RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, MARCH 2021

THIRD YEAR [BATCH 2018-21]

Date : 13/03/2021 **CHEMISTRY [Honours]**

Time : 11.00 am – 1.00 pm **Paper : V [Gr. A]** Full Marks : 50

Attempt **one question** from **each unit**

Unit I

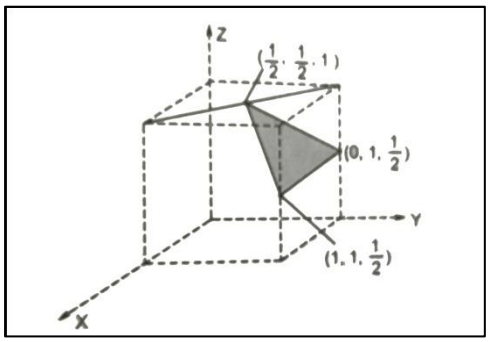
1. a) Consider a special cubic lattice composed of A and B type of atoms, where A atoms are at the points of FCC structure and B atoms are at center of BCC structure.

(i) Draw two planes which are of (100), (110) and (111) types. Mention their Miller indices.

(ii) What is the simplest formula of the crystal?

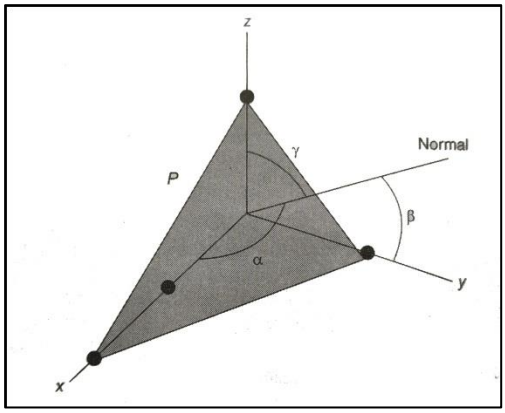
(iii) Calculate the percentage of the void space in the unit cubic cell. [2+1+2]

b) The co-ordinates of the three corners of a shaded face on a cubic unit cell are (½ , ½, 1), (0, 1, 1/2) and (1, 1, ½) as shown below in the figure. Determine the Miller indices of the plane. [2]



c) Dielectric constant of a liquid of molecular weight 112 g mol^{-1} is 4.288. Its refractive index is 1.348 and its density is 1.108 gm/cc at 25°C. Calculate molar polarization and molar refractive index. Also determine the dipole moment of the compound assuming atomic polarization is 5% of electronic polarization. [3]

2. a) Refer the following figure, in which another plane parallel to the P plane (shaded one) and passing through the origin is visualized. The normal line drawn from the origin to the plane is shown, which makes different angles with three axes. From the trigonometric calculation, find out the expression for the interplanar distance when the plane has no intercept with z axis. [3]



b) Cs metal (at.wt. = 0.133kgmol^{-1}) crystallizes in a cubic structure. Using X rays of 0.8 nm wavelength, the sinθ values for the first order reflections from 100, 110 and 111 type planes are 0.133, 0.094 and 0.23, respectively.

(i) Explain which type of cubic unit is present.

(ii) Calculate the density of Cs metal in the structure. [1+2]

c) In a NaCl crystal, the coordination number (CN) of each ion is 6. Which one from the two is correct?

(i) CN is changed to 8 by increasing pressure

(ii) CN does not change by any way. [1]

d) How does one distinguish a polar molecule from a non-polar molecule from the temperature variation of molar polarization? How dipole moment can be determined from such a data? [3]

Unit II

3. a) Explain the principle of determining the total surface area of an adsorbent from the BET adsorption isotherm. [2]

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 100 ml of 0.2 (M) solution of the dye, what will be the equilibrium concentration of the dye in the solution? [3]

c) What is critical micelle concentration (CMC)? CMC of SDS at 25°C is 8.2 mM and 1.4 mM in deionized water and 0.1 M NaCl solution, respectively. Explain such observation. [2]

d) The rate of decomposition of ammonia on electrically heated tungsten follows first order kinetics at low pressure but zero order at high pressure of ammonia. Suggesting a suitable mechanism, explain this mathematically. [3]

4. a) Why is osmotic pressure of colloidal solution always less than that of a true solution? [2]

b) In a particular experiment it is required to have a large amount of gas adsorbed on the surface of solid. Suggest few factors, which may be helpful for the experiment. [2]

c) The surface tension of Hg is 0.485 N/m. If two spherical globules of Hg, each of radius 1 cm, stick together to form one globule, then calculate the change in surface free energy? [2]

d) Suppose ozone adsorbs on a particular surface in accord with a Langmuir isotherm. How could you use the pressure dependence of the fractional coverage to distinguish between adsorption (a) without dissociation, (b) with dissociation into O + O + O? [2+2]

Unit III

5. a) Show that molar free energy of mixing in a binary ideal gas mixture is minimum, when two gases are present in the equimolar ratio i.e. $x_1 = x_2 = 1/2$. [2]

   b) Starting from Gibbs-Duhem equation for a binary solution, achieve a relation concerning the partial vapour pressure and the composition of various components in a solution showing that an increment in mole fraction of component 1 will cause a decrease in the partial pressure of the other component. [Hint: Use the chemical potential of i-th component expressed in terms of fugacity]. [3]

   c) Glucose is added to 1 lit of water to such an extent that $\frac{\Delta T_f}{K_f}$ becomes equal to 1/1000. What is the weight of glucose added? [2]

   d) Which solution from following, at a given temperature, is isotonic with 0.1 M solution of urea? [1]

