

The Q-K model for gas-phase chemical reaction rates

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The quantum-kinetic, or Q-K, model is based on the quantum vibration model that is employed in the computation of gas flows at the molecular level by the direct simulation Monte Carlo (DSMC) method. The Q-K procedure for dissociation is physically realistic within the context of the vibration model in that the reaction occurs upon the selection of the vibrational level that corresponds to dissociation. An analogous, but entirely phenomenological, procedure has been presented for endothermic exchange and chain reactions. These procedures for the endothermic reactions have been well validated, but the existing procedures for the corresponding exothermic reactions have proved to be problematic. This paper presents new procedures for the exothermic reactions that are computationally efficient and provide a near exact match with the equilibrium constant of statistical mechanics. The Q-K model does not depend on the availability of continuum rate coefficients. Instead, the simplicity of the new DSMC procedures allows analytical expressions to be written down for the corresponding rate coefficients in an equilibrium gas. These are used to validate the Q-K model for reactions in high temperature air and in hydrogen-oxygen combustion. The development of the Q-K model has been driven by the need for efficient reaction procedures in DSMC applications that often involve the computation of billions of simulated collisions. It is not intended to compete with the modern theories for gas-phase chemical reactions that employ more accurate physical representations of real reactions. At the same time, the degree of validation of the model is such that the analytical expressions for the rate coefficients that correspond to the model should be useful in their own right. © 2011 American Institute of Physics. [doi:10.1063/1.3650424]

I. INTRODUCTION

Experimental measurements of the speed of gas phase chemical reactions are almost always made at the macroscopic level and are presented in the form of the constants in a modified Arrhenius equation. The resulting expression is called the rate coefficient and is a function of temperature. It would be preferable to have information at the microscopic level that would set out the conditions for the occurrence of a reaction in an individual collision. There have been valuable measurements at the molecular level for particular reactions but, for the vast majority of reactions, information is available only in the form of quantities that have been averaged over all collisions.

Information at the molecular level is often in the form of “steric factors.” The formal definition¹ of a steric factor is that it is “A factor introduced into simple versions of the collision theory of reactions to take care of the fact that the reaction probability depends on the certain mutual orientations of the reactant molecules.” This is hardly useful because simple collision theory employs an inadequate molecular model, assumes equilibrium distribution functions, and may even neglect the need for the collision energy to exceed the activation energy for the reaction. This paper employs a modified definition of the steric factor that it is the fraction of all collisions at a given temperature that results in a reaction. There are several reasons for including all collisions rather than only those with energy above the activation

energy. The modified definition removes the need to define the collision energy and, more importantly, the steric factor is then the average of the ratio of the reaction cross-section to the collision cross-section or reaction probability. Temperature-dependent macroscopic quantities such as the rate coefficient and the steric factor are quasi-equilibrium because, while their values are affected if the distribution functions do not conform to the Maxwell-Boltzmann distributions, they regard temperature as a scalar property and contain no parameters that are sensitive to the degree of non-equilibrium. On the other hand, the reaction probability in an individual collision is unaffected by the distribution functions.

The primary objective of the work that led this paper was to develop procedures for the direct simulation Monte Carlo, or DSMC, method that are not only computationally more efficient than the preceding procedures but do not assume that the gas is in equilibrium. The distribution functions in a reacting gas can be expected to have the equilibrium form if the product of the modified steric factor and the relevant relaxation collision number is small in comparison with unity. The translational relaxation collision number is generally taken to be around five to ten, but it takes many more collisions for the high speed tail of the distribution to come to equilibrium. The product of relaxation collision number and steric factor could well be of order unity or higher in some fast reactions and the velocity distribution would then depart from the Maxwellian form. The relaxation collision number for vibration is very strongly dependent on temperature but is generally orders of magnitude greater

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than that for translation and the distribution of the vibrational levels in a reacting gas can be expected to frequently depart from the Boltzmann distribution. The preceding comments apply to reactions in a homogeneous gas with no macroscopic gradients. The internal structure of, for example, a detonation wave would involve strong non-equilibrium effects that are additional to any non-equilibrium effects caused by the chemical reactions.

