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Accurate rate expressions for simulations of gas-phase chemical reactions

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Abstract

Several of the commonly used expressions giving reaction rates for model chemical reactions, though accurate for very high activation energies (i.e. $E_a \gg k_B T$), are inaccurate for more typical reaction conditions. In this paper we provide the complete and accurate rate expressions for model reactions having cross-sections dependent on translational, line-of-centers translational, and internal energies as well as on combinations thereof. Included are rate expressions for models giving Arrhenius-like temperature dependencies.

Tests of several of the models and their corresponding cross-section expressions were made using Bird's direct simulation Monte Carlo method. These were successful in reproducing the experimentally determined rates over the full range of temperatures for the representative reactions: $HF + H \rightarrow H_2 + F$, $CO + OH \rightarrow CO_2 + H$, $H_2 + O \rightarrow OH + H$ and $H_2 + Cl \rightarrow HCl + H$.

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1. Introduction

In the 1920s Lindemann [1], Christiansen [2], Hinshelwood [3], Fowler [4] and others [5–8] used kinetic theory and statistical mechanics to develop expressions for predicting the rates of chemical reaction for a number of model systems. These included expressions for reactions of species in the gas phase in bimolecular encounters with sufficient energy for reaction available as relative translational energy E_{rel}, translational energy along the line-of-centers at impact E_{cc} and internal energy E_i associated with the number of internal degrees of freedom of the colliding species. Most textbooks of chemical kinetics include some of the expressions. The detailed information required for use of these expressions is available from modern experimental measurements and theoretical predictions for an increasing number of reactions.

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In investigations of chemical reactions using Bird's direct simulation Monte Carlo (DSMC) method [9,10] we have found that the typical rate expressions for model systems found in the kinetics literature are often inadequate.

The expression for the rate constant k of a bimolecular reaction is most often given in the form [1–8]

$$k=\frac{1}{\Gamma\left(\frac{1}{2}s_1+\frac{1}{2}s_2+2\right)}\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}}\sigma\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{\frac{1}{2}s_1+\frac{1}{2}s_2+1}\mathrm{e}^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}},\tag{1}$$

where s_n is the number of square terms representing the available internal energy of molecule n, E_{a} is the activation energy, k_{B} is the Boltzmann constant, T is the temperature, μ is the reduced mass of the colliding pair and σ is a fixed cross-section. The rate expression for a model reaction containing a total of four square terms in the energy representing two rotational degrees of freedom and one vibrational degree of freedom, and reaction occurring with energy E_{rel} and E_{i} exceeding an amount E_{a} is commonly written with the omission of several terms, noting the restriction $E_{\mathrm{a}} \gg k_{\mathrm{B}}T$, as

$$k=\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}}\sigma\mathrm{e}^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}}\left[\frac{1}{6}\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{3}\right].\tag{2}$$

The complete rate expression containing all terms is written as

$$k=\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}}\sigma\mathrm{e}^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}}\left[1+\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{1}+\frac{1}{2}\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{2}+\frac{1}{6}\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{3}\right].\tag{3}$$

For a typical reaction with $E_{\mathrm{a}}/k_{\mathrm{B}}T=10$, the omission of the terms of lower powers introduces an error which is 27% of the correct value for this model.

The complete expressions and their derivations for many of the most useful models are scattered throughout the literature of chemical kinetics and in many cases are simply not to be found. In this article we assemble the full expressions along with their derivations, adding new derivations as required, all in a consistent manner. We explore the effectiveness of each of these models in DSMC calculations for four representative reactions:

$$\mathrm{HF}+\mathrm{H}\rightarrow\mathrm{H}_2+\mathrm{F},$$
$$\mathrm{CO}+\mathrm{OH}\rightarrow\mathrm{CO}_2+\mathrm{H},$$
$$\mathrm{H}_2+\mathrm{O}\rightarrow\mathrm{OH}+\mathrm{H},$$
$$\mathrm{H}_2+\mathrm{Cl}\rightarrow\mathrm{HCl}+\mathrm{H}.$$

The models treated include those with energy requirements based on E_{rel}, E_{cc}, E_{i} and their combinations as well as models giving overall rate expressions having Arrhenius or Arrhenius-like forms $k(T)=AT^{\eta}\mathrm{e}^{-E_{\mathrm{a}}/k_{\mathrm{B}}T}$.

