Parameterization of Pressure- and Temperature-Dependent Kinetics in Multiple Well Reactions

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It is now well confirmed that the influence of temperature on the fall-off behavior of dissociation, recombination and chemically-activated reactions can be dramatic. For single-well, single-product dissociation reactions, it is customary to approximate these fall-off surfaces using extensions of Lindemann's empirical expression. We consider here chemical-activation and dissociation reactions possessing multiple wells and multiple products. We show that direct approximation of the rate coefficients via Chebyshev expansions yields reliable and accurate representations of their pressure and temperature dependences, which are superior to those from a Lindemann approach to fit the form factor representing the fall-off surface. The superiority of the method is demonstrated in a study of seven channels corresponding to four different reactions important in combustion chemistry over the ranges 300–3,000 K and 0.02–200 atm.

Introduction

The prediction of unimolecular reaction rate coefficients and their extrapolation to different temperatures and pressures is particularly attractive to those interested in the quantitative aspects of chemical-kinetic modeling. Indeed, such prediction is possible now that estimates of rate coefficients of sufficient reliability for some applications in atmospheric, combustion and chemical vapor deposition modeling can be carried out. In estimating these temperature- and pressure-dependent rate coefficients, the microcanonical rate coefficients are best obtained from the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (Gilbert and Smith, 1990) and the collisional effects are best treated by an analysis of the master equation (Gilbert and Smith, 1990; Venkatesh et al., 1996a). Mechanistic kinetic models of chemical processes can comprise hundreds of elementary dissociation, recombination, and chemically-activated reactions (Drake and Blint, 1991; Chevalier et al., 1992). For inclusion in predictive gas-phase reactor models, where the coupled equations for flow, energy, and pressure drop must be solved along with the species balances, the total computational effort may become prohibitive if the rate coefficients are calculated from unimolecular theory at each prescribed temperature and pressure. The situation is compounded by stiffness (Gear, 1971; Brown et al., 1989). To expedite the total model calculations, it is necessary to make recourse to computationally efficient approximate expressions for the temperature- and pressure-dependent rate coefficients. Until recently, such approximate expressions for rate coefficients were restricted to single-well, single-product dissociation reactions. Troe's F_{cent} method (Gilbert et al., 1983), the SRI method due to Stewart et al. (1989), and the method due to Poole and Gilbert (1994) are reliable, accurate approximations. However, their performance on multiple-well, multiple-product chemically-activated or dissociation reactions can be unsatisfactory. Recently, Kazakov et al. (1994) have proposed an empirical formalism to parametrize multiple-well chemical activation reactions. Their method, though exhibiting improved accuracy in comparison with the models proposed for single-well reactions, does exhibit large errors for some of the reaction channels considered in this study. This leads to a fundamental problem in approximation theory concerning whether there is any practical and general functional form to employ. The functional form employed must be able to capture topographical structures such as local maxima and minima, and sharp gradients, with as few parameters as possible.

An inherent disadvantage of empirical models is that there is no means of assuring that the models will provide uniform approximation over the entire range of temperatures and pressures for any kind of multiple-well reaction. Furthermore, empirical models do not provide any guidance for the introduction of additional parameters to increase the uniformity and accuracy of approximation along the temperature and pressure axes. One approach is to seek recourse in the mathematical theory of approximation of functions (Powell, 1981). Any function of temperature and pressure can be represented exactly as a sum of orthogonal functions in infinite dimensions. A well-known result from functional analysis is that any periodic function over the support $(-1, 1)$ is represented exactly by its Fourier expansion. Similarly, nonperiodic functions over the support $(-1, 1)$ are represented exactly by their Chebyshev expansions. The finite truncation of such expansions will introduce an error which is rigorously estimated by theoretical methods The truncated expansions, however, guarantee uniformity of approximation over the entire domain and it is possible to obtain quantitative estimates of the reduction in the truncation error due to the increase in the number of terms in the series expansion. An example of such approximation is the use of truncated bivariate Legendre series expansions to approximate Coulomb wave-functions in chemical physics (McWeeny, 1979).

We propose the direct approximation of the reaction rate coefficient as a truncated orthogonal series expansion in temperature and pressure. The basis functions constituting the series expansion are the Chebyshev polynomials (Powell, 1981; Rivlin, 1990). We argue that this approximation technique yields lower maximum relative errors in the approximated rate coefficient when compared with other empirical or interpolation methods. We have also considered the approximation of the reaction rate coefficients by the recently developed radial basis functions (Powell, 1990). Radial basis functions (RBFs) are a generalization of splines, however, in contrast to splines, the complexity of constructing an RBF approximant is *independent* of the number of dimensions of the approximand. Despite the fact that RBF approximants handle steep gradients of the approximands better than Chebyshev approximants, our experience shows that for the class of problems considered here, they typically require more parameters to achieve the same degree of accuracy when compared to Chebyshev approximants.

This article develops the Chebyshev parameterization as follows. The motivation for our selection of reaction channels used to test the various approximation methods considered in this study is explained. Troe's F_{cent} method, the SRI method and the method due to Poole and Gilbert are considered. The performance of these methods on the test channels of the section is exhibited. Modification of Troe's F_{cent} method to account for multiple wells and multiple products is described and its performance is analyzed. A method is also described which is designed for multiple-well systems (Kazakov et al., 1994) and its performance on the test reaction channels is analyzed. Chebyshev approximants and radial basis functions are considered. The performance is discussed of these approximants on the test reaction channels examined earlier, and the superiority of the Chebyshev approximants to all others is established. A summary of our comparative analysis is presented before our conclusions.

