

Approximation of RRKM Falloff Behavior by Interpolation Formulas

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The accuracy of interpolation formulas for reproducing the pressure falloff of unimolecular reaction rate constants as given by master equation–RRKM calculations was studied using the $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ reaction as a test case. It was concluded that the predictive ability of one-parameter formulas is limited to about 20% for a fixed temperature, which degrades substantially for the five formulas tested if the fitting parameter is expressed as a function of temperature over ranges of interest in atmospheric and combustion modeling. A novel two-parameter formula containing a correction term in the denominator of the Lindemann–Hinshelwood expression $k/k_\infty = P_r/[1 + P_r + (P_r/B)^A]$ was shown to give better performance than two previously studied three-parameter formulas. When treated on an equal basis (extended to contain three parameters and fitted at each temperature) with the three-parameter equations, which lead to 10% errors, our formula reproduces RRKM rate constants within an accuracy of 3%. With the two fitting constants expressed as temperature polynomials having a total of five parameters, this formula was able to reproduce falloff behavior of RRKM rate constants with a maximum error of 10% from 300 to 2100 K over the pressure range from 10^{-5} to 10^5 Torr for both weak and strong collider assumptions.

I. Introduction

By specifying appropriate models for reactant and critical configuration geometries and energetics, one can readily compute unimolecular reaction rate constants by RRKM theory. In current practice, values of k_{uni} below the high pressure limit are obtained by solving a master equation.^{1,2} It is found in general that such RRKM results agree well with experiments over a wide range of temperature and pressure. For repetitive recalculations of rate constants as needed for computer modeling of atmospheric and combustion chemistry, however, RRKM calculations are too demanding of computer resources. For these purposes, it is necessary to have a faster, though perhaps less accurate, way to compute unimolecular reaction rate constants over practical intervals of temperature and pressure. The accepted way to do this is to approximate RRKM pressure falloff behavior by analytical formulas.^{3–11} These formulas have in common that the too-narrow pressure falloff of the Lindemann–Hinshelwood formula

$$\frac{k}{k_\infty} = \frac{P_r}{1 + P_r}$$

where the reduced pressure P_r is related to the high- and low-pressure limiting rate constants k_∞ and k_0 by $P_r = k_0 P/k_\infty$, is either multiplied by a correction factor^{3–6,10,11} or replaced by a formula that intrinsically has a more gradual transition between the low and high pressure limits.^{7–9} While not specifically required by any theoretical concept, it has been customary to adjust the parameters of these interpolation formulas so that exact agreement with the RRKM rate constant is forced at the limits and at $P_r = 1$. The formulas that have been tested are successful in accounting for the shape of the pressure falloff curve but do not, as we discuss below, give satisfactory accuracy over the full range of temperature and pressure of interest in computer modeling of complex reactions. We have undertaken a search for the source of this limited quantitative performance and to devise an interpolation formula that would be an improvement upon previous efforts.

For the purpose of testing interpolation formulas, we chose the unimolecular reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$, which has been well characterized experimentally^{12,13} and has been the subject of many theoretical studies.^{14–17} Rate constants were computed using the SMPL3 set of demo parameters supplied with the Gilbert, Jordan, and Smith implementation of RRKM theory.^{2,18} It incorporates full angular momentum conservation, including the falloff regime. Internal rotors in the transition state are treated as free rotors. The equilibrium internuclear distance is 1.54 Å, and the transition state fragment separation is taken as 4.5 Å. The critical energy of 88.0 kcal and the energy of 87.59 kcal at the separation of 4.0 Å are taken to specify a Morse potential for the reaction. Lennard-Jones parameters 4.0 Å and 44 K and the average energy transferred per collision of 500 cm^{-1} model He as the bath gas.

