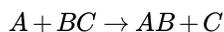
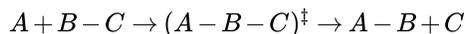


11.11: Transition State Theory

Transition state theory was proposed in 1935 by Henry Eyring, and further developed by Merrideth G. Evans and Michael Polanyi (Laidler & King, 1983), as another means of accounting for chemical reaction rates. It is based on the idea that a molecular collision that leads to reaction must pass through an intermediate state known as the transition state. For example, the reaction



would have an intermediate (ABC) where the $B - C$ bond is partially broken, and the $A - B$ bond is partially formed.



So the reaction is mediated by the formation of an activated complex (denoted with the double-dagger symbol \ddagger) and the decomposition of that complex into the reaction products. Using this theory, the rate of reaction can be expressed as the product of two factors

$$\text{rate} = (\text{transition state concentration}) \times (\text{decomposition frequency})$$

If the formation of the activated complex is considered to reach an equilibrium,

$$K^\ddagger = \frac{[ABC]^\ddagger}{[A][BC]}$$

So the concentration of the transition state complex can be expressed by

$$[ABC]^\ddagger = K^\ddagger [A][BC]$$

Using the relationship from Chapter 9 for the equilibrium constant, K^\ddagger can be expressed in terms of the free energy of formation of the complex (ΔG^\ddagger)

$$K^\ddagger = e^{-\Delta G^\ddagger/RT}$$

And so the reaction rate is given by

$$\text{rate} = (\text{frequency})[A][BC]e^{-\Delta G^\ddagger/RT}$$

and the remaining task is to derive an expression for the frequency factor. If the frequency is taken to be equal to the vibrational frequency for the vibration of the bond being broken in the activated complex in order to form the reaction products, it can be expressed in terms of the energy of the oscillation of the bond as the complex vibrates.

$$E = h\nu = k_B T$$

or

$$\nu = \frac{k_B T}{h}$$

The reaction rate is then predicted to be

$$\text{rate} = \frac{k_B T}{h} [A][BC] e^{-\Delta G^\ddagger/RT}$$

And the rate constant is thus given by

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}$$

An alternative description gives the transition state formation equilibrium constant in terms of the partition functions describing the reactants and the transition state:

$$K^\ddagger = \frac{Q^\ddagger}{Q_A^\ddagger Q_{BC}^\ddagger} e^{-\Delta G^\ddagger/RT}$$

where Q_i is the **partition function** describing the i^{th} species. If the partition function of the transition state is expressed as a product of the partition function excluding and contribution from the vibration leading to the bond cleavage that forms the products and the partition function of that specific vibrational mode

$$Q^\ddagger = Q' q_v^\ddagger$$

In this case, q_v^\ddagger can be expressed by

$$q_v^\ddagger = \frac{1}{1 - e^{-h\nu^\ddagger/RT}} \approx \frac{k_B T}{h\nu^\ddagger}$$

So the equilibrium constant can be expressed

$$K^\ddagger = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A^\ddagger Q_{BC}^\ddagger} e^{-\Delta G^\ddagger/RT}$$

And so the rate constant, which is the product of n^\ddagger and K^\ddagger , is given by

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A^\ddagger Q_{BC}^\ddagger} e^{-\Delta G^\ddagger/RT}$$

which looks very much like the Arrhenius equation proposed quite a few years earlier! Thus, if one understands the vibrational dynamics of the activated complex, and can calculate the partition functions describing the reactants and the transition state, one can, at least in theory, predict the rate constant for the reaction. In the next chapter, we will take a look at how kinetics studies can shed some light on chemical reaction mechanisms.

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