   (i) 0.1 M NaCl solution

   (ii) 0.1 M glucose solution

   (iii) 0.1 M $BaCl_2$ solution

   e) The solubility of AgCl is measured in presence of HNO_3 of 1.28×10^{-5} mol dm^{-3} as 1.28×10^{-6}. Calculate the mean ionic activity coefficient of AgCl. [2]

6. a) Consider a strong electrolyte, M_xA_y, which is completely dissociated into corresponding ions in its aqueous solution. If activity and activity coefficient are respectively expressed as 'a' and 'γ' then prove that the mean ionic activity, can be expressed as –

$$a_{\pm}^{z} = a_M^x a_A^y$$ [3]

   b) Compare the curves for $log\gamma_{\pm}$ vs $\mu^{1/2}$ for very dilute NaCl, $CaCl_2$ and $ZnSO_4$ solutions (not a mixture). Using the Debye Huckel limiting law, show that the theoretical slopes for the curves (above) for Na_2SO_4 and $CaCl_2$ of same concentration are same. [3]

   c) A gas obeys the equation of state $P(V_m - b) = RT$. For this gas b = 0.0391 dm^3 mol^{-1}. Calculate the fugacity and fugacity coefficient for the gas at 1000°C and 1000 atm. Calculate $\mu_{real} - \mu_{ideal}$. [3]

   d) Which of the following colligative properties is associated with the concentration term 'molarity'? [1]

   (i) lowering of vapour pressure

   (ii) Osmotic pressure

   (iii) elevation of boiling point

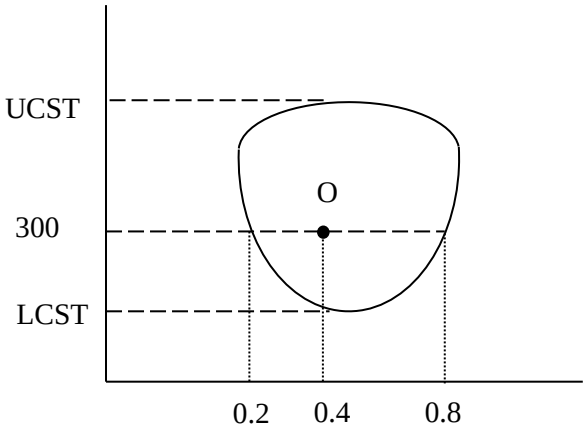
Unit IV

7. a) Given that $\frac{x_A}{p_A}\frac{dp_A}{dx_A} + \frac{x_B}{p_B}\frac{dp_B}{dx_A} = 0$. Show that the vapor would be richer in the component the addition of which increases the total vapor pressure of the solution. [3]

   b) Total vapor pressure over a solution is 0.7 atm . The vapor pressures of the two components A & B in pure states are 0.6 and 0.9 respectively. Calculate mole fraction of A both in the liquid and in the vapor phase. [both components obey the Raoult's law] [2]

   c) From the condition of thermodynamic equilibrium prove that the rate of change of freezing temp with respect to pressure is inversely proportional to the latent heat of vaporisation. Also,plot freezing temperature with pressure for a given substance. [3+2]

8. a) Consider the phase diagram for nicotine-water system (the x-axis represent the mole fraction of water) :



   At O

   (i) What are the phases present ?
   (ii) What are the amounts of the two phases if we start with 100 gm of mixture?
   (iii) What are the mole fractions of water in the two phases ? [4]

   b) Consider the following equilibria :

   $AlCl_3 + 3\,H_2O \longrightarrow Al(OH)_3 + HCl$

   [$Al(OH)_3$ is partly insoluble]

   Calculate the no of phases, components, degrees of freedom and identify them. [3]

   c) Free energy of a system in two phases (α and β) are given by for α : $G_\alpha = G_\alpha(0) - a_\alpha T$ and for β : $G_\beta = G_\alpha(T_{tr}) - a_\beta T$, $G_\alpha(0)$, $G_\alpha(T_m)$ being the free energy of the phase α at T= 0 and T=T_{tr} (phase transition point) respectively, given that $a_\alpha \neq a_\beta$. Identify with reason the order of the phase transition α to β [3]

Unit V

9. a) Consider a system comprised of 3 particles, available energy levels are 1, 3, 5, 7, 9, 11....

   A macrostate is defined by total energy E = 10.

   (i) Identify the microstates. (more than one particles may be accomodated in the same level)

   (ii) Calculating the number of distributions corresponding to every microstate, determine which one is most probable. [1.5 + 3.5]

b) A variable x follows the distribution

$$P(x) = \frac{1}{1+x}$$

Calculate the average value of x in the range 0 to 1. [3]

c) Calculate the residual entropy of the crystal A-A-B (consider B is slightly more electronegative than A). [2]

10. a) Express enthalpy in terms of partition function, volume and temperature . [3]

b) Assuming Barometric distribution law arrive at an expression for how the atmospheric pressure falls with height and then show heavier the gas sharper the fall. [3]

c) Calculate the molar heat capacity of Hydrogen gas at 27°C, vibrational temperature of hydrogen being 6215 K. Also mention the high temperature limiting value of the gas. [3+1]

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