Test Reaction Channels

In order to examine the various methods of approximation considered in our study, reaction channels were primarily chosen to illustrate the contrasting behavior between multiple-well reactions and single-well reactions, as well as that between dissociation reactions and chemically-activated reactions. We consider a select set of three thermal dissociation channels and four chemical-activation channels. The dissociations are of the $C_3H_5O_2$ radical and of ethane. The $C_3H_5O_2$ radical dissociation (Bozzelli and Dean, 1993) occurs through multiple wells and yields a total of 14 pathways. We specifically consider $C_3H_5O_2 \leftrightarrow C_3H_5 + O_2$. The dissociation of ethane is of key importance in combustion and has been thoroughly studied (Larson et al., 1984; Davidson et al., 1995). It is a single-well reaction. We consider both the pathways $C_2H_6 \leftrightarrow CH_3 + CH_3$ and $C_2H_6 \leftrightarrow C_2H_5 + H$. We have chosen four chemical-activation channels of the reaction of the allyl radical with molecular oxygen and that of the methyl radical with itself. In respect of the allyl radical reaction with oxygen we consider two pathways removed from the initially formed adduct in order to assess the effects of multiple wells. These are the $C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$ and $C_3H_5 + O_2 \leftrightarrow C \cdot CyCCOO$ channels (Bozzelli and Dean (1993) for the chemical structure of $C \cdot CyCCOO$). The chemically-activated reaction of the methyl radical with itself occurs through a single well. We have considered both the pathways $CH_3 + CH_3 \leftrightarrow C_2H_6$ and $CH_3 + CH_3 \leftrightarrow C_2H_5 + H$ of this reaction.

Method of computing rate constants

The microcanonical rate coefficients have been computed for all of the reactions considered by using the appropriate chemical-activation or dissociation formalism based on the RRKM theory (Gilbert and Smith, 1990) along with consistent thermodynamic parameters. A direct count method for the density of states has been used in these calculations. The absolute temperature- and pressure-dependent rate coefficients have been derived from a theoretical analysis of the master equation presented in Venkatesh et al. (1996a). The least-eigenvalue hypothesis, which is always valid for the master equation treatment of single-well systems, is valid for multiple-well systems only under certain conditions satisfied by the interplay of the isomerization, dissociation, and collisional time-scales. All of the multiple-well systems studied here satisfy the conditions for the applicability of the least-negative eigenvalue hypothesis. Angular momentum conservation has been treated explicitly. An exponential downward model for the probability density of the intermolecular rotational-vibrational energy transfer has been used. For comparative purposes, we also present the approximation of rate coefficients derived from a steady-state analysis that utilizes the modified strong-collision hypothesis (Gilbert et al., 1983) to account for intermolecular energy transfer. However, in order to test the efficacy of the various approximation schemes, the level of sophistication of the methods of computing the fitted values of the rate coefficients is immaterial. Instead of using the RRKM theory, one could use the statistical adiabatic channel model (SACM) (Quack and Troe, 1981) or the quantum-Rice-Ramsperger-Kassel theory (QRRK) (Dean, 1985) with or without a master equation treatment for the collisional energy transfer.

Temperature and pressure domain of approximation

Our interest is in approximating the surface representing the temperature- and pressure-dependent rate coefficients over a range of temperatures and pressures wide enough to be of value in simulation and optimization of large mechanistic kinetic models. We consider the temperature range of 300 –3,000 K and the pressure range of 0.02–200 atm. In our analyses we compute the rate coefficients at 2,500 points on a 50×50 temperature-pressure grid in these ranges. This grid is equidistant for all the approximation schemes considered here with the exception of Chebyshev approximation which requires a specially chosen nonequidistant grid, the description of which is given the section on Chebyshev expansions.

Criterion for judging the efficacy of approximation

A final issue is the criterion of assessment of the approximation procedures considered. We base our judgment on the maximum relative errors in the approximated rate coefficient over the entire temperature and pressure domain considered. The relative error is defined as

$$\text{Relative Error} = \left| 1 - \frac{[k(T,P)]_{\text{approximated}}}{[k(T,P)]_{\text{RRKM}}} \right|, \quad (1)$$

where $k(T,P)$ is the rate coefficient at temperature T and pressure P. Since the outcome of reactor models can be highly sensitive to the quantitative details of the rates of reactions in the model, it is very desirable that the maximum relative errors in the approximated rate coefficients be no larger than a threshold value. In principle, this threshold value can be set to as conservatively low a value as desired. Chief among the advantages of a Chebyshev approximant or a radial basis function approximant is that the approximation error decreases faster than the total number of basis functions retained in their formalism. Hence, there exists an optimal number of basis functions corresponding to a specified threshold error for these types of approximants. Conventional approaches do not, however, provide such flexibility of tailoring approximants to specified threshold errors. Without loss of generality, we choose an *ad hoc* value of 0.2 for the threshold error in our comparative analysis of the various approximation schemes considered in this study. Because the errors in the species concentration profiles can be exponential functions of the errors in the approximated rate coefficients, it is desirable in practice to choose a prudently low value of the threshold error.

Existing Empirical and Semiempirical Approaches

Although our interest is in multiple-well systems, the methods for single-well systems are examined first in order to show that their accuracy, good as they are for single-well reactions, do not extend to multiple-well systems even when accounting for modifications that allow for more parameters in their formalisms. It is important to note this because chemical-kinetics simulation software such as CHEMKIN II (Kee et al., 1989) approximate the falloff behavior of reactions using methods designed for single-well systems. Chemical kineticists should be aware that these methods, if used for approximating the falloff behavior of multiple-well reactions, can result in unacceptably large approximation errors. The presentation in this section follows the following format. Since all of these methods, with the exception of the extension to Troe's F_{cent} method, are described in detail in their sources, only their formulation is mentioned and their performance on the test reaction channels is described.

Methods for single-well systems

In these methods, the temperature- and pressure-dependent rate coefficient $k(T,P)$ is given by

$$k(T,P) = k_\infty \left(\frac{P_r}{P_r + 1} \right) F(T, P_r), \quad (2)$$

where k_∞ is the temperature-dependent rate coefficient at the high-pressure limit, and $F(T, P_r)$ is the form factor. P_r is the reduced pressure defined by

$$P_r = \frac{k_0}{k_\infty}[M], \quad (3)$$

where k_0 is the temperature-dependent rate coefficient at the low-pressure limit and $[M]$ the bath gas density which may include enhancing effects of third bodies. The limiting rate coefficients are approximated by the modified Arrhenius formalism

$$k_0 = A_0 T^{\beta_0} \exp\left(-\frac{E_0}{RT} \right), \quad (4)$$

and

$$k_\infty = A_\infty T^{\beta_\infty} \exp\left(-\frac{E_\infty}{RT} \right), \quad (5)$$

where A_0, β_0, E_0, A_∞, β_∞, and E_∞ are adjustable parameters.

