RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIFTH SEMESTER EXAMINATION, DECEMBER 2012

THIRD YEAR

Date : 17/12/2012 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : V (Gr. A) Full Marks : 50

[Attempt **one** from each unit]

Unit-I

1. a) Draw a clearly labelled diagram of a simple cubic lattice (edge length '*a*'). Indicate on it the (100) planes. Find the percentage of void space in a unit cell of such a lattice. [4]

   b) Acetic acid dissolves in water to form an apparently homogeneous solution. Draw schematically the relative arrangement of solute and solvent molecules (i) in the bulk (ii) at the surface. Sketch the surface tension versus concentration curve for a series of such solutions. [4]

   c) Write the Debye equation denoting the variation of total polarisation with temperature for a polar molecule. The index of refraction of an ideal gas at STP is 1.000373 and the dielectric constant is 1.00234. Calculate the dipole moment and polarisability of the molecule, assuming atom polarisation to be 5% of electron polarisation. [5]

   d) The distance between two successive parallel planes in a cubic crystal cannot be $a/\sqrt{7}$ – explain. [2]

2. a) Write down the B–E–T equation for a gas–solid absorption case. Explain the significance of the terms involved. What form does the equation take for an adsorbed layer that is only **one molecule** thick? [5]

   b) A metal which crystallizes in the cubic system gives the following Bragg reflections. Explain whether the unit cell is SCC, BCC or FCC and calculate the value of '*a*' if x-rays of wavelength 1.54A° are involved. [3]

θ	Sin θ	$(\text{Sin }\theta)^2$
21.8	0.371	0.138
25.4	0.429	0.185
37.4	0.606	0.369
45.4	0.712	0.510

   c) Distinguish clearly between physisorption and chemisorption for adsorption of a gas on a solid surface. Give one example of each. [4]

   d) For HF the dipole moment is 1.91 D. The bond distance is 92 picometre. Calculate the percentage ionic character of the covalent bond, explaining the basis of your calculation. [1D = 3.336×10^{-30} Cm] [3]

Unit-II

3. a) Derive thermodynamically a relation between the elevation of boiling point and molality of solute in a dilute solution clearly stating the assumptions involved. [4]

   b) State the Nernst Distribution Law.

   The distribution coefficient of solid *A* between an organic solvent and water (an immiscible pair) is 80.00. A 30 ml sample of *A* in the organic solvent (5 g/ 100 ml) is extracted with 100 ml of water in two ways (i) 60 ml followed by 40 ml (ii) 40 ml followed by 60 ml. How much of *A* will remain in the 30 ml sample in each case? [5]

   c) For the dissociating equilibrium system:

$$\text{X (solid)} \rightleftharpoons \text{Y (gas)} + \text{Z (gas)}$$

   Find out the number of phases, components and degrees of freedom using Gibbs phase rule. Clearly explain the concept of dry ice with respect to the phase diagram of carbon dioxide. [6]

4. a) Derive Duhem-Margules equation stating clearly the assumptions. [4]

b) Water and phenol are partially miscible at 323K. When these two liquids are mixed at 323K and 1 atm then at equilibrium one phase is 89% water by weight and the other is 37.5% water by weight. If 6.00 gm of phenol and 4.00 gm of water are mixed at 323k and 1 atm, find the mass of water and that of phenol in each phase at equilibrium. [3]

c) The vapour pressure of *A* is 939.4 mm of Hg and that of *B* is 495.8 mm of Hg at 140ºC. Assuming that they form an ideal solution, what will be the composition of mixture, which boils at 140ºC under 1 atm. What will be the composition of the vapour at this temperature? [3]

d) Two liquids *X* and *Y* mix to form an ideal binary solution of a certain composition. What will be the sign of the following quantities ΔG (mix), ΔH (mix) and ΔV (mix)? Give proper arguments. Hence demonstrate that mixing of the two liquids is entirely entropy driven. Explain, with an example, the term eutectic mixture. [5]

Unit-III

5. a) Write down the Schrodinger equation (time independent case) for the one-dimensional simple harmonic oscillator (SHO), explaining the terms involved. Plot the potential energy function and mention its salient features. What would the spring constant (*k*) signify in the case of a diatomic molecule which is modelled by the SHO? [4]

b) What is meant by orbital? How does it differ from Bohr orbit? [2]

c) The radial wavefunction of the 2s orbital of a hydrogen atom is given by the following expression. $R_{2,0} = N(2 - r/a_0)\ \exp\ (-r/2a_0)$ where a_0 = Bohr radius and *N* is a constant.

(i) Determine the number and location of the nodes in the 2s wavefunction (ii) Write down the expression for the radial distribution function of a 2s electron and sketch the radial distribution curve. [4]

6. a) Show that $\psi = e^{-\alpha x^2}$ is a solution of the Schrowdinger equation for a simple harmonic oscillator. Also find out the eigen value for this choice. [3]

b) Justify or criticize – zero point energy is the manifestation of Heisenberg uncertainty relation. [2]

c) From the probability density of the 1s electron show that the most probable distance of the electron from the nucleus is equal to the Bohr radius (a_0).

[Given: $\psi(1s) = (1/4\pi a_0^3)^{1/2}\ \exp(-r/a_0)$] [3]

d) Draw the graphical plots of ψ and ψ^2 for the ground state of the SHO by superimposing them on the potential energy function. [2]

Unit-IV

7. a) State Nernst Heat Theorem (NHT). Plot the variation of ΔG and ΔH of a reaction with respect to temperature. What can be said about the values of ΔS and ΔC_p of a reaction as $T \to 0$, on the basis of NHT? [4]

b) Define partition function. Express average energy of a system in an ensemble of distinguishable particles in terms of partition function. [3]

c) Consider 12 molecules divided equally among 3 non-degenerate energy levels. What is the thermodynamic probability (W) for this distribution? How does the value of W change if one molecule is removed from one level and added to another? Is the value of W level-specific? [3]

8. a) Einstein's equation for the heat capacity of solid is given as

$$C_v = 3R\left(\frac{h\nu}{K_B T}\right)^2 \frac{e^{h\nu/K_B T}}{(e^{h\nu/K_B T} - 1)^2}$$

where the terms have their usual meaning (i) Arrive at Dulong Petit's equation from the above equation. (ii) Define Einstein's characteristic temperature. [3]

b) Write a short explanatory note on adiabatic demagnetization as a technique that may by utilized to achieve low temperature. [4]

c) For what increase in altitude is the earth's atmospheric pressure reduced to half? Assume average value of temp 250K and the average molar mass 0.029 Kg mol^{-1}. [3]