ST.JOSEPH’S COLLEGE (AUTONOMOUS) BANGALORE

M.Sc CHEMISTRY – II SEMESTER

SEMESTER EXAMINATION, APRIL 2018

CH-8315- Physical Chemistry

**Time: 2.5 hours** **Max.Marks: 70**

This question paper contains two pages and three parts A, B and C

**PART-A**

Answer any **SIX** of the following questions.  **6 x 2 =12 marks**

1. What are the inputs of quantum mechanics to statistical thermodynamics?
2. Write the equation relating pressure and partition function. How does it account for the deviation from the ideal behavior?
3. What is excess volume? Name an experimental method for its determination.
4. Explain the Seebeck effect?
5. What are the limitations of collision theory?
6. Explain the term electro kinetic phenomena.
7. Write the expression for rate constant of a bimolecular reaction in terms of partition functions and explain terms in it.
8. What are the limitations of Lindemann theory of unimolecular reactions?

**PART-B**

 Answer any **FOUR** of the following questions.  **4 x 12 = 48 marks**

1. (a) Using Gibbs- Duhem- Margules equation derive expression for the behavior of ideal and non ideal solution during distillation processes.

(b) Obtain the expressions for the variation chemical potential with respect to temperature and pressure.

(c) What are the criteria for the standard state of gas and liquid?  **(5+4+3)**

1. (a Derive the equation for thermodynamic mixing properties of non ideal binary mixture.

(b) Derive the expression for the free energy in terms of partition function.

(c) How do you calculate electronic partition function?  **(5+4+3)**

1. (a) Derive Bose-Einstein statistics for the molecules present in a system of non-degenerate energy levels.

(b) Calculate the translational and electronic contribution to standard free energy of helium at 298K.  **(8+4)**

1. (a) Explain the influence of internal pressure of the solvent on the rate of a reaction.

(b) Discuss with a suitable example the conditions for the formation of kinetic and thermodynamic products.

(c) Discuss the kinetics of free radical polymerization. **(3+3+6)**

1. (a) Discuss the RRK theory of unimolecular reactions.

(b) Acetaldehyde undergoes thermal decomposition to form methane and carbon dioxide according to the following mechanism:

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$ CH\_{3}CHO → CH\_{3}^{\*} + CHO^{\*}$

 $CH\_{3}^{\*}$ + $CH\_{3}CHO$ $→$ $CH\_{4} + CH\_{3}CO^{\*}$

 $CH\_{3}CO^{\*}$ $→$ $CH\_{3}^{\*}$ + CO

 2 $CH\_{3}^{\*}$ $→$ $C\_{2}H\_{6}$

Obtain an expression for the chain length for the formation of methane. **(6+6)**

1. (a) Discuss the entropy production due to the flow of mass through a semipermeable membrane.

(b) How do you study the kinetics of fast reactions by relaxation methods?  **(6+6)**

PART-C

Answer any **TWO** of the following questions. **2x 5 = 10 marks**

1. The volume (V) of an aqueous sodium chloride at 298K for a series of solutions were plotted against molality (x) and found to fit an equation; V = 1003 + 16.62x + 1.77x3/2 + 0.12x2. Calculate the partial molal volumes of the two components at molality equal to 0.10 molkg-1
2. The rotational spectrum of gaseous HCl has a series of lines separated by 10.6 cm-1. Calculate the rotational partition function explicitly and implicitly. Comment on the results.
3. Consider the reaction: [Co(NH3)5H2O]3+(ClO4―)3 + HNO3 → Products

 This reaction has been carried out at 298K using the initial concentrations of the complex and HNO3 as 0.001M and 0.002M respectively. The same reaction has been carried out by changing the concentrations of the complex and HNO3 as 0.0002M and 0.001M respectively. Calculate the factor by which the rate constant will be affected by the change in the ionic strength of the species involved in the reaction.

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