



(Pages : 3)

**A – 5826**

Reg. No. : .....

Name : .....

**Second Semester M.Sc. Degree Examination, August 2016**

**Branch : Chemistry**

**CH/CL/CA/CM 223 : PHYSICAL CHEMISTRY – II**

**(2013 Admission Onwards)**

Time : 3 Hours

Max. Marks : 75

**SECTION – A**

**(10×2=20 Marks)**

Answer **any ten** among **a, b and c** of **each** question. **Each** sub-question carries **2** marks.

- I. a) Arrange  $O_2$ ,  $O_2^+$  and  $O_2^-$  in the increasing order of stability. Justify your answer.
- b) Write spectroscopic term symbol by
  - I)  $B_2$
  - II)  $O_2$
- c) What do you mean by London dispersion forces ? Explain.
- II. a) Which of the following molecules are microwave active ? Justify your answer.  
 $CH_2Cl_2$ ,  $BCl_3$ ,  $PCl_5$ ,  $COS$ .
- b)  $NO$  shows a Q bands in the vibration-rotation spectrum. Why ?
- c) Explain the term 'normal mode of vibration'.
- III. a) Distinguish between steady state and equilibrium.
- b) State and explain Onsager reciprocal relation.
- c) Explain the term 'isothermal evaporation'.

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- IV. a) Rationalise third law of thermodynamics from statistical point of view.  
b) Define rotational temperature. Explain its significance.  
c) Electrons never follow Maxwell-Boltzman statistics. Why ?
- V. a) What are the factors on which thickness of the ion atmosphere in an electrolyte depend ? Explain.  
b) Write Lippmann equation. Explain the terms.  
c) Write electrode reactions for  $H_2 - O_2$  fuel cell under alkaline conditions.

## SECTION – B

(5×5=25 Marks)

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

- VI. a) Apply HMO method for allyl cations. Find the  $\pi$  (pi) molecular orbitals and their energies.  
b) Find the ground state energy of He by first order perturbation method.
- VII. a) Use particle in a box model to find the energy of  $\pi$  (pi) molecular orbitals of a conjugated hydrocarbon.  
b) With the help of polarizability ellipsoids discuss Raman spectra of  $CO_2$ .
- VIII. a) Define phenomenological coefficient. Show that direct coefficients always dominate indirect coefficients.  
b) Derive an equation for the rate of entropy production of one component system with heat and matter transport.
- IX. a) Calculate residual entropy of para-dichlorobenzene.  
b) Calculate the translational partition function of  $CO_2$  at 0K and 1b pressure.
- X. a) Calculate mean ionic activity coefficient of 0.01 molal  $LaCl_3$  in water at  $25^\circ C$  ( $A = 0.509$ )  
b) Write Tafel equation. Explain the significance of slope and interrupt of a Tafel plot.



SECTION – C

(3×10=30 Marks)

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

XI. Discuss briefly LCAO method of bonding as applied to hydrogen molecule.

XII. a) How would you determine dipole moment of a linear molecule using microwave spectroscopy ? Discuss.

b) Write Morse equation. Represent graphically. Show that real molecules approximates to simple harmonic oscillator approximation for low amplitude vibrations.

XIII. Rationalise a) thermal osmosis b) thermal diffusion using irreversible thermodynamics.

XIV. How would you evaluate equilibrium constant of a chemical reaction from molecular parameters ? Discuss.

XV. Derive Debye Hückel Onsager equation. Discuss.

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