Almost all studies of chemically reacting gas flows by the DSMC method have employed procedures that were first introduced in 1979.² Equilibrium kinetic theory was used to convert the conventional rate coefficients that are defined in terms of the macroscopic gas temperature to collision probabilities that are a function of the energy in the collision. The model that employs these procedures is now called the “total collision energy,” or TCE, model. This model depends on the availability of reliable data for the reaction rate coefficients. This macroscopic data is applied at the microscopic level, but the use of equilibrium theory in its derivation means that it may not be adequate for reactions in gases that have distribution functions that depart markedly from the equilibrium form.

The DSMC chemistry model that is now termed³ the “quantum-kinetic,” or Q-K, model makes no use of existing rate equations, but the procedures are sufficiently simple for the corresponding rate equations to be readily written down and these predicted rates may then be compared with the established continuum rates. The Q-K model was first presented⁴ in the context of a comparison of collision energy based DSMC procedures with the corresponding procedures based on the macroscopic temperature. The procedures for the forward or endothermic reactions have required little modification in subsequent papers, but those for the reverse or exothermic reactions have proved to be problematic. The existing comparisons of the Q-K reaction rate coefficients with the generally accepted rates based on experiment have almost all been concerned with the forward reaction rates and these are largely unaffected by the revised procedures for the reverse reaction that are presented in this paper. Galis, Bond, and Torczynski⁵ have presented the most extensive set of comparisons and have extended the model to include ionization. In addition, Liechty and Lewis⁶ have considered charge exchange reactions, but this paper deals only reactions that involve neutral gases.

The Q-K condition for dissociation is that the energy in a collision should be sufficiently high to permit the selection of the vibrational level that corresponds to dissociation. On the assumption that the reacting gas is in translational and vibrational equilibrium, this condition leads to an analytical expression for the dissociation rate coefficient. While these theoretical rates can be compared with the data that is available for the rate coefficients, they have no role in the implementation of the Q-K model in DSMC programs.

The original paper⁴ proposed a procedure for recombination reactions that related the probability of a recombination to the dissociation rate that occurs within the calculation. This was satisfactory for the high temperature air flows that are dominated by dissociations but could not be implemented for combustion calculations in which recombination reactions

occur in the absence of dissociations. The recombination procedure was revised in Ref. 3 and it was assumed in that the probability of a recombination in a binary collision is equal to the probability of a third molecule being within a “ternary collision volume.” This volume was generally set to the sphere with radius equal to the sum of the radii of the three molecules in the collision. However, this ternary collision volume was an arbitrary choice and it became clear that it did not lead to accurate rates. It is defined unambiguously in this paper as the volume such that the ratio of the dissociation rate to the recombination rate is in agreement with the ratio based on the equilibrium constant from statistical mechanics. It will be shown that a ternary collision volume in the form of a constant times a power law of temperature can lead to almost exact agreement with the equilibrium constant. Note that the employment of the equilibrium constant in the derivation of the DSMC procedures does not amount to an assumption that the gas is in equilibrium. It merely means that the effect of collisions in a non-equilibrium gas is always to move towards the equilibrium state.

The original procedure⁴ for reverse or exothermic exchange and chain reactions employed a condition similar to that for the forward reaction, but in an unnecessarily complex fashion that effectively removed the asymmetry due to the difference in the magnitudes of the activation energies. Because of this, Bird³ employed an alternative procedure that combined the analytical expression for the forward rate with the equilibrium constant that had to be evaluated for every relevant collision. It has now been found that detailed balance is approximately satisfied if the forward procedure is applied also to the reverse reaction and the activation energies are set to the heat of reaction for the forward reaction and zero for the reverse reaction. In addition, the condition for the forward reactions has been simplified and made more explicit. It is no longer necessary to evaluate the equilibrium constant for each collision. The corresponding rate equations are readily written down and the ratio of the forward to the reverse rate can again be compared with the ratio predicted by statistical mechanics. Should the ratio based on the equilibrium constant be higher than that predicted by the model, a finite activation energy can be applied to the reverse reaction. Conversely, should the model ratio be the higher, the activation energy for the forward reaction can be set higher than the heat of reaction. Good agreement is obtained when the activation energy adjustments have a temperature dependence that is similar to that adopted for the ternary collision volume. The required adjustments are generally small in comparison with the heats of reaction but, because it is a phenomenological model, these activation energies do not necessarily apply to the real gas. Section II presents a general discussion of phenomenological molecular models.

