RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2019
THIRD YEAR [BATCH 2017-20]
CHEMISTRY [Honours]
Paper : V [Gr-A]

Date : 12/12/2019
Time : 11 am – 1 pm
Full Marks : 50

[Attempt one question from each Unit]

[Use P = 1 atm, T = 298 K and standard value for physical constants, if otherwise not mentioned]

Unit – I [10 marks]

1. a) Define molar polarisation. How can the dipole moment be determined with the help of Debye-Langevin equation? [3]

   b) From the geometrical arguments and concept of Miller indices, show that for a cubic crystal of dimension 'a'

$$d_{hK0} = \frac{a}{\sqrt{h^2 + k^2}}$$ [4]

   c) Using X-rays of wavelength $\lambda = 154.2$ pm, a face centered cubic lattice produces reflections from the (111) and (200) planes. If the density of copper, which is a face-centered cubic lattice, is 8.935 gm/cc, at what angles will the reflection of copper appear? [3]

2. a) Calculate the fraction of space occupied by particles in a closed packed face centered cubic lattice. [3]

   b) Potassium crystallizes with a body centred cubic lattice and has a density of 0.856 gm cc^{-1}. Calculate the length of the unit cell and the distance between (110) planes. [3]

   c) Show that dimension of polarizability in SI unit matches with the dimension of volume. [2]

   d) The distance between two successive parallel planes in a cubic crystal cannot be $\frac{a}{\sqrt{7}}$ - Comment. [2]

Unit – II [10 marks]

3. a) Show that the excess pressure inside a spherical soap bubble is equal to $\frac{4\gamma}{r}$, where γ = surface tension, $r =$ radius of soap bubble. [3]

   b) 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? [3]

   c) At 20°C, for pure CH_2I_2, γ = 50.76 mJ/m^2 and for pure water γ = 72.75 mJ/m^2 and the interfacial tension is 45.9 mJ/m^2. Will CH_2I_2 spread over water? What will happen in the reverse situation? [3]

   d) Adsorption of gases on solids are always an exothermic process. Explain. [1]

4. a) Stating the required assumptions derive an equation to show the dependence of the surface excess on surface tension of a two component system. [3]

   b) At 20°C, the interfacial tension between glycol and water is 57 dyne cm^{-1}. If for water-vapour and glycol-vapour interfaces surface tensions are 72 and 31 dyne cm^{-1}, respectively, then calculate (i) the work of adhesion between water and glycol (ii) the work of cohesion of two liquids (iii) the spreading coefficient of glycol on water. [1+1+1]

c) Explain hydrophobic effect in the context of micellization. [2]

d) What would be the effect of increase in (i) salt concentration and (ii) temperature on CMC of a surfactant? [2]

Unit – III [10 marks]

5\. a) Derive thermodynamically a relation between the elevation of boiling point of a solution and molal concentration of the solute. State assumption(s) and approximation(s) involved, if any. [4]

b) Calculate the van't Hoff factor and the apparent degree of dissociation of a 0.2 molal aqueous solution $NaNO_3$, which freezes at 0.675°C. [Given K_f = 1.86 K kg.mol^{-1}]. [3]

c) Calculate the ionic strength of a solution obtained by mixing 25 ml of 0.004(M) Na_2SO_4, 25 ml of 0.008(M) K_2SO_4 and 50 ml of 0.01 (M) urea solutions. [3]

6\. a) From the chemical potential versus temperature diagram, justify that $\Delta T_f > \Delta T_b$. Assume that the solute is non-volatile and does not dissolve in solid solvent. [3]

b) Benzoic acid dimerizes when dissolved in benzene. The osmotic pressure of a solution of 5g of benzoic acid in 100 mL of benzene is 5.73 atm, at 10°C. Find the van't Hoff factor and the degree of association. [4]

c) From the thermodynamic consideration, justify, that $\Delta_{mix}V$ and $\Delta_{mix}H$ are zero for ideal binary solution. [3]

Unit – IV [10 marks]

7\. a) Derive Duhem-Margules equation, thermodynamically. [3]

b) (i) Show graphically, how melting point of a solution changes with composition, for a liquid mixture A and B, at a fixed pressure. (A and B form a compound at a stoichiometric ratio 1:2, the melting points are in the order AB_2 > A > B).

(ii) In the diagram locate the melting points of pure species A, AB_2 and B, their melting point curves in the mixture and the eutectic points. [1+3]

c) (i) Draw the typical cooling curves for water (in the range -10^oC to 110°C) for two different pressure P_h and P_l (take $P_h > P_l$).

(ii) In the diagram mark the melting point and boiling point. [1+2]

8\. a) Calculate the number of phases, number of components and degrees of freedom in the following systems:

i) $CaCO_3(s) = CaO(s) + CO_2(g)$ when we start with pure $CaCO_3(s)$ only

ii) $CaCO_3(s) = CaO(s) + CO_2(g)$ when we start with $CaCO_3(s)$ and $CO_2(g)$ [2+2]

b) Derive Clasius-Clapeyron equation. [4]

c) Draw the phase diagram of phenol-water system and explain the various parts of the curve. [2]

Unit – V [10 marks]

9\. a) Consider a canonical ensemble with N, the number of distinguishable systems and E, total energy, both being constant. The possible energy levels in which a system may exists be E(1), E(2), E(3)........ A distribution is given by the set $\{a(1), a(2), a(3).......\}$, where a(i) represents the number of system in the E(i) level.

(i) Derive the generalized expression for the number of microstates corresponding to a given distribution.

(ii) Applying the condition for most probable distribution along with the constancy of total number of system and total energy show that for the most probable distribution with α and β two constants, so far undetermined. [2+3]

b) ΔG is a function of temperature for a reaction and is given by $\Delta G = a + bT + CT^2$.

i) Show that in the limiting zone $T \to 0, b = 0$.

ii) Show schematically the variation of ΔH and ΔG with temperature on the same plot. [1+2]

c) Derive an expression for the internal energy of a system in terms of partition function and temperature. [2]

10. a) Accepting the conventional statement of the Nernst statement of third law show that attainment of absolute zero is not possible. [3]

b) Depict in a diagram how entropy and temperature change stepwise during the process of adiabatic demagnetization. [3]

c) Heat capacity of a solid is given by Einstein's equation as follows

$$C_V = 3R \frac{\left(\frac{h\nu}{kT}\right)^2 \exp\left(\frac{h\nu}{kT}\right)}{\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)^2}$$

Hence, (i) Obtain Dulong-Petit's law.

(ii) Give definition and significance of Einstein's characteristic temperature. [2+2]

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