- (c) "Elevation of boiling point of an ideally dilute solution is an extensive property." Justify and criticize.
- (d) What will be the number of components, when solid CaCO_3 is heated in a closed container and the following equilibrium is attained? Justify your answer.



- (e) What is the probability for finding a particle in the left most 10% of a one-dimensional box for the $n = 1$ state?
- (f) Find the eigenfunctions and eigenvalues of the operator ' $\frac{d}{dx}$ '.
- (g) What does 'ultra-violet catastrophe' mean?
- (h) The motion of a free particle cannot be quantized. Justify and criticize.
- (i) If $|\psi_1\rangle = \begin{pmatrix} 2-3i \\ 6+4i \end{pmatrix}$ and $|\psi_2\rangle = \begin{pmatrix} i \\ 1 \end{pmatrix}$, Find the value of $\langle \psi_1 | \psi_2 \rangle$.
- (j) Sketch the plane $1\bar{1}0$ in a three-dimensional cubic lattice.
- (k) What is the relation between $1\bar{1}$ planes and $\bar{1}1$ planes of a two-dimensional square lattice?
- (l) Why is it difficult to assign the position of 'H' atom through X-ray crystallography?

Please Turn Over

2. (a) Establish Nernst Distribution law from thermodynamic stand point.

(b) A certain solution of benzoic acid in benzene has freezing point of 3.1°C and a boiling point of 82.6°C at 1 atm pressure. Explain these observations and suggest structure of the solute particle at two temperatures.

[Given : Normal freezing point of benzene = 5.5°C

Normal boiling point of benzene = 80.1°C

For Benzene, $K_f = 5.12 \text{ Kkg mol}^{-1}$, $K_b = 2.53 \text{ Kkg mol}^{-1}$

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

3. Using the concept of chemical potential (μ) derive thermodynamically a relation between the depression of freezing point of an ideally dilute solution containing a non-volatile non-electrolyte solute and its molality clearly mentioning the assumptions and approximations you have used. $3+(1+1)$

4. Derive the Clapeyron equation and then proceed on to find the expression for Clausius-Clapeyron equation for a liquid-vapour equilibrium clearly mentioning the assumptions and approximations involved. $(2+2+1)$

5. (a) Draw the phase diagram for CO_2 and hence explain why CO_2 sublimates at normal temperature and pressure.

(b) Draw the phase diagram for sulphur and hence explain why the four phases cannot coexist in equilibrium. $2\frac{1}{2}+2\frac{1}{2}$

6. (a) Consider a particle in a two-dimensional box to determine $[\hat{x}, \hat{p}_x]$ and $[\hat{x}, \hat{p}_y]$ and interpret the result.

(b) For a $1.0 \times 10^{-26} \text{ gm}$ particle in a one-dimensional box whose ends are at $x = 0$ and $x = 2.000 \text{ \AA}$, calculate the probability so that the particles 'x' coordinate lies in between $1.6000 \text{ \AA}$ and $1.6001 \text{ \AA}$ for $n = 1$ state. $3+2$

7. (a) Which of the following wave functions are normalizable over the indicated interval? Justify your answer.

(i) $e^{-x}(-\alpha, \alpha)$

(ii) $xe^{-x}(0, \alpha)$

(iii) $\left(\frac{4}{ab}\right)^{\frac{1}{2}} \sin \frac{\pi x}{a} \sin \frac{\pi y}{b} \left[\begin{matrix} 0 \leq x \leq a \\ 0 \leq y \leq b \end{matrix} \right]$

(b) Obtain the operator $\hat{A}^2$ for

$\hat{A} = (i) \frac{d}{dx} + x$

(ii) $\frac{d^2}{dx^2} - 2x \frac{d}{dx} + 1$

3+2

8. (a) Suppose that a particle in a one-dimensional box of length “ a ” is in the state represented by the normalized state function

$$\psi(x) = \begin{cases} \left(\frac{30}{a^5}\right)^{\frac{1}{2}} x(a-x) & ; [0 \leq x \leq a] \\ 0 & ; \text{otherwise.} \end{cases}$$

Calculate the average energy of the system. [Consider, $V = 0$ inside the box]

- (b) Determine whether the following functions are acceptable or not over the indicated intervals,

(i) $e^{-x} \cos x (0, \alpha)$

(ii) $\frac{\sin x}{x} (0, \alpha)$

3+2

9. (a) Prove that the kinetic energy operator is Hermitian :

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}.$$

- (b) Calculate the uncertainty in the position of a particle of mass 100 gm moving with a velocity $10 \pm 0.005 \text{ ms}^{-1}$. 3+2

10. (a) Determine the probability associated with the ground state for a particle in a one-dimensional box of length ‘ a ’ between $2a/3$ and a .

- (b) Show that the eigenvalue of a Hermitian operator is real. 3+2

11. (a) Determine the Miller indices of the plane that intersects the crystal axes at

(i) $(a, 2b, 3c)$, (ii) $(a, b, -c)$ and (iii) $(2a, b, c)$.

- (b) Derive Bragg equation, $n\lambda = 2d \sin \theta$, where terms have their usual meaning. $1\frac{1}{2}+3\frac{1}{2}$

12. Heat capacity of a solid is given by Einstein’s equation as follows :

$$C_v = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{\left(\frac{h\nu}{kT} \right)}}{\left[e^{\left(\frac{h\nu}{kT} \right)} - 1 \right]^2}$$

Hence :

- (a) Obtain Dulong-Petit’s law.

- (b) Give definition and significance of Einstein characteristic temperature.
- (c) Explain why Einstein's theory of heat capacity of solid fails to explain the experimental temperature variation of heat capacity in the low temperature region. 1+2+2
13. (a) Define space lattice and unit cell. Name all possible types of crystal system.
- (b) In a compound, oxide ions are arranged in CCP. One sixth of the tetrahedral voids are occupied by cations (A) and one-third of octahedral voids are occupied by cations (B). What is the formula of the compound? 3+2
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