## The Transition State Theory or The Theory of Absolute Reaction Rates

The collision theory of reaction rates suffers from the following drawback: (i) It is difficult to calculate the steric factor from molecular geometry for complex molecules; (ii) the theory is applicable essentially to gaseous reactions. An alternate theory called absolute reaction rate theory or frequently known as transition state theory of reaction rates has been developed by Eyring in 1935. This theory attempts to treat the reaction rates from thermodynamic considerations. It is assumed that an equilibrium is established between the reactions and the activated complex. The activated complex is treated formally as a molecule in spite of its transitory existence and the laws of thermodynamics can be applied to it. As stated previously that all the reactions proceeds through an activated or transition state which has energy higher than the reactants or the products. The rate of reaction depends upon two factors, viz, (i) the concentration of the transition state species and (ii) the rate at which the activated complex decomposes. Consider a simple biomolecular reaction between molecules A and B as

$$A + B \rightleftharpoons [AB^{\ddagger}] \xrightarrow{k_2} \text{Products}$$

**The rate of such a reaction = [concentration of activated complex molecule] X [Frequency of decomposition of the activated complex into the products]**

In order to calculate the concentration of activated complex it is assumed that the complex is in equilibrium with the reactant molecules. Hence the equilibrium constant $K^{\ddagger}_{eq}$ is given as

$$K^{\ddagger}_{eq} = \frac{[AB^{\ddagger}]}{[A][B]}$$

$$[AB^{\ddagger}] = K^{\ddagger}_{eq}[A][B] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (80)$$

The activated complex is an aggregate of atoms and is assumed to be similar to an ordinary molecule except that it breaks up into products at a special vibration at which it is unstable. The frequency of such a vibration is something like the rate at which the activated complex decomposes. If ν is the frequency of such a vibration, then the rate of decomposition of the activated complex is given as

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A][B]$$

$$= [AB^{\ddagger}]\,\nu = K^{\ddagger}_{eq}\,[A][B]\nu \qquad \ldots\ldots\ldots\ldots\ldots\ldots (81)$$

Since an activated complex is an unstable species and is held together by loose bonds, therefore the vibration of low frequency will decompose the activated complex. The average energy of such a vibrational degree of freedom is given by kT (where k is the Boltzmann constant and is equal to R/N where N is the Avogadro constant ). The energy of E of this vibration is given by Planck's expression, E=hν.

$$\nu = E/h = kT/h = RT/N_Ah$$

Substituting this value of ν in Eq.(81), we get

$$k_2[A][B] = K^{\ddagger}_{eq}[A][B]\frac{RT}{N_Ah}$$

$$k_2 = K^{\ddagger}_{eq}\frac{RT}{N_Ah} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(82)$$

## Thermodynamic Aspects:

The result given by expression eq.(82) is of importance when the equilibrium constant is interpreted thermodynamically by introducing the terms, free energy of activation, $\Delta G^{\ddagger}$, the enthalphy of activation, $\Delta H^{\ddagger}$ and the entropy of activation ,$\Delta S^{\ddagger}$ ,. These quantities represent the difference between the values of the respective thermodynamic functions between the activated complex and the reactants, all substances being in their standard state , i.e., activity being unity.

Since we have

$$\Delta G^{\ddagger} = -RT\ln K^{\ddagger}_{eq}$$

$$\ln K^{\ddagger}_{eq} = -\Delta G^{\ddagger}/RT \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (83)$$

and

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(84)$$

Putting the value of $\Delta G^{\ddagger}$ in Eq. (83), we get

$$\ln K^{\ddagger}_{eq} = -\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}$$

$$K^{\ddagger}_{eq} = \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)\exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (85)$$

Substituting this value of $K^{\ddagger}_{eq}$ in Eq. (82) gives

$$k_2 = \frac{RT}{N_Ah}\left[\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots (86)$$

Equation (86) can be expressed in a form which involves the experimental activation energy $E_a$ instead of enthalphy of activation $\Delta H^{\ddagger}$ . The variation of $K^{\ddagger}_{eq}$ with temperature is given by

$$\frac{d\ln K^{\ddagger}_{eq}}{dt} = \frac{\Delta E^{\ddagger}}{RT^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(87)$$

Where $\Delta E^{\ddagger}$ represents the increase in energy when the reactants go from the initial state to the activated state. Taking logarithm of Eq. (82) , we get

$$\ln k_2 = \ln T + \ln K^{\ddagger}_{eq} + \ln \frac{R}{N_A h} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(88)$$

