

**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034****M.Sc. DEGREE EXAMINATION – CHEMISTRY****THIRD SEMESTER – APRIL 2024****PCH3MC02 – THERMODYNAMICS AND CHEMICAL KINETICS**

Date: 04-04-2024

Dept. No.

Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

SECTION A – K1 (CO1)**Answer ALL the questions****(5 x 1 = 5)****1 Answer the following.**

- a) How is fugacity related with chemical potential?
- b) What is meant by Peltier effect?
- c) Evaluate $\ln 10^{20}!$ using Stirling's approximation.
- d) Mention the effect of ionic strength on rate constant in the reaction between $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-} .
- e) Give an example of an opposing reaction.

SECTION A – K2 (CO1)**Answer ALL the questions****(5 x 1 = 5)****2 Fill in the blanks.**

- a) The conditions to be satisfied by cross coefficients of coupled reactions is-----
- b) Partition function increases with----- of temperature.
- c) Complex molecules have ----- value of entropy of activation.
- d) ----- is also called a double reciprocal plot.
- e) Branched chain propagation steps are the cause for -----.

SECTION B – K3 (CO2)**Answer any THREE of the following****(3 x 10 = 30)**

- 3 a) Predict the degrees of freedom in all regions of the phase diagram of a ternary system in which one compound forms a hydrate.
b) The emf of the cell $\text{Pt}, \text{H}_2(1\text{atm}) / \text{HBr}(\text{aq}) // \text{AgBr}(\text{s}) / \text{Ag}(\text{s})$ at 298 K is 0.3620 V. Calculate the mean activity coefficient of HCl at a molality of 0.004. E^0 of the cell is 0.0707 V. (6+4)
- 4 State the principle of microscopic reversibility. How can it be used to verify Onsager's reciprocal relation?
- 5 a) Prove that $\beta = 1/kT$ and mention its significance.
b) Obtain the relationship between partition function and entropy. (5+5)
- 6 a) Discuss the effect of pressure and time lag on the kinetics of a unimolecular reaction.
b) Calculate the rate constant for a molecule that exhibits three vibrational degrees of freedom at 300 K. Given: $Z = 5 \times 10^{10} \text{ Ms}^{-1}$ and $E_a = 60 \text{ kJ/mol}$. (6+4)
- 7 Explain the determination of the concentrations of A, B and C in a reaction of the type $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ when they follow first order kinetics. How will you compare its concentration vs time graph with that of a normal first order reaction?

SECTION C – K4 (CO3)

	Answer any TWO of the following	(2 x 12.5 = 25)
8	a) Discuss the determination of partial molar property by intercept method. b) How is the activity of a solvent determined by freezing point method?	(7+5.5)
9	a) Discuss the conservation of mass and energy in an open and closed system. b) The difference in energy between the first excited state, $^2P_{1/2}$ of fluorine atom and the ground state $^2P_{3/2}$ is 0.05 eV. Calculate the electronic partition function of fluorine atom at 1000K. (8+4.5)	
10	Explain the reaction rates in the light of collision theory, statistical and classical thermodynamic forms of transition state theory.	
11	a) How are the kinetic features of the thermal decomposition of acetaldehyde explained? b) Discuss the kinetics of anionic polymerization process.	(7+5.5)

SECTION D – K5 (CO4)

	Answer any ONE of the following	(1 x 15 = 15)
12	a) Discuss the variation of chemical potential with temperature and pressure. b) Derive an expression for translational partition function. Calculate the molecular translational partition function for 1 mol of nitrogen gas at 27 °C and $1.013 \times 10^5 \text{ Nm}^{-2}$ assuming the gas to behave ideally.	(7+8)
13	a) Discuss with suitable examples the influence of ionic strength and dielectric constant in determining reaction rates. b) Show that the Michaelis-Menton mechanism for an enzyme catalysis gives $r = r_{\text{max}} / 2$, when $[S]_0 = K_M$ and calculate the limiting rate of an enzyme catalyzed reaction when the concentration of the enzyme is $3.45 \times 10^{-7} \text{ M}$ and the rate constant is $2.08 \times 10^3 \text{ s}^{-1}$.	(6+9)

SECTION E – K6 (CO5)

	Answer any ONE of the following	(1 x 20 = 20)
14	a) Calculate the fugacity of nitrogen at 0°C and 100 atm. Its density at 0 °C and 1 atm is 1.25 Kg m^{-3} b) Discuss the application of irreversible thermodynamics to biological system with an example. c) What are Fermions? Obtain the most probable distribution of indistinguishable particles using Fermi- Dirac statistics.	(5+5+10)
15	a) The enzyme penicillinase (Mol. wt = $3 \times 10^4 \text{ g/mol}$) catalyzes the decomposition of an antibiotic. The turn over number of the enzyme at 28°C is 2000 s^{-1} . If 6.4 µ g of penicillinase catalyzes the destruction of 3.11 mg of amoxicillin (Mol. Wt = 364 g/mol) in 20 seconds, calculate the number of active sites in the enzyme. b) What are parallel reactions? Obtain an expression for the rate constants of a parallel reaction. c) How are relaxation techniques and flow methods used to study the kinetics of fast reactions?	(6+8+6)