II. One-Parameter Interpolation Formulas

Several one-parameter equations that approximate RRKM results over a wide range of pressures at a given temperature have been proposed.^{3,7,8} These include the semiempirical J formula⁸

$$\frac{k}{k_\infty} = \frac{-(1 + P_r) + [(1 + P_r)^2 + 4(J_{3/2} - 1)P_r]^{1/2}}{2(J_{3/2} - 1)} \quad (1)$$

where

$$J_{3/2} = \left(\frac{k_\infty}{k_{3/2}} - 1 \right)^2$$

the empirical a formula⁷

$$(k/k_\infty)^a = (P_r)^a + 1 \quad (2)$$

where

$$a_{3/2} = \frac{\log 2}{\log(k_{3/2}/k_\infty)}$$

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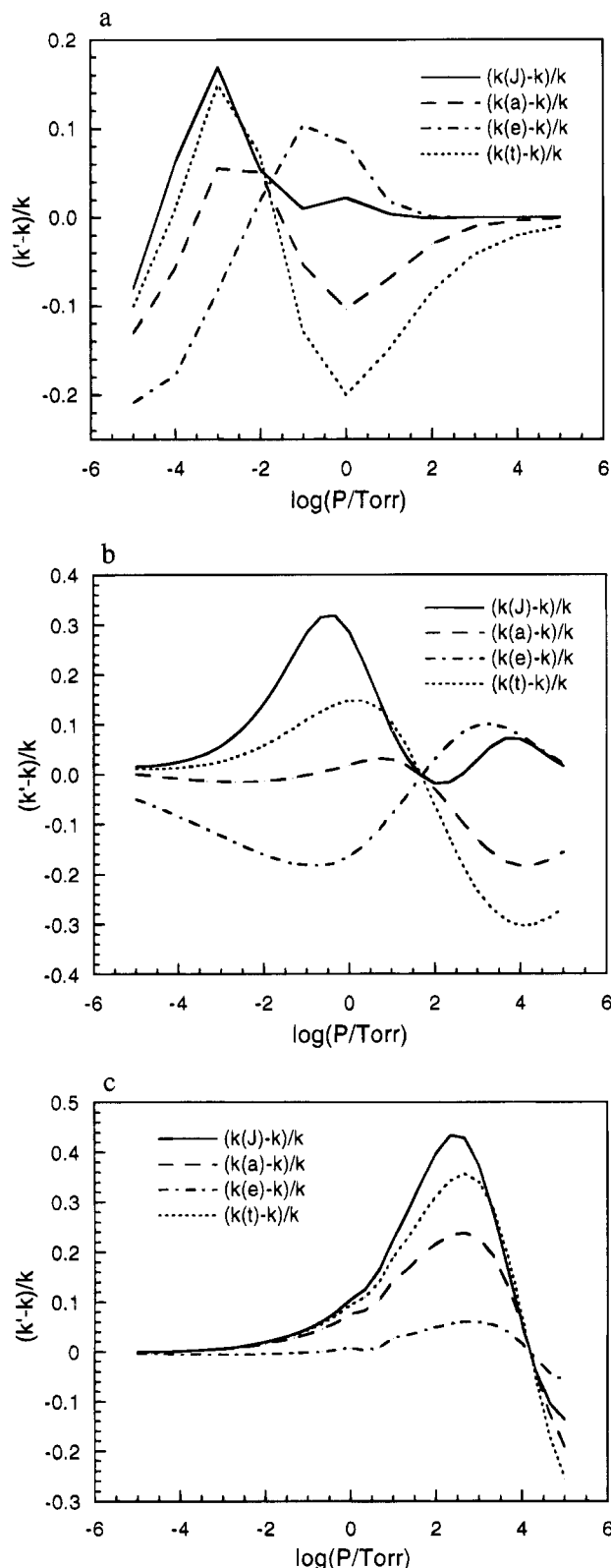


Figure 1. Relative errors in unimolecular reaction rate constants for the one-parameter interpolation formulas given by eqs 1, 2, 4, and 5 for $k(J)$, $2k(a)$, $4k(e)$ and $5k(t)$, respectively; (a) $T = 300$ K; (b) $T = 1200$ K; (c) $T = 2100$ K. Note that over this temperature range, the $P_{3/2}$ value increases from 10^{-2} to 10^4 Torr.

