RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2018

THIRD YEAR [BATCH 2016-19]

Date : 17/12/2018 **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) Calculate the co-ordination number of an atom in (i) a primitive cubic unit cell (ii) a body centered cubic unit cell and (iii) a face centred cubic unit cell. [3]

   b) "The total molar polarization is independent of temperature". Comment on the statement in the light of clausius-Mosotti equation and Debye equation. [2]

   c) A liquid of molecular weight 18 and density 0.995×10^3 kg.m^{-3} has a dielectric constant 78.5 and refractive index 1.383. Calculate the values of its molar polarization, molar refraction and dipole moment. Neglect atomic polarization. [3]

   d) What is the highest order that can be observed in Bragg's reflection from a solid by X-ray. [2]

2. a) A plane makes an intercept of (4,2,6) with the axial directions from the origin. What are miller indices? Find the spacing of 110 planes in a b-c-c crystal having unit cell volume 27×10^{-24}ml. [3]

   b) The diamond has a FCC lattice and there are 8 atom in a unit cell. Its density is 3.51 gm cc^{-1}. Calculate the 1st 3 angles at which reflections would be obtained using an X-ray beam of $\lambda = 71.2$ pm. [3]

   c) Explain the following, starting 'True' or False'. [2+2]

   i) Orientation polarization depends on T as well as the dielectric constant of medium.

   ii) For the cubic crystal, always there is a gap after 6 consecutive lines for the intensity vs. $\sin^2\theta$ plot.

Unit – II

[10 marks]

3. a) A capillary is kept partially immersed into water and is inclined at an angle of 45^0. If the radius of the capillary is 0.03 cm, calculate the length of the water column within the capillary. Given $\gamma_{H_2O} = 72\,\text{dyne cm}^{-1}$ and $\rho_{H_2O} = 1\,\text{gm cm}^{-3}$. [2]

   b) Deduce the condition in terms of surface tension (γ) for spontaneous spreading of one liquid over another immiscible liquid. [3]

   c) Show that when a diatomic gas adsorbs as atom on the surface of a solid, the Langmuir adsorption isotherm becomes, $\theta = \dfrac{\sqrt{K.P}}{1+\sqrt{K.P}}$, Where the symbols have their usual meaning. [3]

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

4. a) A glass capillary sealed at the upper end is of length 0.11m and internal diameter 2×10^{-5}m. The tube is immersed vertically into a liquid of surface tension 5.03×10^{-2} nm^{-1}. To what length the capillary has to be immersed so that the liquid level inside and outside the capillary becomes same. [Atmospheric pressure is 1×10^5 Pascal.] [3]

b) 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]

c) Show that the value of packing parameter P(= $V_t/a_h l_t$) of a surfactant has to be less than or equal to 1/3 to form spherical micelles.(The terms have their usual meaning) [2]

d) Explain the effect of addition of a surfactant in water on its surface tension. [2]

Unit – III

[10 marks]

5. a) Derive thermodynamically a relation between the osmotic pressure of a dilute solution of a solute and its molar concentration. State assumption and approximation involved. [3]

b) When 2 kg of non-volatile hydrocarbon containing 94.4% carbon is dissolved in 100 g benzene, vapour pressure of benzene is lowered from 74.66 mm to 74.01mm. Find out the molecular formula of hydrocarbon. [3]

c) What are the factors on which the Debye-Huckel constant (A) depends? [2]

d) Show that the molar free energy of mixing $\Delta_{mix}\ G_m$ in a binary ideal gas mixture is minimum when two gases are present in the equimolar ratio. [2]

6. a) For a binary solution containing n_A gm moles of A and n_B gm moles of B, show that

$$\frac{df_1}{df_2} = \left(\frac{x_2}{x_1}\right)\frac{f_1 dx_1}{f_2 dx_2}$$

[Terms are carrying the appropriate meaning of respective substance] [3]

b) Derive the expression for the fugacity coefficient, $\gamma = e^{bP/RT}$ of a gas that obeys the equation of state $P(\bar{V} - b) = RT$,where *b* is a constant. [3]

c) "A binary solution may exhibit a depression of boiling point"— Justify or criticize. [2]

d) A solution of NaCl has an ionic strenth of 0.24 unit. What concentration of Na_2SO_4 would have same ionic strength? [2]

Unit – IV

[10 marks]

7. a) Draw the phase diagram of phenol-water system and calculate the number of degrees of freedom at different regions of the diagram with justification. [3]

b) Draw a labeled phase diagram for a two component solid-liquid equillibrium system and hence explain the term "eutectic mixture". [3]

c) A solution of A in B deviates positively from the Raoult's law. In a T-composition diagram show qualitatively how the boiling point of the solution changes with mole fraction of any of the two components. In the diagram label clearly (i) the phases present in the various regions of the phase space. (ii) the azeotropic point (iii) boiling point curves for A and B. [4]

8. a) Starting with the condition for equilibrium between two phases α and β (in terms of chemical potential) show that the phase transition temperature T changes with pressure as

$\frac{dT}{dP} = \frac{\Delta V_{\beta\alpha}}{\Delta S_{\beta\alpha}}$ where $\Delta V_{\beta\alpha}$ and $\Delta S_{\beta\alpha}$ represent the difference in volume and entropy respectively between the two phases. [3]

b) Calculate the number of phases, number of components and degrees of freedom in the following system:

i) $AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 6HCl$ ($Al(OH)_3$ gets partially precipitated)

ii) Solution of sugar in water in equilibrium with water vapour. [4]

c) "Multistep solvent extraction is more effective compared to single step extraction"— explain. [3]

Unit – V

[10 marks]

9. a) Consider a system composed of 3 identical but distinguishable particles. Possible energy levels of each particle are 0,1, 2 and 3 joules. The macrostate is specified by a fixed total energy of 5 Joules.

i) Write down the possible distribution (defined in terms of the set $\{n(E_i)\}$, the number of particles occupying the energy level E_i)

ii) Also calculate the number of microstates for each of the distribution. [3+3]

b) i) Write down definition of partition function.

ii) Derive the expression for partition function for a one dimensional harmonic oscillator. [1+3]

10. a) Starting with the expression for the translational partition function and A= -kT ln Q, show that PV = nRT. [3]

b) Describe Nernst heat theorem. Write down the limitation of this theorem. [3]

c) According to Debye's theory the heat capacity of a crystal is given by

$$\bar{C}_v(T) = 9R\left(\frac{T}{\theta_5}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)} dx$$

Show that (i) at $T \to \infty$, $\bar{C}_V(T) \to 3R$ and ii) at $T \to O$, $\bar{C}_V(T) \propto T^3$. [4]

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