RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2015

THIRD YEAR [BATCH 2013-16]

Date : 15/12/2015

Time : 11 am – 1 pm

CHEMISTRY [Hons]

Paper : V [Group – A]

Full Marks : 50

[Answer <u>**one**</u> question from <u>**each unit**</u>]

<u>Unit - I</u>

1. a) The parameters of an orthorhombic unit cell are $a = 50$ pm, $b = 100$ pm and $c = 150$ pm. Determine the spacing between the (123) planes. [2]

    b) Draw the possible (100), (110) and (111) planes in the FCC lattice and calculate the ratio of $d_{hk\ell}$ for these three planes. [3]

    c) The dielectric constant of $CH_4(g)$ at 0°C and 1 atm pressure is 1·00094. Assuming that methane behaves as an ideal gas, calculate (i) the induced polarization and (ii) the polarizability of the molecule. [3]

    d) Explain why 1,4–dichlorobenzene has no dipole moment whereas the dihydroxy analogue has dipole moment. [2]

2. a) In the cubic crystal of CsCl (d = 3·97 gm/cc) the eight corners are occupied by Cl^- ions with a Cs^+ at the center and vice versa. Calculate the distance between the neighbouring Cs^+ and Cl^- ions. What is the radius ratio of the two ions? [Mol. wt. of CsCl = 168·36 gm/mole] [3]

    b) An element occurs in two crystalline forms α and β. The α form has FCC structure with $a = 3·68\text{Å}$ and the β form has BCC with $a = 2·92\text{Å}$. Calculate the ratio of their densities. [3]

    c) Calculate the percentage packing in a simple cubic lattice. [2]

    d) Explain why K^+ and Cl^- ions have the same scattering power for X-rays. [2]

<u>Unit - II</u>

3. a) Clearly mentioning all the model assumptions derive a relationship which describes how surface tension of a solution changes with concentration of solute at a constant temperature. [4]

    b) Justify or criticize : A finite magnitude of zeta potential is necessary for colloid stability. [2]

    c) If at 20°C, for pure CH_2I_2 $\gamma = 50·76\,mJ/m^2$ and for pure water $\gamma = 72·75\,mJ/m^2$, and the interfacial tension is $45·9\,mJ/m^2$, calculate

    i) the spreading coefficient for CH_2I_2 on water.

    ii) the work of adhesion between CH_2I_2 and H_2O. [4]

4. a) Calculate the energy expended in breaking down one ml of water into droplets having mean radius of 10^{-5}cm. Given $\gamma_{H_2O} = 72\,dyne/cm$. [3]

    b) Derive Langmuir adsorption isotherm mentioning the assumptions involved and discuss its behavior at very low and high pressure. [4]

    c) The absorption of a substance form aqueous solution on charcoal at 25°C is governed by the Freundlich isotherm in which n = 3 and k = 0·5. The concentration of the dye is expressed in gm/lit and the amount being absorbed in gm/gm. What weight of substance will be absorbed by 2 gm of charcoal from 1 lit of a solution containing originally 2gm of the substance? [3]

<u>Unit - III</u>

5. a) Prove that the most probable distance of the electron from the nucleus in the ground state of hydrogen atom is equal to Bohr's first radius. [2]

b) Define radial distribution function. Find out the expressions of radial distribution function and radial equation for 2p orbital of H atom, given $\psi_{210} = \dfrac{1}{\pi^{1/2}}\left(\dfrac{1}{2a}\right)^{-\frac{5}{2}} r e^{-\frac{r}{2a}} \cos\theta$. [3]

c) The wave function for the state of lowest energy of a 1D harmonic oscillator is $\psi = A e^{-\frac{Bx^2}{2}}$, where A is the normalization constant and $B = \dfrac{2\pi\sqrt{\mu k}}{h}$. Derive the total energy (E) by substituting ψ into the Schrodinger equation. Given the potential energy $= \dfrac{1}{2}kx^2$. The terms have their usual significance. [3]

d) Show that a non-zero zero point energy of a quantum mechanical harmonic oscillator is in accordance with Heisenberg's uncertainty principle. [2]

6. a) Consider the following radial parts :

(i) $N_1(C_1 - r)e^{-C_2 r}$; (ii) $N_2 e^{-c_3 r}$

From the plots of these radial parts identify the hydrogenic orbitals. [2+2]

b) What do you mean by real hydrogen like wave functions. Starting from $2p_{-1}$, $2p_1$ and $2p_0$, form the real hydrogen like 2p wavefunction.

