

2023

## CHEMISTRY — HONOURS

Paper : CC-9

(Physical Chemistry - 3)

MURALIDHAR GIRLS' COLLEGE  
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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 practical be.*Answer *question no. 1* and *any eight* questions from the rest.1. Answer *any ten* questions :

1×10

- (a) The function  $f(x) = e^{-ikx}$  is an eigenfunction of an operator  $\hat{A} = -i\hbar \frac{\partial}{\partial x}$ . Find the eigenvalue of the eigenfunction.
- (b) Why for a two-component system, the degree of freedom (F) at the Eutectic point is zero?
- (c) A mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  is used as fusion mixture. Explain.
- (d) Prove that if  $\psi(x)$  is a solution to the Schrödinger equation, then any constant times  $\psi(x)$  is also a solution.
- (e) Show the distance of separation of  $(nh, nk, nl)$  planes from  $d_{hkl}$  value with orthogonal axes.
- (f) "If the degree of dissociation or association of solute molecules in solvent increases, the extent of abnormality in colligative property increases." — Explain.
- (g) For a particular wavelength of X-rays, show that the highest order of reflection made by the lattice planes is directly proportional to the interplaner distance.
- (h) What is the physical significance of  $|\psi|^2$ ?
- (i) What is the significance of normalisation constant?
- (j) What do you mean by expansion of eigenstates?
- (k) Explain Bohr's correspondence principle for particle in an one-dimensional box.
- (l) Why are the number of chemical species and number of components are equal for non-interacting constituents in equilibrium?

2. Using the concept of chemical potential, derive the van't Hoff equation,  $\pi = cRT$ , where the terms have usual significance. Also derive a relationship between osmotic pressure and lowering of vapour pressure of an ideal solution.

3+2

Please Turn Over

3. (a) Let  $\psi_1, \psi_2, \dots, \psi_n$  be a set of linearly independent eigenfunctions.

If  $\phi = c_1\psi_1 + c_2\psi_2 + \dots + c_n\psi_n = \sum_i c_i\psi_i$ , find the coefficients  $c_i$ 's? Assume that  $\psi_i$ 's are orthonormal.

(b) A dilute solution of  $H_2SO_4$  in water. Find its degrees of freedom and components. 3+2

4. (a) Show that the probability of finding a particle in a one-dimensional box of length  $a$  within the interval.

$$\left(0 \leq x \leq \frac{a}{4}\right) \text{ is } \frac{1}{4}, \text{ when } n \text{ is even, and is } \left(\frac{1}{4} - \frac{(-1)^{\frac{n-1}{2}}}{2\pi n}\right) \text{ when } n \text{ is odd.}$$

(b) Calculate the ratio of mole fraction of  $O_2$  and  $N_2$  dissolved in water at  $25^\circ C$ , if Henry's law constant for  $N_2 = 6.50 \times 10^7$  torr and for  $O_2 = 3.30 \times 10^7$  torr. 3+2

5. (a) If  $\psi_1$  and  $\psi_2$  are non-degenerate eigenfunctions of a Hermitian operator, ( $\hat{a}$ ) and given :

$$\hat{a}|\psi_1\rangle = a_1|\psi_1\rangle$$

$$\hat{a}|\psi_2\rangle = a_2|\psi_2\rangle$$

$a_1$  and  $a_2$  being the eigenvalues of  $\psi_1$  and  $\psi_2$ , respectively.

show that  $\langle \psi_1 | \psi_2 \rangle = 0$ .

(b) In a crystalline solid, anion  $C$  is arranged in cubic close packing. Cation  $A$  occupies 50% of the tetrahedral voids and cation  $B$  occupies 50% of octahedral voids. What is the formula of the solid? 3+2

6. (a) State with reasons the degree of freedom (F) inside the bound area, outside the bound area and at the C.S.T. for phenol-water system.

