RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2014

THIRD YEAR

Date : 18/12/2014 **CHEMISTRY (Honours)**

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

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

Unit – I

1. a) Show that the fraction occupied by an fcc lattice is greater than that occupied by a bcc lattice. [2]

   b) Explain, why it is not possible to deduce the position of hydrogen atom from X-ray diffraction. [2]

   c) Density of NH_4Cl is 1·5325 gcm^{-3} and it crystallizes in body-centred cubic lattice. Find out the closest distance of approach of two oppositely charged ions. The ionic radius of Cl^- ion is 181 pm. What is the ionic radius of NH_4^+ ion? [3]

   d) The index of refraction of gaseous paraffin C_nH_{2n+2} is found to be 1·00139 when the gas is at STP. Given the molar refractions as 1·1 and 2·42 cm^3mol^{-1} for H and C respectively, determine the formula of the hydrocarbon. [3]

2. a) If during measurement of dielectric constant, and hence molar polarization, the frequency of the applied electric field is raised to a very high value, orientation polarization is found to cease to exist. Explain. [2]

   b) The dipole moment of bromobenzene is $5{\cdot}17\times10^{-30}\,\text{Cm}$ and its polarizability volume $\left(\dfrac{\alpha}{4\pi\epsilon_0}\right)$ is $1{\cdot}5\times10^{-29}\,\text{m}^3$. Find out its relative permittivity at 298 K when its density is $1491\,\text{kg}\,\text{m}^{-3}$. (at wt. of Br = 79·9; $\epsilon_0 = 8{\cdot}8542\times10^{-12}\,\text{CV}^{-1}\text{m}^{-1}$) [3]

   c) NaCl has a fcc lattice but KCl has a simple cubic lattice. Explain. [3]

   d) The edge length of a unit cell of a body-centred cubic lattice is 390 pm. Which is the minimum value of wavelength of X-ray that can be used for X-ray analysis of this crystal? [2]

Unit – II

3. a) i) Derive Langmuir adsorption isotherm, stating the postulates.

   ii) Show that when a diatomic gas adsorbs as atoms on the surface of a solid, the Langmuir adsorption isotherm becomes, $\theta = (\text{KP})^{1/2} \Big/ \left(1+(\text{KP})^{1/2}\right)$

   where the terms have their usual significance. [3+2]

   b) At 292 K, the surface tensions of solutions of butyric acid in water, γ can be represented accurately by the equation, $\gamma = \gamma_0 - a\ln(1+bc)$ where c is the concentration of butyric acid, γ_0 is the surface tension of water, a and b are two constants. Set up the expression for the excess concentration of solute per sq. cm of surface as a function of c. [3]

   c) What is a micelle? Explain the term 'Kraftt temperature'. [2]

4. a) 1 cm^3 of water is broken into droplets, each having a radius of 10^{-5}cm. If the surface tension of water is $72{\cdot}75\times10^{-3}$N/m at 20°C, calculate the change in Gibbs free energy for the process. [2]

   b) A vertical capillary with inside diameter 0·50 mm is submerged into water so that the length of its part emerging outside the water surface is equal to 25 mm. Find the radius of curvature of the meniscus. [Surface tension of water is 70×10^{-3}N/m.] [3]

   c) At 30°C surface tension of CH_2I_2 is $50{\cdot}76\times10^{-3}$ N/m and that for water is $72{\cdot}75\times10^{-3}$N/m. The interfacial tension is $45{\cdot}9\times10^{-3}$ N/m. Calculate the work of spreading of CH_2I_2 on water and work of adhesion between CH_2I_2 and water. [3]

d) For the decomposition of NH_3 on heated Platinum, the reaction becomes zero-order w.r.t NH_3 at high pressures of NH_3. Explain. [2]

