PSG COLLEGE OF ARTS & SCIENCE (AUTONOMOUS)

MSc DEGREE EXAMINATION MAY 2025

(Third Semester)

Branch - CHEMISTRY

CHEMICAL KINETICS AND STASTICAL THERMODYNAMICS

Time: Three Hours

Maximum: 75 Marks

SECTION-A (10 Marks)

Answer ALL questions

ALL questions carry EQUAL marks

 $(10 \times 1 = 10)$

| Module | Question | THE questions carry EQUAL makes (10 X | 1 - 10) | |
|--------|----------|--|------------|-----|
| No. | No. | Question | K Level | CO |
| 1 | 1 | According to absolute reaction rate theory, the molar entropy of activation ΔS* of an elementary bimolecular reaction is a) Zero b) Positive c) Negative d) Positive for endothermic reaction and negative for exothermic reaction | K1 | CO1 |
| | 2 | Although bimolecular collision is the path through which molecules achieve activation energy, some reactions are unimolecular first order in nature because of the a) solvent b) slow collision rate c) equilibrium in energization step d) fast collision rate | K2 | CO1 |
| 2 | 3 | In acid-base catalysis, the proton transfer is to a solvent molecule like. H ₂ O, then the mechanism is a) prototropic b) protolytic c) isotopic d) hydrolytic | K1 | CO2 |
| | 4 | The order of enzyme catalyzed reactions at higher concentration of substrate. a) One b) Two c) Fractional d) Zero | K2 | CO2 |
| 3 | 5 | What does the G-value represent in the context of radiation chemistry? a) The energy of gamma radiation b) The number of ions produced per 100 eV of absorbed energy c) The intensity of the radiation source d) The rate of photon emission | K1 | CO3 |
| | 6 | In Langmuir-Hinshelwood mechanism, if the reactant B is sufficiently adsorbed, the order of the reaction is a) 1 b) 0 c) -1 d) 2 | K2 | CO3 |
| 4 | 7 | The vibrational partition functional (Q_{vib}) is a) $(1-e^{-x})$ b) $(1-e^{-x})^{-1}$ c) $(1-e^{x})$ d) $(1-e^{x})^{-1}$ | K1 | CO4 |
| | 8 | The Sacker-tetrode equation is a) $S^o = 2.303 R [3/2 log M + 5/2 log T + log Q_e - log P - 0.5055]$ b) $S^o = 4.576 R [3/2 log M + 5/2 log T + log Q_e - log P - 0.5055]$ c) $S^o = 2.303 R [3/2 log M + 5/2 log T + log Q_e - 0.5055]$ d) $S^o = 4.576 R [3/2 log M + 5/2 log T + log Q_e - 0.5055]$ | K2 | CO4 |
| 5 | 9 | In how many ways can two particles be distributed in five states of an energy level if the particles follow Bose-Einstein statistics? a) 30 b) 15 c) 20 d) 10 | K1 | CO5 |
| | 10 | Pick out the fermions i) Electron ii) Proton iii) Neutron iv) Deuteron a) iv is correct b) i and iv are correct c) iii and iv are correct d) i, ii and iii are correct | К2 | CO5 |

Cont...

SECTION - B (35 Marks) Answer ALL questions

ALL questions carry EQUAL Marks

 $(5 \times 7 = 35)$

| Module No. | Question No. | Question | K Level | СО |
|---------------|-----------------|--|------------|-----|
| 1 | 11.a. | Construct the Rice-Herzfeld mechanism for organic decomposition. | | |
| | (OR) | | | CO1 |
| | 11.b. | Build the explosion reaction of hydrogen and oxygen. | | |
| 2 | 12.a. | Illustrate the Arrhenius and Van't Hoff intermediates. | | |
| | (OR) | | | CO2 |
| | 12.b. | Explain about the flash photolysis. | | |
| - | 13.a. | Derive the BET adsorption isotherm and shoe that under certain conditions it reduces to Langmuir isotherm. | | |
| | (OR) | | | ~~~ |
| 3 | 13.b. | One gram of charcoal absorbs 1.36x10 ⁻³ litre of H ₂ (measured at STP) to form a monolayer. If the area covered by a single molecule of H ₂ is 1.3x10 ⁻¹⁹ m ² , calculate the surface area of one gram of charcoal. | K3 | CO3 |
| 4 | 14.a. | Analyze the following. i) Permutation and combination law ii) Ensembles | K4 | CO4 |
| | (OR) | | | 1 |
| | 14.b. | Compare internal energy's thermodynamic functions during translational and rotational partition functions. | | ; |
| 5 | 15.a. | Distinguish between Bose-Einstein and Fermi-Dirac statistics. | | |
| | (OR) | | | CO5 |
| | 15.b. | Explain how the equilibrium constant is related to the free energy change of a system and how temperature affects the equilibrium constant. | K4 | 003 |

SECTION -C (30 Marks)

Answer ANY THREE questions

ALL questions carry EQUAL Marks

 $(3\times10=30)$

| Module No. | Question No. | Question | K Level | CO |
|---------------|-----------------|--|------------|-----|
| 1 | 16 | Examine the kinetics and mechanism of the thermal reaction between H ₂ and Br ₂ . | K4 | CO1 |
| 2 | 17 | Analyze the Michaelis-Menten law and discuss the effect of substrate concentration, pH, and temperature on the rate of an enzyme-catalyzed reaction. | K4 | CO2 |
| 3 | 18 | Compare the Langmuir-Hinshelwood and Langmuir-Rideal mechanisms. | K4 | СОЗ |
| 4 | 19 | Derive the Maxwell-Boltzmann statistics. Write its limitations. | K4 | CO4 |
| . 5 | 20 | Compare and contrast the Einstein and Debye models for the heat capacity of solids. | K4 | CO5 |