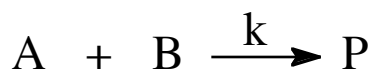


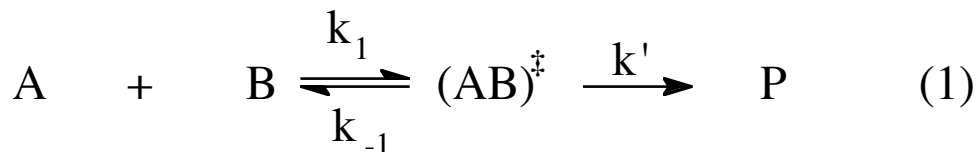
Transition State Theory (Absolute Rate Theory) of Chemical Kinetics

In the following paragraphs, we will outline the derivation of the transition state (Eyring) equation, a fundamental relation between the rate constant for a reaction and the entropy and entropy of activation for that reaction. This is one of the most important equations in physical chemistry; it is one of the few relationships in this course that you should memorize. We will illustrate the derivation using a bimolecular reaction; however, the idea is valid for any elementary reaction. (This derivation follows closely that given in lecture; the transition state (Eyring) equation will be used extensively in Conference #4, when we will study the temperature dependence of the kinetics of dissociation of the anticancer drug Actinomycin D from DNA.)

We will be considering the bimolecular reaction of A with B to form P, as shown below, where k is the second order rate constant describing this reaction:



Now, consider the same bimolecular reaction sequence, but in which A and B reversibly react to form an intermediate complex $(AB)^\ddagger$, which irreversibly decomposes to form final product P. The species $(AB)^\ddagger$ is a so-called transition state (or activated complex) whose lifetime is less than 10^{-13} sec.



We can now write the rate of reaction of A and B to form P in two ways, as in equation (2):

$$d[P]/dt = k[A][B] = k'[AB]^\ddagger \quad (2)$$

In this equation, k is the bimolecular rate constant for conversion of A and B to P and k' is the unimolecular rate constant for decomposition of the activated complex $(AB)^\ddagger$ to form P. Now, the Eyring approach assumes that we can assume a thermodynamic quasi-equilibrium to exist between A, B and $(AB)^\ddagger$. If this is true, we can write an equilibrium constant and an expression for ΔG_0^\ddagger , the free energy of reaction to form the transition state (normally called the standard free energy of activation); these quantities are expressed as immediately below: (note that subsequent to (3), we will leave off the subscripted zero on ΔG_0^\ddagger , as well as for other thermodynamic quantities; this simplifies formula construction).

$$K_{\text{eq}}^\ddagger = \frac{[AB]^\ddagger}{[A][B]}; \quad \Delta G_0^\ddagger = -RT \ln K_{\text{eq}}^\ddagger \quad (3)$$

This transition state is somewhat similar to a normal molecule with one important difference. It has one degree of vibration that is special. The transition state moves along this special vibrational mode to form product P (or to reform reactants A and B). From the above, we can obtain an expression for $[AB^\ddagger]$ in terms of K^\ddagger , $[A]$ and $[B]$, and, thus, an expanded expression for the rate of reaction given in (1) above can be written as equation (4).

$$d[P]/dt = k[A][B] = k'[AB^\ddagger] = k'K_{\text{eq}}^\ddagger[A][B] \quad (4)$$

From this equality, we can write that the bimolecular rate constant k is given by the product $k'K_{\text{eq}}^\ddagger$. Thus, if we can evaluate k' and K_{eq}^\ddagger , we can evaluate k . (We will leave off the eq from the equilibrium constant in the rest of our development.)

$$\ln K^\ddagger = \Delta G^\ddagger/RT = -\Delta H^\ddagger/RT + T\Delta S^\ddagger/RT = \Delta S^\ddagger/R - \Delta H^\ddagger/RT \quad (5)$$

In this equation, ΔH_0^\ddagger is the standard enthalpy of activation and ΔS_0^\ddagger is the corresponding standard entropy of activation. (In general, the term “standard” is usually left off by kineticists and these quantities are simply referred to as the enthalpy of activation and the entropy of activation; it is understood however that these quantities refer to standard state conditions.) From (5), we can write an expression for K^\ddagger as follows:

$$K^\ddagger = e^{\Delta S^\ddagger/R - \Delta H^\ddagger/RT} = e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (6)$$

Then we can write the following expression for the rate constant k_1 .

$$k = k'e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (7)$$

Using statistical mechanical and quantum mechanical reasoning, Professor Henry Eyring calculated that the value of k' was given by $\kappa RT/Nh$, where R is the gas constant, T is the absolute temperature, N is Avogadro's number and h is Planck's constant; κ is a constant known as the transmission coefficient and is often taken to have a value of unity. When the units of the rate constant are in seconds, the value of k' is given fairly closely by $2 \times 10^{10} T$. Thus, the equation for k can be written as in equation (8).

$$k = (RT/Nh)e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} = 2 \times 10^{10} T e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (8)$$

This equation is known as the transition state equation for bimolecular rate constants; it is often termed the Eyring equation or the absolute rate equation.

Questions: Can you rearrange the Eyring equation so that it can be plotted in the form $y = mx + b$? How would you evaluate ΔH_0^\ddagger from the slope and ΔS_0^\ddagger in some manner from the intercept of the corresponding straight line?