and the empirical F formula³⁻⁶

$$\frac{k}{k_\infty} = \frac{P_r}{P_r + 1} F \quad (3)$$

The original form of the F formula³ uses the following expression for F

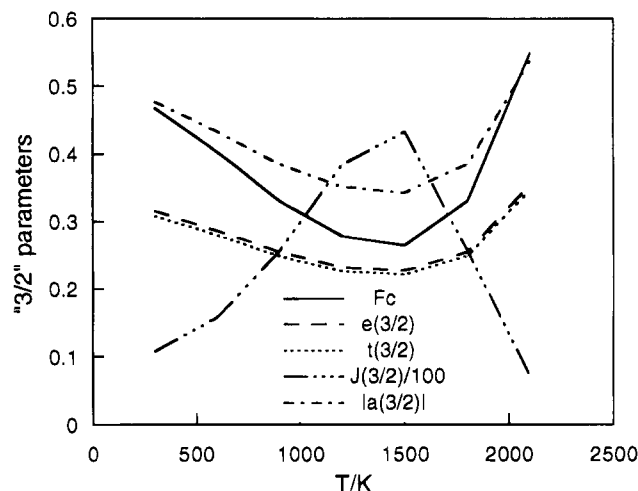


Figure 2. Temperature dependence of parameters fitted at $P_{3/2}$ for five one-parameter formulas. See text for definitions of parameters. The value of $a_{3/2}$ is always negative.

$$\log F = \frac{\log F_c}{1 + [\log(P_r)]^2}$$

where

$$F_c = 2k_{3/2}/k_\infty$$

To give a more accurate result, more advanced versions of eqs 2 and 3 have been proposed.^{3-5,10,11} These intrinsically many-parameter equations are considered in the next section.

We investigated two additional one-parameter equations: an e equation

$$(k/k_\infty)^e = (1 - \exp[-(P_r)^e]); \quad e_{3/2} = \frac{\ln(e-1) - 1}{\ln(k_{3/2}/k_\infty)} \quad (4)$$

and a t equation

$$(k/k_\infty)^t = \frac{2}{\pi} \left(\tan^{-1} \left[\frac{\pi}{2} (P_r)^t \right] \right); \quad t_{3/2} = \frac{\ln \left[\frac{2}{\pi} \tan^{-1} \left(\frac{\pi}{2} \right) \right]}{\ln(k_{3/2}/k_\infty)} \quad (5)$$

The one-parameter equations share two attractive features: they have only a single fitting parameter, which one might hope could eventually be related to molecular properties, and each of their fitting parameters are determined, at least in the forms in which they have been described so far, from the rate constant at a physically meaningful pressure, i.e., at $P_r = 1$, where $k_0P = k_\infty$ and the reaction order is $3/2$.

Comparing each of these formulas by computing rate constants for the methyl recombination reaction, however, confirms that they share several disadvantages. First, 20 to 40% maximum deviations from the RRKM results are consistently observed for each of the equations (Figure 1). Second, the fitting parameters are not simple functions of temperature (Figure 2). Attempting to supplement the one-parameter pressure falloff formulas with formulas that provide the temperature dependence of the fitting parameters, so as to fit RRKM data over both temperature and pressure ranges, increases these errors. While the one-parameter formulas are more accurate than the Lindemann-Hinshelwood formula they were introduced to replace, they are not as accurate as one would wish when parameterized at $P_r = 1$ and used over the full pressure falloff range. It is clearly possible, however, to attain improved accuracy by limiting the pressure and/or temperature range of