Direct simulation Monte Carlo is a stochastic method designed for nonequilibrium flows, and it is very effective at moderate to high Knudsen numbers. DSMC is also valid at low Knudsen numbers and has been shown to converge to the Boltzmann equation in the limit of small cell size and time step [11], but computational requirements become excessive and the method is impractical for very low Knudsen numbers. Originally developed for gas dynamics simulations, the DSMC method has been extended to include chemical reactions [10]. Recent applications include complete simulations of the coupled chemical kinetics and gas dynamics of detonations [12,13]. The DSMC program developed for the simulations reported here employs classical (i.e. continuous) distributions of internal energies to represent the rotational and vibrational motions for molecules having internal degrees of freedom. Energy exchanges are treated with the Borgnakke–Larsen phenomenological model for inelastic collisions [14] with modifications described by Bird to treat only a fraction of the particles as inelastic and to satisfy detailed balancing [10]. Ideally one would use information on cross-sections related to the rotation–vibration levels of the molecules. However, such detailed information on cross-sections is seldom available and the levels are often closely spaced, so that the classical approach is appropriate.

2. Collision rates, reaction rates and distributions

The collision rate between molecules of type A and type B having Maxwellian velocity distributions in three dimensions is given by (see Refs. [10,15] and others)

$$Z_{\mathrm{AB}} = n_{\mathrm{A}} n_{\mathrm{B}} \left(\frac{\mu}{k_{\mathrm{B}}T}\right)^{\frac{3}{2}} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int_0^\infty \mathrm{e}^{-\frac{\mu v_{\mathrm{rel}}^2}{2k_{\mathrm{B}}T}} \sigma_{\mathrm{C}} v_{\mathrm{rel}}^3 \mathrm{d}v_{\mathrm{rel}}, \tag{4}$$

where their cross-section σ_{C} for collisions is dependent on properties of the colliding molecules, v_r is the relative velocity, μ is the reduced mass of the colliding pair, k_{B} is the Boltzmann constant and T is the temperature. Expressed in terms of relative translational energy $E_{\mathrm{rel}} = \frac{1}{2}\mu v_{\mathrm{rel}}^2$, Eq. (4) becomes

$$Z_{\mathrm{AB}} = n_{\mathrm{A}} n_{\mathrm{B}} \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \int_0^\infty \mathrm{e}^{-\frac{E_{\mathrm{rel}}}{k_{\mathrm{B}}T}} \sigma_{\mathrm{C}} \left(\frac{E_{\mathrm{rel}}}{k_{\mathrm{B}}T}\right) \mathrm{d}\frac{E_{\mathrm{rel}}}{k_{\mathrm{B}}T}. \tag{5}$$

For a collision cross-section which has a fixed value σ_{C}, the collision rate is

$$Z_{\mathrm{AB}} = n_{\mathrm{A}} n_{\mathrm{B}} \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma_{\mathrm{C}}. \tag{6}$$

The expression for the reaction rate is the same as Eq. (5) except that the reaction cross-section σ_{R} replaces σ_{C}. We are concerned here with reaction cross-sections which are functions of E_{rel}, E_{cc} and E_{i}. Since E_{cc} is a function of E_{rel} we can write $\sigma_{\mathrm{R}} = \sigma_{\mathrm{R}}(E_{\mathrm{rel}}, E_{\mathrm{i}})$ and the reaction rate $\mathrm{R_{AB}}$ is given by

$$R_{\mathrm{AB}} = n_{\mathrm{A}} n_{\mathrm{B}} \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \int_0^\infty \int_0^\infty \mathrm{e}^{-\frac{E_{\mathrm{rel}}}{k_{\mathrm{B}}T}} \sigma_{\mathrm{R}}(E_{\mathrm{rel}}, E_{\mathrm{i}}) \frac{E_{\mathrm{rel}}}{k_{\mathrm{B}}T} f\left(\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) \mathrm{d}\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T} \mathrm{d}\frac{E_{\mathrm{rel}}}{k_{\mathrm{B}}T}, \tag{7}$$

where $f(\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T})$ is the distribution function for the sum of internal energies E_{i}, expressed as $E_{\mathrm{i}}/k_{\mathrm{B}}T$. The rate constant k for the reaction of A with B is directly related

$$k = \frac{R_{\mathrm{AB}}}{n_{\mathrm{A}} n_{\mathrm{B}}}. \tag{8}$$

The distribution function $f(\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T})$ for the sum of internal energies for two colliding molecules having internal energies available in classical rigid rotations and harmonic vibrations is given in terms of $E_{\mathrm{i}}/k_{\mathrm{B}}T$ by (see Refs. [10,15] and others)

$$f\left(\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right) = \frac{1}{\Gamma\left(\frac{s}{2}\right)} \left(\frac{E_{\mathrm{i}}}{k_{\mathrm{B}}T}\right)^{\frac{s}{2}-1} \mathrm{e}^{-\frac{E_i}{k_{\mathrm{B}}T}}, \tag{9}$$

where $s = s_{\mathrm{A}} + s_{\mathrm{B}}$, the sum of the number of classical internal degrees of freedom of the colliding molecules A and B. The number of degrees of freedom corresponds to the number of square terms in the classical expression for the internal energies. Each rotational mode contributes one degree of freedom and each vibrational mode contributes two. The terms s_{A} and s_{B} may be non-integer. If s is an even integer, the gamma function $\Gamma\left(\frac{s}{2}\right)$ may be replaced by $\left(\frac{s}{2} - 1\right)!$.

