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Reg. No. : ....

Name : ....

Second Semester M.Sc. Degree Examination, September 2014
Branch : Chemistry
CH/CL/CA/CM 223 : PHYSICAL CHEMISTRY – II
(2009 Admission)

Time : 3 Hours

Max. Marks : 75

SECTION – A

Answer **any two** among **a, b** and **c** of **each** question. **Each** subquestion carries **2** marks.

I. a) Arrange O_2, O_2^+ and O_2^- in the increasing order of stability. Justify your answer.

  b) State and explain variation theorem.

  c) What do you mean by 'free valence on carbon atom in a conjugated system' ?

II. a) A solution shows absorbance A = 1.0 what percentage of radiation is absorbed by the solution ?

  b) Find the Doppler shift in frequency when a photon frequency $3.58 \times 10^{18}\ H_z$ is emitted by a source moving with a velocity of 100 ms^{-1}.

  c) Explain the term 'Resonance Raman'. What are its advantages ?

III. a) What is active transport ? Explain its significance.

  b) What do you mean by local equilibrium ? What are the conditions for establishing local equilibrium ?

  c) State and explain Glansdorf-Prigogine theorem.

IV. a) Define thermodynamic probability. How is it related to entropy ?

  b) Show that molecular rotation does not contribute towards pressure of a gas.

  c) Electronic energy does not contribute towards internal energy of molecules. Justify the statement.

V. a) What is concentration overpotential ?

b) Explain the term 'zeta potential'. What is its significance ?

c) Write equation for the activity of the following electrolytes in terms of mean ionic activity coefficient and molal concentration.

    a) $Ca_3(PO_4)_2$ b) $LaCl_3$ **(10×2=20 Marks)**

SECTION – B

Answer either 'a' or 'b' of **each** question. **Each** question carries **5** marks.

VI. a) Find the ground state energy of H atom by variation method use the trial function $\Phi = e^{-\infty r}$. ∞ is the variational parameter.

b) Find the ground state energy of He atom by first order perturbation method.

VII. a) How would you find C = O and C = S bond length of O = C = S using microwave spectroscopy ? Discuss.

b) How would you determine dipole moment of a molecule using microwave spectroscopy ? Explain.

VIII. a) Define phenomenological coefficient. Show that direct coefficients always dominate indirect coefficients.

b) What do you mean by local equilibrium ? What are the conditions under which local equilibrium is established ?

IX. a) Derive an equation for the vibrational contribution towards heat capacity of a gas.

b) Calculate rotational partition function for CO at 300 K. Bond length is 1.13 A°.

X. a) Derive Lippmann equation.

b) Calculate the mean ionic activity coefficient of 0.01 m $CuSO_4$ at 298 K
A = 0.509.   **(5×5=25 Marks)**

SECTION – C

Answer **any three** questions. **Each** question carries **10** marks.

XI. Discuss bonding in H_2 by valence bond method.

XII. How would you predict vibrational Raman activity using Polarizability ellipsoid ? Discuss.

XIII. Rationalise thermal osmosis and thermal diffusion using irreversible thermodynamics.

XIV. Derive Maxwell Boltzman distribution law.

XV. What are the assumptions in Debye Hückel theory ? Use the theory to derive Debye Hückel limiting law.

(3×10=30 Marks)