II Semester M.Sc. Degree Examination, June/July 2014 (NS) (2010-11 & Onwards) CHEMISTRY

C-203: Physical Chemistry - II

Time: 3 Hours Max. Marks: 80

Instruction: Answer question no. 1 and any five of the remaining.

1. Answer any ten of the following:

 $(10 \times 2 = 20)$

- a) Write the phase rule equation and define the terms phase, component and degree of freedom.
- b) Explain the term activity. How is it related to fugacity?
- c) Give the significance of partial molar volume.
- d) Differentiate between canonical and micro-canonical ensembler.
- e) What do you mean by partition function? Define molar partition function.
- f) Calculate the number of ways of distributing distinguishable molecules x, y and z between three energy levels. Each energy level is occupied by one molecule.
- g) Write the Lippmann capillary equation and how do you determine charge density from it ?
- h) Write the Tafel equation and give its significance.
- i) Justify the statement that the thickness of the ionic atmosphere decreases with increase in concentration of the electrolyte.
- j) Calculate the capacitance of the double layer when the thickness of the double layer is 1.5×10⁻⁸cm and dielectric constant of the medium is 80.
- k) Describe the Gouy-Chapmann model and give its significance.
- I) Define the terms "Concentration overpotential" and "activation overpotential".



- 2. a) Obtain Gibbs- Duhem- Margules Equation and give its significance.
 - b) Write the definition of activity coefficient. How do you determine the activity coefficient using EMF method? (6+6=12)
- 3. a) Write the assumptions made by Dulong-Petit, Einstein and Debye for explaining heat capacity of solids. Write the limitation of Einstein's equation.
 - b) Derive the equation for Fermi-Dirac statistics. (5+7=12)
- 4. a) Obtain an expression for translational partition function and give the expression for internal energy E and entropy in terms of partition function.
 - b) What are irreversible processes? Obtain the expressions for entropy production and entropy balance for irreversible processes.
 - c) Calculate the rotational partition function of H_2 at 273 K. (σ = 2 and $I = 4.0 \times 10^{-41} \text{ g.cm}^2$) (5+4+3=12)
- 5. a) Describe the Bjerrum's concept for ion association and explain the formation of triple ions.
 - b) Write the Ilkovic equation and explain how polarographic technique is useful in both qualitative and quantitative estimation? (6+6=12)
- 6. a) Describe the process of electrocatalysis and give the various factors affecting it.
 - b) Describe the experimental technique to measure the interfacial tension as a function of applied potential difference across the interface. (7+5=12)
- 7. a) Under what conditions do electrons tunnel between the electrode and ions in a solution?
 - b) Describe the homogeneous theory of corrosion and give any two methods of prevention of corrosion.
 (7+5=12)
