RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIFTH SEMESTER EXAMINATION, DECEMBER 2013

THIRD YEAR

Date : 16/12/2013 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : V-A Full Marks : 50

[*Answer* _one**_ *question from each unit*]**

Unit - I

1. a) Determine the Miller indices of the planes that intersects the crystal axes at,

   i) $\frac{1}{2}a, \frac{1}{4}b, \propto C$ ii) a, b, –c [2]

   b) Draw diagram showing the variation of surface tension of aqueous solution of the following substances with concentration.

   i) NaCl ii) Sodium dodecyl Sulphate

   Explain using Gibbs adsorption isotherm. [3]

   c) When copper crystal is heated from 293 K to 493K, the glancing angle of the reflection maxima from (III) plane shifts from 20° to 19·92° using X-ray of wavelength 1·4255 Å. Calculate the coefficient of thermal expansion of Cu. [4]

   d) Answer the following : [2×3]

   i) Adsorption of a gas on a solid is an exothermic process. Justify or criticize.

   ii) Molar polarisation values of O_2 and CH_4 are independent of T but those of CH_3Cl and HCl decrease with increase in T. Explain.

2. a) With the help of a diagram show that for a cubic lattice the spacing between the adjacent planes (hKl) is $d = a/\sqrt{h^2+K^2+l^2}$ 'a' being the edge length. [3]

   b) Find the simplest formula of a solid containing A and B atoms in a cubic arrangement in which A occupy corner and B the centre of the faces of unit cell. If side length is 5Å, estimate the density of the solid assuming atomic weights of A and B as 60 and 90, respectively. [3]

   c) i) What is the CGS unit of $\mu^2/3K_BT$, the symbols have their usual meaning. [2]

   ii) Why is this term important? [1]

   d) Explain what do you mean by orientation polarization of a molecule. Why does molar polarization of a polar molecule decrease at high frequencies? [1+2]

   e) The stability of a lyophobic colloid is a consequence of the electrical double layer at the surface of the colloidal particles —explain your answer. [3]

Unit - II

3. a) Write down the Schrodinger equation for one dimensional harmonic oscillator. If the wavefunction for the first excited state of harmonic oscillator is $\psi = Axe^{-\alpha x^2}$,then show that the energy for the corresponding state is $E = \frac{3}{2}h\nu$, where the terms have their usual significance. [5]

   b) The radial wave function for 2s orbital of a hydrogen atom is given by the following expression

   $R_{2,0} = N\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$, N is a constant.

   i) Determine the number and location of node(s) in the given 2s wave function.

   ii) Write down the expression for the radial distribution function of a 2s electron and sketch the radial distribution curve. [2+3]

4. a) Calculate the probability that and electron in the ground state of hydrogen atom will be found within one Bohr radius of the nucleus.

$$\psi_{1S} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$$ [3]

b) For a simple harmonic oscillator, zero point energy is the manifestation of Heisenberg's uncertainty relation. Explain. [2]

c) Consider the following two wave-functions for the H-atom,

$$\psi_{2p+1} = be^{-r/2a}.r\sin\theta e^{i\phi};$$

$$\psi_{2p-1} = be^{-r/2a}.r\sin\theta e^{-i\phi}$$

where, a = Bohr radius, $b = \frac{1}{\sqrt{64\pi}}\left(\frac{1}{a}\right)^{5/2}$

Combine the above two functions to obtain the real ψ_{2px} function assuming that ψ_{2p+1} and ψ_{2p-1} are normalized and orthogonal to each other. Justify your answer mentioning an appropriate quantum mechanical theorem. [5]

Unit - III

5. a) The energy of 1 mol of solid assuming Einstein model is given by,

$E = 3N_A\left(\frac{h\nu_E}{e^{h\nu_E/kT} - 1}\right)$, where terms have their usual significance.

Find, (a) an expression for $\overline{C_V}$ as—

i) $T \to \alpha$ ii) $T \to 0$ [4]

b) Consider a system of a molecules, distributed among non-degenerate energy levels, $\varepsilon_0, \varepsilon_1, \varepsilon_2$ ...etc.

Show that the internal energy (U) of the system can be expressed as $U = NK_B T^2\left(\frac{\partial \ln Z}{\partial T}\right)_V$

[terms have usual meaning] [4]

c) Consider a system of non-interacting particles at constant temperature which are distributed in 3 non-degenerate energy levels in such a way that ε_1, ε_2 and ε_3 consist of 4×10^{23}, 2×10^{23} and 1×10^{23} particles, respectively. Show that the energy levels are equispaced. [2]

6. a) Calculate the number of microstates of arranging 6 identical particles in two boxes, each having 5 compartments without any restriction on occupation such that 4 particles are present in one box and 2 particles are present in the second box. [3]

b) Arrive at the form of Boltzmann distribution by applying the condition of lnW to be a maximum with other necessary constraints. [5]

c) Define partition function and interpret it physically. [1+1]

Unit - IV

7. a) Blue $CuSO_4$. $5H_2O$ crystals release their water of hydration when heated. How many phases and components are present in an otherwise empty heated container? [2]

b) The specific volume of monoclinic sulphur which is stable above the transition temperature is greater than that of rhombic sulphur by 0·0126 cm^3g^{-1}. The transition point at one atm. pressure is 368·65 K and it increases at the rate of 0·035 K atm^{-1}. Calculate the molar heat of transition. [3]

c) i) Sketch the phase diagram of water and mark the following in the diagram : Normal boiling pt., freezing pt., triple point and critical point. [1+2]

ii) How does the phase diagram of water differ from that of carbon-di-oxide? Show by graph also. [2]

d) Draw the phase diagram (T vs mole % of B) of a system consisting of solids A and B forming a stable compound A_2B with congruent melting point. Show that different phases present in the different regions of the diagram. State the degrees of freedom at eutectic point.
[M. Pt of A_2B < M. Pt. of A < M.Pt. of B] [5]

8. a) Derive thermodynamically a relation between the osmotic pressure of a dilute solution of a solute and its molar concentration. State assumptions and approximations involved. [4+1]

b) Explain Konowalloff's rule. [2]

c) Derive Gibbs-Duhem equation. [2]

d) In an ideally dilute solution the solutes obey Henry's law. —Explain. [2]

e) Consider a solute having normal existence in liquid α and associated in liquid β according to the equation, $nA \rightleftharpoons A_n$

How will you determine the value of 'n' experimentally? [4]