❖ Activated Complex Theory

In 1935, an American chemist Henry Eyring; alongside two British chemists, Meredith Gwynne Evans and Michael Polanyi; proposed a new theory to rationalize the rate of different chemical reactions which was based upon the formation of an activated intermediate complex. This theory is also known as the "transition state theory", "theory of absolute reaction rates", and "absolute-rate theory".

The activated complex theory states that the rates of various elementary chemical reactions can be explained by assuming a special type of chemical equilibria (quasi-equilibrium) between reactants and activated complexes.

Before the development of activated complex theory, the Arrhenius rate law was popularly used to determine energies for the potential barrier. However, the Arrhenius equation was based on empirical observations rather than mechanistic investigations as if one or more intermediates are involved in the conversion or not. For that reason, more development was essential to know the two factors present in the Arrhenius equation, the activation energy (E_a) and the pre-exponential factor (A). The Eyring equation from transition state theory successfully addresses these two issues and therefore contributed significantly to the conceptual understanding of reaction kinetics.

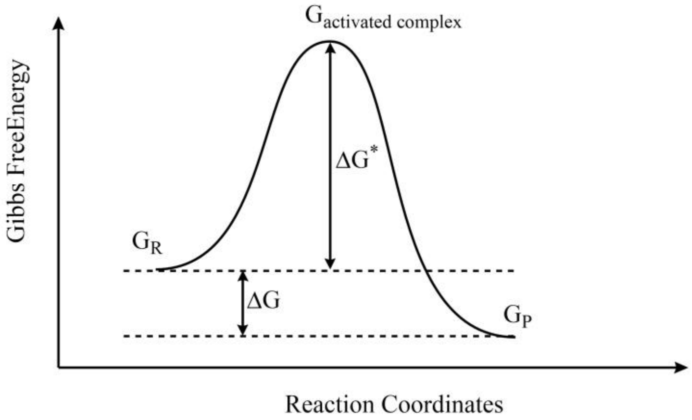


Figure 11. The variation of free energy as the reaction proceeds.

To explore the concept mathematically, consider a reaction between reactant A and B forming a product P via the activated complex X^* as:

$$A + B \overset{K^*}{\rightleftharpoons} X^* \xrightarrow{k} P \tag{178}$$

The equilibrium constant for reactants to activated complex conversion is

$$K^* = \frac{[X^*]}{[A][B]} \tag{179}$$

Henry Eyring showed that the rate constant for a chemical reaction with any order or molecularity can be given by the following relation.

$$k = \frac{RT}{Nh} K^* \tag{180}$$

Where K^* is the equilibrium constant for reactants to activated complex conversion at temperature T. Whereas, R, N and h represent the gas constant, Avogadro number and Planck's constant, respectively. Now, as we know from thermodynamics

$$\Delta G^* = -RT \ln K^* \tag{181}$$

$$-\frac{\Delta G^*}{RT} = \ln K^* \tag{182}$$

$$K^* = e^{-\frac{\Delta G^*}{RT}} \tag{183}$$

Where ΔG^* is the free energy of activation for reactants to activated complex conversion step. Using the value of K^* from equation (183) into equation (180), we get

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} \tag{184}$$

If we put the thermodynamic value of free energy i.e. $\Delta G^* = \Delta H^* - T\Delta S^*$ in equation (184), we get

$$k = \frac{RT}{Nh} e^{-\frac{(\Delta H^* - T\Delta S^*)}{RT}} \tag{185}$$

or

$$k = \frac{RT}{Nh} \times e^{\frac{\Delta S^*}{R}} \times e^{-\frac{\Delta H^*}{RT}} \tag{186}$$

Where ΔH^* and ΔS^* are enthalpy change and the entropy change of the activation step. Equation (186) is popularly known as the Eyring equation. Now, since the equation (186) contains very fundamental factors of the reacting species, that is why this theory got its name of "theory of absolute reaction rates".