Section III outlines the Q-K procedures for DSMC calculations and the derivation of the analytical expressions for the reaction rate coefficients that correspond to them. The operation of the new procedures is demonstrated in Sec. IV with regard to reactions in air and in Sec. V for hydrogen-oxygen reactions. The supplemental material²⁶ includes a visual interactive program QKrates.EXE that includes all the reactions for these two systems as demonstration cases with

pre-set data. This includes most of the parameters associated with the ternary collision volumes and the effective activation energies. The pre-set data also includes up to four sets of Arrhenius rate parameters for each reaction and these demonstrate the degree of agreement between the Q-K rates and the accepted rates that are based either on measurements or on theories such as the transition state theory. Additional rates can be readily added by the user or the program can be used to interactively determine the modified Arrhenius equation that most nearly matches the Q-K rate over the selected temperature range. The default graphical display shows the comparison of either the forward or reverse rates with the Arrhenius rates. Alternative displays show the degree of agreement with the equilibrium constant from statistical mechanics and the steric factors that correspond to the rates. Text files that include the data for the reaction and the information in all displays can be selected as output and all the figures in this paper are based on these files.

II. PHENOMENOLOGICAL MOLECULAR MODELS IN DSMC

A typical application of the DSMC method involves the calculation of many millions of intermolecular collisions and this leads to a requirement for computationally simple molecular models. This has led to the development of “phenomenological” models that focus on the generation of accurate results for the observed gas properties but do not attempt to provide the most realistic model of individual collisions at the microscopic level.

The developers of classical kinetic theory had faced a similar problem in that they required mathematically tractable molecular models that permitted the derivation of analytical expressions for the macroscopic transport properties. The classical models were therefore the obvious choice for early DSMC work but were found to have serious shortcomings that have been overcome by phenomenological models that have been introduced in the context of the DSMC method.

For elastic collisions, the classical hard sphere and Maxwell molecules lead to fixed and unrealistic temperature variations of the coefficient of viscosity and should not be used for problems that involve large variations in temperature. The power-law models are physically realistic and accurately predict the transport properties. On the other hand, they are computationally difficult, and because an arbitrary cut-off must be applied to the effective molecular radius, they do not lead to unambiguous values for the collision rate and mean free path. The developers of kinetic theory had attributed the success of the power-law models to the realistic modeling of the scattering distribution in collisions and made little or no mention of the variation with temperature of the effective molecular size that was implicit in their equations. However, as real gas flows were more intensively studied, it was found that the measurable effects of molecular model correlate almost exactly with the changes in the effective molecular size and that the scattering law has a relatively small effect. This led to the introduction⁷ of the variable hard sphere, or VHS, model which combines the unrealistic but simple isotropic scattering of a hard sphere

with a realistic variation of diameter with the relative speed of the collision pair. This model leads to accurate results for viscosity and heat conduction coefficients, but the Schmidt number that depends on the diffusion coefficient does not match the measured values in real gases. The variable soft sphere, or VSS, model⁸ includes an empirical distortion of the isotropic scattering that can be adjusted to also match the measured Schmidt number. The VSS extension is required only for those applications to gas mixtures in which diffusion is an important factor.

Classical kinetic theory did not lead to any useful models for inelastic collisions. For example, the rough sphere model retains the deficiencies of the hard sphere model with regard to the transport properties, and it is unable to deal with the quantum effects that cause most gases to have fewer than three rotational degrees of freedom and has a fixed and unrealistically fast rotational relaxation time. This problem was solved in the context of the DSMC method by the introduction of the Larsen-Borgnakke, or L-B, model⁹ for rotation which can be regarded as the archetypal phenomenological procedure. It is an add-on to the VHS model and, for a fraction of the collisions that is chosen to match the measured rotational relaxation rate, the post-collision rotational energies are selected from the equilibrium distribution that corresponds to the collision energy. The L-B model was extended to the vibrational modes, but it assumed that the internal energies were continuously distributed and was barely satisfactory. The situation was transformed by the introduction¹⁰ of the quantum version of the L-B model. This model is the foundation of the Q-K model for chemical reactions that is the subject of this paper. It may be compared with the TCE model and the most recent exposition of that model has been provided by Boyd.¹¹

Additional effects such as rotational-vibrational coupling can be included if sufficient physical data is available. At the same time, a phenomenological model is not necessarily improved by a modification that merely aims to improve its physical realism and it is important to not explicitly add effects that have already been implicitly included in a model.