$\psi_{2p_{-1}} = A r e^{-\frac{r}{2a}} \sin\theta e^{-i\phi}$, $\psi_{2p_1} = A r e^{-\frac{r}{2a}} \sin\theta e^{i\phi}$, $\psi_{2p_0} = B r e^{-\frac{r}{2a}} \cos\theta$

Why the new orbitals formed are expressed as $2p_x$, $2p_y$ and $2p_z$? [4]

c) Verify the Heisenberg uncertainty principle for simple harmonic oscillator by computing Δx and Δp. Given (x) = 0, <p>= 0, $<x^2> = \dfrac{h}{\sqrt{mk}}\left(v + \dfrac{1}{2}\right)$ and $<p^2> = h\sqrt{mk}\left(v + \dfrac{1}{2}\right)$. Ther terms have their usual significance. [2]

Unit - IV

7. a) Find out the number of degrees of freedom present in following systems.
   i) A gas in equilibrium with its solution in liquid
   ii) Two partially miscible liquids in the absence of vapour
   ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. [3×1]

b) Benzene and toluene form nearly ideal solutions. At 300K, $p^o_{toluene} = 32 \cdot 06 \, mm \, Hg$ and $p^o_{benzene} = 103 \cdot 01 \, mm \, Hg$.
   i) A liquid mixture is composed of 3 mol of toluene and 2 mol of benzene. If the pressure over the mixture of 300K is reduced, at what pressure does the first vapour form?
   ii) What is the composition of the first trace of water formed? [2+2]

   [Given : $p = p^o_B + (p^o_A - p^o_B)x_A$ and $p = \dfrac{p^o_A p^o_B}{p^o_A + (p^o_B - p^o_A)y_A}$.

   p : vapor pressure of the solution,
   p^o_A, p^o_B : vapor pressure of pure A and pure B;
   x_A : mole fractions of A in liquid phase
   y_A : mole fractions of A in vapor phase]

c) Calculate the vapour pressure of water at 100°C. Given the vapour pressure of water at 95°C is 634 mm and heat of vaporization in this temperature range is 40593 mol^{-1}. [3]

8. a) What is meant by a cooling curve? Draw and discuss the cooling curves for a two component system in which the two components are not miscible in solid state and form a eutectic mixture. [4]

b) A phenol-water system separates into two liquid phases at a temperature of 60°C. The first phase contains 16·8 mass% of phenol, the second phase contains 44·9 mass% of water. If the system contains 90 gm of water and 60 gm of phenol, what is the mass of the each phase? [3]

c) Starting with Gibbs Duhem equation for a liquid mixture, show that $\dfrac{x_A}{p_A}\dfrac{dp_A}{dx_A} = \dfrac{x_B}{p_B}\dfrac{dp_B}{dx_B}$ where

x_A, x_B are the mole fractions of A and B, respectively in the liquid phase, while p_A, p_B are their respective vapor pressures. [3]

Unit - V

9. a) Derive Barometric distribution formula from Boltzmann energy distribution. [3]

b) Calculate lnN_A by using Stirling's approximation, where N_A is the Avogadro's number. Also find the relative error by calculation using calculator. [2]

c) For an ensemble consisting of a mole of particles having 2 energy levels separated by $h\nu = 1 \cdot 00 \times 10^{-20}\,J$. At what temperature will internal energy of the system equal $1 \cdot 00$ KJ? [3]

d) What is Nernst heat theorem? Give the mathematical form in terms of free energy. [2]

10. a) What is thermodynamic probability? Which state function of the system is related to the maximum value of thermodynamic probability and how? [2]

b) Establish the following relations :

i) Internal energy, $U = kT^2 \left(\dfrac{\partial \ln Q}{\partial T}\right)_V$

ii) Heat capacity, $C_V = \dfrac{k}{T^2}\left[\dfrac{\partial^2 \ln Q}{\partial\left(\dfrac{1}{T}\right)^2}\right]_V$ where Q is the partition function. [3+2]

c) Arrive at the expression for heat capacity of solid within Einstein's model and explain the behaviour of C_V at two limiting cases. [3]

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