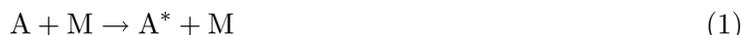


Unimolecular Reactions

A common type of reaction which occurs in combustion is the unimolecular decomposition reaction of the general form: $A + M \rightarrow \text{Products}$. An example of such a reaction is $C_2H_6 + M \rightarrow CH_3 + CH_3 + M$. These reactions are important for two reasons: 1) they can play essential roles in some combustion systems, especially hydrocarbon pyrolysis, and 2) the reaction rates are readily calculated by transition state theory, reducing the uncertainty in the incorporation of such reactions into combustion mechanisms.

The net reaction has three components: 1) the reactant is excited to a state A^* which has enough energy to dissociate, 2) the excited state can then be de-excited by collision, or 3) the excited state can dissociate. Steps 2) and 3) compete with each other. The relevant reactions can be written;



We can thus write expressions for the concentrations of the two species:

$$\frac{d[A]}{dt} = -k_1[A][M] + k_2[A^*][M] \quad (4)$$

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_3[A^*] \quad (5)$$

Using the steady state approximation on equation (5) and solving for $[A^*]$ yields

$$[A^*] = \frac{k_1[A][M]}{k_2[M] + k_3} \quad (6)$$

Plug this into equation (4), and we get:

$$\frac{d[A]}{dt} = -k_1[A][M] + k_2 \frac{k_1[A][M]^2}{k_2[M] + k_3} = \frac{(k_2[M] + k_3)(-k_1[A][M]) + k_2k_1[A][M]^2}{k_2[M] + k_3} \quad (7)$$

$$= \frac{-k_1k_3[M]}{k_2[M] + k_3}[A] = -k_{\text{dissoc}}[A]. \quad (8)$$

Note that the dissociation process is first order in $[A]$, but has a variable order in $[M]$. At high pressures, reactions 1 and 2 are both fast, so the reaction:



is in partial equilibrium (i.e. $k_1[A][M] = k_2[A^*][M]$), and thus the concentration of $[A^*]$ is fixed relative to that of $[A]$ at $(k_1/k_2)[A]$. Then we note that:

$$\frac{d[A^*]}{dt} = \frac{d[A]}{dt} = -k_3[A^*] = \frac{-k_1k_3}{k_2}[A] \quad (10)$$

which has no pressure dependence.

At low pressures, the $[M]$ term in the denominator of k_{dissoc} is small, and thus we get

$$\frac{d[A]}{dt} = -k_1[M][A] \quad (11)$$

which is first order in $[M]$. In this case, the de-excitation step is negligibly slow, and all excited A molecules dissociate.

Lindeman and Troe Formats

No reaction is ever truly in its high temperature or low temperature limit, so we need expressions that allow for accurate computation of reaction rate at any pressure. One such expression was derived on the previous page for a simple unimolecular reaction. Two conventional formats for general, pressure-dependent rate constant expressions are the Lindeman and Troe formats. Both formats start in a similar fashion. Assume a reaction of the form $A + A + M \rightarrow A_2 + M$. Consider, for now, only the forward reaction. In the low pressure limit, the rate should be linearly proportional to pressure. That is:

$$\frac{d[A_2]}{dt} = k_o[A][A][M] \quad (12)$$

and thus, the units for k_o will be $\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$. For the low pressure limit, we can define Arrhenius terms A_o , n_o , and $E_{A,o}$. In the high pressure limit, the reaction becomes independent of pressure, and thus

$$\frac{d[A_2]}{dt} = k_\infty[A][A] \quad (13)$$

and we define A_∞ , n_∞ , and $E_{A,\infty}$ for k_∞ . The units for k_∞ will be $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. We now define a reduced pressure, $P_r = k_o[M]/k_\infty$, then define a pressure dependent rate constant k such that:

$$k = k_\infty \left(\frac{P_r}{1 + P_r} \right) F \quad (14)$$

The two approaches vary in the expression for F . The **Lindemann** form uses $F = 1$, and thus we only need six terms to describe the pressure dependent rate constant (i.e. two sets of Arrhenius terms). For the case that we considered on the previous page, we can see that $k_o = k_1$ and $k_\infty = k_1 k_3 / k_2$. For this case, $P_r = k_2[M] / k_3$, and thus, for $F = 1$,