3. Simulation details

The direct simulation Monte Carlo method was used to explore the use of the reaction models and confirm the validity of the rate expressions obtained analytically. In the subsequent sections we derive the rate expressions for these models. Along with them we report comparisons of analytic and DSMC rates over a range of temperatures for several of the models. The DSMC calculations were made with a 2400-line object-oriented C++ code. Each simulation was carried out for a simple three-dimensional cell with periodic boundaries and a cell width of one mean-free-path. The simulations were run for 24 h on AMD Athlon 2200+ processors with the Free Software Foundation's GNU compiler and required less than 20 MB of RAM. Each case was initialized with 10,000 or 20,000 reactant particles and was run for a total of 240,000 time steps with a step size on the order of 10^{-12} s with a typical reaction half-life of 20,000 time steps.

4. Model reactions

A model reaction is specified by a statement of the energy requirements for reaction in the form of the reaction cross-section $\sigma_R(E_{rel}, E_i)$. In the simplest cases this is expressed as a requirement that E_{rel} or E_i exceed an energy minimum E_a, a quantity at least loosely related to the Arrhenius activation energy. In other cases the requirement may be more complex.

An overall rate expression is obtained by carrying out the integrations indicated in Eq. (7) with insertion of the appropriate function $\sigma_R(E_{rel}, E_i)$. This typically involves transformations and specifying lower limits for the integrations. Further, the specification of σ_R for a specific reaction includes a (constant) cross-section σ, normally less than the total collision cross-section σ_C, allowing for steric and similar effects.

With $\sigma_C \gg \sigma$ the reaction cross-section may be specified independently of σ_C and properties such as viscosity become independent of the reaction model. In the calculations reported here we have used the hard sphere model with a fixed cross-section σ_C. If a different total collision cross-section in used in DSMC calculations (such as the cross-section for the inverse power potential or the variable hard sphere collision model), the distribution of energy in collisions will be altered and the reaction rates will be different.

The rate expressions and their derivations for several models are indicated in the following sections. A key to obtaining relatively simple rate expressions is the use of cross-section expressions with E_{rel} in the denominator to cancel that in the integrand of Eq. (7).

4.1. Translational energy requirement, $E_{rel} > E_a$

The reaction cross-section is specified as

$$\sigma_R = \begin{cases} \sigma & \text{if } E_{rel} \geqslant E_a \\ 0 & \text{if } E_{rel} < E_a \end{cases}. \tag{10}$$

The integral involving E_i in Eq. (7) is separable, equal to unity and may be eliminated. The resulting expression becomes

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}} \sigma \int_{\frac{E_a}{k_BT}}^{\infty} e^{-\frac{E_{rel}}{k_BT}} d\frac{E_{rel}}{k_BT} = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}} \sigma_C e^{-\frac{E_a}{k_BT}} \left(1 + \frac{E_a}{k_BT}\right). \tag{11}$$

4.2. Line-of-centers translational energy requirement, $E_{cc} > E_a$

In the case of collisions of hard spheres the center-to-center translational energy depends on E_{rel} and the impact parameter. Several approaches may be used in consideration of the mechanics, but the requirement that E_{cc} exceed E_a results in the cross-section expression

$$\sigma_R = \begin{cases} \sigma\left(1 - \frac{E_{rel}-E_a}{E_{rel}}\right) & \text{if } E_{rel} \geqslant E_a \\ 0 & \text{if } E_{rel} < E_a \end{cases}. \tag{12}$$

The integration within Eq. (7) is straightforward and leads to

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}} \sigma e^{-\frac{E_a}{k_BT}}. \tag{13}$$

4.3. Internal energy requirement, $E_i > E_a$

In this case the reaction cross-section is independent of E_{rel} and the requirement is that the sum E_i of energies for s degrees of freedom exceed E_a. The cross-section is given by

$$\sigma_R = \begin{cases} \sigma & \text{if } E_i \geqslant E_a \\ 0 & \text{if } E_i < E_a \end{cases}. \tag{14}$$