Unit – III

5. a) For a harmonic Oscillator $<x^2>=\frac{1}{\alpha}\left(n+\frac{1}{2}\right)$ and $<p^2>=\hbar^2\alpha\left(n+\frac{1}{2}\right)$. Find out expressions for σ_x and σ_{p_x} and show that $\sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}$ where $\left[\alpha=\left(\frac{k\mu}{\hbar^2}\right)^{1/2}\right]$. [3]

b) Quantum harmonic oscillators can be found in the classically forbidden region where kinetic energy is negative. Explain. [2]

c) Find out the most probable value of r in 1s-state for a hydrogenic atom. Given $\psi_{1S}=\frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2}\exp\left(-zr/a_0\right)$, where a_0 is the Bohr radius. [3]

d) Explain why the quantum number 'm' is called the magnetic quantum number. [2]

6. a) For the 1s state of the hydrogen atom, $\psi_{1S}=A\exp\left(-r/a_0\right)$

i) Find the normalisation constant A.

ii) Evaluate the probability density for a 1s electron at the nucleus.

Given, $\int_0^{\alpha} x^n e^{-qx}dx=\frac{n!}{q^{n+1}}$, $n>-1, q>0$. [3]

b) Prove that a hydrogen atom energy level having principal quantum number 'n', has a degeneracy equal to n^2. [2]

c) The wave equation of a harmonic oscillator at its ground state is $\psi_0(x)=\left(\frac{\alpha}{\pi}\right)^{1/4}\exp\left(-\alpha x^2/2\right)$, where $\alpha=\left(\frac{k\mu}{\hbar^2}\right)^{1/2}$. Find out the expression of the zero-point energy in terms of oscillation frequency. [3]

d) The fundamental vibrational frequency of $H^{75}Br$ is $2{\cdot}63\times10^3$ cm^{-1}. Calculate the root-mean-square displacement in the ground state. [2]

Unit – IV

7. a) What are the criteria of a first order phase transition? [2]

b) Find the number of components and degrees of freedom for a gas phase mixture of O_2, O, O^+ and e^-, in which all the O comes from the dissociation of O_2 and all the O^+ and e^- come from the ionization of O. Give the most reasonable choice of independent intensive variables. [3]

c) Water and phenol are partially miscible at 50°C. When these two liquids are mixed at 50°C and 1 atm, at equilibrium one phase is 89% water by weight and the other is 37·5% water by weight. If 6·0 g of phenol and 4·0 g of water are mixed at 50°C and 1 atm pressure, find the mass of water and mass of phenol in each phase using lever rule. [3]

d) The antimony-lead system has an eutectic temperature of 246°C and an eutectic composition of 87% lead and 13% antimony by weight. What phases are at equilibrium at the eutectic point? What is the value of ‘F’ at this point? Explain. [2]

8. a) Derive Gibbs phase rule and show that it is valid for any system irrespective of whether all components are present in all phases or not. [3]

b) How can you get a P–T phase diagram from a P–V–T phase diagram? [2]

c) What is the principle of fractional distillation of a liquid mixture? [2]

d) At 363 K the vapour pressure of toluene is 400 mm Hg and that of ortho xylene is 150 mm Hg. What is the composition of a liquid mixture that will boil at 363 K under a pressure of 0·5 atm? What is the composition of the vapour produced? [3]

Unit – V

9. a) Consider a system of four identical particles distributed in three energy states O, $\in$ and $2\in$, having a total energy $E = 4\in$. Find out the different configurations in which these particles may be arranged. Calculate thermodynamic probability and mathematical probability of each configuration. [3]

b) Write and explain the statement of Nernst Heat theorem. [2]

c) Draw a curve showing the variation of entropy when a solid (at temperature T) is heated to form vapour (at temperature T', T' > boiling point). How would you determine the absolute entropy of the substance in the vapour phase at temperature T'? [3]

d) Evaluate ln(N!) for N = 10 using a calculator and compare the result to that obtained using Stirling's approximation. [2]

10. a) Define molecular partition function (q) of a system, having non-degenerate energy states. What are the limiting values of q as $T \to OK$ and $T \to \infty$? How can you interpret these results? [3]

b) Explain the principle of cooling by adiabatic demagnetization of paramagnetic substances (S—T diagram should be given] [3]

c) What is residual entropy? Explain citing an example. [2]

d) What is an ensemble? For the canonical ensemble, what thermodynamic properties are held constant for each system in the ensemble? [2]

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