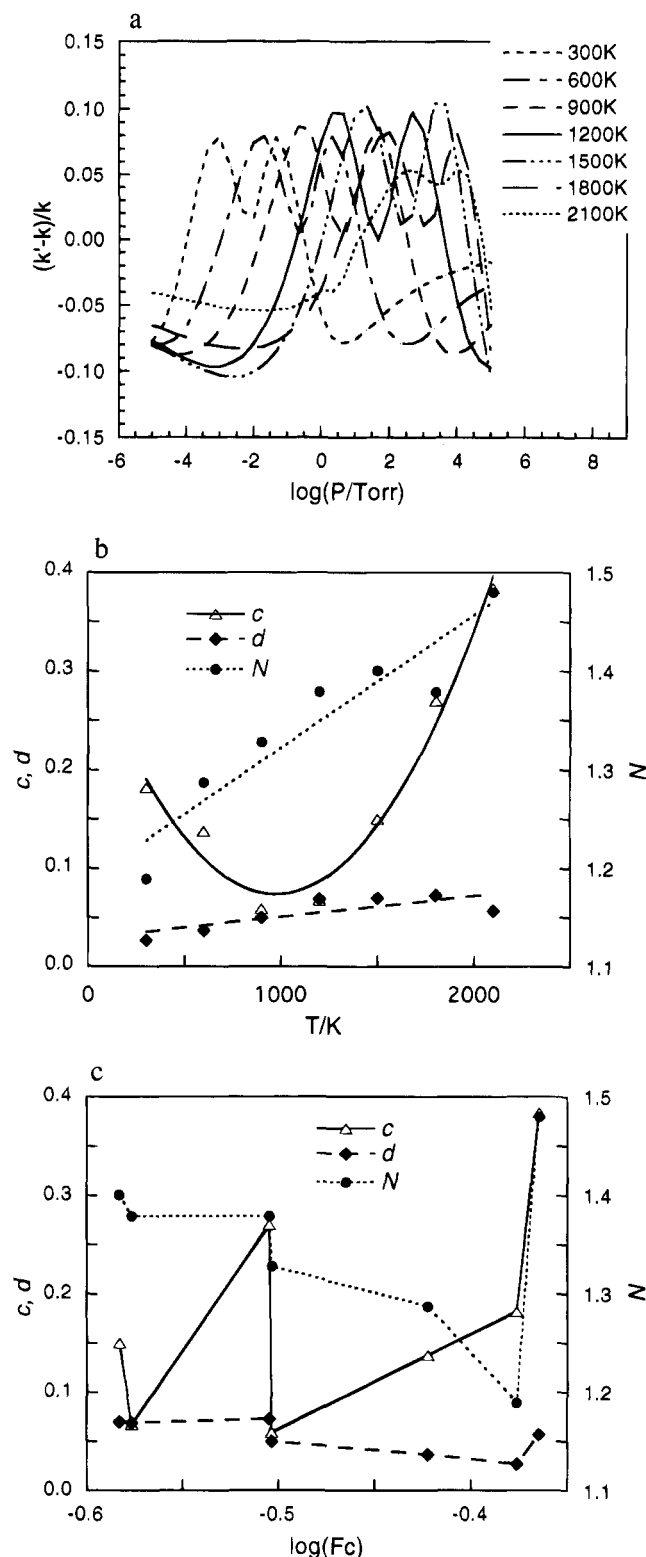


Figure 3. (a) Relative errors in rate constants for eq 6 with parameters fitted at each temperature; (b) temperature dependence of parameters of eq 6; (c) parameters of eq 6 as functions of $\log F_c$, originally proposed relationships (ref 3 $c = -0.4 - 0.67 \log F_c$, $N = 0.75 - 1.27 \log F_c$, $d = 0.14$, and correlations from ref 10 proposed $c = -0.2 - 1.31 \log F_c$, $N = 0.87 - 0.74 \log F_c$, $d = 0.048$).

application and setting the fitting parameter to optimize the fitting accuracy in that range.

III. Many-Parameter Formulas

Formulas with more than one parameter can do a better job fitting RRKM pressure falloff data.