III. THE QUANTUM-KINETIC CHEMISTRY MODEL

A. Dissociation

The total energy in a binary collision is the sum of the relative translational energy and the energies in all internal modes of both molecules. The L-B procedures redistribute this energy to the post-collision values of the relative energy and the internal modes. Physical reasoning would suggest the total collision energy should be redistributed in a parallel fashion to all internal modes of both molecules. However, a mathematical peculiarity of the expressions that comprise the “general Larsen-Borgnakke model”¹² is that exactly the same result is achieved if there are successive and separate redistributions of the sum of the remaining translational energy and the pre-collision energy in a particular internal mode of one molecule to the post-collision energy in that mode and molecule. This is called the “serial” application of the model.

Consider the serial application of the quantum L-B model to a vibrational mode of one of the molecules in a

collision in which the sum of the relative translational energy and the pre-collision vibrational energy of the molecule and mode under consideration is E_C . The maximum vibrational level that can be selected is

$$i_{\max} = \lfloor E_C / (k \Theta_v) \rfloor, \quad (1)$$

where Θ_v is the characteristic vibrational temperature in the harmonic oscillator model and k is the Boltzmann constant. Potential post-collision states i^* are chosen uniformly from the states equal to or below $i_{\max}$ and are selected through an acceptance-rejection routine with probability

$$P = (1 - i^* k \Theta_v / E_C)^{3/2 - \omega}, \quad (2)$$

where ω is the temperature exponent of the coefficient of viscosity. There is a continuous set (i.e., an infinite number) of levels beyond the dissociation limit so that, if $i_{\max}$ is above the dissociation level, it must be selected and dissociation occurs. The condition for dissociation of the molecule AB in the reaction $AB + T \rightarrow A + B + T$ is therefore

$$i_{\max} > \Theta_d / \Theta_v, \quad (3)$$

where Θ_d is the characteristic dissociation temperature. The vibrational collision number is unity¹ at the dissociation limit so that the condition is applied in the DSMC collision routine prior to any L-B selection of a post-collision vibrational state.

The corresponding rate coefficient in an equilibrium VHS gas at temperature T is

$$k_f(T) = g R_{\text{coll}}^{\text{AB},T} \Upsilon(i_{\max})^{\text{AB},T}. \quad (4)$$

The degeneracy g of the reaction is included to cover the case of a polyatomic molecule in which the reaction can occur through more than one mode with the same characteristic vibrational temperature. The collision rate parameter $R_{\text{coll}}^{\text{AB},T}$ is the collision rate for collisions between gas species AB and T divided by the number density product. It can be written for an equilibrium VHS gas as

$$R_{\text{coll}}^{\text{AB},T} = (2\pi^{1/2} / \varepsilon) (r_{\text{ref}}^{\text{AB}} + r_{\text{ref}}^T)^2 (T / T_{\text{ref}})^{1 - \omega^{\text{AB},T}} \times (2kT_{\text{ref}} / m_r^{\text{AB},T})^{1/2}, \quad (5)$$

where r_{ref} is the molecular radius at temperature T_{ref} and m_r is the reduced mass. For dissociations, it is necessary to add the symmetry factor ε that is equal to 1 for like molecules and 2 for unlike molecules. The parameter $\Upsilon(i_{\max})^{\text{AB},T}$ is the fraction of collisions between AB and T that have sufficient energy to meet the condition of Eq. (3). With i as the pre-collision vibrational state of AB, the result for an equilibrium VHS gas is

$$\begin{aligned} \Upsilon(i_{\max})^{\text{AB},T} &= \sum_{i=0}^{i_{\max}-1} \{ Q[(5/2 - \omega^{\text{AB},T}), \\ &\quad \times ((i_{\max} - i) \Theta_v^{\text{AB}} / T)] \exp \\ &\quad \times (-i \Theta_v^{\text{AB}} / T) \} / z_v(T)^{\text{AB}}. \end{aligned} \quad (6)$$