➢ *Significance of Entropy of Activation and Enthalpy of Activation*

As far as the equation (184) is concerned, it can easily be seen that as the free energy change of the activation step increases, the rate constant would decrease. However, if we look at the simplified form i.e. equation (186), we find three factors; one is RT/Nh which is constant if the temperature is kept constant. The second factor involves ΔS^*, and therefore, we can conclude that the reaction rate would show exponential increase if the entropy of activation increases. The third factor includes ΔH^*, and therefore, we can conclude that the reaction rate would show exponential decrease if the enthalpy of activation increases. It is also worthy to note that the first two terms collectively make the frequency factor.

➢ ***Comparison with Arrhenius Rate Constant***

Like the collision theory, the validity of the "activated complex theory" must also be checked against the results of the Arrhenius rate equation. In order to do so, recall the Arrhenius equation i.e.

$$k = A\, e^{-\frac{E_a}{RT}} \tag{187}$$

By looking at the analogy with equation (187), we get

$$A = \frac{RT}{Nh} \times e^{\frac{\Delta S^*}{R}} \tag{188}$$

and

$$e^{-\frac{E_a}{RT}} = e^{-\frac{\Delta H^*}{RT}} \tag{189}$$

Now we can use equation (188) and (189) to determine the value of entropy of activation and enthalpy of activation.

1. Calculation of entropy of activation: In order to determine the entropy change of the activation step, take the natural logarithm of the equation (188) i.e.

$$\ln A = \ln \frac{RT}{Nh} + \ln e^{\frac{\Delta S^*}{R}} \tag{190}$$

$$\ln A = \ln \frac{RT}{Nh} + \frac{\Delta S^*}{R} \tag{191}$$

or

$$\frac{\Delta S^*}{R} = \ln A - \ln \frac{RT}{Nh} \tag{192}$$

$$\Delta S^* = R \ln A - R \ln \frac{RT}{Nh} \tag{193}$$

Thus, higher is the value of the frequency factor, larger will be the entropy of activation.

2. Calculation of enthalpy of activation: In order to determine the entropy change of the activation step, we must look at the equation (189) which suggests that the enthalpy change of the activation step as exactly equal to the activation energy of the reaction dictating the rate considerably i.e. $\Delta H^* = E_a$. However, it has been observed that the exact value of activation energy is slightly different than the enthalpy of activation. In order to prove the aforementioned statement, rewrite the equation (186) as:

$$k = \frac{R}{Nh} e^{\frac{\Delta S^*}{R}} \times T \times e^{-\frac{\Delta H^*}{RT}} \tag{194}$$

or

$$k = C \times T \times e^{-\frac{\Delta H^*}{RT}} \tag{195}$$

Where C is another constant. Now taking natural logarithm both side, equation (195) takes the form

$$\ln k = \ln C + \ln T + \ln e^{-\frac{\Delta H^*}{RT}} \tag{196}$$

or

$$\ln k = \ln C + \ln T - \frac{\Delta H^*}{RT} \tag{197}$$

Now, differentiating both side w.r.t temperature, we get

$$\frac{\mathrm{d} \ln k}{dt} = \frac{1}{T} + \frac{\Delta H^*}{RT^2} \tag{198}$$