$$k = k_\infty \left(\frac{P_r}{1 + P_r} \right) = \frac{k_1 k_3}{k_2} \left(\frac{k_2[M] k_3}{1 + k_2[M] / k_3} \right) = \frac{k_1 k_3 [M]}{k_2 [M] + k_3} [A] \quad (15)$$

which agrees with our derived expression. However, this simplified approach is not valid for all pressure dependent reactions, and a more complex approach is suggested by **Troe**. In this approach, F is obtained from:

$$\log F = \left[1 + \left(\frac{\log P_r + c}{n - d(\log P_r + c)} \right)^2 \right]^{-1} \log F_{cent} \quad (16)$$

using the following terms:

$$c = -0.4 - 0.67 \log F_{cent} \quad (17)$$

$$n = 0.75 - 1.2 \log F_{cent} \quad (18)$$

$$d = 0.14 \quad (19)$$

$$F_{cent} = (1 - \alpha) \exp\left(\frac{-T}{T^{***}}\right) + \alpha \exp\left(\frac{-T}{T^*}\right) + \exp\left(\frac{-T^{**}}{T}\right). \quad (20)$$

In this approach, we need as many as four additional parameters (α , T^* , T^{**} , and T^{***}).

Transition State Theory

If we consider reactions that proceed through a well-defined, short-lived, intermediate 'transition' state, then we can use the 'absolute reaction rate theory' or 'transition state theory' to calculate the rate constant. For this theory, we assume a reaction of the form:



where M^\ddagger is the transition state. For this transition state, we assume that the complex is species for which we can define geometric parameters such as moments of inertia, as well as molecular parameters such as vibrational frequencies. This basic information then allows us to do statistical mechanics on M^\ddagger in the same way that we would on any species to get thermodynamic properties. Furthermore, we assume that one of the vibrational modes of M^\ddagger is a 'special mode' with a vibrational frequency ν along which the complex travels from reactants to products. The reaction from reactants to transition state and back is assumed to be fast both ways so that it is always in partial equilibrium. Using these approximations, we can first get the concentration of M^\ddagger from:

$$K_c = \frac{[M^\ddagger]}{[A][B]} \equiv K_c^\ddagger. \quad (22)$$

The rate at which M^\ddagger goes to products is assumed to be first order in $[M^\ddagger]$ with a rate constant equal to the 'special' vibrational frequency, so that:

$$\frac{d[M^\ddagger]}{dt} = \nu[M^\ddagger] = \nu K_c^\ddagger [A][B] \quad (23)$$

Then, for the reaction $A+B \rightarrow \text{Products}$, we have the rate constant $k = \nu K_c^\ddagger$. The remainder of the problem is to determine K_c^\ddagger . From statistical mechanics, we define for any species i a partition function z_i that includes information on the energy storage modes of a molecule including those for translation, rotation, vibration, and electronic excitation. We assume we can calculate z_{M^\ddagger} given geometrical information and vibrational frequencies. We can break down z_i to $f_i \exp[-E_{o,i}/\hat{R}T]$, where $E_{o,i}$ is the bond energy of the species. From statistical mechanics, we obtain the expression for the equilibrium constant:

$$K_c^\ddagger = \frac{f^\ddagger}{f_A f_B} \exp[-(E_{o,M^\ddagger} - E_{o,A} - E_{o,B})/\hat{R}T] = \frac{f^\ddagger}{f_A f_B} \exp[-\Delta E_o^\ddagger/\hat{R}T] \quad (24)$$

Note that ΔE_o^\ddagger will be greater than zero since there is essentially no bond energy in the complex. We furthermore break up f^\ddagger into two parts, one corresponding to the special vibrational mode f_ν , and the second part containing the remaining modes f^\ddagger . If we consider ν to be a relatively low frequency, then the expression for its partition function component will correspond to the high temperature limit expression, $f_\nu = k_b T/h\nu$, where k_b is Boltzmann's constant, and h is Planck's constant. Then we get our final expression for the rate constant k as:

$$k = \frac{k_b}{h} \frac{f^\ddagger}{f_A f_B} T \exp[-\Delta E_o^\ddagger/\hat{R}T]. \quad (25)$$

Thus, if we can estimate the structure of the transition state for a particular reaction, then calculate its properties, we have a relatively straightforward means to get a reaction rate. The challenge is to identify the appropriate transition state for a given reaction, though there are well established protocols to do so.

