

THIRD SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2017

(CUCSS)

Chemistry

CH 3C 07—PHYSICAL CHEMISTRY—II

(2010 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Part A*Answer all questions.**Each question carries 1 weightage.*

1. How many ways you can distribute two particles among three degenerate energy levels according to (a) Maxwell Boltzman statistics ; (b) Fermi Dirac statistics.
2. Define partition function. Explain its significance.
3. Define rotational temperature. Identify molecule with the highest rotational temperature.
4. Calculate heat capacity of gaseous water molecule using equipartition principle.
5. Define Fermi level. Explain its significance.
6. Both Fermions and Bosons follow Maxwell Boltzman statistics under dilute system conditions. Why ?
7. What do you mean by rate of entropy production ?
8. Define phenomenological coefficient. Explain its significance.
9. Explain pressure jump method of relaxation spectroscopy.
10. Explain the term potential energy surface.
11. Distinguish between activated and non-activated adsorption.
12. How would you distinguish XPS peaks from AES peaks in the electron spectrum ?
13. Spontaneous adsorption is always exothermic. Why ?
14. Unimolecular gas phase surface catalysed reactions follow first order kinetics at low pressures and zero order kinetics at high pressures. Why ?

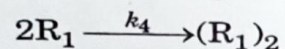
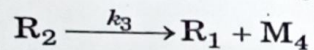
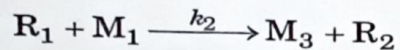
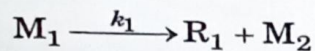
(14 × 1 = 14 weightage)

Part B*Answer any seven questions.**Each question carries 2 weightage.*

15. Derive an equation to show the relationship between internal energy and partition function.
16. Account for the anomalous heat capacity of H₂.

Turn over

17. Briefly discuss Bose-Einstein condensation.
18. Show that direct phenomenological coefficients always dominate indirect phenomenological coefficients.
19. Mechanism for organic decomposition reaction is given below. Derive the rate law :



R_1 and R_2 are radicals intermediates M_3 and M_4 are stable products.

20. The pre-exponential term for a first order reaction is $5 \times 10^{13} \text{ s}^{-1}$. Calculate the entropy of activation at 500 K.
21. Two gases A and B are adsorbed simultaneously on a solid surface. Show that the fractional surface coverage of the gas A, $\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$ P_A and P_B are partial pressures of gases A and B, b_A and b_B are the corresponding equilibrium constants for adsorption.
22. Briefly discuss Eley-Rideal mechanism of bimolecular surface catalysed reactions.
23. Derive equation for translational partition function for a delocalized system.
24. Derive an equation to show the effect of conic strength of the medium on the rate of ionic reactions in solutions.

(7 × 2 = 14 weightage)

Part C

Answer any two questions.

Each question carries 4 weightage.

25. Derive Maxwell-Boltzmann distribution law.
26. Rationalise thermal osmosis and thermal diffusion using irreversible thermodynamics.
27. What are the assumptions of absolute rate theory? Following the theory, derive an equation for bimolecular rate constant.
28. Derive BET adsorption isotherm. Discuss.

(2 × 4 = 8 weightage)