Differentiating the above equation with respect to the temperature, we obtain

$$\frac{d\ln k_2}{dT} = \frac{1}{T} + \frac{d\ln K^{\ddagger}_{eq}}{dT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(89)$$

Substituting the value $d\ln K^{\ddagger}_{eq}/dT$ from Eq. (87)

$$\frac{d\ln k_2}{dT} = \frac{1}{T} + \frac{\Delta E^{\ddagger}}{RT^2}$$

$$= \frac{RT + \Delta E^{\ddagger}}{RT^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (90)$$

Comparison of Eq.(90) with Eq.(65) leads to

**$d\ln k/dT = E_a/RT^2$**.... (65)

$$E_a = \Delta E^{\ddagger} + RT$$

Since $\qquad \Delta E^{\ddagger} = \Delta H^{\ddagger} - P\Delta V^{\ddagger}$

Therefore $\qquad E_a = \Delta H^{\ddagger} + RT - P\Delta V^{\ddagger}$ …………………………….(91)

For ideal gases , Eq. (91) reduces to $\quad E_a = \Delta H^{\ddagger} + RT - \Delta n^{\ddagger}RT$ ( as $P\Delta V^{\ddagger} = \Delta n^{\ddagger}RT$) ……(92)

Where $\Delta V^{\ddagger}$ is the change in volume and $\Delta n^{\ddagger}$ is the change in number of molecules passing from the initial state to the activated state. For a unimolecular reaction, there is no change in the number of molecules as the activated complex is formed. Therefore, $\Delta V^{\ddagger}$ is zero and Eq.(91) reduces to

$$E_a = \Delta H^{\ddagger} + RT \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (93)$$

and the rate Eq. (86) becomes

$$k_2 = \frac{RT}{N_A h}\left[\exp\left(-\frac{E_a - RT}{RT}\right)\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\right]$$

$$= \frac{RT}{N_A h}\left[\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{E_a}{RT}\right) e\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (94)$$

For a biomolecular reaction $\Delta n^{\ddagger} = -1$ and Eq. (92) becomes

$E_a = \Delta H^{\ddagger} + 2RT$ …………………………… (94)

The rate Eq. (86) now becomes

$$k_2 = \frac{RT}{N_A h}\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{E_a - 2RT}{RT}\right)$$

$$= \frac{RT}{N_A h}\left[\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{E_a}{RT}\right)e^{2}\right]$$

……………(95)

The entropy of activation can be calculated from the experimental values of rate constant and activation energy. It has been found that the difference between $\Delta H^{\ddagger}$ and $E_a$ is small and in fact, for reactions in solutions and for unimolecular reaction $\Delta H^{\ddagger} \approx E_a$. In other cases involving gases , an additional term $\Delta n^{\ddagger}RT$ has been included. Hence without much error, we may write

$$k_2 = \frac{RT}{N_A h}\left[\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{E_a}{RT}\right)\right]$$

………………(96)

$$= \frac{RT}{N_A h}\left[\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)\right]$$

……………(97)

The expression resembles the Arrhenius equation except that $\Delta H^{\ddagger}$ appears instead of $E_a$. The quantity $\Delta H^{\ddagger}$ is often called the enthaphy of activation. A comparison of Eq. (97) with Eq. (68) shows that the pre-exponential factor A is related to the entropy of activation as

$k=Ae^{-E_a/RT}$…(68)

$$A = \frac{RT}{N_A h}\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$$

…………………………………(98)

An exact calculation of A needs the evaluation of $\Delta S^{\ddagger}$. A negative value of $\Delta S^{\ddagger}$ means that the activated complex is more ordered than the reactants. A more negative value of $\Delta S^{\ddagger}$ indicates that A will have smaller value which means the reaction will be slower. A positive value of activation entropy $\Delta S^{\ddagger}$ means that the entropy of the complex is greater than the entropy of the reactants. A loosely bound complex has a higher entropy than a tightly bound one. More often there is a decrease in entropy in passing through the activated complex. The steric (probability) factor used in the collision theory is more or less analogous to the entropy of activation in the transition state theory. It should be noted that the quantity $RT/N_0h$ does not depend on the nature of the reactant or activated complex and , therefore, will be same for all reactions at the same temperature.

