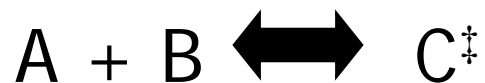


The transition state

The activated complex is a distorted structure that is intermediate between the structure of the reactants and that of the products. Today we call this the transition state, which is the structure at the peak of the potential energy surface between the reactants and products. The fundamental assumption of transition state theory is that the transition state is in equilibrium with the reactants and products.



The assumption of equilibrium between the reactants and the transition state

Since the formation of the transition state C^\ddagger occurs in equilibrium with the reactants we can express the equilibrium constant as

$$K^\ddagger = \frac{[C^\ddagger]}{[A][B]}$$

and the rate constant is given by the product of a frequency factor $k_B T/h$ for the formation of the complex times the equilibrium constant.

Relationship of transition state rate constant to Arrhenius parameters

The transition state rate constant

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

is

$$k = (k_B T/h) e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

and the Arrhenius rate constant is

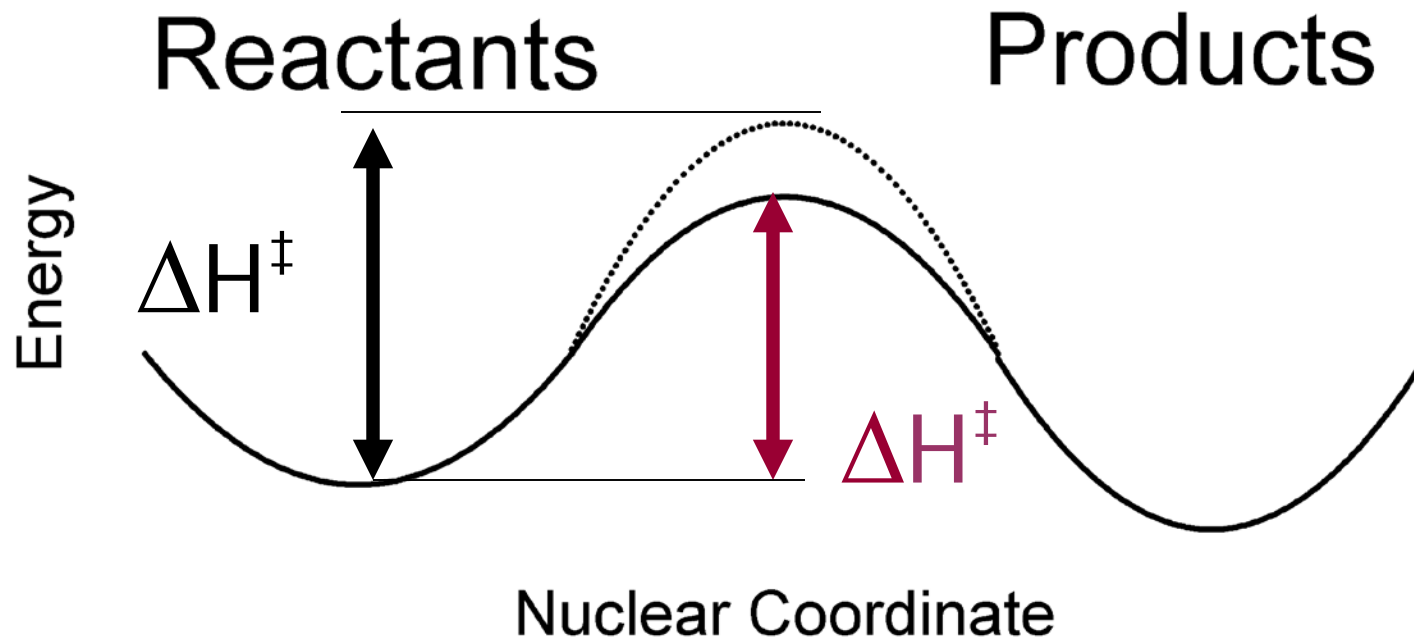
$$k = A e^{-E_a/RT}$$

which leads to the identification

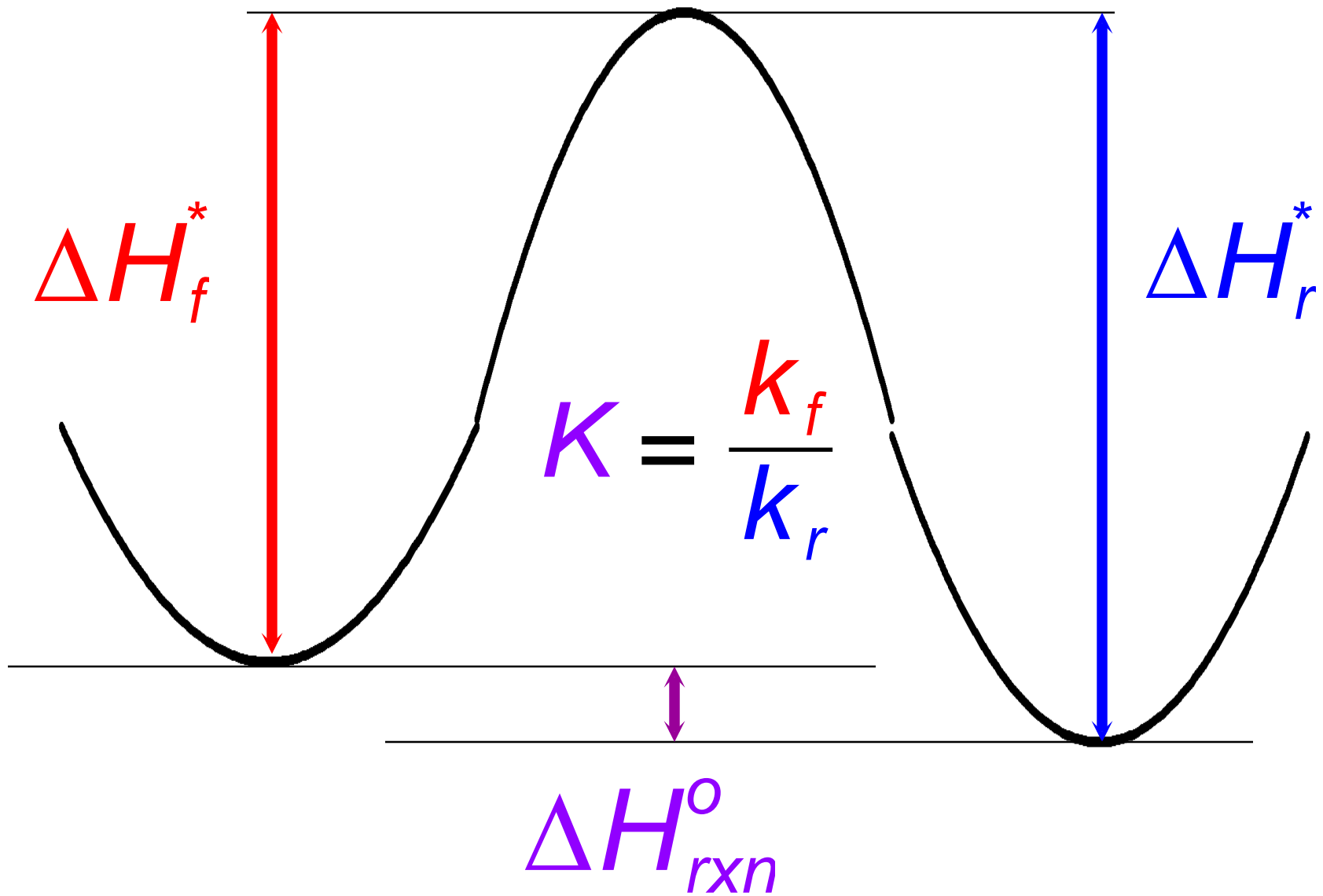
$A = (k_B T/h) e^{\Delta S^\ddagger/R}$ The frequency factor depends on the exponential of the activation entropy.

$E_a = \Delta H^\ddagger$ where E_a is the activation enthalpy.

Catalysis involves lowering of the energy barrier



A catalyst provides an alternative reaction pathway with a lower activation energy or activation enthalpy.



