

2022

CHEMISTRY — HONOURS

Paper : CC-9

MURALIDHAR GIRLS' COLLEGE
LIBRARY (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
- What is the essential weakness of the Debye Theory of heat capacity of crystals?
 - How many octahedral and tetrahedral holes are possible in a fcc structure?
 - A powder diffraction photograph from a metal (M) shows lines, which shows indices as (110), (200), (211), (220), (310), (222), (321), (400)...
- Identify, what the symmetry of the unit cell should be.
- Using Einstein's heat capacity of solid, obtain the Dulong-Petit's Law.
 - What is the relation between $\bar{1}1$ and $1\bar{1}$ planes of a square lattice?
 - Calculate and explain the number of components of phenol-10% NaCl aqueous solution system, pertaining to the determination of the consolute temperature.
 - Does Compton shift depend on the material of the scattering? Justify your answer.
 - Show $(\hat{A}^\dagger)^\dagger = \hat{A}$.
 - What is the essence of the superposition of states in quantum mechanics?
 - Fusion mixture is used in quantitative analysis for fusion. — Why? (Answer in the light of phase rule)
 - Check the acceptability of $\psi = e^{-x^2}$ in the range $(-\infty, +\infty)$.
 - Prove that if $\psi(x)$ is a solution to the Schrödinger equation, then any constant times $\psi(x)$ is also a solution.
2. (a) Derive Duhem-Margules equation and show that if one component obeys Raoult's Law, then the other will also obey.
- (b) What do you mean by phase transition of first order? Show using diagram how C_p changes with temperature (T). 3+2

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3. (a) State with reasons the degrees of freedom (F) inside the bound area, outside the bound area and at the critical solution temperature for phenol-water system.
- (b) Calculate the osmotic pressure at 300K of a solution formed by dissolving 1 gm of glucose and 1 gm of sucrose in 1 litre of water. 3+2
4. (a) 0.01 M acetic acid aqueous solution shows depression of freezing point by 0.0194°C while 0.01 M solution in benzene shows the depression by 0.0216°C. Given $K_f = 5.12 \text{ kg mol}^{-1}$ for benzene. Predict the state of acetic acid in these two solutions.

- (b) If ψ_1, ψ_2 (orthonormal) be the eigenfunctions of a Hermitian operator \hat{A} with eigenvalues a_1 and a_2 respectively, then the linear combination $(c_1\psi_1 + c_2\psi_2)$ is not necessarily an eigenvalue of \hat{A} . Then what is the expectation value of \hat{A} ? 3+2

5. (a) Find the simplest formula of a solid containing 'X' and 'Y' atoms in a cubic arrangement in which 'X' atoms occupy the corners and 'Y' atoms occupy the centres of the faces of the unit cell.

If the side of the unit cell is 50 nm, estimate the density of the solid assuming atomic masses of 'X' and 'Y' to be 60 and 90 respectively.

- (b) State with reason if the following function is acceptable :

$$\psi(x) = \sin^{-1} x \left[\text{where, } (-1 \leq x \leq 1) \text{ and } \left(-\frac{\pi}{2} \leq \psi(x) \leq \frac{\pi}{2} \right) \right] \quad 3+2$$

6. (a) Prove that any operator defined as product of two non-commuting operators is not Hermitian even if when the operators themselves are hermitian. How will you make the operator hermitian in this case?

- (b) What is the consequence if two operators do not commute? 3+2

7. (a) For a two component solutions (say, A and B) that obeys Raoult's Law, vapour pressure problems involve as many as four mole-fractions and five vapour pressures. Obviously, we have five unknown pressures, two unknown independent mole-fractions. To solve the problem, explain at least how many pieces of information you require to solve the problem.

- (b) If two operators \hat{A} and \hat{B} commute, then show that they have the same set of eigenfunctions, ψ_i (where $i = 1, 2, 3, \dots$) 3+2

8. (a) Show that for ideal solution, $\Delta H_{\text{solution}} = 0$.

- (b) (i) How did Debye modify the Einstein theory of heat capacity of monatomic crystal?
 (ii) Draw the curves that show the plots of frequency distribution of normal modes in a crystal for both the Einstein and the Debye theories. 2+3

9. (a) The energy state of a particle in a cubicle box ($V=0$) is $\frac{38h^2}{8ma^2}$. State the degrees of degeneracy and assign the states.
- (b) Prove that if $\hat{\alpha}$ and $\hat{\beta}$ are two linear operators, then $(\hat{\alpha} + \hat{\beta})$ and $(\hat{\alpha}\hat{\beta})$ are also linear operators. 3+2
10. (a) Why is x-ray used to get diffraction pattern of a solid? Can we use electron beam for the same?
- (b) The (2 2 2) planes of cubic tantalum unit cell gives a reflection at $21^\circ 5'$ for $\lambda = 0.71 \text{ \AA}$. What is its edge length? 2+3
11. (a) In CaF_2 crystal, Ca^{+2} is arranged in a fcc type crystal structure, while the flouride ions occupy all the tetrahedral holes. Justify the formula of CaF_2 .
- (b) Verify that the wave functions of a particle in a one-dimensional box of width 'a' and infinite height are orthogonal. 3+2
12. (a) Derive the Nernst Distribution Law using the concept of chemical potential.
- (b) A certain mass of substance when dissolved in 100 gm of Benzene, lowers the freezing point by 13°C , which when dissolved in water, the same mass lowers the freezing point by 14°C . If the substance has a normal molecular weight in benzene and in water it is completely dissociated, how many ions in water does it dissociate into? 3+2
13. (a) How would you distinguish an azeotrope from a compound?— Give an argument only. What is the degree of freedom of an azeotrope (of a binary liquid)?
- (b) Show that $\langle x \rangle = \frac{a}{2}$ for all the states of a particle in a box, where 'a' is the length of the box. Is this result physically reasonable? 2+3