Either Eq. (7) may be used or one may simply multiply the collision rate Z_{AB} of Eq. (6) by the probability that E_i exceeds E_a obtained from Eq. (9)

$$f\left(\frac{E_\mathrm{i}}{k_\mathrm{B}T} > \frac{E_\mathrm{a}}{k_\mathrm{B}T}\right) = \frac{1}{\Gamma\left(\frac{s}{2}\right)}\int_{\frac{E_\mathrm{a}}{k_\mathrm{B}T}}^{\infty}\left(\frac{E_\mathrm{i}}{k_\mathrm{B}T}\right)^{\frac{s}{2}-1} \mathrm{e}^{-\frac{E_\mathrm{i}}{k_\mathrm{B}T}}\,\mathrm{d}\frac{E_\mathrm{i}}{k_\mathrm{B}T} = \frac{\Gamma\left(\frac{s}{2},\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)}{\Gamma\left(\frac{s}{2}\right)}, \tag{15}$$

where $\Gamma(j,\alpha)$ is the incomplete gamma function. The result is

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}}\sigma\frac{\Gamma\left(\frac{s}{2},\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)}{\Gamma\left(\frac{s}{2}\right)}. \tag{16}$$

In the case of $\frac{s}{2} = 1$, this reduces to

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}}\sigma\mathrm{e}^{-\frac{E_\mathrm{a}}{k_\mathrm{B}T}}. \tag{17}$$

Similar reductions occur for other integer values of $\frac{s}{2}$ and lead to the general expression

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}}\sigma\mathrm{e}^{-\frac{E_\mathrm{a}}{k_\mathrm{B}T}}\left\{1 + \left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)^{1} + \frac{1}{2}\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)^{2} + \cdots + \frac{1}{\left(\frac{s}{2}-1\right)!}\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)^{\frac{s}{2}-1}\right\}. \tag{18}$$

Series expressions may also be found for $\frac{s}{2} = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

This model was tested in calculations for the reaction $\mathrm{HF} + \mathrm{H} \rightarrow \mathrm{H}_2 + \mathrm{F}$ for which Cohen and Westberg [16] measured rates fit by an Arrhenius-like expression $k = 2.73 \times 10^{-12}T^{0.6}\mathrm{e}^{-32{,}510/RT}$ (k in cm^3 molecule^{-1} s^{-1}, T in K and E_a in cal/mole) over the range 650–7000 K. The reaction is known to be dependent on vibrational excitation of the HF species corresponding to two degrees of freedom. A slight adjustment of the three constants of the experimental rate expression gave a more convenient expression, $k = 6.90 \times 10^{-12}T^{0.5}\mathrm{e}^{-33{,}094/RT}$, incorporating $T^{0.5}$ and corresponding to the energy requirement matching Eq. (14). The values of k were negligibly different from those of the original expression. The DSMC simulations with $s = 2$ gave excellent agreement with the original rate expression as well as with the revised rate expression as shown in Fig. 1.

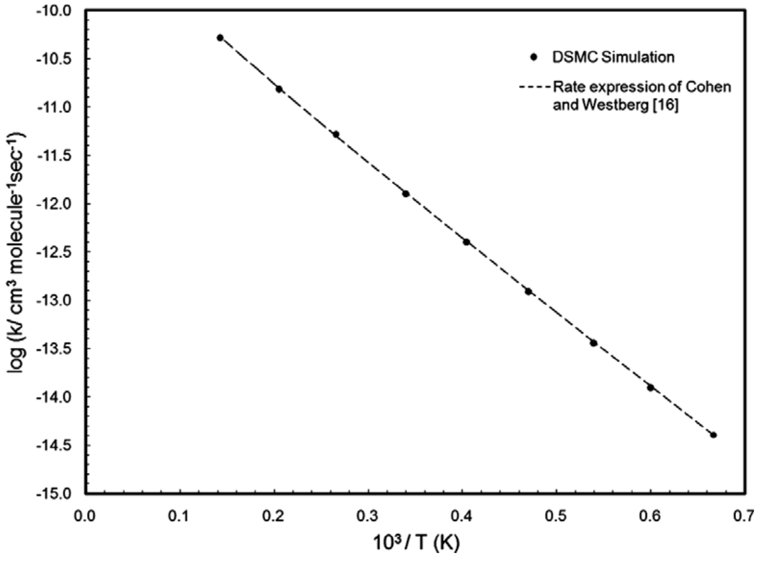

Fig. 1. Comparison of rate constants for the reaction $\mathrm{HF} + \mathrm{H} \rightarrow \mathrm{H}_2 + \mathrm{F}$ simulated using the internal energy reaction model [Eq. (14); $E_\mathrm{i} > E_\mathrm{a}$] over a temperature range of 1500–7000 K.

