UNIT-V

9. (a) What do you mean by fast reactions? Discuss the Flash Photolysis Method for studying the kinetics of fast reactions. (1+3=4)

(b) What is meant by the term relaxation time? For a general reaction

$$A \rightleftharpoons B$$

which is first order in both directions. Obtain the relaxation time expression using the principle of the temperature jump technique. (1+5=6)

(b) The relaxation time for the fast reaction $A \rightleftharpoons B$ is 10 μs (*i.e.* microsecond) and the equilibrium constant is 1.0×10^{-3} mol dm^{-3}. Calculate the rate constant for the forward and reverse reaction. (4)

10. (a) Derive a mathematical relation between the rate and the concentration of the substrate of the enzyme-catalyzed reaction. Discuss the variation of the concentration of the substrate on the rate of the reaction. (3+2=5)

(b) Discuss the effect of reactants concentrations on the rate of homogeneous acid-catalyzed hydrolysis reaction with a suitable example. (4)

(c) Using the Rice-Herzfeld mechanism for the reaction

$$H_2 + Br_2 \rightarrow 2HBr$$

Derive the rate law expression for the formation of HBr. (5)

★★★

PG (CBCS) ODD SEMESTER EXAMINATION, 2022

CHEMISTRY

1st Semester

Course No. : CHMCC - 103

(Physical Chemistry - I)

Full Marks : 70

Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

(Answer any five questions, taking one from each unit)

UNIT - I

1. (a) State and explain the zeroth law of thermodynamics. How the concept of temperature isintroduced from the zeroth law of thermodynamics? 1+1+4 = 6

(b) Explain the term Clausius inequality in terms of reversible and irreversible changes. 4

(c) State and prove Euler's reciprocity relation for the exactness and hence show that for an ideal gas work function (W) is not an exact differential. 4

2. (a) Clearly stating the assumptions involved, show that for an adiabatic change of an ideal gas PV^{γ}= constant. 2+4=6

(b) What are the different types of Maxwell's relations? 4

(c) Give a graphical presentation of the Carnot cycle in a P-V diagram and hence, calculate the efficiency. 1+3=4

UNIT-II

3. (a) Calculate the change in entropy when the two ideal gases are mixed. 7

(b) Show that "G for any phase transition is always zero. 3

(c) what is fugacity and explain its variation with temperature and pressure? 1+3=4

4. (a) What is meant by chemical potentials? Derive the Gibbs-Duhem equation. 2+5=7

(b) State the phase rule. Discuss the derivation of the phase rule. 2+5 =7

UNIT-III

5. (a) Derive the expression for entropy production due to heat flow in an open system 7

(b) Derive Saxen's relation of the electrokinetic effect and show the interrelation between these effects. 2+5=7

6. (a) What is the principle of detailed balancing of chemical reactions? How does it lead to the principle of microscopic reversibility? 7

(b) Obtain the expression of the entropy production in chemical reaction. 7

UNIT-IV

7. (a) Derive a rate expression of a reaction between ions influenced by the ionic strength. (5)

(b) Show that for a gaseous bimolecular reaction

$A(g) + B(g) \rightarrow (AB)^{\#} \rightarrow$ Products,

$$E_a = \Delta H_m^{\#} + 2RT$$

Where subscript m stands for molar. (5)

(c) For the first-order isomerization of an organic compound at 130 °C, the activation energy is 108.4 kJmol^{-1} and the rate constant is 9.12×10^{-4} s^{-1}.Calculate the standard entropy of activation of the reaction. (4)

8. (a) Discuss the statistical mechanical derivation of the rate constant of a gaseous bimolecular reaction. (5)

(b) Drive the rate expression for the influence of solvent on the rates of ionic reactions. (5)

(c) The rate constant of a second-order reaction is 5.70×10^{-5} dm^{-3} mol^{-1} s^{-1} at 25 °C and 1.64×10^{-4} dm^{-3} mol^{-1} s^{-1} 40 °C. Calculate the activation energy and the pre-exponential factor. (4)