The form factor $F(T, P_r)$ in the Troe formalism (Gilbert et al., 1983) is expressed in terms of F_{cent}, the form factor at the center of the falloff, where $P_r = 1$. It requires ten parameters, which can be estimated by the least-squares minimization. Table 1 shows the results of approximating the RRKM rate coefficients of the various reaction channels using Troe's F_{cent} method using the master equation and modified strong collision approaches. For the temperature and pressure domains considered in this study, Troe's F_{cent} method yields maximum relative errors greater than or equal to 0.2 for each of the channels. In particular, the maximum relative error for the

Table 1. Maximum Relative Errors in the Rate Coefficient over Temperature and Pressure Ranges for Empirical Approximants Designed for Single-Well Systems with Master Equation Analysis of the Collisional Energy Transfer*

Channel	Troe's F_{cent} Method	SRI Method	Modified Troe's F_{cent} Method	Modified SRI Method	Method of Poole and Gilbert
$C_3H_5O_2 \leftrightarrow C_3H_5+O_2$	0.4 (0.31)	0.68 (0.53)	0.34 (0.26)	0.61 (0.53)	0.7
$C_2H_6 \leftrightarrow CH_3+CH_3$	0.23 (0.19)	0.41 (0.29)	0.19 (0.18)	0.4 (0.24)	0.02
$C_2H_6 \leftrightarrow C_2H_5+H$	0.23 (0.26)	0.17 (0.20)	0.19 (0.21)	0.14 (0.16)	0.02
$C_3H_5+O_2 \leftrightarrow H_2CCCH_2+HO_2$	3.6 (2.7)	21.2 (16.3)	3.1 (2.3)	19.1 (15.8)	0.3
$C_3H_5+O_2 \leftrightarrow C\cdot CyCCOO$	0.85 (1.15)	3.1 (7.3)	0.6 (1.13)	2.3 (6.1)	0.28
$CH_3+CH_3 \leftrightarrow C_2H_6$	0.29 (0.21)	0.6 (0.23)	0.23 (0.21)	0.5 (0.21)	0.13
$CH_3+CH_3 \leftrightarrow C_2H_5+H$	0.21 (0.19)	0.13 (0.08)	0.21 (0.19)	0.09 (0.08)	0.09

*The numbers in parentheses indicate errors for an identical analysis except that the intermolecular energy transfer is modeled using the strong collision treatment.

multiple-well chemical-activation channel $C_3H_5+O_2 \leftrightarrow H_2CCCH_2+HO_2$ modeled using the master equation analysis is 3.6.

At the onset, it is unclear how one should modify the Troe formalism to obtain more accurate approximations. In our analysis of many reaction channels, some of which are described by Venkatesh et al. (1996b), we have observed that in general, the temperature dependences of the rate coefficients are more complex than their pressure dependences. Furthermore, it is desirable that the temperature-dependent limiting rate coefficients $k_0(T)$ and $k_\infty(T)$ be modeled accurately because the form factor must approach unity at the limiting pressures. Accordingly, we have considered enhancements to the Troe formalism by modeling the pre-exponential term for the limiting rate coefficients as fourth-degree polynomials in the inverse square root of temperature. Although such a pre-exponential form does not resemble the T^n dependence from the transition-state theory, it was found to exhibit good accuracy. The limiting rate coefficients now adopt the expression given by

$$k_0(T)=\left(a_0+\frac{a_1}{\sqrt{T}}+\frac{a_2}{T}+\frac{a_3}{T\sqrt{T}}+\frac{a_4}{T^2}\right)\exp\left(-\frac{E_0}{RT}\right) \quad (6)$$

$$k_\infty(T)=\left(b_0+\frac{b_1}{\sqrt{T}}+\frac{b_2}{T}+\frac{b_3}{T\sqrt{T}}+\frac{b_4}{T^2}\right)\exp\left(-\frac{E_\infty}{RT}\right). \quad (7)$$

Here a_0, a_1, a_2, a_3, a_4, E_0, b_0, b_1, b_2, b_3, b_4, and E_∞ are adjustable parameters. Such a functional form was found to be appropriate based on comparative numerical experimentation on a number of empirical forms. Note that the Modified Troe's F_{cent} method requires a total of sixteen parameters.

As seen in Table 1, the performance of the Modified Troe method is only marginally better than the original Troe formalism despite the increase in the number of parameters.

In the SRI method (Stewart et al., 1989), the form factor $F(T, P_r)$ is approximated by a sum of exponents. The SRI method requires a total of nine parameters, including three each for the low- and high-pressure limiting rate coefficients. It can be seen from Table 1 that the SRI method is less accurate than Troe's F_{cent} method. This is true even if the limiting rate coefficients are modeled using Eqs. 6 and 7 resulting in a total of 15 parameters for this method. The rate coefficient based on the master equation analysis for the reaction $C_3H_5+O_2 \leftrightarrow H_2CCCH_2+HO_2$ exhibits errors as large as 21.2. The original Troe and SRI methods were designed for single-well unimolecular dissociation reactions. For reactions such as HONO and N_2H_4 dissociation, they perform exceedingly well (Venkatesh et al., 1996b), yielding maximum relative errors of no more than 0.04. The reaction $C_3H_5+O_2 \leftrightarrow H_2CCCH_2+HO_2$ is a multiple-well chemical-activation reaction, and the unsatisfactory performance of the Troe and SRI methods and their modifications suggest taking the number of wells explicitly into account in the approximation procedure.

