

MSc DEGREE EXAMINATION MAY 2019
(Third Semester)

Branch - **CHEMISTRY**

PHYSICAL CHEMISTRY - III

Time : Three Hours

Maximum : 75 Marks

Answer **ALL** questions
ALL questions carry **EQUAL** marks (5 x 15 ~ 75)

- 1 a Compare collision theory and ARRT. Which one is superior? Why? (6)
- b With suitable mechanisms, obtain the first order and 3/2 order rate expression for thermal decomposition of acetaldehyde. (6)
- c Write a note on Kinetic isotopic effect. (3)
- OR
- d Discuss Rice - Herzfeld mechanism for decomposition of organic molecule. (5)
- e With neat sketch, account of first and second explosion limit in the reaction between H₂ and O₂. (5)
- f Discuss the statistical thermodynamic approach to AART. (5)
- 2 a Account on : Secondary salt effect and obtain Bronsted -Bjeruum equation. (4)
- b What do you mean enzyme catalysis? Explain the effect of pH in enzyme catalysis. (4)
- c Describe (i) Flash photolysis method and (ii) T-jump method in studying fast reaction kinetics. (4+3)
- OR
- d How does the rate of reactions depend on the following : (i) Internal pressure (i i) dielectric constant? (2+2)
- e Compare and contrast : Arrhenius intermediates and Van't Hoff intermediates. (4)
- f What is the need for the special techniques for the study of kinetics of fast reaction?
Describe stopped flow method in studying fast reaction kinetics. (2+5)
- 3 a Explain the method of determining surface areas of an absorbent from BET adsorption isotherm. (4)
- b Explain the term : G - value.
Write a note on : Dosimetry. (2+ 4)
- c Define the term quantum efficiency. Write the photochemical reaction mechanism for the following reaction and give the reason for high quantum yield. H₂(g) + Cl₂(g)→2HCl (g).
- " " OR
- d Deduce Langmuir adsorption isotherm and comment on its applications. (5)

- 3 Cont...
- e What are hydrated electrons? Briefly explain the mechanism of Radialysis of water. (2+4)
- f Calculate the number of moles of HCl produced by the absorption of one joule of radiant energy of wave length 480 nm in the photochemical reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$, if the quantum yield of the reaction is 1.0×10^6 . (4)
- 4 a What are ensembles? Give its different types and explain. (6)
- b Obtain the expression for Maxwell - Boltzmann statistics. (4)
- c Derive the expression for vibrational contribution to the thermodynamic function E. (5)
- OR
- d State and explain permutation and combination of statistical thermodynamics. (4)
- e Distinguish micro and macro states. (5)
- f Derive the expression for rotational contribution to the thermodynamic function C_v . (6)
- 5 a Derive expression for Bose - Einstein distribution law. (4)
- b Briefly discuss on heat capacity of solids. (6)
- c Account on : negative absolute temperature. (5)
- OR
- d Derive expression for Fermi - Dirac distribution law. (4)
- e Highlight the heat capacity of H_2 and NO gases. (6)
- f What do you mean phase space? (5)

Z-Z-Z**END**