4.4. Combination of translational and internal energies, $E_{rel} + E_i > E_a$

In this case reaction occurs for collisions with $E_{\mathrm{tot}} = E_{\mathrm{rel}} + E_{\mathrm{i}}$ greater than E_{a} and the cross-section is given by

$$\sigma_{\mathrm{R}} = \begin{cases} \sigma & \text{if } E_{\mathrm{tot}} \geqslant E_{\mathrm{a}} \\ 0 & \text{if } E_{\mathrm{tot}} < E_{\mathrm{a}} \end{cases}. \tag{19}$$

Using Eq. (9) in Eq. (7), substituting ($E_{\mathrm{tot}} - E_{\mathrm{i}}$) for E_{rel} and integrating over $E_{\mathrm{i}}/k_{\mathrm{B}}T$ in the range *0* to $E_{\mathrm{tot}}/k_{\mathrm{B}}T$ gives

$$k = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \frac{1}{\Gamma\left(\frac{s}{2}+2\right)} \int_0^{\infty} \mathrm{e}^{-\frac{E_{\mathrm{tot}}}{k_{\mathrm{B}}T}} \left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{\frac{s}{2}+1} \sigma_{\mathrm{R}}\left(\frac{E_{\mathrm{tot}}}{k_{\mathrm{B}}T}\right) \mathrm{d}\frac{E_{\mathrm{tot}}}{k_{\mathrm{B}}T}. \tag{20}$$

With $E_{\mathrm{a}}/k_{\mathrm{B}}T$ as the lower limit of integration the rate constant becomes

$$k = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \frac{\Gamma\left(\frac{s}{2}+2, \frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)}{\Gamma\left(\frac{s}{2}+2\right)}. \tag{21}$$

As before, series expressions may be obtained for integer values of *s*. For even values of *s* the expression is

$$k = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \mathrm{e}^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}} \sum_{n=0,2,4,\ldots}^{s+2} \frac{1}{\left(\frac{n}{2}\right)!} \left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{\frac{n}{2}}, \tag{22}$$

or

$$k = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \mathrm{e}^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}} \left\{ 1 + \left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{1} + \frac{1}{2}\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{2} + \cdots + \frac{1}{\left(\frac{s}{2}+1\right)!}\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{\frac{s}{2}+1} \right\}. \tag{23}$$

For odd values of *s* the series expression is

$$k = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \left\{ \mathrm{e}^{-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}} \sum_{n=1,2,3,\ldots}^{s-1} \frac{1}{\Gamma\left(n+\frac{1}{2}\right)} \left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{n-\frac{1}{2}} + \mathrm{erfc}\left[\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)^{\frac{1}{2}}\right] \right\}, \tag{24}$$

or

$$k = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \left\{ \mathrm{e}^{-\alpha} \left(\frac{2}{\sqrt{\pi}}(\alpha)^{\frac{1}{2}} + \frac{4}{3\sqrt{\pi}}(\alpha)^{\frac{3}{2}} + \frac{8}{15\sqrt{\pi}}(\alpha)^{\frac{5}{2}} + \cdots + \frac{1}{\Gamma\left(s-\frac{1}{2}\right)}(\alpha)^{\frac{s}{2}+1} \right) + \mathrm{erfc}\left[(\alpha)^{\frac{1}{2}}\right] \right\}, \tag{25}$$

where α is $E_{\mathrm{a}}/k_{\mathrm{B}}T$, erfc($\alpha$) is the complementary error function 1-erf(α), and $\Gamma\left(n+\frac{1}{2}\right)$ may be written as $1 \cdot 3 \cdot 5 \cdots (2n-1)\sqrt{\pi}/2^n$.

For comparisons we chose the reaction $\mathrm{CO} + \mathrm{OH} \rightarrow \mathrm{CO_2} + \mathrm{H}$ with rates measured by Boni and Penner [17] who obtained an Arrhenius rate expression of $k = 6.64 \times 10^{-12} T^0 \mathrm{e}^{-8008/RT}$ (k in cm^3 molecule^{-1} s^{-1}, T in K, and E_{a} in cal/mole). Using the reaction cross-section specified by Eq. (22) with $s = 4$, the DSMC simulations give very good agreement with the rate expression by Boni and Penner as shown Fig. 2. The $\mathrm{CO} + \mathrm{OH}$ reaction demonstrates the differences in reaction rates described in the Introduction with Eqs. (2) and (3). At a temperature of 2000 K ($E_{\mathrm{a}}/k_{\mathrm{B}}T = 2$), Eq. (2) predicts a reaction rate only about 1/5 the correct value given by Eq. (3).