$Q(a, x) = \Gamma(a, x) / \Gamma(a)$ is a form of the incomplete Gamma function and $z_v(T) = 1 / [1 - \exp(-\Theta_v / T)]$ is the contribution of the relevant mode to the vibrational partition function.

B. Recombination

The DSMC condition for recombination in a collision between species A and B is that there is another atom or molecule within the “ternary collision volume” V_{coll} . The probability of recombination is therefore

$$P_{\text{rec}} = n V_{\text{coll}}, \quad (7)$$

where n is the number density. The corresponding rate equation is

$$k_r(T) = R_{\text{coll}}^{\text{A,B}} n V_{\text{coll}}. \quad (8)$$

The ratio $k_f(T) / k_r(T)$ from Eqs. (4) and (8) may be equated to the equilibrium constant from statistical mechanics in order to determine the ternary collision volume. It has been found that a volume in the form

$$V_{\text{coll}} = a T^b V_{\text{ref}} \quad (9)$$

allows an almost exact fit of this ratio to the equilibrium constant. The reference volume V_{ref} is most conveniently set to the volume of the sphere with radius equal to the sum of the reference radii of the three molecules.

The values of the constants a and b are determined in the context of the macroscopic temperature, but the evaluation of the ternary collision volume in the DSMC implementation should preferably be based on the quantities associated with the collision. The “collision temperature” based on the relative translational energy in a collision with relative speed c_r is

$$T_{\text{coll}} = (m_r^{\text{A,B}} c_r^2 / (2k)) / (5/2 - \omega^{\text{A,B}}). \quad (10)$$

The average of this temperature over all collisions in an equilibrium gas is equal to the macroscopic temperature, but Eq. (9) contains the temperature to the power b and the average over all collisions of T_{coll}^b is not equal to T^b unless b is zero or unity. The difference is readily calculated from elementary kinetic theory and the factor a must be replaced by

$$a' = \left[(5/2 - \omega^{\text{A,B}})^b \Gamma(5/2 - \omega^{\text{A,B}}) / \Gamma(5/2 - \omega^{\text{A,B}} + b) \right] a. \quad (11)$$

This conversion factor is small if b is in the range -0.5 to 1.5 but goes to zero when $b = -2.5 + \omega^{\text{A,B}}$. The DSMC implementation will therefore have to resort to the macroscopic gas temperature rather than a collision temperature if large negative values of b are unavoidable. It would be preferable to base the collision temperature on E_C rather than just the relative translational energy, but an analytical conversion would not then be possible and a numerical conversion would involve modifications to both coefficients.

C. Exchange and chain reactions

These are binary reactions and an exchange reaction has one stable molecule and one radical both before and after the reaction. A reaction between two stable molecules that leads to one or more radicals is, like thermal dissociation, a chain-initiating reaction. When a pre-reaction pair comprised of one stable molecule and one radical leads to two radicals, it is a chain-branching reaction, while the opposite is a chain-terminating reaction.

Consider the forward and reverse reaction pair $A + B \leftrightarrow C + D$ in which A and C are the molecules that split, while B and D are either molecules or atoms. The phenomenological DSMC procedure for these reactions is analogous to that for the dissociation model. For both the forward and reverse reactions, the reaction probability is equal to that of Eq. (2) with i^* set to the $i_{\max}$ defined by Eq. (1) and with E_c replaced by the activation energy that applies to the reaction. This is a relative probability that must be normalized through division by the sum of probabilities from the ground state to $i_{\max}$. Therefore

$$P = (1 - i_{\max} k \Theta_v / E_c)^{3/2-\omega} / \sum_{i=0}^{i_{\max}} (1 - i k \Theta_v / E_c)^{3/2-\omega}.$$

