

PSG COLLEGE OF ARTS & SCIENCE
(AUTONOMOUS)

MSc DEGREE EXAMINATION DECEMBER 2024
(Third Semester)

Branch - CHEMISTRY

CHEMICAL KINETICS AND STATISTICAL THERMODYNAMICS

Time: Three Hours

Maximum: 75 Marks

SECTION-A (10 Marks)

Answer ALL questions

ALL questions carry EQUAL marks

(10 × 1 = 10)

Module No.	Question No.	Question	K Level	CO
1	1	According to Lindemann's theory of unimolecular reactions, at very high pressure the gaseous reactions follow: a) Zero order kinetics b) Pseudo first order kinetics c) First order kinetics d) Second order kinetics	K1	CO1
	2	Collision theory of a chemical reaction explains a) Rate of a reaction b) Order of a reaction c) Molecularity of a reaction d) Rate, order and molecularity	K2	CO1
2	3	For enzymatic reaction which follows Michaelis-Menten kinetics the condition for the reaction rate to be half its maximum value is a) $K_m = \frac{1}{2}[S]$ b) $K_m = 2[S]$ c) $K_m = [S]^2$ d) $K_m = [S]$	K1	CO2
	4	Acid-base catalyzed reactions are a) homogeneous solid phase reactions b) homogeneous liquid phase reactions c) heterogeneous reactions d) enzyme catalyzed reactions	K2	CO2
3	5	Which of the following statements best describes the hydrated reaction mode of the hydroxyl radical in the radiolysis of water? a) It rapidly combines with oxygen to form water. b) It acts as a strong reducing agent. c) It reacts with other molecules by abstracting hydrogen atoms. d) It remains stable in water for a long period.	K1	CO3
	6	The photochemical reaction is mainly of a) I order b) II order c) III order d) Zero order	K2	CO3
4	7	The rotational partition function (Q_{rot}) is a) $8\pi^2IkT/\sigma h$ b) $8\pi^2kT/\sigma Ih$ c) $8\pi^2IkT/\sigma h^2$ d) $8\pi^2IkT/\sigma^2h^2$	K1	CO4
	8	For H_2 assuming characteristic rotational as 100 K, q_{rot} at 2000 K is a) 15 b) 20 c) 30 d) 10	K2	CO4
5	9	According to Debye theory, specific heat at high temperature is proportional to: a) T b) T^2 c) T^3 d) Independent of T	K1	CO5
	10	Which one of the following is not obeying Bose-Einstein statistics? a) Hydrogen b) Proton c) Nitrogen d) Deuterium	K2	CO5

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SECTION - B (35 Marks)Answer **ALL** questions**ALL** questions carry **EQUAL** Marks

(5 × 7 = 35)

Module No.	Question No.	Question	K Level	CO
1	11.a.	Apply Lindemann's theory to explain the kinetics of unimolecular reactions.	K3	CO1
		(OR)		
	11.b.	Make use of the ARRT to analyze the reaction kinetics between atoms and molecules.		
2	12.a.	Explain the primary and secondary kinetic isotopic effects with examples.	K2	CO2
		(OR)		
	12.b.	State and explain the Michaelis-Menton law.		
3	13.a.	Organize the G-value and hydrated electrons.	K3	CO3
		(OR)		
	13.b.	Discuss the Langmuir-Hinshelwood mechanism for the unimolecular reactions.		
4	14.a.	Derive the Sekur-Tetrode equation.	K4	CO4
		(OR)		
	14.b.	Calculate the translational partition function for benzene (molar mass = 78.0 g mol ⁻¹) in a volume of 1 m ³ at 25 °C.		
5	15.a.	Explain the concept of the heat capacity of diatomic gases.	K4	CO5
		(OR)		
	15.b.	Interpret the negative absolute temperature.		

SECTION -C (30 Marks)Answer **ANY THREE** questions**ALL** questions carry **EQUAL** Marks

(3 × 10 = 30)

Module No.	Question No.	Question	K Level	CO
1	16	Compare the collision theory and ARRT.	K4	CO1
2	17	Simplify the steps involved in flow methods for fast reaction studies, comparing stopped-flow and continuous-flow techniques.	K4	CO2
3	18	Analyze how H ₂ -Cl ₂ reactions are regulated by the photochemical mechanism and kinetics.	K4	CO3
4	19	The vibrational frequencies in m ⁻¹ for CO ₂ are $\bar{\nu}_1 = 1350 \times 10^2$, $\bar{\nu}_2 = 672.2 \times 10^2$ and $\bar{\nu}_3 = 2396 \times 10^2$. The second mode of vibration has a degeneracy of 2. Calculate the following for CO ₂ (g) at 298 K, i) Vibrational partition function (fv) ii) Vibrational contribution to Cv iii) Vibrational contribution to entropy and iv) Characteristic temperature for vibration for each vibrational frequency.	K4	CO4
5	20	Derive the equilibrium constant expression using the partition function.	K4	CO5

Z-Z-Z

END