4.5. Combination of line-of-centers translational and internal energies, $E_{cc} + E_i > E_a$

For the requirement that the sum of the line-of-centers energy E_{cc} and the internal energies E_{i} exceed E_{a} the reaction cross-section is

$$\sigma_{\mathrm{R}} = \begin{cases} \sigma & \text{if } E_{\mathrm{cc}} + E_{\mathrm{i}} \geqslant E_{\mathrm{a}} \\ 0 & \text{if } E_{\mathrm{cc}} + E_{\mathrm{i}} < E_{\mathrm{a}} \end{cases}. \tag{26}$$

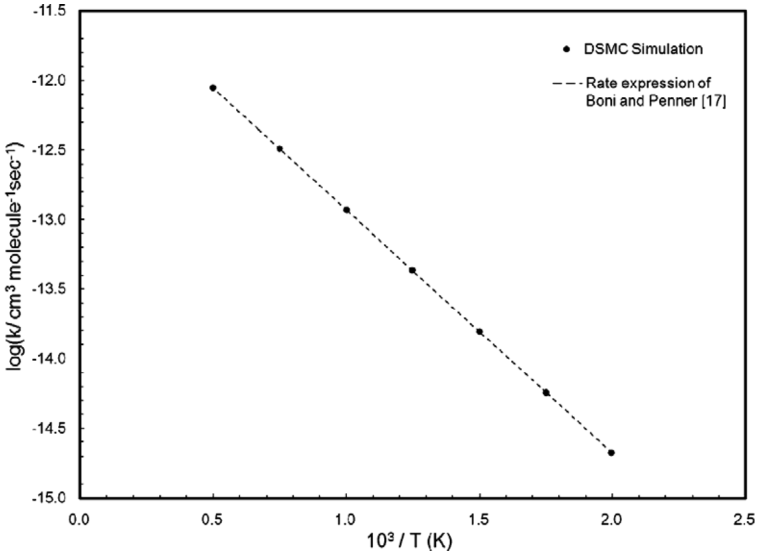

Fig. 2. Comparison of rate constants for the reaction $CO + OH \rightarrow CO_2 + H$ simulated using the combination model [Eq. (19); $E_{rel} + E_i > E_a$] over a temperature range of 500–2000 K.

The rate expression may be derived as in the previous section. An alternative is simply to combine the line-of-centers result in Eq. (13), substituting $E_a - E_i$ for E_a of Eq. (13), with the distribution for E_i of Eq. (9). The rate constant is then obtained as

$$k = \left(\frac{8k_B T}{\pi\mu}\right)^{\frac{1}{2}} \frac{\sigma}{\Gamma\left(\frac{s}{2}\right)} \left\{ \int_{\frac{E_a}{k_B T}}^{\infty} \left(\frac{E_i}{k_B T}\right)^{\frac{s}{2}-1} e^{-\frac{E_i}{k_B T}} d\frac{E_i}{k_B T} + \int_0^{\frac{E_a}{k_B T}} e^{-\frac{E_a - E_i}{k_B T}} \left(\frac{E_i}{k_B T}\right)^{\frac{s}{2}-1} \times e^{-\frac{E_i}{k_B T}} d\frac{E_i}{k_B T} \right\}. \tag{27}$$

For integer values of $\frac{s}{2}$ the results may be expressed in series form. For an even number of square terms ($\frac{s}{2} = 1, 2, 3, \ldots$) the integrations yield

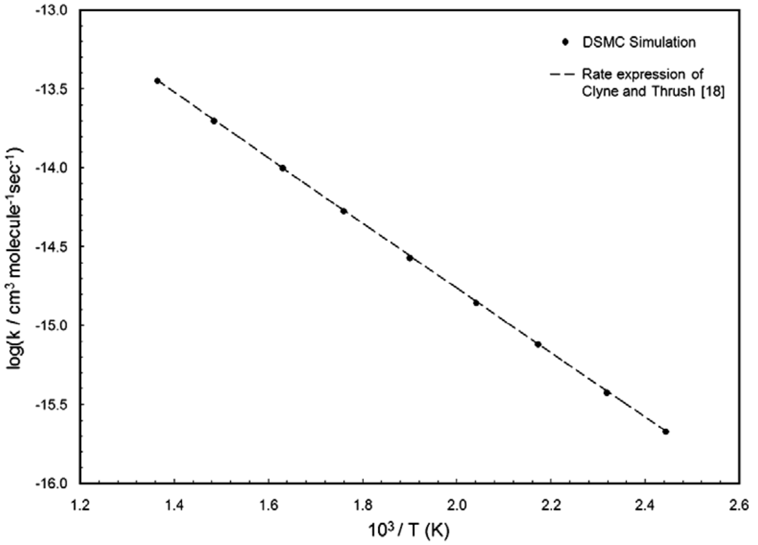

Fig. 3. Comparison of rate constants for the reaction $H_2 + O \rightarrow OH + H$ simulated using the combination model [Eq. (26); $E_{cc} + E_i > E_a$] over a temperature range of 409–733 K.