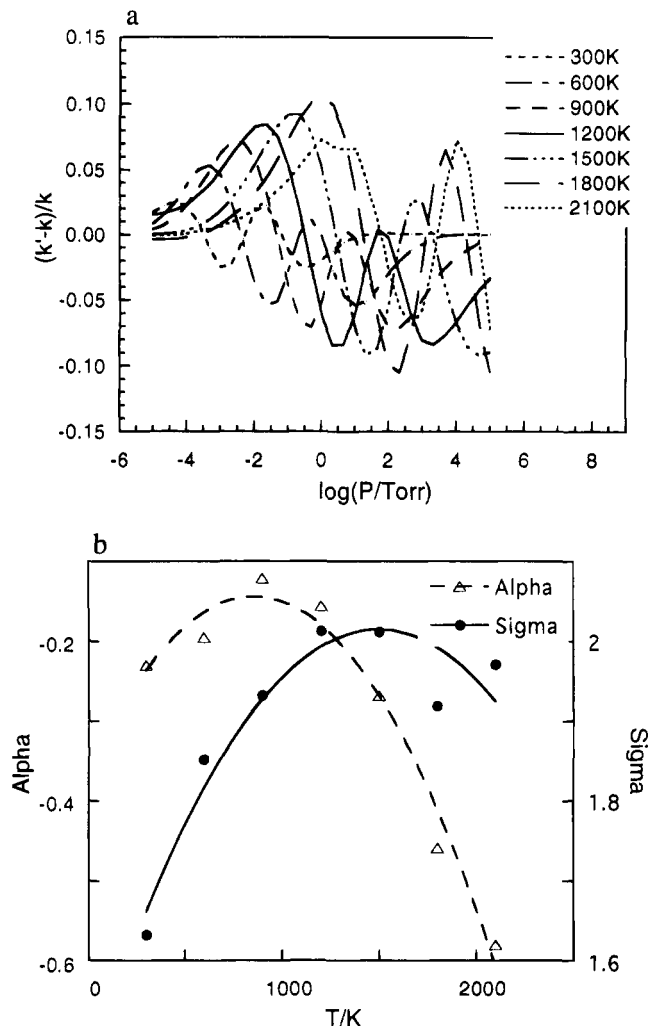


Figure 4. (a) Relative errors for eq 7 with parameters fitted at each temperature; (b) temperature dependence of parameters in eq 7.

Several many-parameter extensions of the F equation (3) have been proposed. The earliest was an extension of the F formula itself to give it the Lorentzian form³⁻⁵

$$\log F = \frac{\log F_c}{1 + [(\log P_r + c)/(N - d[\log P_r + c])]^2} \quad (6)$$

F_c , N , d , and c being parameters and the latest being the Gaussian form¹⁰

$$\log F = \frac{\log F_c}{\exp[(\log P_r - \alpha)/\sigma]^2} \quad (7)$$

F_c , α , and σ being parameters.

Applied to the same set of data with all parameters fitted at each temperature, these formulas show maximum deviations of about 10% (Figures 3a and 4a, respectively). The temperature dependence of the parameters, however, is again quite complex (Figures 3b and 4b). Thus, errors will increase if the parameters are fitted by functions of temperature.

Originally, the parameters in eq 6 were correlated with $\log F_c$. It was claimed that once these correlations were established they could be applied universally.³⁻⁶ The parameters in eq 6 are plotted as functions of $\log F_c$ in Figure 3c. Neither the original relationships³⁻⁶ nor the later ones¹⁰ describe the data for the methyl recombination reaction. From the data displayed, one has to conclude that it seems unlikely that universal

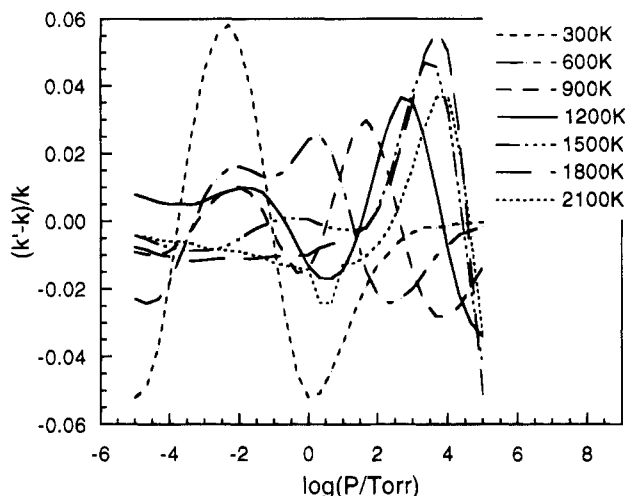


Figure 5. Relative errors for eq 8 with the parameters a and b fitted at each temperature.

expressions for the parameters in eq 6 exist; they must depend on the reaction under study.

