 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

 **M.Sc.** DEGREE EXAMINATION - **CHEMISTRY**

SECOND SEMESTER – **APRIL 2012**

# CH 2816/2810 - THERMODYNAMICS AND STATISTICAL MECHANICS

 Date : 21-04-2012 Dept. No. Max. : 100 Marks

 Time : 9:00 - 12:00

 **PART A**

**Answer ALL the questions: (10 x 2 = 20 Marks)**

1. Show that μi (Chemical potential) = (δU/δni)S,V,nj
2. What are the conditions for the uncoupled chemical reactions in terms of forces and fluxes and phenomenological coeffcients?
3. Explain Soret effect.
4. The partial molar volume of glycerol in a glycerol-water solution (the mole fraction of glycerol is 0.5), is 72.8 cm3 mol-1 at 15.60C. If the total volume of the solution is 45.05 cm3, calculate the partial molar volume of water in the solution.
5. Calculate the mean activity coefficient 0.1 m CaCl2 (aq) at 25OC.
6. Calculate the number of ways of distributing 20 identical objects with the arrangement {1,0,3,5,10,1}
7. Differentiate thermodynamic probability from mathematical probability.
8. Evaluate the characteristic vibrational Einstein temperature for diamond if ν = 46.5 x 1012 Hz.
9. What is residual entropy? Give one example.
10. Mention four phenomena that cannot be explained by Maxwell-Boltzmann statistics.

#  PART – B

**Answer ANY EIGHT questions: (8 x 5 = 40 Marks)**

1. Draw and explain the isobaric fractional distillation of a non-ideal solution of water and nitric acid exhibiting maximum boiling point.
2. The apparent molal heat capacityΦC of an aqueous solution of a glucose as a function of molality is given by ΦC (J K-1 mol-1) = 633.9 + 4.728 m – 0.195 m2. Calculate the partial molar heat capacity of the glucose and that of water in 1 molal solution. The heat capacity of pure of water is 75.31 J K-1 mol-1.
3. State Konowaloff’s rule and derive it thermodynamically.
4. Discuss the application of irreversible thermodynamics to biological systems.
5. Write about the entropy production in an open system.
6. How is fugacity of a gas determined?
7. Compare the three statistical distributions.
8. Calculate the vibrational contribution to the energy of Cl2(g) at 500 K if the vibrational frequency is 560 cm-1.
9. Show that rotational energy of diatomic rigid rotor is equal to RT per mole.
10. State and explain Nernst heat theorem.
11. A certain atom has a three fold degenerate electronic ground level, a non-degenerate excited state at 3500 cm-1 and a three fold degenerate level at 4700 cm-1. Calculate the electronic partition function at 1900 K.
12. Calculate the equilibrium constant (KP) for the reaction S2(g) ⬄ 2 S(g) at 2000 K. The dissociation energy of S2 found spectroscopically is 429.7 kJ/mol and the free energy functions for S(g) and S2(g) are – 1941.4 and – 265.5 J K-1 mol-1 respectively? Also calculate KC for the same reaction.

##  PART – C

**Answer ANY FOUR questions: (4 x 10 = 40 Marks)**

1. a) Derive Gibbs-Duhem equations (6)

b) When n2mol of a solute A is dissolved in 1 kg of water, ΔH can be expressed as,

 ΔH (J mol-1) = 20.5 m2 + 8.4 m22. Calculate  when m2 = 2 (4)

24. a) Draw and explain the phase diagram of a ternary system consisting of two solids A and B and water forming a ternary compound. (5)

b) How will you determine the partial molar volumes in solutions of liquids by measuring the densities at different concentrations? (5)

25. a) What is Onsager reciprocal relation? (2)

 b) Prove the Onsager reciprocal relation by the principle of microscopic reversibility. (8)

26. Derive the following:

a) Sackur-Tetrode equation (5)

b) Molecular translational partition function (5)

27. Explain any two of the following: (5+5)

 a) Macro states and micro states

 b) Dependence of fugacity on temperature

 c) Application of Bose-Einstein statistics

 d) Separation of partition functions

28. a) Explain Einstein’s theory of heat capacity of mono atomic crystals and hence derive an expression for CV(vibration) as per this theory. (6)

 b) Compare Einstein’s theory with Debye’s theory of heat capacity of crystals. (4)

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