M SC DEGREE END SEMESTER EXAMINATION 2014 -15 SEMESTER -1: CHEMISTRY COURSE CODE; P1CHET04/P1CPHT04, TITLE: CLASSICAL AND STATISTICAL THERMODYNAMICS

Time: 3 hrs

Max. Marks: 75

Section A

(Answer any 10 questions. Each question carries 2 marks)

- 1. Heat (Q) and work (w) are not static functions but become so under certain conditions. Why?
- 2. State and explain "Clausius inequality".
- 3. Explain the term "fugacity" as applied to real gases.
- 4. Define thermodynamically the term " partial molar free energy"
- 5. State third law of thermodynamics and mention any two applications of it.
- 6. What is 'phenomenological coefficient'? What is its use in non-equilibrium process?
- 7. Explain the de Donder inequality concept in irreversible thermodynamics.
- 8. What is phase space? Explain with an example.
- 9. Define cluster integral. What is its significance in statistical thermodynamics?
- 10.Explain the concept of ensembles in statistical thermodynamics
- 11.Define the term ' symmetry number' used in statistical mechanics with suitable example
- 12.What is the difference between bosons and fermions? Give two examples for each.
- 13. What is Fermi energy? Explain its significance.

 $(10 \times 2 = 20)$

Section B

(Answer **any 5** questions by attempting not more than **3** questions from each bunch. Each question carries **5** marks)

Bunch 1 (Short essay type)

- 14.What do you mean by partial molar volume? Describe any one method for the determination of partial molar volume.
- 15.Draw the triangular phase diagram of a three component system of three liquids, one pair of which is partially miscible, the other pair being completely miscible. Mark in the diagram the important features and explain them.
- 16. What is the criterion for spontaneity of a reaction on the basis of entropy and Gibbs free energy? Which is the better criterion? Why?

17. Through appropriate equations show how partition function can be used in calculating thermodynamic functions.

Bunch 2 (Problem type)

- 18.Calculate ΔS (mixing) when two moles of H₂, 3 moles of He and 2 moles of O₂ are mixed at fixed T assuming ideal behavior and no chemical change.
- 19.An aqueous solution of alcohol, in which mole fraction of alcohol is 0.05 gave partial pressure of water and alcohol is 23.2 and 10.8 mm. respectively. The vapour pressure in the pure state are $p_{alc} = 21.76$ mm and $p_{water} = 23.8$ mm at the same temperature. Calculate the activity and activity coefficient of water and alcohol.
- 20.Calculate the partition function of a unit in which the energies associated with the various levels are 0, 2 kT, 4kT, 6 kT and 8 kT, etc., at temperature T. Assume that the levels are not degenerate. If there are 1000 particles, calculate the number in each level.
- 21.If the valence electrons of sodium form a perfect Fermi-Dirac gas, calculate the fraction of electronic specific heat contribution at 298 K (the Fermi energy is 3.21 ev).

(5 x 5 = 25)

Section C

(Answer any 2 questions. Each question carries 15 marks)

- 22.Derive Maxwell's relations. Discuss any two of their applications
- 23.Explain the concept of entropy production in open systems.
- 24.Discuss the Debye theory of heat capacities of solids. Point out its superiority over Einstein's theory. Criticize the Debye approach.
- 25.Apply Fermi-Dirac statistics to (i) electron gas in metals and (ii) thermionic emission of electrons from metals.

 $(2 \times 15 = 30)$