The relationship of kinetics and thermodynamics

The principle of microscopic reversibility requires that:

$$K = \frac{k_f}{k_r}$$

Using definitions from thermodynamics and from transition state theory:

$$e^{-\Delta G^{\circ}/RT} = \frac{e^{-\Delta G_f^*/RT}}{e^{-\Delta G_r^*/RT}}$$

Note that at constant temperature the prefactor $k_B T/h$ is the same for each of the rate constants.

The math behind the comparison

Using the definition of free energy:

$$\Delta G = \Delta H - T\Delta S$$

for each free energy gives:

$$e^{\Delta S^0/R} e^{-\Delta H^0/RT} = \frac{e^{\Delta S_f^*/R} e^{-\Delta H_f^*/RT}}{e^{\Delta S_r^*/R} e^{-\Delta H_r^*/RT}}$$

which can be separated into:

$$e^{\Delta S^0/R} = \frac{e^{\Delta S_f^*/R}}{e^{\Delta S_r^*/R}} \quad \text{and} \quad e^{-\Delta H^0/RT} = \frac{e^{-\Delta H_f^*/RT}}{e^{-\Delta H_r^*/RT}}$$

The connection of entropy and enthalpy

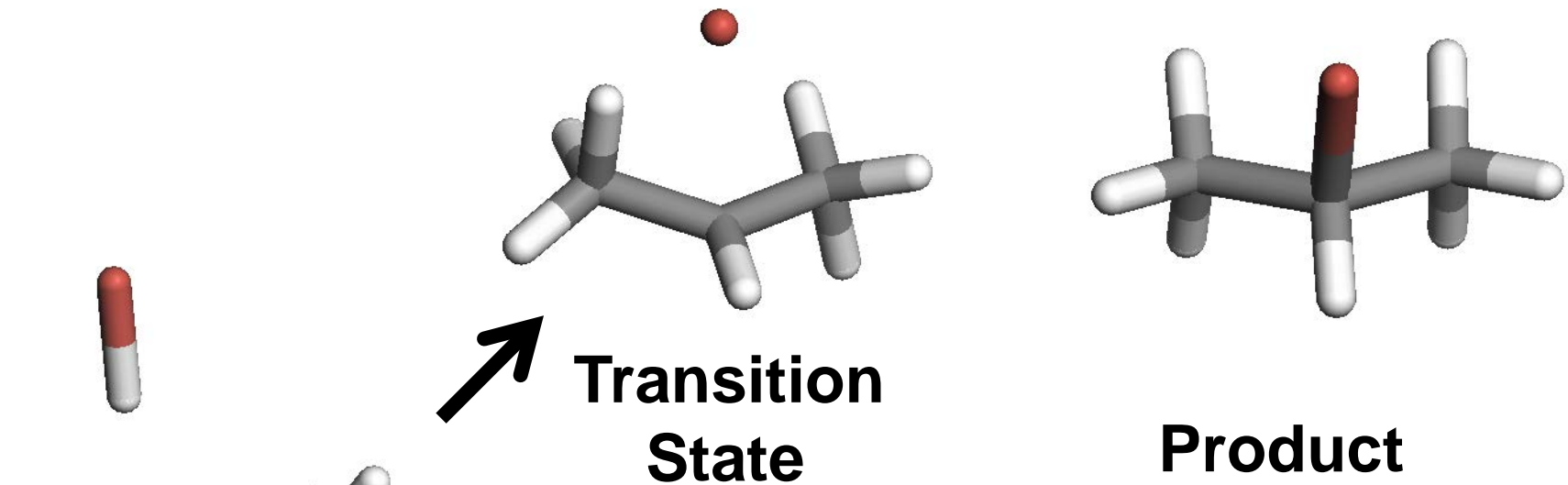
These equations imply simply that:

$$\Delta S^\circ = \Delta S_f^* - \Delta S_r^*$$
$$\Delta H^\circ = \Delta H_f^* - \Delta H_r^*$$

Note that the relationship between the enthalpies can be seen graphically in the energy diagram that we started with.

Note: ‡ and * have the same meaning.

Markovnikov



Product

Reactant

Anti-Markovnikov

