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M.Sc. DEGREE (C.S.S.) EXAMINATION, FEBRUARY 2014

First Semester

Faculty of Science

Branch : Chemistry

ANIC 04/APIC 04/CHIC 04/PHIC 04/POHI 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.

- Comment on the statement "Entropy of the universe is always increasing".
- Explain the term fugacity. How is the fugacity of a real gas determined?
- Explain how the absolute entropy of a substance can be determined with the help of the third law of thermodynamics.
- 4. Explain coupled reactions.
- Depict a phase diagram for two pairs of partially miscible liquids and explain.
- 6. What are thermodynamic excess functions? Give the experimental determination of excess volume.
- 7. What are the Onsagar relation? Explain.
- 8. Explain the terms canonical ensembles, occupation number and statistical weight factor.
- 9. Define partition functions the partition function of system A and B one Q_A and Q_B. The total energy E of the system is E_A + E_B. What is the partition function of the entire system?
- 10. Derive an equation for the translational partition function.
- Briefly explain the statistical formulation of third law of thermodynamics.
- Write short note about supercooled liquids.
- 13. Explain the limitations of Einstein theory of heat capacity of solids.

 $(10 \times 1 = 10)$

Turn over

Section B

Answer any five question by attempting not more than three question from each bunch.

Each question carries a weight of 2.

Bunch 1 (Short Essay Type)

- 14. Derive Gibbs Helmholtz equation. Explain its application.
- 15. Explain the Norst heat theorem. How does it lead to the enunciation of the third law of thermodynamics?
- 16. Derive Maxwell-Boltzmann distribution law.
- 17. Explain the postulates of equal a priori probabilities"

BUNCH 2 (PROBLEM TYPES)

- Calculate the free energy change which occurs when one mole of an ideal gas expands reversibly and isothermally at 300 K from the initial volume of 5 lines to 50 liters.
- Calculate the free energy of mixing Δh_(mx) enthalpy of mixing ΔH_{mx} and ΔS_{mx} at 25°C and later when
 - (a) 10 moles of H are mixed with 10 moles of Ne
 - (b) 10 moles of He are mixed with 20 moles of Ne
- Calculate the translational partition function of a molecule of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24.4 dm³.
- 21. Calculate the translational entropy of gaseous iodine at 298 K and 1 atm.

 $(5 \times 2 = 10)$

Section C

Answer any two questions.

Each question carries a weight of 5.

- 22. Using the principle of microscopic reversibility show that the cross coefficients are equal.
- 23. Derive Gibbs-Duhem-Margules equation. Give its importance.
- 24 (a) Compare Bose-Einstein and formi Dirac statics.
 - (b) Derive Bose-Einstein statistics.
- 25 (a) Derive Sackur-Tetrode equation applicable to monoatomic gas.
 - (b) Get expression for free energy and partition function.

 $(2 \times 5 = 10)$