(b) Evaluate the commutators of the operators  $A$  and  $A^\dagger$ , where  $A = x + i \frac{h}{2\pi} \frac{d}{dx}$ . 3+2

7. Consider the phase diagram (drawn here) for lead-silver system :

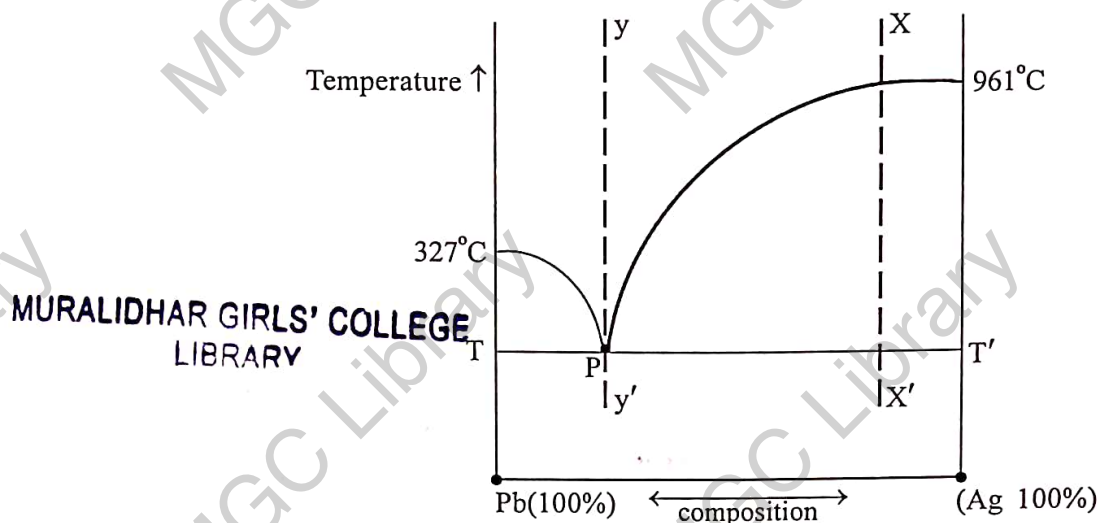
5

(a) Describe the TT' line.

(b) What are the phases present at P?

(c) Describe the changes which occur when the liquid mixture (melt) X (nearly 80% Ag) is cooled along the dashed line (XX').

- (d) Describe the changes along the dashed line
- $yy'$



8. (a) Show that the error in the de Broglie wavelength ( $\lambda$ ) is related to the error in velocity ( $v$ ) by the relation  $d\lambda = -\frac{\lambda}{v} dv$ .
- (b) The eigenfunction for the particle in a one-dimensional box of length  $a$  be  $\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ . Show that the said wavefunction is an eigenfunction of  $\hat{p}_x^2$  but not of  $\hat{p}_x$ . (The notations have their usual significance). 2+3
9. (a) State and explain Konowaloff's rule.
- (b) What is the cause of positive deviations from Raoult's law? What are its consequences? 3+2
10. (a) Show that  $\psi(x) = A \cdot e^{\pm 2\pi i x / \lambda}$  represents a de Broglie wave. Use this relation to derive an expression for  $x$  component of the linear momentum operator  $\hat{p}_x$ .
- (b) If there exists a set of functions which are eigenfunctions of two operators  $\hat{A}$  and  $\hat{B}$ , they must commute : that is,  $\hat{A}\hat{B} = \hat{B}\hat{A}$ . 2½+2½
11. (a) Consider a particle in a two-dimensional box. Determine  $[\hat{x}, \hat{p}_y]$ ,  $[\hat{x}, \hat{p}_x]$ . (notations have got their usual significance).
- (b) Show that the length of the box is an integral multiple of  $\frac{\lambda}{2}$ , where  $\lambda$  is the wavelength associated with the particle wave. 3+2

Please Turn Over

12. (a) KCl crystallizes as FCC. At certain temperature the density of KCl is 2gm/cc and the edge length of the unit cell is 6.3 Å. Find the number of  $K^+$  and  $Cl^-$  ions per kg of KCl.
- (b) 'Experiment shows that KCl has a simple cubic lattice structure. However we expect that KCl should have the same structure of NaCl, that is FCC, as both of them form a continuous series of solid solution, where  $Na^+$  replaces  $K^+$  in any proportions.'— Comment. 3+2
13. (a) 'The void space of FCC lattice is greater than the void space of BCC lattice.'— Justify or criticize.
- (b) Debye's theory is better at predicting low temperature behaviour of heat capacity than that of Einstein's.— Why?

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