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THIRD SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2015

(CUCSS)

Chemistry

CH 3C 07—PHYSICAL CHEMISTRY—II

(2010 Admissions)

Time: Three Hours

Maximum: 36 Weightage

Part A

Answer all questions.

Each question carries a weightage of 1.

- 1. Define thermodynamic probability. How does it differ from mathematical probability.
- 2. Arrange translational, rotational, vibrational and electronic partition functions in the increasing order of magnitude. Justify your answer.
- 3. Account for the 3:1 ratio of Ortho-para-hydrogens.
- 4. Define characteristic temperature. Explain its significance.
- 5. Electrons never follow Maxwell-Boltzman Statistics. Why?
- 6. Explain the term 'communal entropy'.
- 7. What do you mean by 'local equilibrium'?
- 8. State and explain Onsagar Reciprocal relation.
- 9. For the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, derive an equation for the steady-state concentration of B.
- 10. What is secondary salt effect?
- 11. Distinguish between diffusion controlled and activation controlled reactions.
- 12. Unimolecular gas phase reactions follow first order kinetics at high pressures and second order kinetics at low pressures. Why?
- 13. Define isosteric heat of adsorption.
- 14. What is Michaelis Menton constant? Explain its significance.

 $(14 \times 1 = 14 \text{ weightage})$

Part B

Answer seven questions.

Each question carries a weightage of 2.

- 15. Calculate residual entropy of H₂O.
- 16. Calculate heat capacity of diamond at 1000 K. Characteristic temperature is 1860 K.
- 17. Derive Bose-Einstein distribution law.
- 18. Derive an equation for the rate of entropy production for one component system with heat and matter transport.
- 19. Briefly discuss relaxation method of studying fast reactions.
- 20. Show that for a rigid sphere model of bimolecular reaction. Absolute Rate theory agrees with simple collision theory.
- 21. Derive an equation for the surface coverage for dissertaive chemisorption of the type $A_2(g) \xrightarrow{k_1 \atop k_2} 2A$ (ads) in terms of the pressure of A_2 .
- 22. Briefly discuss Lotka-Volterra model of oscillating chemical reactions.
- 23. How do you calculate equilibrium constant of a chemical reaction from molecular parameters?

 Discuss.
- 24. Calculate rotational partition function for CO at 300 K. Bond length is $1.13\ \text{Å}$.

 $(7 \times 2 = 14 \text{ weightage})$

Part C

Answer any two questions.

Each question carries a weightage of 4.

- 25. Discuss briefly Debye's theory of heat capacity of solids.
- 26. Apply Fermi-Dirac Statistics for electrons in metals. Discuss.
- 27. Discuss briefly molecular beam methods of evaluating reaction cross-section.
- 28. Derive Langmuir adsorption isotherm from statistical point of view.

 $(2 \times 4 = 8 \text{ weightage})$