Recently, Poole and Gilbert (1994) have presented a new method for fitting falloff data based on expressing F_{cent} in terms of the average energy transferred in collisions where the molecule loses energy. We found this method to be the most superior semi-empirical formalism for describing the temperature- and pressure-dependence of the single-well reactions considered here with maximum relative errors in the approximated rate coefficient being no more than 0.09. However, the method does not fare as well for multiple-well reactions and, as seen in Table 1, exhibits a maximum relative error of 0.28 for the rate coefficient of the reaction $C_3H_5+O_2 \leftrightarrow C\cdot CyCCOO$ and a maximum relative error of 0.7 for the rate coefficient of the reaction $C_3H_5O_2 \leftrightarrow C_3H_5+O_2$.

Methods for Multiple-Well Systems

In this section we consider two empirical approaches for multiple-well systems. The first method is an extension of Troe's F_{cent} method and was originally presented by Dean et al. (1993). A similar method has been presented by Wang and Frenklach (1993). The second method considered here is the recently proposed generalized-mean-of-limits formalism proposed by Kazakov et al. (1994).

Extension of Troe's F_{cent} method for multiple-well systems

We consider chemically-activated bimolecular reactions (an analogous formalism for dissociation reactions may similarly be derived) where the reactants R and R' combine to form a chemically-activated complex A_0. This entrance isomer A_0 can dissociate irreversibly into products, undergo collisional stabilization, and dissociate back into reactants. The entrance isomer can also undergo reversible isomerization into the energized complex A_1. Typically, there will exist a set of isomers A_i, $i>0$. Each of the isomers A_i can dissociate irreversibly into products, undergo collisional stabilization and reversibly isomerize to the energized complexes A_{i-1} and A_{i+1}. The overall bimolecular rates of reactants to the ith stabilized adduct or to any of the products can be written as

$$\frac{d}{dt}[A_i] = k_i^{\text{stab}}[R][R'], \tag{8}$$

and

$$\frac{d}{dt}[\text{Products}_i] = k_i^{\text{prod}}[R][R']. \tag{9}$$

Stabilization rate coefficients k_i^{stab} and product dissociation rate coefficients k_i^{prod} are functions of temperature, pressure, and the collision parameters of the surrounding molecules. Our objective is to approximate these rate coefficients k_i^{stab} and k_i^{prod} as functions of temperature, pressure and the well-index, which we define to be equal to one plus the minimum number of isomerizations required from the entrance isomer before the specified product channel can occur.

In order to postulate a generalized Lindemann form that takes the well-index into account, we first examine the low- and high-pressure rates of formation of the stabilized adducts and products. In the low-pressure limit, product rates are independent of pressure, and stabilization rates are directly proportional to pressure. This can be observed (Gilbert and Smith, 1990) by an explicit formulation of the master equation. One may then define the low-pressure limiting rate coefficients by the following equations

$$\frac{d}{dt}[A_i] = k_{i,lp}^{\text{stab}}[R][R'][M], \tag{10}$$

$$\frac{d}{dt}[\text{Products}_i] = k_{i,lp}^{\text{prod}}[R][R'], \tag{11}$$

where the low-pressure rate coefficients $k_{i,lp}^{\text{stab}}$ and $k_{i,lp}^{\text{prod}}$ are independent of pressure. In the high-pressure limit, the output channel for each isomer is dominated by the stabilization rate. Let δ_i represent the well-index corresponding to the complex A_i. Then, the following limiting forms hold

$$\frac{d}{dt}[A_i] = k_{i,hp}^{\text{stab}}\frac{[R][R']}{[M]^{\delta_i-1}}, \tag{12}$$

$$\frac{d}{dt}[\text{Products}_i] = k_{i,hp}^{\text{prod}}\frac{[R][R']}{[M]^{\delta_i}}, \tag{13}$$

where the high-pressure rate coefficients $k_{i,hp}^{\text{stab}}$ and $k_{i,hp}^{\text{prod}}$ are independent of pressure. Having defined the high- and low-pressure limits, a generalization of the Lindemann form can be specified. This is done by postulating the simplest form which provides a smooth transition from one limit to another, with a shape factor introduced to account for any deviations.

$$P_r^i = \frac{k_{i,lp}}{k_{i,hp}}[M]^{\delta_i}, \tag{14}$$

$$k_i^{\text{stab}} = \frac{k_{i,hp}^{\text{stab}}}{[M]^{\delta_i-1}}\left(\frac{P_r^i}{P_r^i+1}\right)F, \tag{15}$$

$$k_i^{\text{prod}} = \frac{k_{i,hp}^{\text{prod}}}{[M]^{\delta_i}}\left(\frac{P_r^i}{P_r^i+1}\right)F. \tag{16}$$

Here F represents the equivalent of the Lindemann form factor, and P_r^i is the equivalent Lindemann reduced pressure corresponding to the ith adduct. Equations 14–16 constitute the modified Lindemann formalism. Only F remains to be specified. We model the form factor F as a function of temperature T and pressure P, and, as Gilbert et al. (1983) have done, we postulate it to be of the form

$$F(T,P) = \exp(-L(T,P)F_{\text{cent}}(T)). \tag{17}$$

Here the centering function F_{cent} is purely a function of temperature. L, the line-shape parameter, is a function of temperature and pressure. We model F_{cent} as a fourth-degree polynomial in the inverse square root of temperature

$$F_{\text{cent}}(T) = f_0 + \frac{f_1}{\sqrt{T}} + \frac{f_2}{T} + \frac{f_3}{T\sqrt{T}} + \frac{f_4}{T^2}. \tag{18}$$