The limited accuracy achieved with eqs 6 and 7 led us to search for alternative many-parameter interpolation formulas. The most successful of the ones we studied turned out to have but two fitting parameters. It nonetheless outperformed both eqs 6 and 7.

Equations 6 and 7 exploit the idea of multiplying the Lindemann–Hinshelwood falloff expression by a broadening factor of either a Lorentzian (eq 6) or a Gaussian (eq 7) type. In our approach, we also used the Lindemann–Hinshelwood formula as a starting point. We eventually found that, instead of multiplying it by a factor, a better result could be obtained by adding a two-parameter modification term to its denominator:

$$\frac{k}{k_\infty} = \frac{P_r}{1 + P_r + (P_r/B)^A}; \quad 0 < A < 1 \quad (8a)$$

where the limits on the fitting parameter A are required so that the high and low pressure limits are reached correctly.

Equation 8a can also be reformulated in several ways as a Lindemann–Hinshelwood formula with reparameterized P_r introducing either an effective pressure P' or an effective low k'_0 or high k'_∞ pressure rate constants:

$$\frac{k}{k_\infty} = \frac{P'_r}{P'_r + 1} \quad (8b)$$

$$P'_r = \frac{k_0 P'}{k_\infty}; \quad P' = \frac{P}{1 + (P/B)^A} \quad (8b)$$

$$P'_r = \frac{k'_0 P}{k_\infty}; \quad k'_0 = \frac{k_0}{1 + (P/B)^A} \quad (8c)$$

$$P'_r = \frac{k_0 P}{k'_\infty}; \quad k'_\infty = k_\infty [1 + (P/B)^A] \quad (8d)$$

A final way of rewriting eq 8 is

$$\frac{k}{k_\infty} = \frac{P_r F(P)}{P_r F(P) + 1}; \quad F(P) = \frac{1}{2} (1 - \tanh[a(\log(P) - b)]) \quad (8e)$$

The constants a and b in eq 8e relate to the constants A and B in eqs 8a–d as $A = 2a/\ln 10$, $B = (k_0/k_\infty)10^b$.

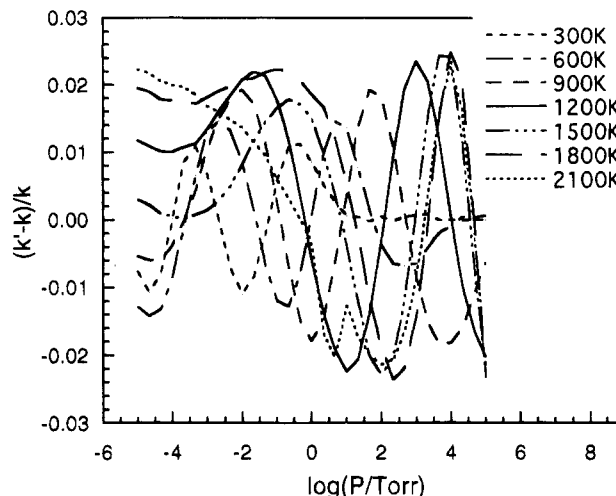


Figure 6. Relative errors for eq 9 with the parameters a , b_1 , and b_2 fitted at each temperature.

