RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2017

THIRD YEAR [BATCH 2015-18]

Date : 18/12/2017 **CHEMISTRY [Honours]**

Time : 11 am – 1 pm **Paper : V [Gr-A]** Full Marks : 50

[Attempt <u>one question</u> from <u>each Unit</u>]

Unit – I

[10 marks]

1. a) Show that for a square lattice the separation of successive (hko) planes is $\frac{a}{\sqrt{h^2 + K^2}}$, where a is the side length. [3]

   b) Draw the typical (III) type of planes in BCC and FCC. Also comment on the possibility of finding these planes in the above crystals. [4]

   c) A liquid of molecular weight 18 and density $0{\cdot}99 \times 10^3 \, Kg\, m^{-3}$ has a dielectric constant 78·5 and refractive index 1·383. Calculate the values of its molar polarisation, molar refraction and dipolemoment neglecting atomic polarisation. [3]

2. a) Find out the SI unit of polarisability. [2]

   b) The density of lithium metal is $0{\cdot}53 \, g\, cm^{-3}$ and the separation of the 100 planes of the metal is 350 pm. Determine whether the lattice is fcc or bcc. [Atomic weight of Li = 6·941] [3]

   c) From Debye plot, explain the T dependence of P_m and hence find out the dipolemoment of substance from the plot. [3]

   d) Explain **<u>any one</u>** : [1×2]

      i) For a SCC, intensity vs. $\sin^2\theta$ plot has a gap after six consecutive peaks.

      ii) The BCC and SCC have different amount of void space.

Unit – II

[10 marks]

3. a) Define, with an example, a lyophilic colloid. How many such a colloid help in stabilising a lyophobic colloid like a gold sol? Explain what do you mean by the term 'Gold number'? [3]

   b) The adsorption of a dye [MW 150 g/mol] from its solution by charcoal is governed by Freundlich isotherm with n = 2·0 and k = 4·5. If 1 gram of charcoal powder were shaken with 100ml of 0·2 (M) solution of the dye, what will be the equilibrium concentration of the dye in the solution? [3]

   c) Write down the BET adsoption isotherm mentioning the terms involved. Plot volume of the gas adsorbed vs equilibrium pressure when heat of condensation is greater than heat of adsorption. [2]

   d) Deduce Langmuir adsorption isotherm from BET isotherm mentioning the special conditions. [2]

4. a) Define spreading coefficient and then find out the condition of spreading of a liquid over another one. [2]

   b) At 25ºC the vapour pressure of water is 23·74mm. What is the size of water droplet that can remain stable at a vapour pressure of 24 mm at 25°C. [3]

   c) A sphere of water of radius 1 mm is divided into two drops of radius r and 2r. Find out the change in surface energy. [$\gamma_{water} = 72 \, dyne/cm$] [3]

   d) What is zeta potential? Why is a finite magnitude of zeta potential necessary for colloid stability? [2]

Unit – III

[10 marks]

5. a) Verify that the wave function $A\exp\left(-Bx^2/2\right)$ is an eigen function of the simple harmonic oscillator (in one dimension) Hamiltonian. Here $B = 2\pi\sqrt{\frac{mK}{h}}$ (the terms have their usual significance). Find the expression of eigen value (E_0). From the value of E_0, make an estimate of the positions of the classical turning points using proper arguments. [3+2]

   b) Prove that the most probable distance of the electron from the nucleus in the groundstate of hydrogen atom is equal to Bohr's first radius. $\left[R_{1S}(r) = \frac{2}{a_0^{3/2}} e^{-\frac{r}{a_0}}\right]$ [3]

   c) Instead of p_{+1} and p_{-1} orbitals, p_x and p_y orbitals are used —explain. [2]

6. a) Schrödinger equation for Hydrogen atom is given as

$$-\hbar^2\left[\frac{\partial}{\partial r}r^2\frac{\partial\psi}{\partial r} + \frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] = 2m_e r^2\left[\frac{e^2}{4\pi\varepsilon_0 r} + E\right]\psi(r,\theta,\phi)$$

   Carry out the 'separation of variable' method to obtain the three independent equation, each containing only one variable r, θ or ϕ. [4]

   b) For the 1S wavefunction for H-atom, $\psi_{1S} = \left(\pi a_0^3\right)^{-1/2} e^{-r/a_0}$, a_0 is the Bohr radius find out the average distance of the electron from the nucleus. [3]

   c) What do you mean by zero point energy? Justify the existence of a non-zero zeropoint energy in case of a quantum harmonic oscillator in the light of Heisenberg Uncertainty principle. [3]

Unit – IV

[10 marks]

7. a) i) Calculate no. of component, no. of phases and the no. of degrees of freedom for water at its boiling point.
      ii) How do those quantities change when some NaCl is added to the water and then it is allowed to boil. [4]

   b) At 27°C, 10g of phenol-water mixture is produced containing 30% phenol by weight. The mixture contains two conjugate solutions one having 20% phenol by weight and the other having 80% phenol by weight. Find out the weight of the two conjugate solutions. [3]

   c) Starting with the appropriate form of the Gibbs'-Duhem equation show that in case of a mixture of two liquids the vapor phase is richer in the component, addition of which raises the total vapor pressure. [3]

8. a) Draw qualitative graph showing how vapor pressure of A, vapor pressure of B and total vapor pressure change with mole fraction of A for the three cases—
      i) A – B obeys Raoult's law
      ii) Shows positive deviation to it
      iii) Shows negative deviation to it. [3]

   b) Four phases of a substance do not coincide in a single point —justify. [2]

   c) With the help of the phase rule show that at a given pressure, the critical solution temperature is non-variant. [2]

   d) The vapour pressure of H_2O at 25°C is 24 mm. N_2 gas is introduced into the container containing water such that total pressure becomes 10 atm. Calculate the vapour pressure of water. [Density of water = 1 g/cc]. [3]

Unit – V

[10 marks]

9. a) What is residual entropy? Find out its value for CO. [1+1]

   b) If the molecular partition function q of a monoatomic gas is given by $q = e^{(A+B\ln T)}$, where A and B are constants, then find out the expression of molar heat capacity $(\bar{C}_v)$ of the gas and show that $B = \frac{3}{2}$. [Given, $U = NK_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$] [3]

   c) Discuss the principle of adiabatic demagnetisation with S – T diagram. [3]

   d) State Nernst heat theorem. [2]

10. a) If the energy difference between the first excited state and ground state is $3\in_0$, ($\in_0$ = energy of the ground state), find out the population ratio between first excited state (g_1 = 3) and non degenerate ground state at 300K. [3]

    b) A 2-level system is characterized by an energy gap of $1{\cdot}3\times10^{-18}$ J. At what temperature will the population of ground state be 5 times greater than that of excited state? [2]

    c) Entropy is a logarithmic function of thermodynamic probability — Justify. [3]

    d) C_V vs. T/θ plot for diamond maintains large difference w.r.t the experimental curve. [2]

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