This choice of the functional form for F_{cent} has been found to be superior to the other empirical forms tested in our numerical experiments. The line-shape parameter $L(T,P)$ is modeled as a Gaussian. This Gaussian needs to account for offset, asymmetry, and width of the temperature and pressure dependence and is modeled as

$$L(T,P) = \exp\left[-\left(\frac{\log P + p_{\text{offset}}}{p_{\text{width}}(T) + p_{\text{asym}}(T)\log P}\right)^2\right], \tag{19}$$

where the asymmetry and width parameters are modeled as low degree polynomials in inverse square root of temperature and are given by

$$p_{\text{asym}}(T) = c_0 + \frac{c_1}{\sqrt{T}} + \frac{c_2}{T}, \tag{20}$$

$$p_{\text{width}}(T) = d_0 + \frac{d_1}{\sqrt{T}} + \frac{d_2}{T}. \tag{21}$$

In this formalism the form factor is modeled by twelve parameters—c_0, c_1, c_2, d_0, d_1, d_2, f_0, f_1, f_2, f_3, and f_4. We model the limiting low- and high-pressure rate coefficients using the fourth-order polynomial in inverse temperature shown in Eqs. 6 and 7. Hence, this method requires a total of 22 parameters. With these definitions, Eq. 17 does not approach unity at infinite-pressure, but remains a univariate function of temperature. Such a definition of the form factor allows for more accuracy and flexibility in the fits than an alternative where Eq. 17 was forced to be unity at the high-pressure limit.

Table 2 presents the performance of this scheme, which we call the extended Troe's F_{cent} method, on all of the reaction channels considered. It shows significant improvements on

Table 2. Maximum Relative Errors in the Rate Coefficient over Temperature and Pressure Ranges for Empirical Approximants Designed for Multiple-Well Systems with Master Equation Analysis of the Collisional Energy Transfer*

Channel	Extended Troe's F_{cent} Method	Method due to Kazakov et al.
$C_3H_5O_2 \leftrightarrow C_3H_5 + O_2$	0.31 (0.38)	0.23 (0.27)
$C_2H_6 \leftrightarrow CH_3 + CH_3$	1.6 (2.1)	0.18 (0.21)
$C_2H_6 \leftrightarrow C_2H_5 + H$	0.23 (0.18)	0.18 (0.13)
$C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$	0.19 (0.2)	0.31 (0.29)
$C_3H_5 + O_2 \leftrightarrow$ C·CyCCOO	0.20 (0.19)	0.25 (0.21)
$CH_3 + CH_3 \leftrightarrow C_2H_6$	0.20 (0.20)	0.07 (0.11)
$CH_3 + CH_3 \leftrightarrow C_2H_5 + H$	0.18 (0.20)	0.13 (0.04)

*The numbers in parentheses indicate errors for an identical analysis except that the intermolecular energy transfer is modeled using the strong collision treatment.

most of the chemical-activation channels when compared to the Troe and SRI formalisms. On the multiple-well chemical-activation reaction $C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$, the maximum relative errors in the rate coefficient are a little under 0.2 for this case, both for the master equation and the modified strong collision analysis. The performance of this method on the multiple-well C_3H_5OO dissociation reaction and the single-well C_2H_6 dissociation reaction is unsatisfactory. Additionally, if the goal is to obtain approximations with less than maximum relative errors of 0.2, it is not met for most of the channels considered.

Method of Kazakov, Wang and Frenklach

For the ith well, $i \geq 1$, let $k_0^i(T)$ and $k_\infty^i(T)$ denote the limiting low- and high-pressure rate coefficients which are approximated by the modified Arrhenius expressions given by Eqs. 4 and 5. The generalized reduced pressure P_r^i for the ith well is defined as

$$P_r^i = \left(\frac{k_0^i(T)}{k_\infty^i(T)} \right)^{1/i}, \tag{22}$$

and is proportional to the bath gas density. The generalized-mean-of-limits (GML) formula (Kazakov et al., 1994) for approximating the temperature and pressure dependence of the stabilization or a product dissociation rate coefficient $k_i(T, P)$ for the ith well is given by

$$k_i(T,P) = \left([k_0^i(T)]^a + [k_\infty^i(T)]^a \right)^{1/a} \tag{23}$$

where the parameter a is modeled as

$$a = h \exp\left\{ -(\log P_r^i - \alpha)^2 / \sigma^2 \right\} - \frac{1}{i}. \tag{24}$$

Here, h, α, and σ are polynomials in the temperature T.

In our tests of this method we have assumed that h, α, and σ are tenth-order (or of degree nine) polynomials in temperature. This results in a total of 36 parameters for this model when the limiting rate coefficients are taken into account. Table 2 depicts the performance of this method on all of the single- and multiple-well reactions considered in this study. For multiple-well reactions, the performance of this method is better than any of the empirical methods seen thus far in this article. However, the method exhibits relative errors greater than 0.20 in the rate coefficient for the multiple-well dissociation reaction $C_3H_5O_2 \leftrightarrow C_3H_5 + O_2$. On the multiple-well chemical-activation reaction $C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$, the maximum relative errors in the rate coefficient are over 0.28 for this case, both for the master equation and the modified strong collision analysis. On the reaction channels considered by Kazakov et al. (1994), this method exhibits very low relative errors in the range of 0.01 to 0.07 for the temperature range examined by them.

Proposed Approaches from Theory of Approximation of Functions

We now consider two methods from the analytic theory of approximation. The first is a global approximation technique using the Chebyshev expansions (Powell, 1981). The second is a local approximation technique using radial basis functions (Powell, 1990).

Chebyshev expansions

We consider the direct approximation of the logarithm of the rate coefficients as a truncated bivariate Chebyshev series in the inverse temperature and logarithm of the pressure. The rationale for choosing the inverse temperature as an argument of the Chebyshev series follows from the fact that any Arrhenius or modified-Arrhenius form for reaction rate coefficients may be expanded asymptotically in the inverse temperature. The complete effect of the falloff behavior becomes evident only over the entire range of pressure, and since pressure varies over wide magnitudes, the logarithm of the pressure is adopted as the second argument of the Chebyshev series. It is assumed that we desire approximations to the rate coefficients in a range of temperature and pressure given by the following inequalities

$$T_{\min} \leq T \leq T_{\max}, \tag{25}$$

$$P_{\min} \leq P \leq P_{\max}, \tag{26}$$

The Chebyshev polynomial (Powell, 1981; Rivlin, 1990) of degree $i - 1$ is given by