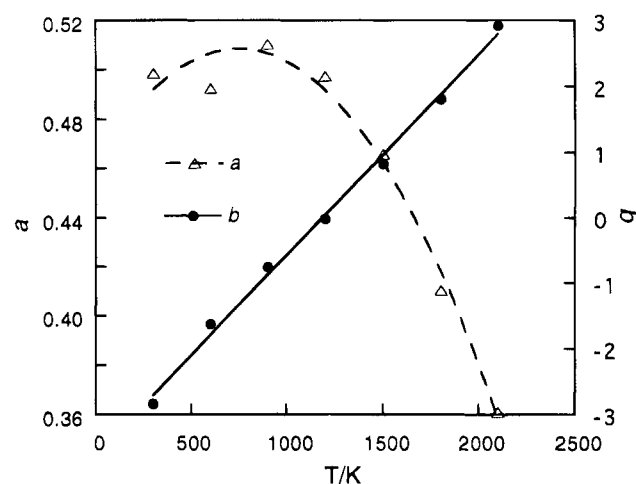


Figure 7. Temperature dependence of the a and b parameters of eq 8 fitted at each temperature.

This equation has only two parameters, one less than eq 7, but still shows good performance. For parameters fitted at each temperature, the maximum errors lie within 6% (Figure 5). Looking at the function $F(P)$ of eq 8e, it is easily seen how a third parameter can be introduced; that is, $F(P)$ can be taken in the form

$$F(P) = \frac{1}{2} \left(1 - \frac{\sinh[a(\log(P) - b_1)]}{\cosh[a(\log(P) - b_2)]} \right) \quad (9)$$

In this case (Figure 6), the maximum error is less than 2.5%, much better than for eq 7, which employs the same number of parameters.

Moreover, by approximating the temperature dependence of the parameters a and b by second- and first-order polynomial forms (Figure 7), we find that the maximum errors still remain at 10% (Figure 8).

So far, the reference set of falloff data has been the array of rate constants calculated by RRKM theory for a weak collider model simulating a reaction in He bath gas with an average energy transferred per collision of 500 cm^{-1} and a fragment separation in the transition state of 4.5 \AA . To test eq 8 further, we computed RRKM rate constants for the same reaction assuming a strong collider model, simulating butane as the bath gas, with 2500 cm^{-1} as the average energy transfer per collision and 5 \AA as the transition state separation. Formula 8 is indeed flexible enough to show similar performance for these substan-

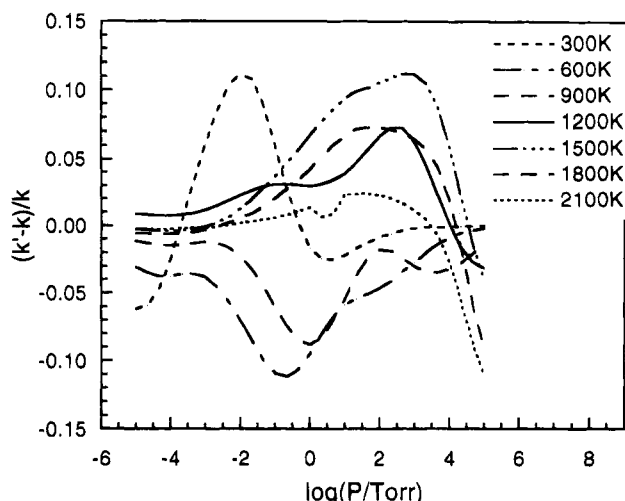


Figure 8. Relative errors of eq 8 with the parameters a and b expressed as functions of temperature by second- and first-order polynomials (Cf. Figure 7).

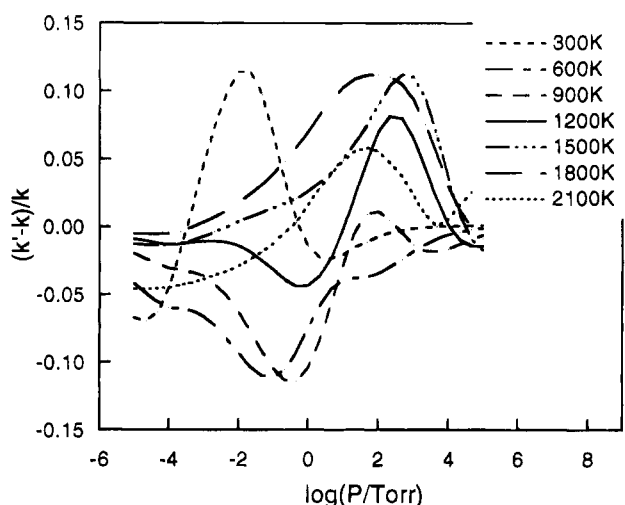


Figure 9. Relative errors for eq 8 with the parameters a and b expressed as functions of temperature by second- and first-order polynomials. A strong collider model was used for the RRKM calculations.

