PSG COLLEGE OF ARTS & SCIENCE
(AUTONOMOUS)

MSc DEGREE EXAMINATION DECEMBER 2018
(Third Semester)

Branch - **CHEMISTRY**

<u>PHYSICALCHEMSTRY - III</u>

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   i
    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 :
        $H_2 + Br_2 \longrightarrow 2\,HBr$. 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
        HClat1OOK.   ...   (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)