$$\varphi_i(x) = \cos[(i-1)\operatorname{acos}(x)]; \quad i = 1, 2, \ldots, \tag{27}$$

where x is the variable of interest defined to lie in the closed interval $[-1, +1]$. Hence, it is necessary to map the temperature and pressure domain onto the unit square. This is achieved by the transformations

$$\tilde{T} \leftarrow \frac{2T^{-1} - T_{\min}^{-1} - T_{\max}^{-1}}{T_{\min}^{-1} - T_{\max}^{-1}}, \tag{28}$$

$$\tilde{P} \leftarrow \frac{2\log P - \log P_{\min} - \log P_{\max}}{\log P_{\max} - \log P_{\min}}, \tag{29}$$

and we note that the rate coefficients $k(T, P)$ remain unchanged due to the mapping

$$k(\tilde{T}, \tilde{P}) \leftarrow k(T, P). \tag{30}$$

The logarithm (to the base 10) of the rate coefficient is thus approximated as

$$\log k(\tilde{T}, \tilde{P}) \approx \sum_{i=1}^{N} \sum_{j=1}^{M} a_{ij} \varphi_i(\tilde{T}) \varphi_j(\tilde{P}). \tag{31}$$

Here, the integer N denotes the number of basis functions along the temperature axis, the integer M denotes the number of basis functions along the pressure axis, and the $\{a_{ij}\}$ are the NM coefficients to be determined from a least-squares fit of the approximant to a set of data points at which the rate coefficients $k(T, P)$ have been computed from a detailed theory. The data points at which the rate coefficients are computed for input to the least-squares fit should be the roots of a high-order Chebyshev polynomial. Such a grid of data points is termed as the *Gauss-Chebyshev grid* (Powell, 1981; Rivlin, 1990). This is necessary (Powell, 1981; Rivlin, 1990; Venkatesh et al., 1996b) to ensure that the approximation is uniform over the whole domain of the temperature and pressure interval. The integers N and M are chosen in advance. Their choice serves to control the accuracy of the approximant, which increases monotonically with N and M. In our analysis we computed the rate coefficients $k(\tilde{T}, \tilde{P})$ on a $d \times d$ *Gauss-Chebyshev grid* where d was taken to be 50. This grid is given by

$$\tilde{T}_i = \cos\left[\frac{2i-1}{2d}\pi\right], \tag{32}$$

$$\tilde{P}_i = \cos\left[\frac{2i-1}{2d}\pi\right], \tag{33}$$

$$1 \leq i \leq d. \tag{34}$$

N and M were varied to construct approximants of different orders of accuracy.

Table 3 displays the performance of the Chebyshev approximants on all of the reaction channels considered in this study. Depending upon the number of basis functions retained along the temperature and pressure axes, the maximum relative errors may be brought down to as low as 0.01. For the multiple-well chemical-activation channel $C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$ fitted by a Chebyshev polynomial with six temperature basis functions and four pressure basis functions, the maximum relative error in the rate coefficient determined by the master equation analysis exhibited for this channel is 0.15, which is much smaller than the errors exhibited by the empirical methods considered earlier. This is true even for the modified strong collision analysis. For the multiple-well dissociation channel $C_3H_5OO \leftrightarrow C_3H_5 + O_2$, a Chebyshev approximant with seven temperature basis functions and three pressure basis functions exhibits far lower errors than those exhibited by the empirical methods, as seen in Table 1.

A noteworthy point is the explicit control of the temperature and pressure dependence in the Chebyshev approximation scheme. By simply increasing the number of basis functions along one axis, while keeping the number of basis functions along the other constant, one may observe the effects of increased accuracy in the representation of either the temperature or pressure dependences. Consider the $C_2H_6 \leftrightarrow CH_3 + CH_3$ reaction channel in Table 3. A Chebyshev approximant with five basis functions along the temperature axis and four basis functions along the pressure axis exhibits a maximum relative error of 0.32 for this channel while a Chebyshev approximant with six basis functions along the temperature axis and three basis functions along the pressure axis exhibits a maximum relative error of 0.23. A suitable balance is achieved in a Chebyshev approximant with seven temperature basis functions and three pressure basis functions to yield a maximum relative error of 0.09 in the rate coefficient. In principle, one may construct Chebyshev approximants of arbitrarily high accuracy by choosing the integers N and M to be sufficiently large to meet the required level of accuracy. A straightforward evaluation of the Chebyshev approximant given by Eq. 31 requires NM Chebyshev polynomial evaluations, $2NM$ multiplications, and $NM-1$ summations. For all values of N and M, a partial summation technique (Venkatesh et al., 1996b) that decreases the number of multiplications by $NM-1$ can be used to evaluate the approximant.

It is important to note that extrapolation should not be attempted on Chebyshev approximants outside the interval of approximation. If an approximation outside of the interval is desired, then one may either recompute the approximant on a wider approximation interval or map the temperature and pressure intervals of $(0, \infty)$ onto $[-1, +1]$ via a semi-infinite to finite mapping function and then construct an approximant in terms of the mapped variables. In the latter ap-

Table 3. Maximum Relative Errors in the Rate Coefficient over Temperature and Pressure Ranges for Chebyshev Approximants With Master Equation Analysis of the Collisional Energy Transfer*

