Chapter 2

Chemical Kinetics Lecture/Lession Plan -3

Chemical Kinetics

2.1 Effect of temperature on reaction rate

Rate of a chemical reaction increases with increase in temperature. But this increase of reaction rate is not uniform with every same change of temperature. Generally with every 10^{o}C increase in temperature, reaction rate increases by two to three fold. This fold change of reaction rate is known as temperature co-efficient.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

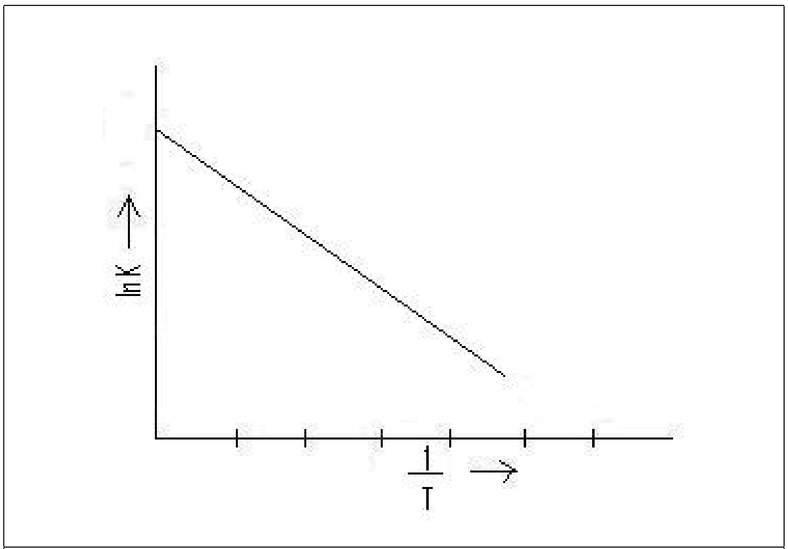
where k_t and k_{t+10} is the rate constant of a chemical reaction at t^0C and $(t + 10)^0$C respectively. Generally 25^0C and 35^0C temperature have been selected for this purpose.

Arrhenius proposed an empirical formula that correlates rate constant of a chemical reaction (k) with temperature at kelvin (T) also known as Temperature dependent rate equation .

$$k = A.e^{-E_a/RT}$$

where, k is the rate constant of a reaction at T kelvin; A is a constant called pre-exponential factor or sometime called frequency factor; E_a is activation energy and R is universal gas constant. By taking natural logarithm, the above reaction can be written as

$$\ln k = \ln A - \frac{E_a}{RT}$$



Plot lnk vs 1/T

If we plot this equation (lnk vs 1/T), we will get a straight line with a negative slope ($-E_a/R$)and the straight line will cut y axis at lnA point. So, from Arrhenius equation and corresponding graph we can get the value of pre-exponential factor (A). From the slope ($-E_a/R$) of the graph the value of activation energy can be determined. We can also say that if the value of activation energy (E_a) increases, the graph will be more steeper and hence the value of rate constant will decreases. So, activation energy have a direct effect on rate of a reaction. We can determine the value of activation energy if we know rate constant of a reaction at two different temperature.
If at T_1 and T_2 temperature, the rate constant of a chemical reaction is k_1 and k_2, then according to Arrhenius equation, we can write

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$
$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

or substracting both equation,

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}[\frac{1}{T_1} - \frac{1}{T_1}]$$

From this equation the value of activation energy (E_a) can be determined.

2.2 Activation Energy

In a chemical reaction reactant molecule does not directly goes to product in terms of energy; rather there is a high energy state compared to both reactant and product so that the all the reactant molecule must overcome this hight energy state and then they may be converted to product. This high energy state is known as transition state and the energy difference between reactant and transition state is known as activation energy (E_a). For a chemical reaction to happen all reactant

molecules must cross this energy barrier.
Let us consider for a chemical reaction the average energy of reactant molecules, product molecules and transition state are E_R, E_P and E_X respective. Now the activation energy E_{a1} will be the energy difference between transition state and reactant and E_{a2} is the energy difference between transition state and product.

