

PSG COLLEGE OF ARTS & SCIENCE
(AUTONOMOUS)

MSc DEGREE EXAMINATION DECEMBER 2022
(Third Semester)

Branch – CHEMISTRY

PHYSICAL CHEMISTRY-III

Time: Three Hours

Maximum: 50 Marks

SECTION-A (5 Marks)

Answer ALL questions

ALL questions carry EQUAL marks (5 x 1 = 5)

- 1 Which of the following is incorrect about transition state theory?
 - (i) It is based on statistical mechanics
 - (ii) The formation of activated complex is rapid
 - (iii) The decomposition of activating complex is slow
 - (iv) The formation of activated complex is the rate determining step
- 2 Flash photolysis is a
 - (i) Pump-probe technique
 - (ii) Jump-probe technique
 - (iii) Temperature-probe technique
 - (iv) Pressure-technique
- 3 The surface coverage (θ), related to pressure and equilibrium constant by Langmuir adsorption isotherm is
 - (i) $\theta = bP / (1+bP)$
 - (ii) $\theta = bP / (1+bP^2)$
 - (iii) $\theta = (1+bP) / bP$
 - (iv) $\theta = bP$
- 4 Maxwell-Boltzmann statistics cannot be applied to
 - (i) Atoms
 - (ii) Molecules
 - (iii) Photons
 - (iv) Lattice
- 5 Phase-Space is a
 - (i) 3-dimensional space
 - (ii) 1-dimensional space
 - (iii) 2-dimensional space
 - (iv) 6-dimensional space

SECTION - B (15 Marks)

Answer ALL Questions

ALL Questions Carry EQUAL Marks (5 x 3 = 15)

- 6 a Show that Lindemann's hypothesis helps to understand the change in the order of reaction due to changes in pressure with some gaseous reactions.
OR
b Distinguish primary and secondary kinetic isotopic effects with examples.
- 7 a How does Michaelis-Menten equation, explains the observed kinetics of enzyme catalyzed reactions?
OR
b Compare and contrast stopped flow and continuous flow techniques for the study of kinetics of fast reactions.
- 8 a. Deduce a BET adsorption isotherm equation. Mention its applications.
OR
b. What are hydrated electrons? Explain their characteristics and importance.

Cont...

- 9 a. Calculate the translational partition function of NO molecule at 300 K in a volume 1000 m^3 . Assuming that NO behaves ideally.

OR

- b. Derive Seckur-Tetrode equation.

- 10 a. Compare the salient features of Bose-Einstein and Fermi-Dirac statistics.

OR

- b. What is meant by negative absolute temperature? How it is achieved?

SECTION -C (30 Marks)

Answer ALL questions

ALL questions carry EQUAL Marks (5 x 6 = 30)

- 11 a. Derive an expression for the rate constant of a bimolecular reaction based on absolute reaction rate theory. In what way ARRT is superior to other theories.

OR

- b. Deduce an expression for the kinetics of $\text{H}_2 - \text{Br}_2$ thermal reaction.

- 12 a. Derive the rate law of Arrhenius and Van't Hoff intermediate complexes.

OR

- b. Apply the double sphere model and deduce a relationship between the solvent dielectric constant and rate constant.

- 13 a. Sketch a schematic diagram of Fricke dosimeter. Explain its mode of functioning and applications.

OR

- b. Describe the Langmuir-Hinshelwood theory for a bimolecular surface reactions. Mention its merits and limitations.

- 14 a. Prove that complete partition function for a system is the product of translational, rotational vibrational and electronic partition functions.

OR

- b. Distinguish the following pairs:

- (i) Classical statistical mechanics and Quantum statistical mechanics (2)
 (ii) Distinguishable particles and indistinguishable particles (2)
 (iii) Canonical ensemble and grand canonical ensemble (2)

- 15 a. Derive Einstein's equation of heat capacity of solids in terms of partition function.

OR

- b. Propose a distribution law applicable to bosons. Derive it.

Z-Z-Z

END