We also know from the Arrhenius equation that

$$k = A\, e^{-\frac{E_a}{RT}} \tag{199}$$

Now taking natural logarithm both side, equation (199) takes the form

$$\ln k = \ln A + \ln e^{-\frac{E_a}{RT}} \tag{200}$$

or

$$\ln k = \ln A - \frac{E_a}{RT} \tag{201}$$

Now, differentiating both side w.r.t temperature, we get

$$\frac{\mathrm{d} \ln k}{dt} = \frac{E_a}{RT^2} \tag{202}$$

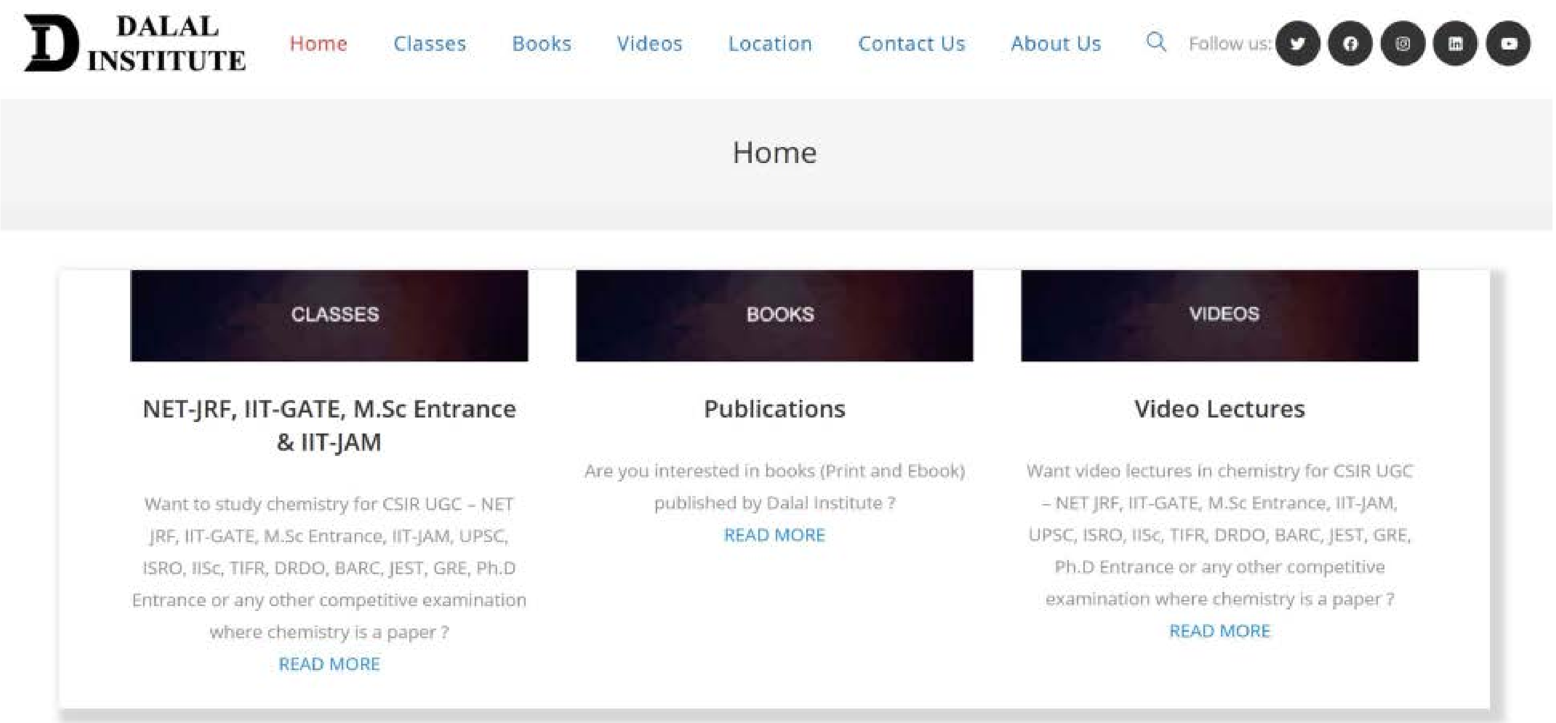
Comparing (198) and (202), we get

$$\frac{1}{T} + \frac{\Delta H^*}{RT^2} = \frac{E_a}{RT^2} \tag{203}$$

$$\frac{RT + \Delta H^*}{RT^2} = \frac{E_a}{RT^2} \tag{204}$$

$$\Delta H^* = E_a - RT \tag{205}$$

If n is the change in the number of moles of gas in going from reactant to activated complex, the result of equation (205) takes the form $\Delta H^* = E_a - \Delta n_g RT$.