Channel	6×3	5×4**	7×3	6×4	8×3	7×4	9×4
$C_3H_5O_2 \leftrightarrow C_3H_5 + O_2$	0.13 (0.14)	0.15 (0.14)	0.10 (0.11)	0.07 (0.09)	0.07 (0.09)	0.05 (0.09)	0.03 (0.04)
$C_2H_6 \leftrightarrow CH_3 + CH_3$	0.23 (0.19)	0.32 (0.27)	0.09 (0.10)	0.18 (0.12)	0.11 (0.10)	0.09 (0.09)	0.02 (0.06)
$C_2H_6 \leftrightarrow C_2H_5 + H$	0.23 (0.19)	0.29 (0.27)	0.17 (0.13)	0.11 (0.10)	0.15 (0.11)	0.13 (0.10)	0.05 (0.05)
$C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$	0.20 (0.17)	0.18 (0.15)	0.18 (0.15)	0.15 (0.14)	0.17 (0.15)	0.09 (0.11)	0.07 (0.02)
$C_3H_5 + O_2 \leftrightarrow C \cdot CyCCOO$	0.19 (0.17)	0.09 (0.13)	0.11 (0.14)	0.09 (0.13)	0.15 (0.13)	0.10 (0.10)	0.05 (0.07)
$CH_3 + CH_3 \leftrightarrow C_2H_6$	0.17 (0.19)	0.33 (0.29)	0.15 (0.18)	0.19 (0.18)	0.11 (0.15)	0.09 (0.13)	0.05 (0.09)
$CH_3 + CH_3 \leftrightarrow C_2H_5 + H$	0.15 (0.13)	0.13 (0.13)	0.16 (0.12)	0.11 (0.12)	0.15 (0.08)	0.08 (0.08)	0.01 (0.01)

*The numbers in parentheses indicate errors for an identical analysis except that the intermolecular energy transfer is modeled using the strong collision treatment.

**Note: 5×4 means the Chebyshev approximant has 5 basis functions along the temperature axis and 4 basis functions along the pressure axis, etc.

proach, care must be taken in choosing a suitable mapping function to preserve the convergence properties of the Chebyshev expansions. This is discussed in further detail in Venkatesh et al. (1996b).

We may note that the Chebyshev polynomials possess many important theoretical properties, in particular, the minimax property. The minimax approximation has the smallest maximum deviation from the true function among all polynomial approximants. A Chebyshev approximating polynomial obtained simply by minimizing the least-square deviation is almost identical to the true minimax polynomial.

Radial basis functions

RBFs are local approximants. We assume that the range of the temperature T and pressure P for which the rate coefficient $k(T,P)$ has to be approximated is given by Eqs. 25 and 26. We also assume that the temperature and pressure are mapped onto the unit square as shown in Eqs. 28 and 29. Let the vector Y denote

$$Y \equiv [\tilde{T}, \tilde{P}]. \tag{35}$$

We denote the logarithm (to base 10) of the rate coefficient $k(\tilde{T}, \tilde{P})$, scaled to lie between -1 and $+1$, by $S(Y)$. In the RBF approach, we fit $S(Y)$ to the special form

$$S(Y) = \lambda_0 + \sum_{i=1}^{m} \lambda_i \phi(\|Y - Y_i\|) \tag{36}$$

with the constraint

$$\sum_{i=1}^{m} \lambda_i = 0. \tag{37}$$

Here, $\|Y - Y_i\|$ denotes the Euclidean norm of the vector $Y - Y_i$. The m parameters λ_i, $i = 1, \ldots, m$, are to be determined by least-squares fitting such that Eqs. 36 and 37 hold. As long as the Y_i, $i = 1, \ldots, m$ (called the centers of the radial bases) are distinct, such systems will be nonsingular for many choices (Micchelli, 1986) of $\phi(r)$ including the following

$$\phi(r) = r^3 \quad \text{Duchon radial cubics,} \tag{38}$$

$$\phi(r) = \sqrt{r^2 + 1} \quad \text{Hardy multiquadrics,} \tag{39}$$

$$\phi(r) = \frac{1}{\sqrt{r^2 + 1}} \quad \text{Inverse multiquadrics,} \tag{40}$$

$$\phi(r) = r \quad \text{Piecewise linear functions,} \tag{41}$$

$$\phi(r) = r^2 \log r \quad \text{Thin-Plate splines.} \tag{42}$$

In one-dimension, cubic splines, which minimize the Euclidean norm of the second derivatives of the approximant, arise as a special case of RBFs. In any number of dimensions, RBFs preserve most of the attractive approximation properties of one-dimensional splines. RBF approximants will accept arbitrarily scattered data and can be used for either interpolation or regression. A comparative survey (Franke, 1982) of 34 different algorithms for scattered data interpolation ranked the *multiquadric* RBF as the most impressive method included in the tests. More recently, Powell (1992) has observed that, similar to cubic splines in one-dimension, thin-plate splines are optimal for approximating two-dimensional surfaces in the sense of minimizing the Euclidean norm of the second derivatives of the approximant. Furthermore, RBF approximants consisting of thin-plate splines may be evaluated rapidly (Powell, 1992) through a truncated Laurent-expansion technique.

The RBF method is unconditionally stable in any number of dimensions under very mild restrictions. In this approach, the computational cost of modeling d data points using m basis functions in D dimensions is $O(dm^2)$ operations, which is independent of D. This is in direct contrast to polynomial approximation, where the cost of computing m basis function coefficients is $O(m^{3D})$. In the RBF approach the data points can be scattered unlike the case of Chebyshev approximants. The only remaining issue is the choice of the centers $\{Y_i, i = 1, \ldots, m\}$. The number of data points d at which the rate coefficients are computed is usually much larger than the number of centers m. We have to select a subset of only m of the d sample points to center the RBFs. To improve conditioning and minimize extrapolation errors, this subset should contain as widely spread out data points as possible. A slow but excellent selection strategy is: (i) include a randomly selected point; (ii) search the whole data set to find and include the point which lies furthest from any point included so far; and (iii) repeat until m points are selected.