$$\begin{aligned} \frac{dN}{N} = & \frac{1 - \exp(-\Theta_v/T)}{\Gamma(5/2 - \omega)} \sum_{j=0}^{\infty} \left\{ \exp\left(-\frac{j\Theta_v}{T}\right) \int_{(E_a/k - j\Theta_v)/T > 0}^{\infty} \left[\frac{m_r c_r^2}{2kT} \left(1 - \frac{E_a}{m_r c_r^2/2 + jk\Theta_v}\right) \right]^{3/2-\omega} \right. \\ & \times \left[\sum_{i=0}^{\lfloor (m_r c_r^2/2 + jk\Theta_v)/(k\Theta_v) \rfloor} \left(1 - \frac{ik\Theta_v}{m_r c_r^2/2 + jk\Theta_v}\right)^{3/2-\omega} \right]^{-1} \exp\left(-\frac{m_r c_r^2}{2kT}\right) d\left(-\frac{m_r c_r^2}{2kT}\right) \Bigg\}, \end{aligned}$$

and the corresponding rate coefficient is

$$k(T) = g R_{\text{coll}} (dN/N). \quad (13)$$

This is an unwieldy result, but it is possible to write down an alternative expression that is based on physical reasoning rather than formal kinetic theory. The selection of possible post-collision vibrational levels through Eq. (2) is from an equilibrium distribution so that the rate coefficient is simply the product of the degeneracy g , the collision rate parameter, and the fraction of the vibrational level $i_{\max}$ in the Boltzmann distribution.

This is satisfactory if the level $i_{\max}$ is very large in comparison with unity, but some endothermic reactions and all exothermic reactions have either zero or small activation energies. The use of discrete levels then leads to unacceptably abrupt changes in the rate coefficients and it is impossible to obtain a near exact agreement between the ratio of forward to reverse rate coefficients and the equilibrium constant. The level $i_{\max}$ is the highest level with energy below the activation energy E_a and a smooth curve is obtained for the rate coefficients if the energy $i_{\max} k \Theta_v$ in the numerator is replaced by E_a . The DSMC probability of an exchange or chain reaction in a collision with $E_c > E_a$ is then

$$P_{\text{reac}} = (1 - E_a/E_c)^{3/2-\omega} / \sum_{i=0}^{i_{\max}} (1 - i k \Theta_v / E_c)^{3/2-\omega}. \quad (12)$$

The summation in the denominator is unity when E_a/k is less than Θ_v and only a few terms need to be calculated when the activation energy is small. While there are many terms when the activation energy is large, the sum is then a near linear function of $E_c - E_a$ and the summation may be replaced by a simple expression.

An exact expression can be written down for the fraction of collisions that satisfy the condition of Eq. (12) in an equilibrium VHS gas. With j as the pre-collision vibrational level, this is

The term $i_{\max} k \Theta_v$ in the exponential should be replaced by E_a in order to maintain consistency with Eq. (12) and the normalizing factor is simply the vibrational partition function, so that

$$k_f(T) = g^A R_{\text{coll}}^{A,B} \exp(-E_a^{A,B}/(kT)) / z_v(T)^A \quad (14)$$

and

$$k_r(T) = g^C R_{\text{coll}}^{C,D} \exp(-E_a^{C,D}/(kT)) / z_v(T)^C. \quad (15)$$

Typical results from the two approaches are compared in Table I.

TABLE I. Reaction rate coefficients $k(T)$ ($\text{m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for $\text{NO} + \text{O} \leftrightarrow \text{O}_2 + \text{N}$

