RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2016
THIRD YEAR [BATCH 2014-17]
CHEMISTRY [Honours]
Paper : V [Group – A]

Date : 14/12/2016
Time : 11 am – 1 pm
Full Marks : 50

UNIT I

(*Answer any one question*) [1×10]

1. a) The Miller indices are very useful for expressing the separation of planes (hkl). Consider the (hko) planes of a square lattice built from a unit cell with sides of length '*a*'.

(i) Show that $d_{hko} = \dfrac{a}{(h^2+k^2)^{1/2}}$ for square lattice, with the pictorial description of unit cell.

(ii) Find the Miller indices of the plane that intersects the crystallographic axes at the distance $(2a, \infty b, \infty c)$. [3+1]

b) Show with the help of diagrams, the planes in two adjacent cubic unit cells having the following Miller indices: [3]

(i) Primitive Cubic Cell (111)
(ii) Body Centre Cubic Cell (200)
(iii) Face Centred Cubic Cell (220)

c) The diamond has a Fcc lattice, and there are 8 atoms 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]

2. a) A face centred lattice has all the positions occupied by atom A. The body centre octahedral hole in it is occupied by an atom B. For such a crystal calculate the void space per unit volume of unit cell. Also predict the formula of the compound. [3]

b) Justify or criticise: No cubic crystal is found with the line corresponding to $h^2+k^2+l^2=7$ in Powder diffraction. [2]

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

d) Explain the variation of the molar polarization of a polar molecule with the frequency of the alternating electric field with proper diagram. [2]

UNIT II

(*Answer any one question*) [1×10]

3. a) Show that the work of adhesion between two liquid phases α and β is given by,

$$W_A^{\alpha\beta} = \frac{1}{2}\left(W_c^{\alpha} + W_c^{\beta}\right) - \gamma^{\alpha\beta}$$

Where, W_c^{α} and W_c^{β} be the work of cohension for α and β phases respectively. [3]

b) Write down BET adsorption isotherm mentioning the terms involved. How will you determine the surface area of adsorbent using BET isotherm. [1+3]

c) Prove that surface excess for any of the components (Γ_i) is related to the surface tension of the solution as

$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln C_i}\right)_{T,P} \quad [Ci = \text{concentration of the component}]$$

Provided if we consider the solution dilute. [3]

4. a) (i) In a graphical plot, show how the magnitude of electrical potential in the solution changes with distance from the metal in case of a metal-solution interface in accordance with Stern double layer model.

(ii) In the above diagram point out the part of the potential, known as 'ξ' potential. [2+1]

b) On the basis of an equilibrium between adsorbed gas and adsorbing surface, show that if a monatomic gas is adsorbed as dimer then $\theta = K^{1/2} P^2 / (1+KP^2)$.

Mention all the assumptions required for the derivation. [3]

c) Discuss the stability and coagulation of lyophobic sol. [2+2]

UNIT III

(*Answer __any one__ question*) [1×10]

5. a) Schrödinger equation for hydrogen atom – is

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

Carry out the 'separation of variable' method to obtain the three independent equations, each containing only one variable. [4]

b) Explain in the light of Heisenberg's uncertainty equation why the zero-point energy of a harmonic oscillator can not be zero. [2]

c) Consider the following first excited state wave function for harmonic oscillator, $\Psi = Axe^{-\beta x^2}$ where A is the normalisation constant. If the wave function is the accepted wave function for the harmonic oscillator, then find the value of β and the energy of the first excited state. [4]

6. a) For the 1s state of the hydrogen atom, $\Psi_{1s} = A.e^{-r/a_0}$

(i) Find the normalisation constant A.

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

Given, $\int_0^{\alpha} x^n e^{-qx}dx = \frac{n!}{q^{n+1}},\ \begin{matrix} n>-1 \\ q>0 \end{matrix}$. [4]

b) Although the probability of finding an electron on the nucleus for H-atom is maximum but the corresponding radial distribution function is zero at the nucleus — explain. [2]

c) Consider the following two 2p wave function for H-atom,

$$\Psi_{2p_{+1}} = \frac{1}{8\pi^{1/2}}\left(\frac{1}{a_0}\right)^{5/2} r.e^{-r/2a_0}\sin\theta e^{+i\phi}$$

$$\Psi_{2p_{-1}} = \frac{1}{8\pi^{1/2}}\left(\frac{1}{a_0}\right)^{5/2} r.e^{-r/2a_0}\sin\theta e^{-i\phi}$$

Combine the above two complex wave function to construct real Ψ_{2p_x} wave function. [4]

UNIT IV

(*Answer __any one__ question*) [1×10]

7. a) Derive Gibbs' phase rule. Discuss whether this rule is valid for a system of C components, all of which are not present in each of P phases. [3+1]

b) A saturated solution of Na_2SO_4, with excess of solid, is present at equilibrium with its vapour in a closed vessel.

(i) How many phases and components are present?

(ii) What is the degrees of freedom of the system? Identify the independent variables. [3]

c) Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 600 torr, the mole fraction of A in the vapour phase is 0.35 and in the liquid phase is 0.70. What are the vapour pressures of pure A and pure B at temperature T? [3]

8. a) Draw the phase diagrams for H_2O and CO_2 systems. Indicate the differences between the two diagrams. [4]

b) Write down the thermodynamic criteria for a first order phase transition. [2]

c) In an ideally dilute solution solutes obey Henry's law — explain. [2]

d) Ice melts while dry ice sublimes under ordinary conditions. Explain. [2]

UNIT V

(*Answer <u>any one</u> question*) [1×10]

9. a) Consider a system containing three distinguishable particles distributed between four quantized energy levels having energies 0, $\in$, $2\in$ and $3\in$ in such a way that the total energy of the system is fixed at $3\in$. How many distributions will be possible for the above system and which distribution will be the most probable distribution? [4]

b) Define partition function.

What is the physical meaning of the term 'partition function'?

Show that the internal energy (u) of the system is related to the partition function (z) through the relation, $u = NKT^2\left(\frac{\partial \ln z}{\partial T}\right)_V$, where the terms have their usual significance. [4]

c) A 2-level system is characterized by an energy gap of $1.3\times10^{-18} J$. At what temperature will the population of ground state be 5 times greater that of excited state? [2]

10. a) Show that Einsteins equation for heat capacity of solid reduces to Dulong-Petit law at high temperature. [2]

b) A paramagnetic substance containing F_c is taken in a chamber and magnetization and demagnetization are performed under a specific condition, repeatatively, so that very low temperature is achieved.

(i) Explain the steps with thermodynamics involved.

(ii) Draw a suitable curve (labelled) to reach low temperature. [3+2]

c) State and explain the "Third law of Thermodynamics". 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). [3]

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