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**AI—188—2017**

**FACULTY OF SCIENCE**

**M.Sc. (First Year) (First Semester) EXAMINATION**

**MARCH/APRIL, 2017**

**(CBCS PATTERN)**

**CHEMISTRY**

**Paper-III, CH-413**

**(Physical Chemistry-I)**

**(Tuesday, 25-4-2017)**

**Time : 10.00 a.m. to 1.00 p.m.**

*Time— Three Hours*

*Maximum Marks—75*

- N.B. :—*
- (i) Attempt All questions.
  - (ii) All questions carry equal marks.
  - (iii) Solve Q. No. 5 (A) MCQ in one attempt only.

Given : (1)  $h = 6.626 \times 10^{-34}$  Js.

(2) Mass of electron,  $m_e = 9.1091 \times 10^{-31}$  kg.

(3) Velocity of light,  $c = 3 \times 10^8$  ms<sup>-1</sup>

(4) Gas constant,  $R = 8.314$  JK<sup>-1</sup> mole<sup>-1</sup>

(5) Boltzmann constant,  $k = 1.38 \times 10^{-23}$  J/K.

(6) Avogadro's number,  $N = 6.022 \times 10^{23}$  moles.

1. Solve any *three* (out of five) : 15
- (a) Explain Orthogonality and normalisation of wave functions.
  - (b) State the Gibb's phase rule equation, reduce it for three component systems and explain the terms involved in it with examples.
  - (c) Calculate the ionic strength of a solution prepared by mixing 50 ml of 0.2M KNO<sub>3</sub>, 20 ml 0.15M K<sub>2</sub>SO<sub>4</sub> and 30 ml of 0.05M Cu(NO<sub>3</sub>)<sub>2</sub>.

P.T.O.

- (d) Write an account on :
- Schottky defect
  - Frenkel defect.
- (e) Define Zeta-Potential and explain Gouy-Chapman theory of electrical double layer.
2. Attempt any *three* (out of five) : 15
- Define Ladder operators and prove that :  

$$[L_+, L_-] = 2\hbar L_z.$$
  - Explain three component system involving two pairs of partially miscible liquids using phase diagram.
  - What are partition function ? Derive an expression for electronic partition function.
  - Define (i) Electron affinity and (ii) Lattice energy and explain Lattice energy using Born-Haber cycle for the formation of ionic solid, MX.
  - Derive the Lipmann equation of surface excess phenomenon.
3. Solve the following :
- State the Schrodinger's wave equation in Hamiltonian form and solve it for a linear harmonic oscillator. Show that zero-point energy for linear harmonic oscillator is,  $E_0 = \frac{1}{2}h\nu$ .
- Or
- Write an account on first order and non-degenerate perturbation theory. 8
- For particle in one-dimensional box problem, show that :

$$\Psi_n = A \sin\left(\frac{n_x \pi x}{l}\right)_{n_x=1,2,3,4,\dots}$$

An electron is confined in a one-dimensional box as length  $1\text{\AA}$ . Calculate its ground state energy in eV. Is quantisation of energy levels observable.

*Or*

What is degeneracy of energy states? Calculate degeneracies of a particle of mass ' $m$ ' in three-dimensional cubical box of width ' $a$ ' having the energies :

- (i) 6
- (ii) 9
- (iii) 11
- (iv) 14

in units of  $\frac{h^2}{8ma^2}$

Explain zero-point energy for that particle.

4. Solve the following :

- (a) What is fugacity? Explain the graphical method of its determination.

*Or*

Explain Debye-Hückel limiting law.

Calculate the activity coefficients of sodium and sulphate ions and the mean activity coefficient of 0.01 molal solution of sodium sulphate in water at room temperature.

- (b) Define (i) Activity and (ii) Activity coefficient.

Describe solubility method for determination of activity coefficients of electrolytic solutions.

*Or*

The rotational partition constant  $B$  of  $\text{HCl}$  ( $g$ ) determined by microwave spectroscopy is  $10.6\text{ cm}^{-1}$ . Calculate rotational partition function of  $\text{HCl}$  at (i)  $1000\text{K}$  & (ii)  $2273\text{K}$ . (Symmetry number of  $\text{HCl} = 1$ .)

P.T.O.

5. (a) Select the *correct* alternatives.

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(i) For spin-angular momentum, which of the following commutation is wrong ?

- (a)  $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$  (b)  $[\hat{S}^2, \hat{S}_x] = 0$   
 (c)  $[\hat{S}_z, \hat{S}_x] = -i\hbar\hat{S}_y$  (d)  $[\hat{S}_y, \hat{S}_z] = -i\hbar\hat{S}_x$ .

(ii) In three component systems, Tie-lines are not used in the region of.....

- (a) One phase (b) Two phases  
 (c) Three phases (d) Both (a) & (c).

(iii) In micro-canonical ensemble, the constants are.....

- (a) E, V, N (b) T, V, N  
 (c) T, V, u (d) None of the above (a), (b) & (c).

(iv) Generally, Transition metal compounds exhibit.....

- (a) Metal excess defects (b) Metal deficiency defects  
 (c) Stoichiometric defects (d) Both (a) and (b).

(v) According to Debye-Hückel theory, which of the following relation is *true* ?

- (a)  $\Lambda_v > \Lambda_\infty$  (b)  $\Lambda_v < \Lambda_\infty$   
 (c)  $\Lambda_v = \Lambda_\infty$  (d)  $\Lambda_v$  is never equal to  $\Lambda_\infty$

where,  $\Lambda_v$  &  $\Lambda_\infty$  are equivalent conductances at dilution V and at infinite dilution for strong electrolytes.

(B) Write short notes on any *two* :

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- (a) Ternary systems containing two solid and one liquid components.  
 (b) Wien effect  
 (c) Spin-orbit coupling.