T (K)	Forward, Eq. (13)	Forward, Eq. (14)	Reverse, Eq. (13)	Reverse, Eq. (15)
1000	$0.1034507 \times 10^{-23}$	$0.1034505 \times 10^{-23}$	$0.3579352 \times 10^{-15}$	$0.3579347 \times 10^{-15}$
3000	$0.4161669 \times 10^{-18}$	$0.4161663 \times 10^{-18}$	$0.2676447 \times 10^{-15}$	$0.2676443 \times 10^{-15}$
5000	$0.4493306 \times 10^{-17}$	$0.4493298 \times 10^{-17}$	$0.2052196 \times 10^{-15}$	$0.2052187 \times 10^{-15}$
7000	$0.1138287 \times 10^{-16}$	$0.1138285 \times 10^{-16}$	$0.1673790 \times 10^{-15}$	$0.1673787 \times 10^{-15}$
9000	$0.1814120 \times 10^{-16}$	$0.1814117 \times 10^{-16}$	$0.1421784 \times 10^{-15}$	$0.1421779 \times 10^{-15}$
11 000	$0.2363457 \times 10^{-16}$	$0.2363452 \times 10^{-16}$	$0.1241490 \times 10^{-15}$	$0.1241490 \times 10^{-15}$
13 000	$0.2776087 \times 10^{-16}$	$0.2776082 \times 10^{-16}$	$0.1105671 \times 10^{-15}$	$0.1105665 \times 10^{-15}$
15 000	$0.3073301 \times 10^{-16}$	$0.3073295 \times 10^{-16}$	$0.9993737 \times 10^{-16}$	$0.9993699 \times 10^{-16}$

The small differences are almost certainly due to errors in the evaluation of Eq. (13) and the comparatively simple result that was based on physical reasoning is evidently identical to the exact result, but there is little prospect of an analytical rather than a numerical proof.

The default activation energy for the forward reaction is the heat of reaction and that for the reverse reaction is zero. The ratio of the forward to the reverse rate is compared with the equilibrium constant and, as noted in Sec. I, the two are brought into the best possible agreement by the upward adjustment of either the forward or reverse activation energy. These adjustments are temperature dependent through a relation similar to that in Eq. (9) for the ternary collision factor. In addition to these phenomenological adjustments, there may be experimental or theoretical evidence for activation energies above the default values. Should a phenomenological adjustment fall short of the desired value, both the forward and reverse activation energies may be increased to meet the higher value while keeping the forward to reverse rate ratio in agreement with the equilibrium constant.

The DSMC implementation employs the adjusted activation energies in a similar manner to the use of the adjusted ternary collision volume in recombination reactions. The collision temperature is again defined by Eq. (10) and a must again be replaced by a' . The rates that employ either the default or adjusted activation energies are essentially the collision theory rates divided by the vibrational partition function of the molecule that splits in the reaction. The exponential term is identical to that in the Arrhenius equation and the collision term is proportional to a fixed power of the temperature. However, the partition function leads to a more complex temperature dependence of the rate coefficient and the activation energy may itself be temperature dependent.

IV. REACTIONS IN AIR

A. Dissociation and recombination

Consider the dissociation of oxygen in a collision with another oxygen molecule. Figure 1 compares the dissociation rate coefficient from the Q-K theory with rate equations that are tabulated in Boyd,¹¹ Kang and Dunn,¹³ and Park and Menees.¹⁴ The Q-K rate has a complex dependence on temperature but, for this reaction, it is notable that there is very close agreement with the rates of Refs. 13 and 14 that have a temperature power of -1 , while the power of -1.5 in the rate of Ref. 11 leads to lower rates at the higher temperatures. The degree of uncertainty associated with existing rate coefficients for high temperature air is generally considered to be a factor of five, so that the very close agreement of the Q-K rate with two of these rates in Fig. 1 has to be, to some extent, fortuitous. This is confirmed by Fig. 2 which shows the corresponding comparison for the dissociation of nitrogen in a collision with another nitrogen molecule.

The rate data in Ref. 11 presents separate dissociation rates for atoms or molecules as the collision partner and the other references provide species-dependent rates. The only effect of the collision partner in the Q-K theory is through the collision rate. Figures 3 and 4 repeat the comparisons of Figs. 1 and 2 with the corresponding atom as the collision partner.

