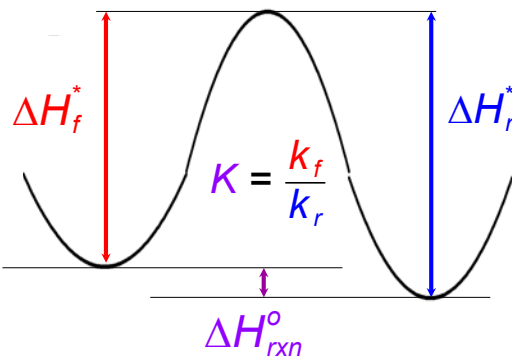


Kinetics



Transition state rate constant



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:

$$e^{-\Delta G^0/RT} = \frac{e^{-\Delta G_f^\ddagger/RT}}{e^{-\Delta G_r^\ddagger/RT}}$$

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:

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

which can be separated into:

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

The connection of entropy and enthalpy

These equations imply simply that:

$$\begin{aligned} \Delta S^0 &= \Delta S_f^\ddagger - \Delta S_r^\ddagger \\ \Delta H^0 &= \Delta H_f^\ddagger - \Delta H_r^\ddagger \end{aligned}$$

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.

Relationship to the 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.

Relationship to the Arrhenius parameters

The reaction rate can also be written

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

where ΔG^\ddagger is the activation Gibbs energy.

This provides an interpretation for the Arrhenius parameters:

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

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