# 3.6   Pressure-dependent Reactions

Under certain conditions, some reaction rate expressions depend on pressure as well as temperature. GAS-PHASE KINETICS provides for two kinds of such reactions: unimolecular/recombination fall-off reactions and chemically activated bimolecular reactions. Generally speaking, the rate for unimolecular/recombination fall-off reactions increases with increasing pressure, while the rate for chemically activated bimolecular reactions decreases with increasing pressure. In both cases, GAS-PHASE KINETICS makes available various expressions that blend smoothly between high- and low-pressure limiting rate expressions.

3.6.1   Unimolecular/Recombination Fall-off Reactions

As an example of a unimolecular/recombination fall-off reaction, consider methyl recombination. In the high-pressure limit, the appropriate description of the reaction is $CH_3 + CH_3 \Leftrightarrow C_2H_6$. In the low-pressure limit, a third-body collision is required to provide the energy necessary for the reaction to proceed, i.e., the appropriate description is $CH_3 + CH_3 + M \Leftrightarrow C_2H_6 + M$. When such a reaction is at either limit, the (solely temperature-dependent) rate expressions discussed in the preceding paragraphs are applicable. However, when the pressure and temperature are such that the reaction is between the limits, the rate expressions are more complicated. To denote a reaction that is in this "fall-off" region, we write the reaction with the positive + M enclosed in parentheses,

$$CH_3 + CH_3(+ M) \Leftrightarrow C_2H_6(+ M)$$
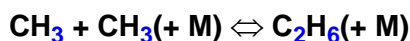
There are several methods of representing the rate expressions in this fall-off region. The simplest one is due to Lindemann.[5] There are also now two other (and related) methods that provide a more accurate description of the fall-off region than does the simple Lindemann form. The GAS-PHASE KINETICS package handles all three of these forms as options.

We begin with the Lindemann approach. Arrhenius rate parameters are required for both the high- and low-pressure limiting cases, and the Lindemann form for the rate coefficient relates them in a pressure-dependent rate expression. In Arrhenius form, the parameters are given for the high-pressure limit k_∞ and the low-pressure limit k_0 as follows:

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5. F. Lindemann, *Trans. Faraday Soc.* **17**:598 (1922).

Equation 3-23

$$k_0 = A_0 T^{\beta_0} \exp(-E_0 / R_c T)$$

Equation 3-24

$$k_\infty = A_\infty T^{\beta_\infty} \exp(-E_\infty / R_c T)$$

The rate constant at any pressure is then taken to be

Equation 3-25

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

where the reduced pressure P_r is given by

Equation 3-26

$$P_r = \frac{k_0 [M]}{k_\infty}$$

and $[M]$ is the concentration of the mixture, possibly including enhanced third-body efficiencies.

> It is also possible that the third body in the fall-off region could be a specific species rather than the mixture as a whole. In such a case, the reaction could be written, for example, as $CH_3 + CH_3 (+N_2) \Leftrightarrow C_2H_6 (+N_2)$. In this case, the concentration of Nitrogen $[N_2]$ would replace the total concentration in the mixture $[M]$ in these equations.

For this example, note that the units for k are 1/sec, k_0 are cm^3/(mole $\bullet$ sec), and k_∞ are 1/sec. If the F in *Equation 3-10* is unity, then this is the Lindemann form. The other descriptions involve more complex expressions for the function F.

In the Troe form,[6] F is given by

Equation 3-27

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

The constants in *Equation 3-27* are

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6. R. G. Gilbert, K. Luther, and J. Troe, *Ber. Bunsenges. Phys. Chem.* **87**:169 (1983).

Equation 3-28

$$c = -0.4 - 0.67 \log F_{\text{cent}}$$

Equation 3-29

$$n = 0.75 - 1.27 \log F_{\text{cent}}$$

Equation 3-30

$$d = 0.14$$

and

Equation 3-31

$$F_{\text{cent}} = (1 - \alpha)\exp(-T/T^{***}) + \alpha\exp(-T/T^{*}) + \exp(-T^{**}/T)$$

The four parameters α, T^{***}, T^{*}, and T^{**} must be specified as auxiliary input to the GAS-PHASE KINETICS Pre-processor, as described in Neutral Third Body and Pressure Dependent Parameters (*Section 3.5.3.1* of the *CHEMKIN Input Manual*). It is often the case that the parameter T^{**} is not used. Thus GAS-PHASE KINETICS provides for the use of either three or four parameters.

