

## Il Semester M.Sc. Examination, June 2016 (CBCS) CHEMISTRY

C 203: Physical Chemistry - II

Time: 3 Hours

Max, Marks: 70

Instruction: Answer question number 1 and any five of the remaining.

Answer any ten questions of the following :

 $(2 \times 10 = 20)$ 

 a) Calculate the thickness of ionic atmosphere for 0.01 M NaOH using the following data:

D = 78.6

T=298°K

 $k = 1.38 \times 10^{-6}$ 

 $\varepsilon = 4.802 \times 10^{-10} \text{ esu.}$ 

- b) Give the Debye Huckel equation for higher concentration and comment on the constants A and B.
- c) Describe the Helmholtz double layer theory.
- d) What is meant by surface excess and how it can be measured graphically?
- e) Justify the presence of trible ions in a medium of low dielectric constant.
- f) What is meant by concentration overpotenital?
- g) State phase rule and define the term phase and degree of freedom.
- h) What is the difference between a canonical and microcanonical ensemble?
- i) Mention the physical significance of partition function.
- Define the terms 'apparent molar volume' and 'partial molar volume', write the expression for both.
- k) Calculate the partition function of a system at 298 K which has energy levels at 0, 2 x 10<sup>-21</sup> J and 8 x 10<sup>-21</sup> J with a degeneracy of 1, 3 and 5 respectively.
- I) What is de-Donder's inequality?



- 2. a) How do you estimate metal lons qualitatively and quantitatively by polarographic technique?
  - b) Derive the Butler-Volmer equation and show that small changes in 'q' produces large changes in 'l'. (5+5=10)
- 3. a) Describe the thermodynamic aspects of surface excess.
  - b) Describe the theory of quantum aspects of charge transfer at electrode solution interface. (5+5=10)
- 4. a) Derive the Debye-Huckel equation for the problem of activity coefficient.
  - b) Give the Lipmann's equation and calculate the charge density, if the value of the slope is 0.735. (6+4=10)
- a) What are thermodynamic excess functions obtain the equation for G<sup>E</sup>, S<sup>E</sup> and H<sup>E</sup>?
  - b) Calculate the rotational partition function and rotational entropy values for nitrogen at 300 K. Given, I moment of Inertia = 1.39 x 10<sup>-46</sup> Kg m<sup>2</sup>. (5+5=10)
- 6. a) How are the values of activity and activity coefficient determined by solubility method?
  - b) Explain the concept of uncompensated heat and relate it to various thermodynamic quantities. (5+5=10)
- a) Derive the equation for Maxwell-Boltzmann distribution for a system containing N distinguishable non-interacting particles.
  - b) Calculate the translational partition function for one mole of nitrogen at 2 atms and 300 K, assuming the gas to behave ideally. (6+4=10)
- 8. a) Derive Onsagar's reciprocity relation.
  - b) Write a note on ::
    - i) Semiconductor-solution interface
    - ii) Electrocatalysis:

(4+6=10)