2023

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 practicalbe.

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 Na_2CO_3 and K_2CO_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

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

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

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

(b) Calculate the ratio of mole fraction of O_2 and N_2 dissolved in water at 25°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 ψ_1 and ψ_2 are non-degenerate eigenfunctions of a Hermitian operator, ($\hat{\alpha}$) and given :

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

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

a_1 and a_2 being the eigenvalues of ψ_1 and ψ_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

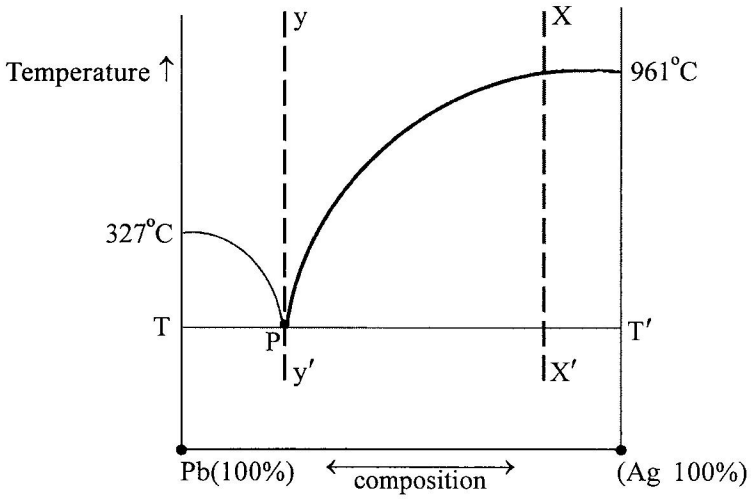
7. Consider the phase diagram (drawn here) for lead-silver system : 5

(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 (λ) 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 λ is the wavelength associated with the particle wave. 3+2

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12. (a) KCl crystalizes 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? 2½+2½