

## First Periodical Test, July-December, 2021

Class.....M.Sc. I SEMESTER.....

Subject.....CHEMISTRY.....

Paper (with code).....CHEM408 PHYSICAL CHEMISTRY.....

Max Marks. **10**

No. of Students: **40**

**Note:** Students are required to attempt **Three** questions. Question No. **1** is **compulsory**.

Q.1 (a) “Unimolecular reactions are not always of first order.” –Justify the statement using Lindmann mechanism. **[2]**

(b) The energy of activation for a bimolecular gaseous decomposition is 20000 Cal/ mol. Calculate the fraction of the molecule having sufficient energy to decompose at 27<sup>0</sup>C and at 227<sup>0</sup>C. **[2]**

Q.2 (a) Arrhenius factor “A” always have the same unit as the rate constant. Comment. **[1]**

(b) The rate of reaction is given by

$$\log k = A - \frac{B}{T} + C \log T.$$

Find the value of activation energy. **[2]**

**OR**

Q.3 The gas phase reaction  $\text{CO} + \text{Cl}_2 \xrightarrow{k} \text{COCl}_2$  is second order (first order in each reactant). If  $P_{\text{CO}}^0 = P_{\text{Cl}_2}^0 = 0.1$  atm and  $t_{1/2}$  is 1 hour at 25<sup>0</sup>C but 30 min and 35<sup>0</sup>C. then (a) Calculate  $k$  at 25<sup>0</sup>C (b) Calculate  $E$  and  $A$  of the Arrhenius equation and  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  of the transition state theory. **[3]**

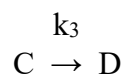
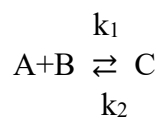
Q.4(a) Why is the transition state theory also termed as the absolute theory of reaction rates. **[1]**

(b) All collisions between activated molecule may not be successful. Why? **[1]**

(c) Calculate the rate constant for decomposition of HI at 500K, if energy of activation is 15 kJmol<sup>-1</sup> and collision diameter of HI is 3.5Å. **[1]**

OR

Q.5(a) For the mechanism,



- (i) Derive the rate law assuming the steady state approximation to eliminate the concentration of C.
- (ii) Assuming that  $k_3 \ll k_2$ , express the pre-exponential factor A and the overall activation energy E for the formation of D in terms of  $A_1, A_2$  and  $A_3$  and  $E_1, E_2$  and  $E_3$  for the three steps [2]
- (b) The value of  $\Delta S^\ddagger$  for a reaction has been obtained as  $-80.5 \text{ J K}^{-1} \text{ mol}^{-1}$  at 400K. Find the value of A for the reaction. [1]