LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

THIRD SEMESTER – **NOVEMBER 2013**

CH 3814 - THERMODYNAMICS & CHEM. KINETICS

Date : 07/11/2013 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

Part-A

Answer all questions. Each question carries two marks.

1. Define: Chemical potential.
2. What are tie lines? Mention their significance.
3. Calculate the ionic strength of 0.25 m stannous chloride.
4. What is residual entropy? How does it arise?
5. Calculate the number of ways of distributing eight helium atoms among 5 energy levels.
6. Obtain the relation of partition function with enthalpy.
7. Write an expression for the rate constant of the reaction involving linear and non-linear activated complex formation on the basis of ARRT.
8. What is the influence of pH on enzymatic reactions?
9. Calculate the time at which the concentration of B is maximum for a consecutive reaction, $A \rightarrow B \rightarrow C$ with rate constants of 0.28 min^{-1} and 0.16 min^{-1} for the first and second step respectively.
10. Write the mechanism for the thermal decomposition of acetaldehyde.

Part-B

Answer eight questions. Each question carries five marks.

11. Derive Gibbs-Duhem equation and highlight its importance.
12. A 4.84 molal aqueous solution of a non-volatile solute has a vapour pressure of 2466 Nm^{-2} at 25°C.At the same temperature, the vapour pressure of pure water is 3146 Nm^{-2}. Assuming ideality, calculate the activity and activity coefficient of water in the solution.
13. Predict the degree of freedom in all the regions formed in the phase diagram of a ternary system in which one compound forms a hydrate.
14. Calculate the translational partition function of an oxygen molecule confined in a 1 litre vessel at 27°C.

15. Discuss the influence of molecular symmetry on rotational partition function withrelevant examples.
16. Derive Sackur-Tetrode equation and mention its significance.
17. Write a note on Electrokinetic phenomena.
18. Calculate the number of collisions per second between N_2 and O_2 molecules in one cm^3 ofequvimolar mixture of gases at a total pressure of 202.6 kPa (each at 101.3 kPa) and atemperature of 27□C. (d_{O2} = 1.58 A□ and d_{N2} = 1.46 A□)
19. Derive Eyring equation relating the rate constant and entropy of activation for areaction.
20. Discuss any one mechanism for bimolecular surface reactions with a specific example.
21. For a parallel first order reaction, A → B, C derive the expression for the concentrations of A, Band C at time t.
22. Explain flash photolysis technique for studying the kinetics of fast reactions.

Part-C

Answer four questions. Each question carries ten marks.

23. Obtain an expression for the variation of fugacity with temperature.
24. a) How will you establish a relation between partition function and energy?
    b) What is the entropy of a collection of N identical molecules at 0K, if the energy levels are non-degenerate. (7+3)
25. a) Derive Maxwell-Boltzmann distribution law using its assumptions.
    b) How will you differentiate between ortho and para hydrogen molecules? (7+3)
26. a) Explain the kinetics of single substrate enzymatic reaction and derive the rate law.
    b)TheLineweaver-Burk plot for the hydrolysis of lactose by β-galactosidase has a straight line with the slope 3.65×10^{-5} min and y-intercept of 8.25×10^{-3} $Lmol^{-1}min$. Evaluate ν_{max} and K_M for the reaction. (7+3)
27. a) Derive the general equation for the rate of unimolecular gas reactions using steady state hypothesis proposed by Hinshelwood.
    b) Explain electrostriction. (6+4)
28. Discuss the kinetics of branched chain explosion reactions.