2021

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*** from the rest.

1. Answer ***any ten*** questions : 1×10

(a) If $\hat{\alpha}$ and $\hat{\beta}$ are two operators such that $\left[\hat{\alpha},\hat{\beta}\right]=1$, then find $\left[\hat{\alpha},\hat{\beta}^2\right]$.

(b) What is the difference between the tie lines in phenol–water system and those in acetic acid–chloroform–water system?

(c) If $|\psi_1\rangle=\begin{pmatrix}1\\ i\\ 0\end{pmatrix}$ and $|\psi_2\rangle=\begin{pmatrix}-i\\ 0\\ 2i\end{pmatrix}$, Find $\langle\psi_1|\psi_2\rangle$.

(d) Is cos $|x|$ an acceptable wave function in the range $(-2\pi, 2\pi)$?

(e) Scattering of x-rays by electrons in diffraction work is analogous to the Compton scattering— Justify or criticized.

(f) In ordinary algebra, $(P + Q)(P - Q) = P^2 - Q^2$. Expand $\left(\hat{P}+\hat{Q}\right)\left(\hat{P}-\hat{Q}\right)$. Under what conditions do we find the same result as in the case of ordinary algebra?

(g) Determine the Miller indices of the planes that intersect the crystal axes at
   (i) a, $2b$, $3c$ and
   (ii) a, b, $-c$.

(h) Elevation of boiling point is an entropy effect. — Comment.

(i) Depression of freezing point is always observed. — Justify or criticized. Assume the solute does not dissociate or associate.

(j) A metallic element exists in simple cubic structure. Each edge of the unit cell is 3Å. The density of metal is 10 gm^{-3}. How many unit cells will be there in 16·2 g of the metal?

(k) Determine the number of components when $AlCl_3$ is added to water.

(l) A 10(m) aqueous solution of urea is cooled to –13·02ºC. What amount of urea will separate out if the mass of solution taken is 100 g? [K_f (water) = 1·86 K kg mol^{-1}].

2. (a) A compound made of particles *A*, *B* and *C* form ccp lattice. In the lattice, ion A occupies the lattice points and ions B and C occupy the alternate tetrahedral voids. If all the ions along one of the body diagonals are removed, then find the formula of the compound.

(b) Let $\phi = x$. If ϕ is expanded in terms of $\sin kx$ such that

$$\phi = \sum_{k=1}^{n} C_k \sin kx \qquad [-\pi \le x \le \pi],$$

show that, $C_n = \frac{2}{n}(-1)^{n+1}$ 2+3

3. (a) Show that the operator $\hat{A} = i\left(\hat{X}^2 + 1\right)d/dx + i\hat{X}$ is hermitian.

(b) A photon of energy 3 keV collides elastically with an electron initially at rest. If the photon emerges at an angle of 60º, calculate —

(i) the kinetic energy of the recoiling electron, and

(ii) the angle at which the electron recoils.

[Given : $m_c = 9{\cdot}1 \times 10^{-31}$ kg] 2+3

4. (a) Check the acceptability of the following functions in the given domain :

(i) $e^{im\phi}(0, 2\pi)$

(ii) $e^{-x}\cos x(0, \infty)$

(b) Suppose a metal crystal forms a cubic unit cell. The first six observed Bragg diffraction angles, using the powder method and *x*-rays with $\lambda = 165{\cdot}8$ pm, be as follows :

21·96º, 25·59º, 37·65º, 45·74º, 48·2º and 59·7º

Determine the type of the cubic unit cell.

(Arrange your calculations in a Tabular form). 2+3

5. (a) Two liquids *A* and *B* form an ideal solution. At a particular temperature, the vapour pressure of *A* is 200 torr while that of pure *B* is 75 torr. If the vapour over the solution consists of 50 mole percent *A*, what is the mole percent of *A* in the liquid phase?

(b) Locate the point inside the graph for a ternary mixture with 50% of *A*, 20% of *B* and 30% of *C*. 2+3

6. (a) Find out the number of phases for (i) a dilute solution of the salt NaH_2PO_4 in water, (ii) a saturated solution in contact with the solid salt, at equilibrium with the vapour phase.

Find out the degrees of freedom in each case.

(b) For an operator $\hat{S}$, the following expansion (Taylor Series) is valid :

$$e^{\hat{S}} = 1 + \hat{S} + \frac{\hat{S}^2}{2!} + \frac{\hat{S}^3}{3!} + \ldots$$
$$= \sum_{n=0}^{\infty} \frac{\hat{S}^n}{n!}$$

Show under what condition $e^{\hat{A}+\hat{B}} = e^{\hat{A}}.e^{\hat{B}}$ where $\hat{A}$ and $\hat{B}$ are two operators. 2+3

7. (a) For a particle in a one-dimensional box, the wave function is

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \; 0 \le x \le a$$

But obviously, this is not an eigenfunction of the operator $\hat{p}_x$. If so, how would you determine the linear momentum of the particle?

