Code No. : B/2058(C)

Fourth Semester Examination, May 2017

M.Sc. CHEMISTRY

Paper - IV

CHEMICAL KINETICS

Time : 3 Hrs.   Max.Marks : 80

Note : Section 'A' consists of 10 very short answer type questions, all of which are compulsory and should be attempted first. Section 'B' consists of four short answer type questions with internal options. Section 'C' consists of four long answer type questions with internal choice.

Section - 'A'

Answer the following very short-answer-type questions in one or two sentences :   **(2x10=20)**

Q.1   What is meant by complex reactions?

Q.2   Define microscopic.

Q.3   Differentiate between rate of reaction and specific rate of reaction.

Q.4   Write the expression for calculation of entropy of activation.

Q.5   For a reaction both ΔH and ΔS are positive. Under what condition, reactions will be spontaneous?

Q.6   What is the significance of Grunwald-Weinstein parameter?

Q.7   What is tunneling effect?

Q.8   Write Taft equation.

Q.9   What is Swain-Lupton equation?

Q.10   Write the Michaelis-Menten equation.

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Section - 'B'

Answer the following short-answer-type questions with word limit 200-250 :   (5x4=20)

Q.1   Discuss the kinetics and mechanism of thermal para-ortho hydrogen conversion.

OR

Derive an expression for the rate constant for an opposing reaction, when both the reactions are of first order.

Q.2   The rate constant of a reaction at 30° C is found to be exactly double than that of 20° C. Calculate the energy of activation for the reaction.

OR

Can the activation energy for a reaction be zero or negative? Explain.

Q.3   Define isotopic effect. Explain the semi-classical theory of primary kinetic isotopic effect.

OR

What would be the effect of increase in solvent polarity on the rate of a SN_1 Reaction?

Q.4   Explain the substituent effect on rate of a chemical reaction. How the acidity constant of a carboxylic acid is affected by replacing substituent?

OR

Discuss Linear Free Energy relationship giving appropriate examples.

Section - 'C'

Answer the following long-answer-type questions with word limit 400-450 :   (10x4=40)

Q.1   Give various types of Acid-Base catalysis with suitable examples and discuss its proposed mechanism.

OR

Describe the kinetics of formation and decomposition of phosgene.

Q.2   For the thermal combination of hydrogen and iodine at 283° C, at a concentration of one mole/dm^3, the number of molecules of hydrogen and iodine colliding per second is 6×10^{31}/cm^3. The actvation energy of the reaction is 187 kJ. Calculate the number of molecules reacting per cm^3.

OR

What is Hammett acidity function? Explain how it is useful in studying the dynamics of a chemical reaction?

Q.3   Explain the effect of solvent on elimination and nucleophilic substitution reactions.

OR

Describe the effect of solvent on reaction rate in terms of dielectric constant.

Q.4   Define substituent constant. Give a method of its estimation.

OR

Discuss Hammett Equation and explain its deviation. Mention the modifications proposed for it.

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