PSG COLLEGE OF ARTS & SCIENCE
(AUTONOMOUS)

MSc DEGREE EXAMINATION DECEMBER 2018
(Third Semester)

Branch - **CHEMISTRY**

PHYSICALCHEMSTRY - III

Time : Three Hours Maximum : 75 Marks

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

1 a Discuss the modified form of Lindemann theory. (5)
b Account on : (i) Transmission coefficient (ii) Isokinetic temperature (6)
c Account on : Autooxidation. (4)

OR

d Apply statistical thermodynamics to study ARR theory. (6)
e With Rice - Herzfeld mechanism, discuss the reaction mechanism of thermal decomposition of CH_3CHO. (6)
f Obtain rate constant for the reaction :
$H_2 + Br_2 \rightarrow 2\ HBr$. with reaction mechanism (3)

2 a Apply AAR theory to study the role of solvent in chemical reactions. (6)
b Explain Bronsted catalytic law. (5)
c Discuss the relaxation theory in the study of fast reaction kinetics. (4)

OR

d Discuss secondary salt effect and obtain Bronsted - Bjerrum equation. (5)
e Highlight the effects of substrate concentration and pH of the medium in the determination of reaction rate. (4)
f Compare the techniques of stopped flow method and of continuous flow method. (5)

3 a What are hydrated electron? Mention its colour. (2)
b Mention the reactions taking place in radialysis of water. (4)
c Discuss Langmuir - Hinshelwood mechanism of surface reactions. (9)

OR

d Differentiate physisorption from chemisorption. (4)
e Write the reaction mechanism for the photochemical formation of HC1 for H_2 and Cl_2 molecules. (5)
f Highlight the importance of radiation chemistry in industry. (5)

4 a Compare microstate and macrostate. (6)
b The rotational constant of gaseous HC1 determined by microwave spectrum is 10.59 cm^{-1}. Calculate the rotational partition function of HC1atlOOK. (4)
c Evaluate the thermodynamic properties C_v and S from partition functions. (5)

OR

d Derive the expression for the translational partition function. (6)
e Write the general equations for (i) partition function and (ii) entropy in terms of partition function. (5)
f Hint on Combination and Permutation laws. (4)

5 a Explain with examples : Heat capacity of diatomic gases. (7)
b Obtain equilibrium constant from partition function. (5)
c Where is Fermi - Dirac statistics applied? (3)

OR