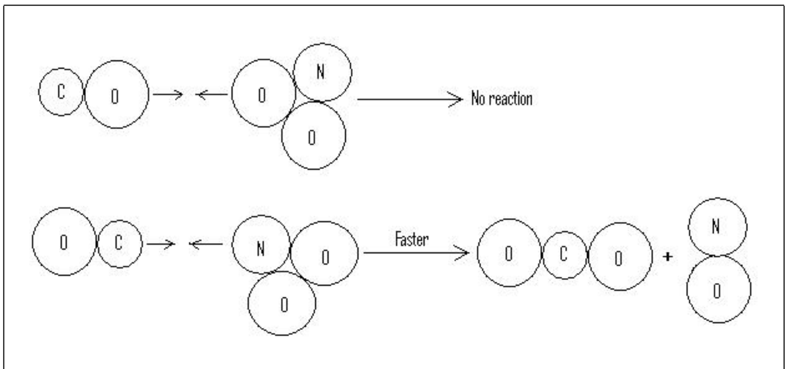
$$\begin{aligned} E_{a1} &= E_X - E_R \\ \text{and },E_{a2} &= E_X - E_P \end{aligned}$$

Now, if $E_{a1} < E_{a2}$, then the reaction will be exothermic reaction or heat will be released during reaction. if $E_{a1} > E_{a2}$, then the reaction will be endothermic reaction or heat will be absorbed during reaction.

2.3 Mechanism of Reaction

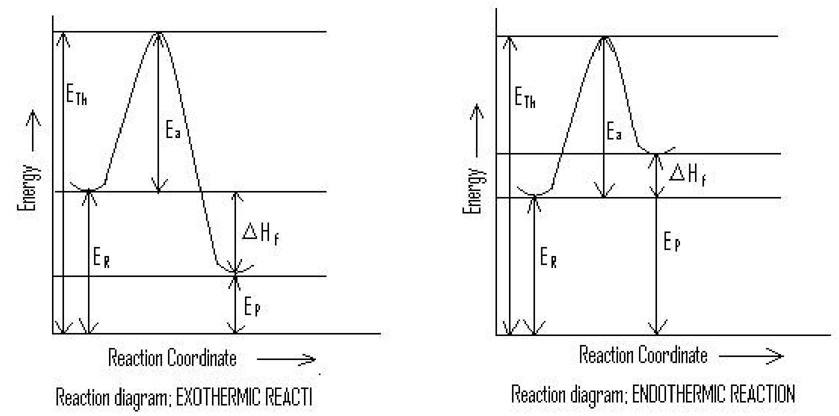
2.3.1 Postulates of Collision theory

Reactant molecules must collide with each other for a chemical reaction to happen; without collision, mixing of reactants does not lead to product formation.
All collision is not effective to transform reactants into products. Only effective collision transform reactants to products.
Only those collisions are effective where the colliding molecule's translational kinetic energy along the centre is equal or more than the activation energy of the reaction.
Drawback of collision theory: In collision theory reacting molecules are considered as hard sphere but this is true only for ideal gas.
The translational energy along the line of collision is considered as activation energy but the contribution other energy like vibrational or rotational motion have been ignored here.



Effective and ineffective collision

2.3.2 Postulates of transition state theory



Different transition state

According to transition state theory, reacting molecules are transformed into intermediate high energy state which is called transition state or activated complex. Now to form activated complex, reacting molecules must approach each other and during this approach constant continuous changes happens in bond length, bond angle of the reacting molecules and hence energy level increases.
The activated complex is a loose association of multiple reacting molecules. In activated complex both the bond breaking and new bond forming happens simultaneously.
The activated complex is unstable as it is highest energy state in the course of total reaction. Activated complex finally breaks into products.