# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

**M.Sc.** DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER – **NOVEMBER 2014**

**CH 3814 - THERMODYNAMICS & CHEMICAL KINETICS**

Date : 01/11/2014 Dept. No. Max. : 100 Marks

Time : 09:00-12:00

## Part-A

***Answer all the questions. Each question carries two marks:*** ***( 10 X 2 = 20 )***

1. How will you account for the positive slopes obtained in Ellingham's plot?
2. Mention the significance of chemical potential.
3. Define rate of internal entropy production. Mention its unit.
4. What is a flux? How does it arise?
5. Calculate the electronic partition function for an atom at its ground electronic state $^2P_{3/2}$.
6. The translational heat capacity at constant volume is 12.471 J/K/mol. Obtain its translational energy at 500 K.
7. The rate of a reaction between the aqueous solutions of two singly charged cations in an ionic strength of 0.0241 moldm$^{-3}$ is 1.55 L$^2$mol$^{-2}$min$^{-1}$. Find the rate constant at zero ionic strength using Bronsted-Bjerrum equation.
8. What are the limitations of collision theory?
9. Draw the potential energy diagram for Arrhenius type intermediates formed in the homogeneously catalyzed reactions.
10. What are stationary and non-stationary chain reactions?

## Part-B

***Answer any eight questions. Each question carries five marks:*** ***( 8 X 5 = 40 )***

11. The vapor pressure of 6.32 molal aqueous solution of KCl is 2186 Nm$^{-2}$ and the vapor pressure of pure water is 3142 Nm$^{-2}$ at 25 ºC. Assuming ideality, calculate the activity and activity coefficient of the solute in the solution.
12. Discuss the variation of fugacity with temperature.
13. Explain: (a) Peltier effect and (b) thermomechanical effect.
14. Discuss the entropy production in chemical reactions.
15. The vibrational frequency of CO molecule is 6.5x10$^{13}$s$^{-1}$. Calculate the fraction of molecules present in vibrational level v=1 and v=2 at 25°C.
16. How is partition function used to offer a microscopic insight into the average energy of a molecule?
17. Calculate the translational partition function of an oxygen molecule confined in a 1litre vessel at 27°C.
18. Using appropriate diagrams discuss the role of potential energy surfaces in reaction kinetics.
19. Compare the rate constants calculated by TST and collision theory for the reaction between two atoms.
20. Discuss any one mechanism for bimolecular surface reactions with a specific example.
21. A gas-phase bimolecular reaction has a rate constant of 2.34 × 10$^{-2}$ dm$^3$mol$^{-1}$s$^{-1}$ at 400°C and its activation energy is 150 kJmol$^{-1}$. Calculate the entropy and enthalpy of activation at 400°C.
22. Derive the expressions for the concentrations of A, B, and C for a first order parallel reaction, A giving two parallel products, B and C at time t.

## Part-C

***Answer any four questions. Each question carries ten marks:*** ***( 4 X 10 = 40 )***

23. a.Explain Onsager theory in the light of phenomenological coefficients.
    b.Write a note on electrokinetic effects. (6 + 4)
24. a.Arrive at the degrees of freedom in all the regions of the phase diagram ofa ternary system leading to the formation of two hydrates. (6 + 4)
    b.Calculate the ionic strength of a solution containing 0.1m $KNO_3$ and 0.15m $K_2SO_4$
25. a.Derive the relation between partition function and entropy.
    b.Evaluate the rotational partition function for NO molecule at 100 K. Given the rotational constant = 1.70 $cm^{-1}$. (6 + 4)
26. a.Explain the kinetics of single substrate enzymatic reaction and derive the rate law.
    b.For an enzyme catalyzed reaction, the rate is found to be $2.3 \times 10^{-4}$ $Ms^{-1}$ when the substrate concentration is $2.5 \times 10^{-4}$ M. Calculate the limiting rate by applyingMichaelis-Menten equation. (7 + 3)
27. a.Describe the influence of dielectric constant on the rate of ionic reactions insolution.

    b.Explain any one reversible inhibition reaction. (7 + 3)
28. a.Discuss the kinetics of branched chain explosion reactions.
    b.The rate constant for a reaction doubles when the temperature increased from 22.50°C to 27.47°C. Determine the activation energy of the reaction. (7 + 3)

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