tially different conditions (Figure 9). Thus, given high- and low-pressure limiting rate constants as well as five empirical values, which define the parameters a and b as functions of temperature (Figure 7), eq 8 is able to reproduce RRKM falloff results over a wide range of pressure (10^{-5} – 10^5 Torr) and temperature (300–2100 K) with maximum errors of about 10%, substantially less than the expected systematic errors of the corresponding experimental measurements.

Equation 8 can be tested directly against experimental data. Reference 13 provides measured rate constants for methyl–methyl recombination from 296 to 906 K. We took the values of the high- and low-pressure limiting rate constants suggested in ref 15 and applied eq 8 to the data in ref 13 at two representative temperatures for which a substantial part of the falloff region was covered (Figure 10). Equation 8 describes the experiments as well as more detailed RRKM calculations.¹⁵ In both cases, the fitting accuracy is mainly determined by the quality of the experimental data.

IV. Conclusions

Interpolation formulas describing the pressure falloff of unimolecular reaction rate constants computed by an RRKM–master equation program for the reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ were compared for accuracy over the temperature range 300 to

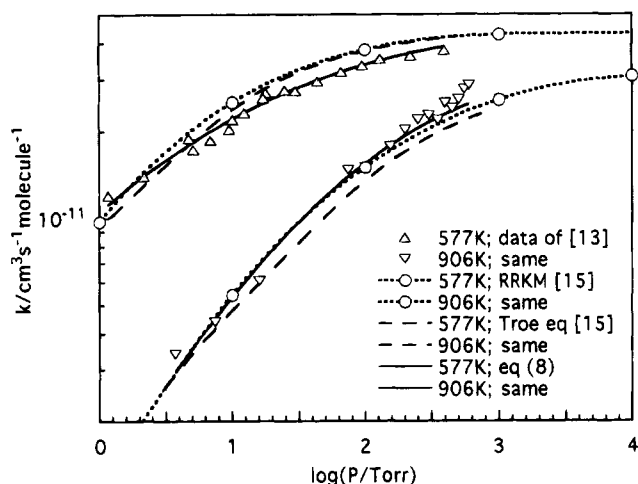


Figure 10. Methyl–methyl recombination experimental rate constants¹³ fitted by eq 8 together with the RRKM data and analytical fits to the Troe formula (6).¹⁵ The constants of eq 8 were $a = 0.51$, $b = -2.41$ at 577 K and 0.40 and -1.43 at 906 K.

2100 K for pressures from 10^{-5} to 10^5 Torr. It was found that the best performance was obtained for a new interpolation equation in which a two-parameter correction is added to the denominator of the Lindemann–Hinshelwood falloff formula.

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- Program *Unimol* Gilbert, R. G.; Jordan, M. J. T.; Smith, S. C. 1990, Department of Theoretical Chemistry, Sydney University, NSW 2006, Australia. The data set we used is the demo provided as *SMPL3* in the distribution. It was found that convergence to the high pressure limit was not obtained automatically by the program. The k/k_∞ values used for our analysis were obtained by multiplying the k/k_∞ values computed by the *MASTER* program by the ratio of the output k_∞ value to the k_{uni} value computed by the program at $P = 10^{10}$ Torr. The full array of falloff data used in our work can be obtained over the Internet by anonymous ftp; log in to lioness.cm.utexas.edu and grab (or get) the ASCII text file methyl-falloff in the directory /pub/Falloffdata.