(b) The normal boiling point of a saturated solution of bezanilide in ethanol is 82·00ºC. The melting point of benzanilide is 161ºC, the melting point and normal boiling points of ethanol are –117ºC and 80·00ºC. K_b for ethanol is 1·22 K kg mol^{-1}. Molecular weights are 46 for ethanol and 197 for benzanilide.

(i) Calculate the composition of this saturated solution of benzanilide.

(ii) Calculate the molar heat of fusion of benzanilide.

You may select the appropriate colligative-property equations so that your answers will be accurate only to about 1%, and you may assume ideal solution behaviour. 2+3

8. (a) An aqueous solution of sucrose freezes at –0·210ºC. Calculate the normal boiling point and the molality of an aqueous dilute sodium chloride solution having the same vapour pressure. Assume ideal solution behaviour. Given, K_b for water = 0·51 K kg mol^{-1}.

(b) How many octahedral voids are present in a fcc lattice? Indicate the location of all octahedral voids with proper explanation. 2+3

9. (a) For Al metal, the Einstein characteristic temperature is 240 K. Calculate $C_{v,m}$ of Al, using the Einstein model of heat capacity at (i) 50 K, and (ii) 300 K.

(b) If $\hat{\alpha}$ and $\hat{\beta}$ are two commutating and Hermitian operators, and ψ_1 and ψ_2 are eigenfunctions of $\hat{\alpha}$ with a_1 and a_2 eigenvalues respectively, then show that, $\int \psi_1 \hat{\beta} \psi_2 d\psi = 0$, (unless $a_1 = a_2$). 2+3

10. (a) Calculate the separation of the (133) planes of an orthorhombic unit cell with a = 0·82 nm, b = 0·941 nm, and c = 0·75 nm. Also find the separation of the 399 planes for the same lattice, using argument only.

(b) $\psi(x) = A \sin kx + B \cos kx$, where A and B are arbitrary constants, and $k = \left(8\Pi^2 m E / h^2\right)^{1/2}$ represents a wave function for a free particle (in x-direction). Justify the energy is not quantized. Why can not the wave function of a free particle be normalized? 2+3

11. (a) Consider the states

$$|\psi\rangle = 9i|\phi_1\rangle + 2|\phi_2\rangle \text{ and}$$
$$|\chi\rangle = -\frac{i}{\sqrt{2}}|\phi_1\rangle + \frac{1}{\sqrt{2}}|\phi_2\rangle,$$

where two vectors $|\phi_1\rangle$ and $|\phi_2\rangle$ form a complete and orthonormal basis.

Calculate the operators $|\psi\rangle\langle\chi|$ and $|\chi\rangle\langle\psi|$. Are they equal?

(b) Calculate the Eutectic temperature and the Eutectic composition for a binary solid-liquid system if $\Delta H_{fus,A} = 2.1\ \text{kJ mol}^{-1}$ and $\Delta H_{fus,B} = 4.18\ \text{kJ mol}^{-1}$, and the melting points of pure A and pure B are 400ºC and 600ºC respectively. 2+3

12. (a) Show that if $\hat{\alpha}$ and $\hat{\beta}$ are Hermitian operators, then $\hat{\alpha}\,\hat{\beta}$ will be Hermitian if $[\hat{\alpha}, \hat{\beta}] = 0$.

(b) Metals A and B form the compounds AB_3 and A_2B_3. Solids A, B, AB_3 and A_2B_3 essentially are immiscible in each other, but are completely miscible as liquids. A and B melt at 600ºC and 1100ºC, respectively. Compound A_2B_3 melts congruently at 900ºC and gives a simple eutectic with A at 450°C. Compound AB_3 decomposes at 800ºC to give the other compound and a melt. There is a eutectic at 650ºC.

Draw the simplest phase diagram consistent with this information, and label all phase regions. 2+3

13. (a) Write down the effective number of atoms present in a hcp unit cell with proper explanation.

(b) Two solutions of non-volatile solutes A and B are prepared. The molar mass ratio $M_A / M_B = 1/3$. Both are prepared as 5% solutions by weight in water. Calculate the ratio of freezing point depressions $\left(\Delta T_f\right)_A / \left(\Delta T_f\right)_B$ of the solutions. If the two solutions are mixed to prepare two new solutions, S_1 and S_2, the mixing ratio being 2 : 3 and 3 : 2 by volume for S_1 and S_2 respectively, what would be the ratio $\left(\Delta T_f\right)_{S_1} / \left(\Delta T_f\right)_{S_2}$? 2+3