Entropy of Activation

On a side note, starting with the expression for k , we can isolate terms for the complex minus the special vibration. We denote this construct with a ' \ddagger ' superscript, and thus

$$k = \frac{k_b T}{h} \frac{f^\ddagger}{f_A f_B} \exp[-\Delta E_o^\ddagger / \hat{R}T] = \frac{k_b T}{h} K_c^\ddagger \quad (26)$$

where we have assumed $\Delta E_o^\ddagger \approx \Delta E_o^\ddagger$. From the definition of the equilibrium constant and the Gibbs free energy, we get:

$$K_c^\ddagger = e^{-\Delta G^\ddagger / \hat{R}T} = e^{-\Delta H^\ddagger / \hat{R}T} e^{\Delta S^\ddagger / \hat{R}} \quad (27)$$

If we note that $\Delta H^\ddagger \approx \Delta E_o^\ddagger$, then we can rewrite our expression as:

$$k = e^{\Delta S^\ddagger / \hat{R}} \left(\frac{k_b T}{h} \right) e^{-\Delta E^\ddagger / \hat{R}T} \quad (28)$$

which is close to Arrhenius form. In this case we note that the pre-exponential factor A is related to the entropy of activation ΔS^\ddagger . For transition states with greater disorder (greater number of quantum states available), this term is greater, and the reaction proceeds faster.

Rate-limiting Step

Not all reactions in a reaction chain are of equal importance. In some cases, all one needs to know is the single critical reaction rate in a sequence to determine the overall reaction rate of the entire chain. This critical step is called the rate-limiting step. As an example consider the 2-step reaction chain $A \rightarrow B$ followed by $B \rightarrow C$, such that A are the reactants, C are the products, and B is some intermediate species. We're typically interested in the overall reaction rate for $A \rightarrow C$.

If both steps are first order reactions, then we have for the first step ($A \rightarrow B$):

$$\frac{d[A]}{dt} = -k_1[A] \quad \Rightarrow \quad [A] = [A]_0 e^{-k_1 t} \quad (29)$$

where $[A]_0$ is the initial concentration of A. For the intermediate species B, we have both source and sink terms, so we get

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad \Rightarrow \quad \dot{[B]} + k_2[B] = k_1[A]_0 e^{-k_1 t}. \quad (30)$$

This is a more complex ODE, but it still has a fairly simple solution which can be shown to be:

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} e^{-k_1 t} + C e^{-k_2 t}. \quad (31)$$

Applying the boundary condition that $[B] = 0$ at $t = 0$, we get:

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}). \quad (32)$$

Now since $d[C]/dt = k_2[B]$, we can write:

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}). \quad (33)$$

Looking at two limiting cases where $k_2 \gg k_1$ and where $k_1 \gg k_2$, we can simplify the expression. For $k_2 \gg k_1$, the denominator in (33) is k_2 , so the rate term in front of $[A]_0$ becomes k_1 . Except for very short times, the first of the two exponential terms will dominate the other, and so we will get:

$$\frac{d[C]}{dt} = k_1 [A]_0 e^{-k_1 t} \quad (34)$$

and all the k_2 dependence drops out of the rate for C production. Similarly, for $k_1 \gg k_2$, equation (33) reduces to

$$\frac{d[C]}{dt} = k_2 [A]_0 e^{-k_2 t} \quad (35)$$

and all the k_1 dependence is gone. This result holds in general for reaction sequences of arbitrary form. The slowest step in the sequence sets the rate for the entire sequence, and thus that is the only rate that needs to be known to determine the rate for the entire chain.