LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2024**

PCH3MC02 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 09-11-2024 Dept. No. Max. : 100 Marks

Time: 01:00 pm-04:00 pm

	SECTION A – K1 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
1	**Answer the following**	
a)	Define chemical potential.	
b)	What are drag coefficients?	
c)	Write the relationship between pressure and partition function.	
d)	Define the rate of reaction in the light of Christiansen's concept.	
e)	What is an opposing reaction?	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**Fill in the blanks**	
a)	For ideal gas, the fugacity is equal to its_____.	
b)	The flux-force relationship is_____.	
c)	The number of microstates corresponding to its macrostate is known as _____.	
d)	The limiting rate constant K_∞ is given by _____	
e)	Chain length refers to _____	
	SECTION B – K3 (CO2)	
	Answer any THREE of the following	**(3 x 10 = 30)**
3	Derive Gibbs-Duhem equation for a binary system. Mention its significances.	
4	Discuss the validity and verification of Onsager equation in irreversible thermodynamics.	
5	a) Obtain the relationship between internal energy and partition function. b) Calculate the translational partition function of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24.4 dm^3.	(5+5)
6	a) Discuss the construction of potential energy surface with an example and mention its significance. 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 maximum rate.	(6 + 4)
7	Discuss the kinetics of thermal chain reaction with an example.	

SECTION C – K4 (CO3)

	Answer any TWO of the following	**(2 x 12.5 = 25)**
8	a) Define fugacity. How is the fugacity of real gas determined by graphical method? b) Calculate the rational activity coefficient of 4.5 molal aqueous solution of a non-volatile solute with an activity of 0.4982. (10+2.5)	
9	a) What is internal entropy production? Predict the condition for internal entropy production to be positive to maintain equilibrium. b) The difference in energy between the first excited state, $^2P_{1/2}$ of bromine atom and the ground state $^2P_{3/2}$ is 0.19 eV. Calculate the electronic partition function of bromine atom at 1100 K. (8 + 4.5)	
10	a)Discuss the influence of time-lag on the order of a reaction in Lindemann's hypothesis b) For a first order reaction, the rate constant at 298 K is 4.0×10^{-6} s^{-1} and its activation energy is 71kJ/mol. Calculate the frequency factor and entropy of activation. Given: Δn = 1. (7 + 5.5)	
11	a) Obtain the rate expression for the reversible conversion of cis 2-butene to *trans* 2-butene that follows first order in both the directions and 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) Draw and explain the phase diagram for the formation of two pairs of partially miscible liquids. b) The rotational constant of gaseous HCl is 10.59 cm^{-1}. Calculate the rotational partition function of HCl at 100 K. c) How does the concept of irreversible thermodynamics apply to biological process? (5+5+5)	
13	a) Obtain an expression to study the influence of ionic strength on the rates of reaction between ions. Comment on the magnitude of the parameters of A and $\Delta S^{\neq}$ for the following reactions i) $S_2O_3^{2-} + SO_3^{2-} \rightarrow$ Products ii) $[Co(NH_3)_5Br]^{2+} + OH^- \rightarrow$ Products. b) Derive an expression for the rate of anonic polymerization. (10 + 5)	

SECTION E – K6 (CO5)

	Answer any ONE of the following	**(1 x 20 = 20)**
14	a) Calculate the fugacity of H_2 at 100 °C and 300 atm. The density of H_2 at the above condition is 16.79 g dm^{-3}. b) State Peltier effect and obtain the phenomenological equations and coefficient. c) Explain the postulates of Einstein's theory of heat capacity of solids. Compare it with Debye theory. (5 + 5 + 10)	
15	a) The entropy of activation and frequency factor for reactions in solutions are found to differ by 42 $JK^{-1}mol^{-1}$ and 10^2 respectively for each unit of Z_AZ_B. Justify with examples. b) Calculate the rate constant at 298 K for the following reaction with E_a 15.5kJ/mol Atom + Diatomic molecule → Triatomic non-linear molecule Given the Partition functions: $Q_{trans} = 10^8$, $Q_{rot} = 10$, $Q_{vib} = 1$. c) How are electric field and magnetic field jump methods used to study the kinetics of rapid reactions? (7 + 6 + 7)	
