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 27^0C and at 227^0C. **[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 $CO+Cl_2 \xrightarrow{k} COCl_2$ is second order (first order in each reactant). If $P^0_{co}=P^0_{Cl2}=0.1$ atm and $t_{1/2}$ is 1 hour at 25^0C but 30 min and 35^0C. then (a) Calculate k at 25^0C (b) Calculate E and A of the Arrhenius equation and $\Delta S^{\#}$ and $\Delta H^{\#}$ 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 $kJmol^{-1}$ and collision diameter of HI is 3.5A. **[1]**

OR

Q.5(a) For the mechanism,

$$A+B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C$$

$$C \xrightarrow{k_3} D$$

(i) Derive the rate law assuming the steady state approximation to eliminate the concentration of C.

(ii) Assuming that $k_3 << k_2$, 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 $\Delta S^{\#}$ for a reaction has been obtained as $-80.5 Jk^{-1}mol^{-1}$ at 400K. Find the value of A for the reaction. **[1]**