It is important to note that in this method the selection strategy is executed only once and the total number of parameters constituting the approximant are the m basis coefficients and the m centers. In our computations we have considered only the thin-plate splines RBF. The least-squares fit was performed on an equidistant grid of 2,500 points in the inverse temperature and the logarithm of pressure. Table 4 displays the minimum number of thin-plate RBFs required for each of the channels to achieve a maximum relative error of 0.2 in the approximation to the rate coefficient determined from a master equation analysis. In terms of the number of parameters required for acceptable approximation, it is clear that the Chebyshev approximants are superior to RBFs. The utility of RBFs lies in scattered data interpolation where one does not have explicit control in choosing the points in the domain at which the approximant can be computed exactly. On the other hand in the case of interest here, the approximation of rate coefficients generated by the RRKM or SACM theories, there is complete flexibility in choosing the temper-

Table 4. Minimum Number of Thin-Plate Splines Required to Achieve Maximum Relative Errors of 20% in the Rate Coefficient over Temperature and Pressure Ranges with Master Equation Analysis of the Collisional Energy Transfer

Channel	No. of Radial Bases
$C_3H_5O_2 \leftrightarrow C_3H_5 + O_2$	187
$C_2H_6 \leftrightarrow CH_3 + CH_3$	120
$C_2H_6 \leftrightarrow C_2H_5 + H$	117
$C_3H_5 + O_2 \leftrightarrow H_2CCCH_2 + HO_2$	170
$C_3H_5 + O_2 \leftrightarrow C \cdot CyCCOO$	154
$CH_3 + CH_3 \leftrightarrow C_2H_6$	107
$CH_3 + CH_3 \leftrightarrow C_2H_5 + H$	99

ature- and pressure-domain at which the rates are explicitly computed. However, RBF approximants are amenable to extrapolation unlike Chebyshev approximants.

Results

(a) For multiple-well systems, Troe's F_{cent} method, the SRI method, and the method due to Gilbert and Poole provide approximants of low accuracy for the ranges of temperature and pressure tested here. Modification of the Troe's F_{cent} method and the SRI method to account for increased temperature dependence in the limiting rate coefficients does not result in approximants of uniform and acceptable accuracy. An empirical extension of Troe's F_{cent} method to account for multiple-wells provides approximants which, though exhibiting better accuracy, are also not uniformly accurate.

(b) The generalized-mean-of-limits formula due to Kazakov et al. (1994), which was specifically designed for multiple-well systems, provides accurate approximants only if the range of temperature and pressures considered is narrow. For the 2,500-point grid over the ranges of temperature and pressure specified in the section on temperature and pressure domain of approximation, it has exhibited larger errors on the multiple-well channels considered here.

(c) The Chebyshev approximants described earlier provide approximants of acceptable accuracy for single-well as well as multiple-well systems. The radial basis function approximants provide accurate approximants for single- and multiple-well systems. They require more parameters since they are local approximants, but the radial basis function approximants are amenable to extrapolation.

(d) Some of the empirical methods tested here have exhibited large errors on some of the reactions considered when compared with similar studies in the literature. This is due to two reasons. We have considered a very wide range of temperature and pressure and additionally considered a densely spaced grid over these ranges. Any empirical approximation technique can prove to work well when considering a few domain points over a wide range of the domain or a large number of domain points over a small range of the domain. If one were analyzing shock-tube data over a limited range or limited number of data points, it is perfectly reasonable to use any of the empirical models to approximate the rate constants. In the simulation of mechanistic models, one usually considers a large number of reactions over a wide range of temperatures and pressures.

(e) It should be noted that the empirical approaches construct approximants in terms of the temperature and reduced pressure, both of which are not independent variables. The reduced pressure is a function of temperature and pressure. The motivation (Gilbert et al., 1983) for modeling in terms of the reduced pressure was to facilitate the establishment of correlations with the quantity F_{cent} of Eq. 10. However, it is clear from our studies on multiple-well systems that such correlations do not exist for the universal application of the F_{cent} method. Our motivation for using Chebyshev approximants is in their incorporation into mechanistic kinetic models for the purposes of simulation. The Chebyshev approximants have been constructed in terms of temperature and pressure which are independent variables and are related only through the ideal gas law. In the simulation of mechanistic kinetic models, the variables of explicit control are the temperature and pressure. The reduced pressure is different for each reaction and hence cannot act as a quantity of explicit global control.

Conclusions

We conclude that the method of falloff approximation due to Poole and Gilbert is the most accurate method for the approximation of the temperature- and pressure-dependence of single-well reactions. For multiple-well systems, our investigation reveals that none of the proposed empirical approaches in the literature and suitable for the approximation over wide ranges of temperature and pressure as required in the simulation models for chemical-kinetics problems. We surmise that empirical or semi-empirical approaches to approximating the falloff behavior of multiple-well reactions offer no means of assuring that the approximation errors will always be minimal over fine grids defined over broad ranges of temperature and pressure.

The Chebyshev approximants provide accurate approximants over any temperature and pressure domain for single- and multiple-well reactions. These approximants should not be used for extrapolative studies. Similarly, the radial basis approximants which are suited for extrapolation provide accurate approximants for any kind of reaction over any range of temperature and pressure conditions although they require more parameters. The Chebyshev approximants, as well as the radial basis approximants, provide us with the ability to (i) control independently the accuracy of approximation along the temperature and pressure axes; (ii) construct approximations to a user-specified degree of accuracy; (iii) analyze the maximum interpolation errors over the entire temperature and pressure domain (not just including the points used in the fits); and (iv) increase or decrease the number of parameters in the approximant by means of rigorous sensitivity analysis methods.

The determination of the unknown parameters in a Chebyshev approximant requires the solution of a straightforward linear least-squares problem which is computationally very facile to implement. On the other hand, the empirical approaches studied in this article require the solution of a nonlinear least-squares problem which is less trivial to solve numerically. Nonlinear least-squares problems can possess multiple minima which may be difficult to detect (Poole and Gilbert, 1994).

Spectral approximations such as the Chebyshev approximation provide a mathematical framework for estimating the interpolation and approximation errors. This is not the case with the Lindemann or generalized Lindemann approach where it is impossible to provide an upper bound on the interpolation errors of the rate coefficients for the postulated functional forms of the falloff surface. In Venkatesh et al. (1996b), we provide a comprehensive discussion of estimating the worst-case interpolation errors of Chebyshev approximants, and discuss the relationships between the topography of the function being approximated and the minimum number of basis functions required in a Chebyshev approximant to achieve a specified order of accuracy. We also show how sensitivity measures of interest may be computed in order to study the importance of approximations along the temperature or pressure axes. This is achieved via a variational perturbation analysis. These sensitivity measures can then enable the user to rank the importance of the reactions in a mechanism to a user-specified degree of approximation.

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