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BR—229—2016

FACULTY OF SCIENCE

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

NOVEMBER/DECEMBER, 2016

(CBCS Course)

CHEMISTRY

Paper III (CH-413)

(Physical Chemistry—I)

(Monday, 21-11-2016) **Time : 10.00 a.m. to 1.00 p.m.**

Time—Three Hours *Maximum Marks*—75

N.B. :— (*i*) Attempt *All* questions.

(*ii*) Use of log table and calculator is allowed.

(*iii*) Solve Question No. **5** (A) MCQ in one attempt only.

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

(2) Mass of an electron, $m_e = 9.109 \times 10^{-31}$ kg.

(3) Velocity of ligth, $c = 3 \times 10^{8}$ ms^{-1}.

(4) Gas constant, R = 8.314 J/K/mole.

(5) Avogadro's number, N = 6.022×10^{23} molecules

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

1. Solve any *three* : 15

(*a*) Explain Spin-Orbit coupling with reference to multiplet structure of sodium-D line.

(*b*) Explain by quantum mechanical approach : 'No two electrons are in the same quantum state'.

(*c*) Explain a three-component system involving three pairs of partially miscible liquids with a suitable phase diagram.

P.T.O.

(*d*) Calculate the ionic strength of :

(*i*) 0.01 M aluminium sulphate

(*ii*) A solution of (0.1 M NaCl + 0.02 M $BaCl_2$).

(*e*) State and explain Mitscherlich's law of isomorphism.

2. Attempt any *three* : 15

(*a*) Prove that :

$$\left[\hat{S}^2,\ \hat{S}_x\right] = \left[\hat{S}^2,\ \hat{S}_y\right] = \left[\hat{S}^2,\ \hat{S}_z\right] = 0 .$$

(*b*) Draw a phase diagram for the eutectic systems containing three components. Explain it.

(*c*) Define a partition function and derive an expression for translational partition function.

(*d*) Explain octahedral and tetrahedral voids in close packed structure of solids.

(*e*) Derive Lipmann equations of surface excess phenomenon.

3. Solve the following :

(*a*) State the Schrödinger's wave equation in terms of Hamiltonian form and describe its application to a system of linear harmonic oscillators.

Or

Describe a first-order and non-degenerate perturbation theory for the system of H-atom. 8

(*b*) What is the wavelength of light absorbed when an electron in a linear molecule 10 Å long make a transition from ground to first excited state ?

Or

Set up and solve the Schrödinger wave equation to a particle in three-dimensional box problem and calculate degeneracies for it when energy equal to 9 and 14 in the units of $h^2/8\ ml^2$. 7

4. Solve the following :

(*a*) What is activity and activity coefficient ? Describe Debye's Hückel theory for activity coefficient of electrolytic solutions.

Or

What is meant by fugacity of a gas ? Explain the graphical method of its determination. 8

(*b*) The rotational partition constant B of HCl(g) determined by microwave spectroscopy is 10.59 cm^{-1}. Calculate rotational partition function of HCl at 100 K temperature.

(Symmetry number for HCl = 1).

Or

What are Extensive properties ? Explain chemical potential and partial molar heat content with their significance. 7

5. (A) Select the correct alternatives : 5

(*i*) In case of Lader operators which of the following communications are true :

(1) $[L_z, L_{\pm}] = \pm \hbar L_{\pm}$

(2) $[L_z, L_{\pm}] = 2\hbar L_z$

(3) $[L_z, L_{\pm}] = i\hbar L_y$

(4) $[L_z, L_{\pm}] = i\hbar L_x$

(*a*) Only (1)

(*b*) Only (2)

(*c*) (1), (2) and (3)

(*d*) (1), (2), (3) and (4)

P.T.O.

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

(*a*) three-phases (*b*) two-phases

(*c*) one-phase (*d*) both (*a*) and (*c*)

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

(*a*) E, V, N (*b*) T, V, N

(*c*) T. V, μ (*d*) None of these

(*iv*) Lattice energy and dissociation energy for the ionic crystals are of with ..... .

(*a*) Same magnitude only

(*b*) Same magnitude but opposite in sign

(*c*) Opposite in sign only

(*d*) None of the above

(*v*) For a solution of strong electrolyte, higher the frequency of alternating current, higher the conductance is known as ..... .

(*a*) Debye-Hückel theory of strong electrolytes

(*b*) Onsager effect

(*c*) Debye-Falkenhagen effect

(*d*) Wien effect

(B) Write short notes on any *two* : 10

(*a*) Helmholtz-Perrin theory of electrical double layer

(*b*) Wien effect

(*c*) Two-solid and one-liquid component systems : formation of binary compounds, one double salt formation

(*d*) Orthogonality and normalisation of wave functions.