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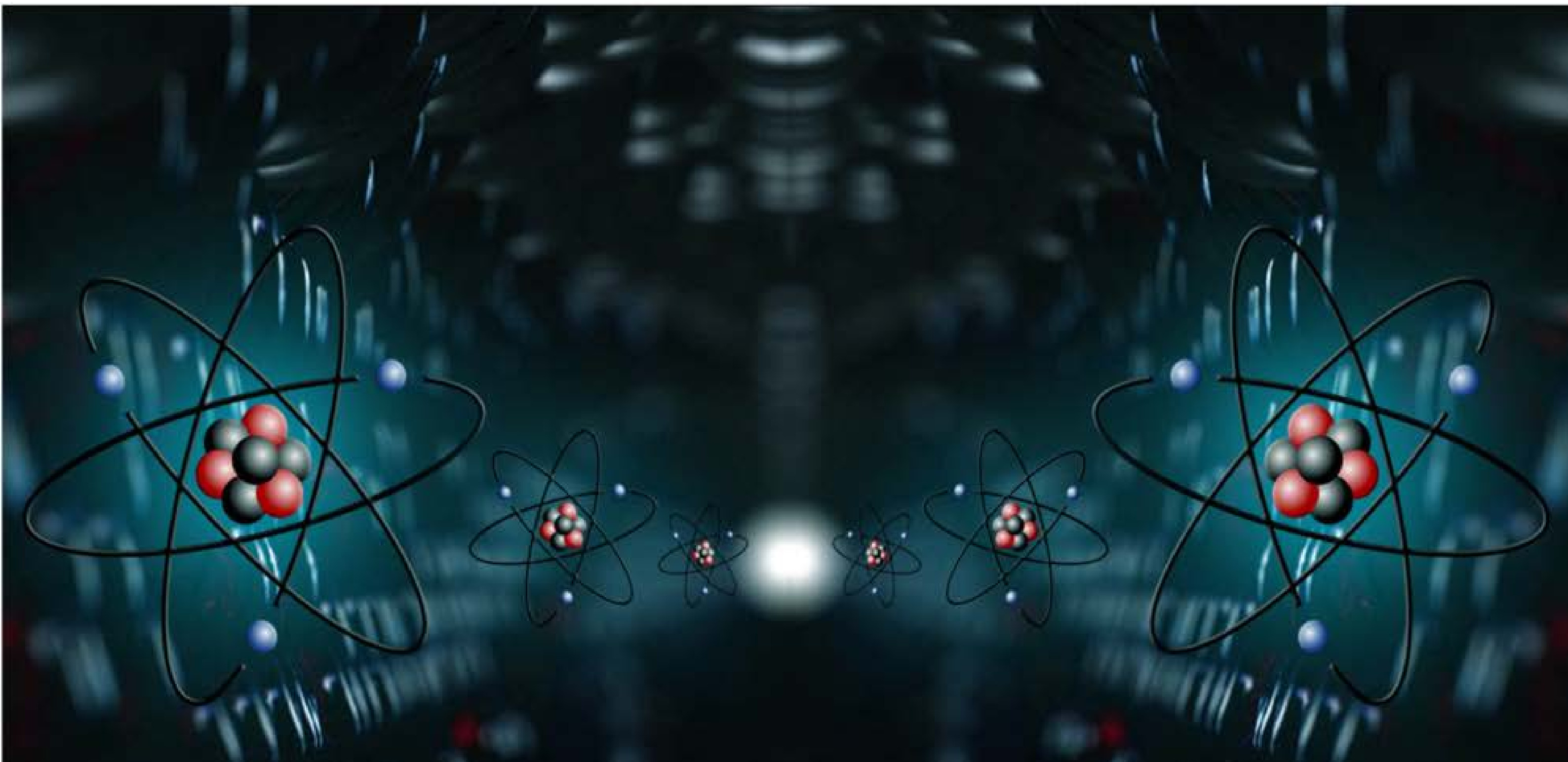

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