

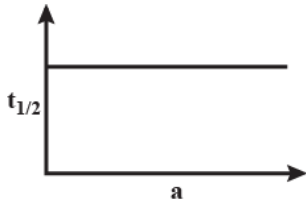

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2023-24 & thereafter)

M.Sc. DEGREE EXAMINATION, NOVEMBER 2024
BRANCH IV- CHEMISTRY
FIRST SEMESTER

COURSE : CORE
PAPER : ADVANCED PHYSICAL CHEMISTRY
SUBJECT CODE : 23CH/PC/PC14
TIME : 3 HOURS

MAX.MARKS :100

Q.N o.	SECTION-A Answer all questions (10x1=10 marks)	C O	K L
1.	Particles with half integral spin are known as a) Bosons b) Fermions c) Nuons d) Mesons	1	1
2.	For hydrogen molecule the number of translational, rotational and vibrational degrees of freedom at high temperature are: a) 3,3,3 b) 3,2,1 c) 3,2,2 d) 3,1,1	1	1
3.	Cell potential is an _____ property. a) extensive b) colligative c) intensive d) nuclear	1	1
4.	The Arrhenius rate equation is a) $k=Ae^{-E_a/RT}$ b) $k=Ae^{E_a/RT}$ c) $k= 2.303 A/RT$ d) $k= E_a /RT$	1	1
5.	In a consecutive reaction, $A \rightarrow I \rightarrow P$ $A \rightarrow I \quad v = k_a [A]$ $I \rightarrow A \quad v = k'_a [A]$ $I \rightarrow P \quad v = k_b [A]$ When $k_b \gg k'_a$, a) The formation of the product depends only on the k_a b) The formation of the product depends only on the k_b c) The formation of the product depends only on [I] d) The formation of the product depends on both k_a & k_b	1	1
6.	According to Rice-Herzfeld mechanism of decomposition of acetaldehyde, the rate of decomposition is directly proportion to a) $[CH_3CHO]^{1/2}$ b) $[CH_3CHO]^{3/2}$ c) $[CH_3CHO]$ d) $[CH_3CHO]^{2/3}$	1	1
7.	The equation for the rate constant of a diffusion-controlled reaction between two different molecules is a) $K_D = 4RT/3\eta$ b) $K_D = 8RT/3\eta$ c) $K_D = 3RT/8\eta$ d) $4RT/9\eta$	1	1
8.	Activity of a solid is always taken to be _____. a) 1 b) 0 c) same as amount d) moles	1	1
9.	In Freundlich adsorption isotherm, the slope of the straight-line graph between $\log(x/m)$ and $\log P$ for adsorption of a gas on solid is a) $1/n$ b) $\log k$ c) n d) k	1	1
10.	In electrochemistry, the transfer coefficient (α) is a quantity that has a value _____. a) one b) more than 1 c) between 0 and 1 d) less than zero		

SECTION- B			
	Answer all questions (10 x 1 = 10 Marks) Fill in the blanks-	CO	KL
11.	The units of partition function is _____.	2	2
12.	The process of catalytically induced fragmentation of the long chain hydrocarbons(drawn from earth as petroleum) is called _____.	2	2
13.	The symmetry number for HCl molecule is _____.	2	2
14.	According to Dulong and Pettit's law, for a monatomic crystal, C_v (calK^{-1}) is _____	2	2
15.	Variation of the rate of the reaction between ions in the presence of an added electrolyte acting as catalyst is called as _____ .	2	2
Answer in a line or two:			
16.	The following is graph of $t_{1/2}$ verses concentration of reactant 'a'. What  is the order of the reaction?	2	2
17.	Identify type and give an example of the following isotherm. 	2	2
18.	Consider a system of distinguishable particles having only two non-degenerate energy levels separated by an energy which is equal to kT at 25K. Calculate the ratio of populations in states at 25K.	2	2
19.	Evaluate using Stirling approximation $\ln N!$. Where $N = 6.023 \times 10^{23}$	2	2
20.	Indicate whether the reaction is spontaneous or not. Given: $E_{\text{cell}} = 1.314\text{V}$. ($n=2$)	2	2

