

c. Multistep Reactions Have Rate-Determining Steps

Since chemical reactions commonly consist of several elementary reaction steps, let us consider how transition state theory treats such reactions. For a multistep reaction such as



where I is an intermediate of the reaction, there is an activated complex for each elementary reaction step; the shape of the transition state diagram for such a reaction reflects the relative rates of the elementary reactions involved. For this reaction, if the first reaction step is slower than the second reaction step ($k_1 < k_2$), then the activation barrier of the first step must be higher than that of the second step, and conversely if the second reaction step is the slower (Fig. 14-5). Since the rate of formation of product P can only be as fast as the slowest elementary reaction, if one reaction step of an overall reaction is much slower than the other, the slow step acts as a "bottleneck" and is therefore said to be the rate-determining step of the reaction.

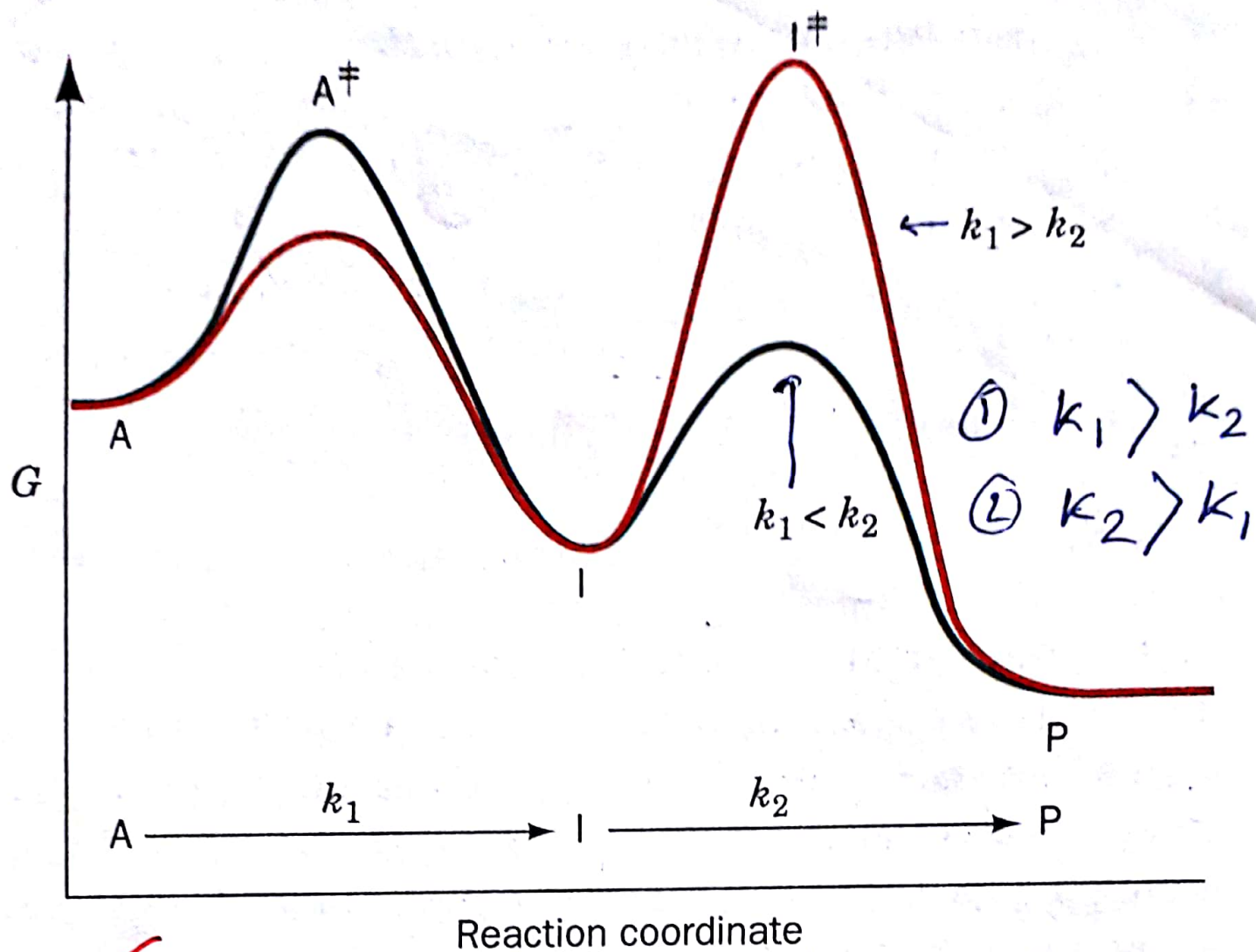
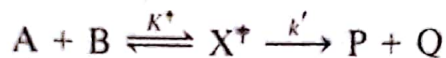


FIGURE 14-5 Transition state diagram for the two-step overall reaction $A \rightarrow I \rightarrow P$. For $k_1 < k_2$ (green curve), the first step is rate determining, whereas if $k_1 > k_2$ (red curve), the second step is rate determining.

b. 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:



where X^\ddagger represents the activated complex. Therefore, considering the preceding discussion,

$$\frac{d[P]}{dt} = k[A][B] = k'[X^\ddagger] \quad [14.7]$$

where k is the ordinary rate constant of the elementary reaction and k' is the rate constant for the decomposition of X^\ddagger 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^\ddagger is in rapid equilibrium with the reactants; that is,

$$K^\ddagger = \frac{X^\ddagger}{[A][B]} \quad [14.8]$$

where K^\ddagger 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^\ddagger is an equilibrium constant it can be expressed as:

$$-RT \ln K^\ddagger = \Delta G^\ddagger \quad [14.9]$$

where ΔG^\ddagger is the Gibbs free energy of the activated complex less that of the reactants (Fig. 14-4b), 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. [14.7] through [14.9] yields

$$\frac{d[P]}{dt} = k' e^{-\Delta G^\ddagger/RT} [A][B] \quad [14.10]$$

This equation indicates that the rate of a reaction depends not only on the concentrations of its reactants but also decreases exponentially with ΔG^\ddagger . 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.