The approach taken at SRI International by Stewart, et al.[7] is in many ways similar to that taken by Troe, but the blending function F is approximated differently. Here, F is given by

Equation 3-32

$$F = d\left[a\exp\left(\frac{-b}{T}\right) + \exp\left(\frac{-T}{c}\right)\right]^{X} T^{e}$$

where

Equation 3-33

$$X = \frac{1}{1 + (\log P_r)^2}$$

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7. P. H. Stewart, C. W. Larson, and D. M. Golden, *Combustion and Flame* **75**:25 (1989).

In addition to the six Arrhenius parameters—three each for the low-pressure limit k_0 and high-pressure limit k_∞ expressions—the user must supply the parameters a, b, and c in the F expression. The parameters d and e were not discussed by Stewart, et al., but we have included them as additional optional parameters to increase flexibility. If one wishes, d and e can be considered parameters that define a weak-collision efficiency factor, in the event that one wants to compute strong-collision rate parameters and correct them with such a factor.

Figure 3-1   Rate constant as a function of pressure at fixed temperature for a unimolecular fall-off reaction
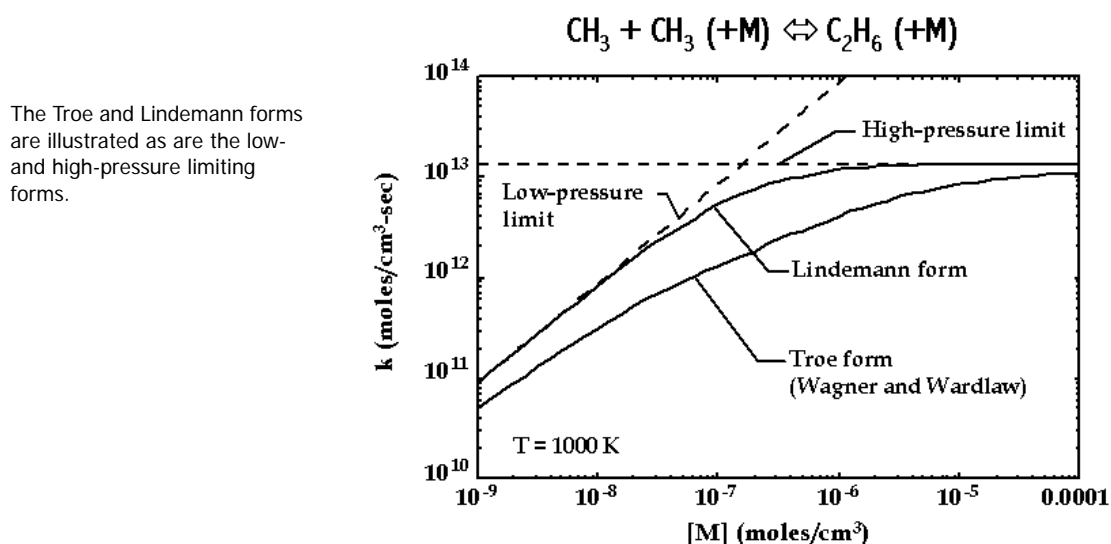
The Troe and Lindemann forms are illustrated as are the low- and high-pressure limiting forms.

$CH_3 + CH_3 \ (+M) \Leftrightarrow C_2H_6 \ (+M)$

$T = 1000$ K

Figure 3-1 illustrates the pressure dependence of rate expressions for the example reaction, $CH_3 + CH_3(+ M) \Leftrightarrow C_2H_6(+ M)$, evaluated at a fixed temperature of 1000 K. Both the Lindemann and the Troe forms are shown, as well as the low- and high-pressure limits. The specific constants in fits to the Troe form ($A_0 = 1.135E36$, $\beta_0 = -5.246$, $E_0 = 1704.8 \text{cal/mole}$, $A_\infty = 6.22E16$, $\beta_\infty - 1.174$, $E_\infty = 653.8 \text{cal/mole}$, $\alpha = 0.405$, $T^{***} = 1120$K, $T^* = 69.6$K) are taken from Wagner and Wardlaw.[8] For the relatively simple Lindemann case ($F = 1$), the limiting behavior is apparent. In the low-pressure limit, $[M] \rightarrow 0$, the denominator in *Equation 3-25* approaches unity and the rate expression becomes $k \rightarrow k_0[M]$. In the high-pressure limit, $[M] \rightarrow \infty$, the pressure-ratio factor approaches one, and the rate expression becomes $k \rightarrow k_\infty$, i.e., a constant. For both the Troe and SRI forms, F approaches unity for both high and low pressures. Thus, all expressions recover the correct limiting behavior.

8. A. F. Wagner and D. M. Wardlaw, *Journal of Physical Chemistry* **92**:2462 (1988).