Transition state diagram is no longer symmetrical because there is an energy difference between reactants and products.

Thermodynamics of the Transition State

The realization that the attainment of the transition state is the central requirement in any reaction process led to a detailed understanding of reaction mechanisms. For example, consider a bimolecular reaction that proceeds along the following pathway:

$$A + B \overset{k^+}{\rightleftharpoons} X^+ \overset{k}{\rightarrow} P + Q$$

where $X^+$ represents the activated complex. Therefore, considering the preceding discussion,

$$\frac{d[P]}{dt} = k[A][B] = k'[X^+] \quad [13.7]$$

where $k$ is the ordinary rate constant of the elementary reaction and $k'$ is the rate constant for the decomposition of $X^+$ to products.

In contrast to stable molecules, such as $A$ and $P$, which occur at energy minima, the activated complex occurs at an energy maximum and is therefore only metastable (like a ball balanced on a pin). Transition state theory nevertheless assumes that $X^+$ is in rapid equilibrium with the reactants; that is,

$$K^+ = \frac{[X^+]}{[A][B]} \quad [13.8]$$

where $K^+$ is an equilibrium constant. This central assumption of transition state theory permits the powerful formalism of thermodynamics to be applied to the theory of reaction rates.

If $K^+$ is an equilibrium constant it can be expressed as:

$$-RT \ln K^+ = \Delta G^+ \quad [13.9]$$

where $\Delta G^+$ is the Gibbs free energy of the activated complex less that of the reactants (Fig. 13-4b), $T$ is the absolute temperature, and $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is the gas constant (this relationship between equilibrium constants and free energy is derived in Section 3-4A). Then combining Eqs. [13.7] through [13.9] yields

$$\frac{d[P]}{dt} = k'e^{-\Delta G^+/RT}[A][B] \quad [13.10]$$

This equation indicates that the rate of a reaction depends not only on the concentrations of its reactants but also decreases exponentially with $\Delta G^+$. Thus, the larger the difference between the free energy of the transition state and that of the reactants, that is, the less stable the transition state, the slower the reaction proceeds.

In order to continue, we must now evaluate $k'$, the rate of passage of the activated complex over the maximum in the transition state diagram (sometimes referred to as the activation barrier or the kinetic barrier of the reaction). This transition state model permits us to do so (although the following derivation is by no means rigorous). The activated complex is held together by a bond that is associated with the reaction coordinate and that is assumed to be so weak that it flies apart during its first vibrational excursion. Therefore, $k'$ is expressed

$$k' = k\nu \quad [13.11]$$

where $\nu$ is the vibrational frequency of the bond that breaks as the activated complex decomposes to products and $k$, the transmission coefficient, is the probability that the breakdown of the activated complex, $X^+$, will be in the direction of product formation rather than back to reactants. For most spontaneous reactions in solution, $k$ is between 0.5 and 1.0; for the colinear $H + H_2$ reaction, we saw that it is 0.5.

We have nearly finished our job of evaluating $k'$. All that remains is to determine the value of $\nu$. Planck's law states that

$$\nu = \frac{e}{h} \quad [13.12]$$