F 5541 (Pages : 3) Reg. No.....

Name.....

M.Sc. DEGREE (C.S.S.) EXAMINATION, FEBRUARY 2016

First Semester

Faculty of Science

Branch : Chemistry

AN1 C04/AP1 C04/CH1 C04/PH1 C04/POH1 C04—CLASSICAL AND STATISTICAL THERMODYNAMICS

[Common to all Branches of Chemistry]

(2012 Admission onwards)

Time : Three Hours Maximum Weight : 30

Section A

Answer any **ten** *questions.*
Each question carries a weight of 1.

1. Derive the expression for thermodynamic equation of state.
2. Give one application of Gibbs-Helmholtz equation and explain.
3. Explain the experimental determination of excess volume.
4. Sketch and explain the graphical representation of a two pairs of partially miscible liquids.
5. State third law of thermodynamics. Explain its importance.
6. Prove the theorem of minimum entropy production.
7. Explain the role of ATP in bioenergetics.
8. Explain the postulates of 'equal a priori probability'.
9. Derive the expression for the following thermodynamic functions in terms of partition function :
   (a) Enthalphy ; (b) Heat capacity, C_4.
10. Derive expression for rotational partition function.
11. Explain the statistical formulation of third law of thermodynamics.
12. Write note on thermionic emission.
13. Find the relation between fugacity and pressure.

(10 × 1 = 10)

Turn over

Section B

Answer **five** *questions by attempting not more than three questions from each bunch.*
Each question carries a weight of 2.

Bunch 1 (Short Essay Type)

14. Write a short essay on determination of partial molar volume and enthalpy.

15. Derive Maxwell's relation $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$. What is the significance of Maxwell's relation ?

16. Derive Bose-Einstein distribution law.

17. Explain Bose-Einstein conversation taking liquid helium as example.

Bunch 2 (Problem Type)

18. For the Weston standard cell, calculate ΔG, ΔH and ΔS using the following data :

$E = 1.01463$ V at 25°C, $n = 2$, $F = 96500$ C $\left(\frac{\partial E}{\partial T}\right)_P = -5.0 \times 10^{-5}$ V K^{-1}.

19. 4 dm^3 of methane and 1 dm^3 of argon each at 1 atm and 27°C are mixed isothermally in a vessel of 3 dm^3 capacity. Find ΔG mix, ΔS mix, and ΔH mix. Assume that gases behave ideally.

20. Calculate the rotational contribution to H°, S° and G° for oxygen gas at 298 K. The moment of inertia for $O_{2(g)}$, $I = 1.937 \times 10^{-46}$ kgm^2.

21. Calculate the molar residual entropy of a crystal in which the molecules can adopt 6 orientations of equal energy at 0K.

$(5 \times 2 = 10)$

Section C

Answer any **two** *questions.*
Each question carries weight of 5.

22. Discuss carefully the phase diagram for a three component system consisting of two salts and water at a fixed temperature and pressure.

23. Explain the following :

    (a) Thermo electric phenomena.

    (b) The principle of microscopic reversibility.

    (c) The Onsagar reciprocal relation.

24. Distinguish between Einstein solids and Debye solids. Also explain their limitations.

25. Derive Maxwell-Boltzmann distribution law. Also obtain the value of β used in statistical mechanies.

$(2 \times 5 = 10)$