



**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034**

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

THIRD SEMESTER – APRIL 2018

**6PCH3MC02/CH3814 - THERMODYNAMICS AND CHEMICAL KINETICS**

Date: 26-04-2018  
Time: 09:00-12:00

Dept. No.

Max. : 100 Marks

**Part-A**

*Answer ALL questions.*

**(10 × 2 = 20)**

1. Define Chemical potential.
2. Show that  $\left(\frac{\partial \ln a}{\partial T}\right)_{P, n_1, n_2} = -\bar{H}_j / T^2$
3. What are coupled and uncoupled reactions?
4. State Prigogine's principle of minimum entropy production.
5. Obtain the relationship between internal energy and partition function.
6. The entropy of activated complex increases for the reaction between two oppositely charged ions in solution – Justify.
7. What is the effect of temperature on the rate of enzymatic reactions?
8. Draw the potential energy diagram of a catalysed reaction forming van't Hoff intermediate.
9. The rate constant for the reaction,  $H^+ + OH^- \rightarrow H_2O$  is  $1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the half-life for the neutralisation process if  $[H^+] = [OH^-] = 0.1 \text{ M}$ .
10. How are chain reactions classified based on the number of radicals produced in propagation step?

**Part-B**

*Answer any EIGHT questions.*

**(8 × 5 = 40)**

11. Explain the three important uses of Ellingham diagram with suitable examples.
12. Obtain the phenomenological equations and their cross coefficients for streaming potential and electro-osmosis.
13. Calculate the vibrational partition function for nitrogen gas at 300 K, if the vibration frequency is  $2360 \times 10^2 \text{ m}^{-1}$ .
14. How does a concept of irreversible thermodynamics apply to biological process?
15. Discuss the Einstein theory for specific heat capacity of solids.
16. Derive the Sackur–Tetrode equation for a monoatomic gas.
- 17a. Calculate the number of collisions per second in one cubic centimetre of iodine containing  $1.04 \times 10^{19}$  molecules at 300 K. (Given: Collision diameter,  $\sigma = 4.6 \text{ \AA}$  and  $M_{\text{Iodine}} = 254 \text{ g mol}^{-1}$ ).
- b. Differentiate time and true order of a reaction with the relevant graphs. (2+3)

18. Explain the effect of added salt on the rates of ionic reactions in solution.
19. Discuss the kinetics of free radical polymerization reactions.
20. Describe any one mechanism for a bimolecular surface reaction with an example.
21. Explain the kinetics of hydrogen-bromine reaction.
22. Compare the rate constant expressions obtained by TST and collision theory for the reaction between two atoms

### Part-C

*Answer any FOUR questions.*

(4 × 10= 40)

- 23a. Sketch the phase diagram and arrive at the degrees of freedom for all the regions of a ternary system leading to the formation of double salts.
  - b. Discuss any two methods of determining the fugacity of a real gas. (5+5)
- 24a. State Peltier effect and obtain their phenomenological equations and coefficient.
  - b. Explain Onsager theory in the light of phenomenological reciprocal relationship. (5+5)
- 25a. What are Bosons? Obtain the most probable distribution of indistinguishable particles using Bose-Einstein statistics.
  - b. Calculate the translational partition function of NO molecule at 500 K in a volume of 100 m<sup>3</sup> assuming the gas to behave ideally. (5+5)
- 26a. Explain the kinetics of atom and radical combination reactions.
  - b. Find the value of  $\Delta^\ddagger H^\circ$  for a bimolecular reaction having 115 kJ mol<sup>-1</sup> of activation energy. (7+3)
- 27a. Explain the principle of flash photolysis to study the kinetics of fast reactions.
  - b. Explain the kinetics of consecutive reactions with a relevant graph. (5+5)
- 28a. Discuss the effect of substrate concentration on enzymatic reaction.
  - b. The rate of an enzymatic reaction is  $2.48 \times 10^{-4}$  mol L<sup>-1</sup> min<sup>-1</sup> and is decreased by a factor of 2.4 if a competitive inhibitor is present. Calculate the degree of inhibition. (7+3)

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