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

**M.Sc. DEGREE EXAMINATION, NOVEMBER 2023**
**BRANCH IV- CHEMISTRY**
**FIRST SEMESTER**

**COURSE : CORE**
**PAPER : ADVANCED PHYSICALCHEMISTRY**
**SUBJECT CODE : 23CH/PC/PC14**
**TIME : 3 HOURS MAX.MARKS :100**

| SNO | SECTION A (10 x 1 = 10 marks)<br>**Answer ALL Questions** | K LEVEL |
|---|---|---|
| 1. | In an adsorption process if an unimolecular layer is formed then it is<br>a) Physisorption b) Chemisorption c) ion exchange d) None | K1 |
| 2. | Solvents can influence reaction rates, conversion and product selectivity by<br>a) directly participating in the reaction steps<br>b) competing with the reactant for interaction with the catalysts,<br>c) changing the relative stabilization of the reactant, the transition state (TS) and/or the product,<br>d) all of these | |
| 3. | According to molecular collision theory, the reaction is subjected to _____<br>a) Number of molecular collisions of reactant<br>b) Number of collisions between Transition state and reactants<br>c) Number of effective collisions or reactants<br>d) None | K1 |
| 4. | The ionic strength of a solution of molality $m_i$ and valency of the ion Zi is ____<br>a) $\mu = 1/2\, miZi^2$ b) $\mu = \sum miZi^2$ c) $\mu = 1/2 \sum Zi^2$ d) $\mu = 1/2 \sum miZi^2$ | |
| 5. | Physisorption _____ with increase in temperature<br>a) Increases b) decreases c) remains unchanged d) none of these | |
| 6. | _____ phenomena arise from movement of ions in the electric double layer under a pore pressure gradient.<br>a) Electrokinetic b) double layer c) Osmosis d ) none of these | |
| 7. | The_____ mechanism explains unimolecular reactions that take place in the gas phase.<br>a) Lindemann-Hinshelwood b) Pre-Equilibria<br>c) transition state d) none of these | |
| 8. | In a Hydrogen Oxygen fuel cell, Hydrogen enters through the anode.<br>a) True b) False | |
| 9. | Catalyst changes the equilibrium constant of the reaction<br>a) True b) False | |
| 10. | In a complex photochemical reaction involving a secondary process the quantum yield might exceed 1<br>a) True b) False. | |

| SNO | SECTION – B (10 x 1 = 10 marks)<br>**Answer ALL Questions** | K LEVEL |
|---|---|---|
| 11. | Explain Zeta potential. | K2 |
| 12. | Explain the hydrogenation reaction with an example. | K2 |
| 13. | What is the significance of exchange current density? | K2 |
| 14. | Illustrate chain reaction with an example. | K2 |
| 15. | What is a Phenomenological Equation? | K2 |
| 16. | Explain microstate | K2 |

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|---|---|---|
| 17. | What are distinguishable systems? | K2 |
| 18. | Rephrase Electrochemical Interface. | K2 |
| 19. | Given example to illustrate Chemisorption. | K2 |
| 20. | What are consecutive reactions. | K2 |

| SNO | SECTION C (4 x 6 = 24 marks)<br>ANSWER ANY FOUR QUESTIONS | K LEVEL |
|---|---|---|
| 21. | Show pre-equilibrium approximation and steady-state approximation | K3 |
| 22. | Demonstrate the physical origin of the kinetic salt effect | K3 |
| 23. | How is ensemble applied in statistical thermodynamics, | K3 |
| 24. | Clasify electrocapillary measurements and electrocapillary curves? Write the application of electrocapillary curves. | K3 |
| 25. | Present Gibbs adsorption isotherm. | K3 |

| SNO | SECTION – D (4 x 8 = 32 marks)<br>ANSWER ANY FOUR QUESTIONS | K LEVEL |
|---|---|---|
| 26. | Compare Guoy Chapman and Stern Models of double layer. | K4 |
| 27. | Outline Potential Energy Surfaces and analyse the following statement: 'Reaction with attractive potential energy surfaces proceeds more efficiently if the energy is translational.' | K4 |
| 28. | Investigate Boltzmann parameters using Lagrange's method of undetermined multipliers. | K4 |
| 29. | Derive and examine Sackur Tetrode equation for the monoatomic gas. | K4 |
| 30. | Examine the explosion behavior of a chain reaction.<br>$H_2 + O_2 \longrightarrow 2H_2O$ | K4 |

| SNO | SECTION – E (2 x 12 = 24 marks)<br>ANSWER THE FOLLOWING | |
|---|---|---|
| 31a | Derive Butler- Volmer Equation for one electron transfer and explain the significance of symmetry factor **β.**<br>**(OR)** | K5 |
| 31b | Compare Maxwell- Boltzmann, Bose-Einstein and Fermi - Dirac statistics. | |
| 32a | Deduce the postulates BET theory. How will you determine the surface area of a solid using BET theory and explain the limitations of this method.<br>**(OR)** | K5 |
| 32b | a) Explain Lindemann-Hinshelwood mechanism for unimolecular reactions. (8 Marks)<br>b) Using steady state approximation devise the rate law for the decomposition of $N_2O_5$ (4 Marks)<br>$N_2O_5 \longrightarrow NO_2 + NO_3 \quad k_a$<br>$NO_2 + NO_3 \longrightarrow N_2O_5 \quad k'_a$<br>$NO_2 + NO_3 \longrightarrow NO_2 + O_2 + NO \quad k_b$<br>$NO + N_2O_5 \longrightarrow NO_2 + NO_2 + NO_2 \quad k_c$ | |

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