LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

THIRD SEMESTER – **APRIL 2025**

PCH3MC02 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 26-04-2025 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 PM

	SECTION A – K1 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
1	**Answer the following**	
a)	Define activity coefficient.	
b)	Write the conditions to be satisfied by cross coefficients of coupled reactions.	
c)	Evaluate ln 10 ! using Stirling's approximation .	
d)	Mention the order of a unimolecular reaction at low concentration.	
e)	What is straight chain explosion?	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**Fill in the blanks**	
a)	The fugacity of helium is always _____than the pressure.	
b)	The _____function describes how far a system is from equilibrium during an irreversible process.	
c)	The relation between entropy 'S' of a given system and the thermodynamic probability 'W' is given by _____.	
d)	_____is the slowest step when the time-lag is huge.	
e)	Chain length refers to_____	
	SECTION B – K3 (CO2)	
	Answer any THREE of the following	**(3 x 10 = 30)**
3	a) Show that $(\partial \mu_i / \partial T)_{p,n_i} = -\bar{S}i$ b) How is the activity of a solute determined by vapour pressure method?	(5+5)
4	What is Onsager reciprocal relation? How is it verified by the principle of microscopic reversibility?	
5	a) Compare Maxwell-Boltzmann, Bose-Einstein and Fermi- Dirac Statistics. b) Calculate the vibrational partition function for nitrogen gas at 300 K, if the vibration frequency is $2360 \times 10^2\ m^{-1}$.	(5+5)
6	a) Discuss the conversion of para hydrogen to ortho hydrogen in terms of potential energy surface. b) Predict the order of the average vibrational energy of an activated complex.	(7+3)
7	Determine the concentrations of A, B & C in a reaction of the type $A \xrightarrow{k1} B \xrightarrow{k2} C$.	

	SECTION C – K4 (CO3)	
	Answer any TWO of the following	**(2 x 12.5 = 25)**
8	a) Define partial molar property. How is it determined by intercept method? b)The fugacity coefficient of a gas at 200 K and 80 atm is 0.92. Calculate the difference in chemical potential of the real gas and an ideal gas.	(9 + 3.5)
9	a) Discuss the conservation of mass and energy in open and closed system. b) Obtain the expression for vibrational partition function.	(8 + 4.5)
10	a) Discuss the Lindemann-Christiansen's mechanism to study the influence of concentration on the order of a unimolecular reaction. b) The rate constant of a first order reaction in solution at 313 K is 1.6×10^{-4} s^{-1} and its activation energy is 55 kJ/mol. Calculate the frequency factor and entropy of activation. Given: $\Delta n = 1$.	(7+5.5)
11	a)) Obtain the rate expression for the reversible conversion of Fumaric acid to Maleic acid that follows first order in both the directions. Prove that the rate expression is similar to an irreversible first order reaction. b) ^{227}Ac has a half-life period of 22 years. It follows two parallel paths, one leading to ^{227}Th and the other leading to ^{223}Fr. The percentage yield of the two products are 2 and 98 respectively. Calculate the rate constants for the two parallel paths and their halve life periods.	(6 + 6.5)
	SECTION D – K5 (CO4)	
	Answer any ONE of the following	**(1 x 15 = 15)**
12	a) Predict the degrees of freedom in all regions of the phase diagram of a ternary system in which two compounds form a hydrate. b) Discuss the flux-force relationship with an example. c) Determine the rotational temperature and the rotational partition function for oxygen at 300 K. The bond length of the molecule is 1.207 Å.	(5 + 5 + 5)
13	a) Obtain an expression to show the effect of dielectric constant of the medium on the rate constant and discuss the salient features of the equation with suitable examples. b) Derive an equation for the rate of cationic polymerization process.	(10 + 5)
	SECTION E – K6 (CO5)	
	Answer any ONE of the following	**(1 x 20 = 20)**
14	a) Calculate the fugacity and fugacity coefficient of ammonia at 50 atm and 298 k, given that the gas obeys the equation of state P (V-b) = RT and b= 0.0391 dm^3 mol^{-1}. b) Obtain the phenomenological equations and their cross coefficients for electrokinetic phenomenon. c) What are Bosons? Obtain the most probable distribution of indistinguishable particles using Bose-Einstein statistics.	(5 + 5 + 10)
15	a) What is the effect of ionic strength on the rate of reaction if the slowest step involves oppositely charged species? b) What is Lineweaver-Burk plot? The intercept and slope of the plot are 5.0×10^{-3} and 1.5×10^{-5} respectively. Calculate the value of K_M and maximum rate. c) How are flow and relaxation techniques used to study the kinetics of fast reactions?	(7 + 5 + 8)