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \mathrm{e}^{-\frac{E_\mathrm{a}}{k_\mathrm{B}T}} \sum_{n=0,2,4,\ldots}^{s} \frac{1}{\Gamma\left(\frac{n}{2}+1\right)} \left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)^{\frac{n}{2}}. \tag{28}$$

For an odd number of square terms the expression is

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \left\{ \mathrm{e}^{-\frac{E_\mathrm{a}}{k_\mathrm{B}T}} \sum_{n=1,2,3,\ldots}^{s-2} \frac{1}{\Gamma\left(n+\frac{1}{2}\right)} \left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)^{n-\frac{1}{2}} + \mathrm{erfc}\left[\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)^{\frac{1}{2}}\right] \right\}. \tag{29}$$

Comparisons with DSMC calculations were made for the combustion reaction $H_2 + O \rightarrow OH + H$ studied by Clyne and Thrush [18] who obtained an Arrhenius-like expression of $k = 6.0 \times 10^{-13} T^{0.5} \mathrm{e}^{-8900/RT}$ (k in cm^3 $\mathrm{molecule}^{-1}$ s^{-1}, T in K, and E_a in cal/mole) over a temperature range of 409–733 K. Using the reaction model defined by Eq. (26), the DSMC method was capable of accurately simulating the reaction as shown in Fig. 3 with both E_cc and E_i ($s = 4$) contributing to the energy available for reaction.

4.6. Models giving Arrhenius-like rate expressions, no internal energy

Since rate expressions derived from experimental measurements are often represented in Arrhenius and Arrhenius-like forms incorporating T to the power η, $k = A\mathrm{e}^{-E_\mathrm{a}/k_\mathrm{B}T}$ and $k = AT^\eta \mathrm{e}^{-E_\mathrm{a}/k_\mathrm{B}T}$, it is useful to have models giving matching rate expressions. A number of these have been developed for reactions independent of internal energies (i.e. without E_i) by LeRoy [19], Menzinger and Wolfgang [20], and others. We consider one example here.

The cross-section is given by the expression (using σ_C in this case)

$$\sigma_\mathrm{R} = \begin{cases} \sigma_\mathrm{C} \frac{c}{E_\mathrm{rel}} (E_\mathrm{rel} - E_\mathrm{a})^{\eta+\frac{1}{2}} & \text{if } E_\mathrm{rel} \geqslant E_\mathrm{a} \\ 0 & \text{if } E_\mathrm{rel} < E_\mathrm{a} \end{cases}, \tag{30}$$

where c is a constant. Insertion into Eq. (7) leads to

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}} \int_{\frac{E_\mathrm{a}}{k_\mathrm{B}T}}^{\infty} \mathrm{e}^{-\frac{E_\mathrm{rel}}{k_\mathrm{B}T}} \sigma_\mathrm{C}\, c (k_\mathrm{B}T)^{\eta+\frac{1}{2}} \left(\frac{E_\mathrm{rel} - E_\mathrm{a}}{k_\mathrm{B}T}\right)^{\eta+\frac{1}{2}} \mathrm{d}\frac{E_\mathrm{rel}}{k_\mathrm{B}T}, \tag{31}$$

and after integration gives

$$k = \left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma_\mathrm{C}\, c (k_\mathrm{B}T)^{\eta+\frac{1}{2}} \mathrm{e}^{-\frac{E_\mathrm{a}}{k_\mathrm{B}T}} \Gamma\left(\eta + \tfrac{3}{2}\right), \tag{32}$$

or $k = AT^\eta \mathrm{e}^{-E_\mathrm{a}/k_\mathrm{B}T}$ with

$$A = \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}} \sigma_\mathrm{C} c k_\mathrm{B}^\eta \Gamma\left(\eta + \tfrac{3}{2}\right). \tag{33}$$

4.7. Models giving Arrhenius-like rate expressions with internal energies, $E_{rel} + E_i > E_a$

Several models with reaction depending on translational and internal energies and giving Arrhenius-like rate expressions have been reported [21,22]. These have reaction cross-sections of the form (using σ_C)

$$\sigma_\mathrm{R} = \begin{cases} \sigma_\mathrm{C} c (E_\mathrm{tot} - E_\mathrm{a})^{\eta-\frac{1}{2}} \left(\frac{E_\mathrm{tot} - E_\mathrm{a}}{E_\mathrm{tot}}\right)^{\frac{s}{2}+1} \\ 0 \end{cases}, \tag{34}$$

if $E_{tot} \geqslant E_\mathrm{a}$ and $E_{tot} < E_\mathrm{a}$, respectively, where $E_{tot} = E_\mathrm{rel} + E_\mathrm{i}$. The derivation is the same as that giving Eq. (21). With σ_R above substituted in Eq. (20) and specification of $E_\mathrm{a}/k_\mathrm{B}T$ as the lower limit of integration Eq. (20) becomes