SECTION- C		CO	KL
Answer any four questions (4 x 6 = 24 Marks)			
21.	Derive the expression for Maxwell- Boltzmann Statistics.	3	3
22.	a) Explain in detail the potential energy diagram of surfaces. (4) b) A average human DNA molecule has 5×10^8 bio-nucleotides (rungs on DNA ladder) of four different kinds. If each rung were a random choice of one of these four possibilities, what would be the residual entropy associated with this typical DNA molecule? (2)	3	3
23.	a) Explain the dynamics of molecular collisions. (3) b) Explain the sedimentation potential. (3)	3	3
24.	a) Explain the role of catalytic oxidation in pollution control with an example. k_a k_b (3) b) Show that the pre-equilibrium mechanism - $A + B \leftrightarrow C \rightarrow P$ (3) results in a second order reaction, k_a' Arrive at a rate law when $k_b \ll k_a'$		
25.	Obtain an expression for internal energy and partition function of an ideal gas. Show that the internal energy of a monatomic gas is $3RT/2$.		

SECTION- D		CO	KL
Answer any four questions (4x 8= 32 marks)			
26.	a) Derive an expression for molecular translational partition function of an ideal gas. (5) b) Calculate the translational partition function for D_2 molecule confined to 100cm^3 vessel at 25°C . Given: $m = 4.028\text{u}$, $u = 1.67 \times 10^{-27}\text{Kg}$ (3)	4	4
27.	a) Describe the Rice-Herzfeld mechanism in decomposition of acetaldehyde. (4) b) Compare Eley Rideal mechanism and Langmuir Hinshelwood mechanism for surface catalysed reaction. (4)	4	4
28.	Discuss the application Bose Einstein equation in derivation of Planck's equation for distribution of energy in black body radiation.	4	4
29.	What do you mean by diffusion-controlled reactions? Prove that the diffusion rate of the reaction is inversely proportional to the viscosity.	4	4
30.	Explain the Helmholtz-Perrin and Stern models for structure of electrified surfaces.	4	4

SECTION E		CO	KL
Answer the following (2 x 12 = 24 Marks)			
31.	<p>a) Starting from the expression of entropy and partition function derive Sackur Tetrode equation. Calculate the standard molar entropy of Argon at 25°C. Given molar mass of Ar= 39.95 [4+3]</p> <p>b) Evaluate the vibrational partition function at 1500K. The wave numbers of three normal modes of CO₂ are 1388 cm⁻¹, 667.4 cm⁻¹, and 2349 cm⁻¹, the second being doubly degenerate. (5)</p> <p style="text-align: center;">OR</p> <p>a) What are phenomenological equations? Discuss the Onsager reciprocity relation and verify the same. (6)</p> <p>b) Discuss the Lindemann-Hinshelwood mechanism for unimolecular reactions. (6)</p>	5	5
32.	<p>a) Derive Tafel equation. In the electrolysis of 2N sulphuric acid using Ni electrodes the hydrogen over voltage was found to be 0.35V for a given current density. What will be the hydrogen over voltage for the same cathode under same conditions if the current density is increased 8 times its preset value? Given b = 0.12V at 298K (4+3)</p> <p>b) Discuss in brief the influence of solvent on reaction rate. (5)</p> <p style="text-align: center;">OR</p> <p>a) Discuss in detail the Debye specific heat equation of solids. (8)</p> <p>b) A monolayer of N₂ molecules is adsorbed on the surface of 1.00g of an Fe/Al₂O₃ catalyst at 77K, the boiling point of liquid nitrogen. Upon warming, the nitrogen occupies 2.86cm³ at 0°C and 760Torr. What is the surface area of the catalyst? The effective area of a N₂ molecule is 0.167nm². (4)</p>	5	5