From the collision theory, $k_2=PZ_{11}\exp(-E_a/RT)$ i.e., the activation energy determines $k_2$,while in transition state theory it is determined by the free energy of activation, $\Delta G^{\ddagger}$. For slower reactions, a higher value of $\Delta G^{\ddagger}$ will be observed at a given temperature. Since

$k_2=PZ_{11}\exp(-E_a/RT)$ (from collision theory) ……… (99)

and $k_2 = \frac{RT}{N_A h}\left[\exp\left(\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)\right]$ (from transition state theory) …… (100)

Hence the orientation factor P is related to $\Delta S^{\ddagger}$, i.e., the entropy of activation. The steric (probability) factor A in the Arrhenius equation is equal to $Z_{11}$ of the collision theory and is equal to $RT/N_Ah \exp(\Delta S^{\ddagger}/R)$.

For simple molecules these values are identical. For more complex reactant molecules where the collision theory fails the transition state theory still gives satisfactory value of A.

## ❖ Theory of Unimolecular Reactions

The collision theory and the absolute reaction rate theory satisfactorily account for the biomolecular reaction. However, a number of unimolecular gaseous reactions have been studied, which were found to be of first order as , for example, the decomposition of $N_2O_5$

$$N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$$

If the energy of activation of these first order reactions is believed to come from biomolecular collisions then the question that arises is how these reactions occur. To investigate the kinetics of such reactions , Lindemann in 1922 proposed that the behavior of unimolecular reactions can be explained on the basis of biomolecular collisions. It is proposed that when the reactant molecules are activated by collisions with other molecules there may be a time lag before decomposition of the activated molecules. In other words, the activated molecules do not decompose immediately into products but remain in the activated state for a finite time. During this time –lag, the energized molecules may lose their extra energy in a second biomolecular collision or it may be deactivated to ordinary molecules. Consequently, the rate of the reaction will not be proportional to all the molecules activated but only to those which remain active. The process of activation or deactivation by collisions may be represented by the following mechanism:

$$A+A \xrightarrow{k_1} A+A^* \qquad \text{(activation)}$$

$$A+A^* \xrightarrow{k_2} A+A \qquad \text{(deactivation)}$$

$$A^* \xrightarrow{k_3} \text{Products} \qquad \text{(decomposition)}$$

where A is an inactive molecule and $A^*$ the activated molecule. The rate at which A will disappear is proportional to the concentration of $A^*$ , viz.,

$$-\frac{d[A]}{dt} = k_3[A^*] = k_1[A]^2 - k_2[A][A^*] \qquad \text{…………………..(101)}$$

Since $[A^*]$ is not known and it is necessary to obtain it in terms of [A] this can be done with the help of steady state principle. According to this, it is assumed that in the steady state the concentration of the intermediate (activated complex) is small and does not change with time , i.e, the rate of formation and the rate of decomposition of the intermediate are equal, i.e,

$$k_1[A]^2 - k_2[A][A^*] - k_3[A^*] = 0$$

$$k_1[A]^2 - k_2[A][A^*] = k_3[A^*]$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3}$$

Hence,

$$-\frac{d[A]}{dt} = \frac{k_3 k_1[A]^2}{k_3 + k_2[A]} \qquad \text{……………………………(102)}$$

Equation (102) predicts two limiting possibilities.

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**Case I:** When $k_2[A] >> k_3$ Eq. (102) reduces to

$$-\frac{d[A]}{dt} = \frac{k_3 k_1}{k_2}[A]$$

which is a first order rate equation. This corresponds to a situation in which the concentration of A is high enough to produce appreciable deactivation of $A^*$ by collisions with A so that the rate of deactivation $k_2[A][A^*]$ is appreciably large in comparison to the rate of decomposition, $k_3[A^*]$.

**Case II:** When $k_3 >> k_2[A]$ i.e rate of decomposition is large as compared to the rate of deactivation Eq. (102) becomes

$$-\frac{d[A]}{dt} = k_1 [A]^2$$

In such cases the reaction should be of second order. This situation corresponds to low concentration of A where the rate of activation becomes slow and hence the rate controlling.

In gaseous reaction as the pressure of the system is decreased, the deactivation, $k_2[A][A^*]$, decreases . At low pressure, therefore, the conditions for the first order kinetics fail and $k_2[A]$ is no longer greater than $k_3$. Thus the first order kinetics is replaced by the second order kinetics.

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