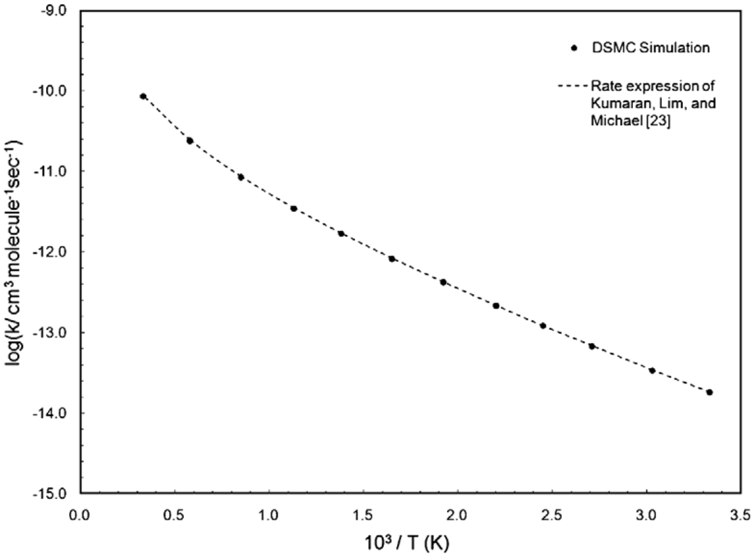

Fig. 4. Comparison of rate constants for the reaction $H_2 + Cl \rightarrow HCl + H$ simulated using the Arrhenius reaction model [Eq. (34); $E_{rel} + E_i > E_a$] over a temperature range of 296–3000 K.

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}}\sigma_C c\frac{1}{\Gamma\left(\frac{s}{2}+2\right)}\int_{\frac{E_a}{k_BT}}^{\infty} e^{-\frac{E_{tot}}{k_BT}}\left(\frac{E_{tot}}{k_BT}\right)^{\frac{s}{2}+2}(E_{tot}-E_a)^{\eta-\frac{1}{2}}\times\left(\frac{E_{tot}-E_a}{E_{tot}}\right)^{\frac{s}{2}+1} d\frac{E_{tot}}{k_BT}. \tag{35}$$

The integration gives

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{\frac{1}{2}}\sigma_C c(k_BT)^{\eta-\frac{1}{2}}e^{-\frac{E_a}{k_BT}}\frac{\Gamma\left(\frac{s}{2}+\eta+\frac{3}{2}\right)}{\Gamma\left(\frac{s}{2}+2\right)}, \tag{36}$$

or $k = AT^{\eta}e^{-E_a/k_BT}$ with

$$A = \left(\frac{8}{\pi\mu}\right)^{\frac{1}{2}}\sigma_C ck_B^{\eta}\frac{\Gamma\left(\frac{s}{2}+\eta+\frac{3}{2}\right)}{\Gamma\left(\frac{s}{2}+2\right)}. \tag{37}$$

For this model the reaction cross-section σ_R given by Eq. (34) has the possibility of increasing beyond the collision cross-section σ_C for large values of E_{tot}. Since this may be unrealistic, care must be taken in choosing the values of σ_C and c, such that c is sufficiently low to avoid the problem. The cross-section of Eq. (34) was used in DSMC calculations for the reaction $H_2 + Cl \rightarrow HCl + H$ for which Kumaran, Lim, and Michael [23] found the Arrhenius-like expression $k = 4.78 \times 10^{-16}T^{1.58}e^{-3198/RT}$ (k in cm^3 molecule^{-1} s^{-1}, T in K, and E_a in cal/mole) for a temperature range of 296–3000 K. The calculations were carried out with $s = 4$, $\sigma_C = 1.099 \times 10^{-15}$ cm^2, and $E_a = 3.198$ kcal/mole. As shown in Fig. 4, the reaction rates were accurately simulated using the indicated cross-section expression.

5. Discussion

The expressions listed and their corresponding models offer a variety of possibilities for fitting to experimental measurements of reaction rate. They provide the connections between reaction rates and the cross-sections needed in DSMC calculations. The complete rate expressions presented here give better fits with experimental data than the approximate expressions, and they are necessary for an accurate determination of cross-sections for use in DSMC calculations.

The complete expressions can and should be used in both Navier–Stokes and related continuum codes as well as in developing DSMC codes. The Navier–Stokes equations, however, are only valid for flows near equilibrium and give only approximate solutions to most chemically reacting flows. Direct simulation Monte Carlo calculations, which are applicable to nonequilibrium flows, can, in turn, provide convenient standards for checking such calculations.

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