LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2023**

PCH3MC02 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 01-11-2023 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)	The fugacity of helium gas is always more than its pressure-Justify.
b)	What is meant by Seeback effect?
c)	Indicate the relationship between pressure and partition function.
d)	Mention an example of a reaction with a high $\Delta S^{\neq}$.
e)	Give any two minor products of the thermal decomposition of acetaldehyde.
	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 non-coupled reactions is----------
b)	The unit of partition function is----------
c)	Simple reactant molecules have ---------- value of frequency parameter.
d)	The efficiency of an enzyme is determined in terms of ----------.
e)	The chain length of a reaction refers to ----------.
	SECTION B – K3 (CO2)
	Answer any THREE of the following **(3 x 10 = 30)**
3	a) Draw and explain the phase diagram of a ternary system consisting of two solids and water with the formation of a double salt. b) Calculate the fugacity coefficient of ammonia at 1000 K and 100 atm pressure, given that the gas obeys the equation of state P (V-b) = RT. Given, b = 0.037 dm^3 mol^{-1}. (6+4)
4	Prove the relationship, $L_{ik} = L_{ki}$ and mention its significance.
5	a) Compare Einstein's theory with Debye's theory of heat capacity of crystals. b) Calculate the ratio of molecules in the first excited state and ground state at 3000 K. Given that the energy of the first excited electronic state of oxygen molecule is 15.7×10^{-20} J. ($g_0 = 3$ and $g_1 = 2$). (6+4)
6	a) Discuss the construction of potential energy surface for a reacting system with an example and mention its importance. b) Entropy of activation observed for the reaction $CH_3N_2CH_3 \rightarrow C_2H_6 + N_2$ at 300 K is 71 J/K. Calculate the value of pre-exponential factor. (6+4)
7	What are opposing reactions? Obtain the rate expression for a cis ⇌ trans isomerization reaction that follows first order in both the directions. Prove that the rate expression is comparable to an irreversible first order reaction

	SECTION C – K4 (CO3)
	Answer any TWO of the following **(2 x 12.5 = 25)**
8	a) Derive Gibbs-Duhem equation. Mention its significances. b) What is the change in chemical potential of toluene at 25 ^{0}C when a solute is added at a mole fraction of 0.60. (8+4.5)
9	a) Discuss the entropy production and entropy flow in open systems. b) Calculate the molar residual entropy of a crystal in which the molecules can adopt seven orientations of equal energy at 0 K. (8+4.5)
10	How will you discuss reaction rates in the light of collision theory, partition function and the thermodynamic forms of transition state theory?
11	a) What are Eadie and Woolf plots? How are they obtained? Mention their advantages. 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 half-life periods. (6+6.5)
	SECTION D – K5 (CO4)
	Answer any ONE of the following **(1 x 15 = 15)**
12	a) How is the fugacity of gases determined by graphical method? b) Obtain an expression for rotational partition function. Calculate the molecular rotational partition function for nitrogen gas at 27 ^{0} C. The moment of inertia of nitrogen is 13.9 x 10^{-47} Kg m^2. (7+8)
13	a) How will you interpret the mechanism of a reaction in terms of the magnitudes of A and $\Delta S^{\neq}$? Give examples. b) A consecutive first order reactions of the type A → B → C have rate constants k_1 and k_2. Given that $[A_\circ]$ = 2M, $k_1 = 0.19\ s^{-1}$ and $k_2 = 0.1\ s^{-1}$. Calculate t_{max} and $[B]_{max}$. c) Prove that the photochemical reaction between molecules of hydrogen and bromine has virtually the same algebraic form as the thermal reaction. (5+4+6)
	SECTION E – K6 (CO5)
	Answer any ONE of the following **(1 x 20 = 20)**
14	a) The emf of the cell Pt, H_2(1atm) /HCl // AgCl (s), Ag (s) at 298 K is 0.8526 V. Calculate the mean activity coefficient of HCl at a molality of 0.1. E^0 of the cell is 0.2244 V. b) Obtain the phenomenological equations and their cross coefficients for streaming potential and electro-osmosis. c) Highlight the postulates of Maxwell-Boltzmann statistics and derive the expression for the most probable distribution of particles. (5+5+10)
15	a) What are kinetic parameters? How are they evaluated in an enzymatic reaction? Mention their significance. b) Discuss the kinetics of cationic polymerization process. c) How are relaxation techniques and flow methods used to study the kinetics of rapid reactions? (8+5+7)

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