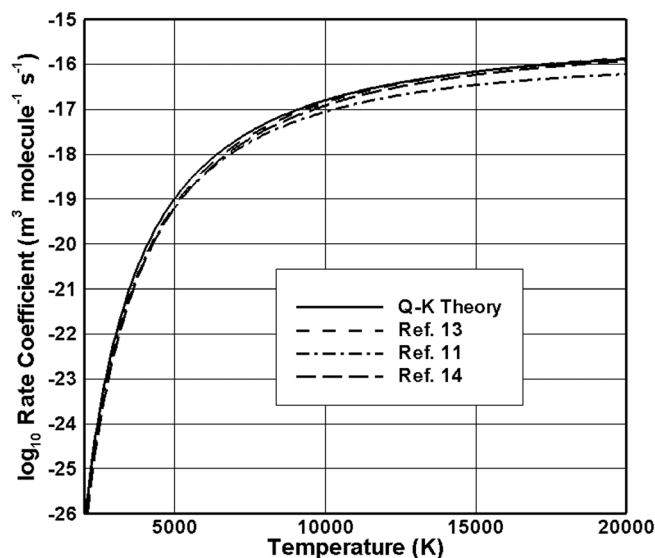


FIG. 1. Dissociation rate coefficient for $\text{O}_2 + \text{O}_2 \rightarrow \text{O} + \text{O} + \text{O}_2$.

The uncertainty associated with the fitting of measured or theoretical rates to the empirical Arrhenius equation does not allow definitive conclusions, but it is clear that the predicted rates from the Q-K theory are consistent with the currently accepted rates.

The effective volume of a ternary collision sets the recombination rate and it is adjusted through the coefficients of Eq. (9) to bring the ratio of the dissociation to the recombination rate into agreement with the equilibrium constant of statistical mechanics. Equation (9) is of the form of the pre-exponential term of the modified Arrhenius equation and Fig. 5 shows that the agreement can be almost exact. The ratio has been normalized through the multiplication of the recombination rate coefficient by Loschmidt's number (the number of molecules in one cubic meter of gas at standard temperature and pressure).

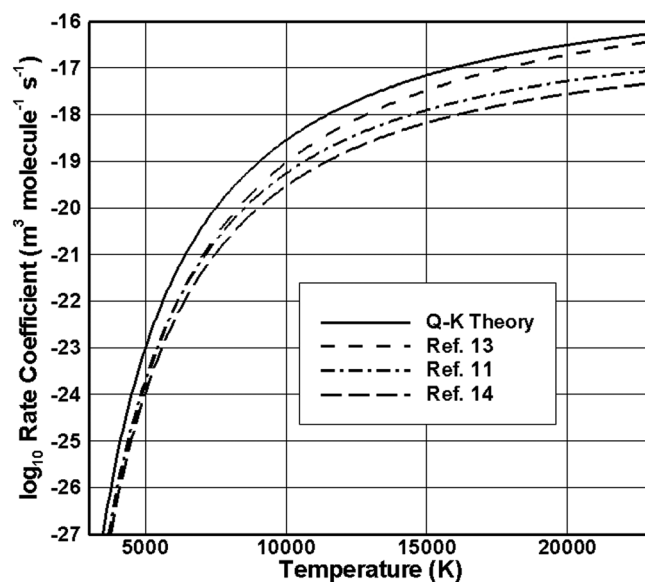
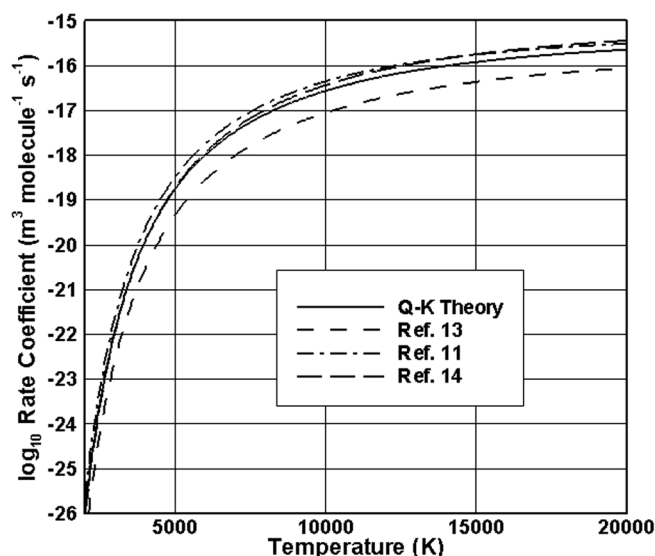
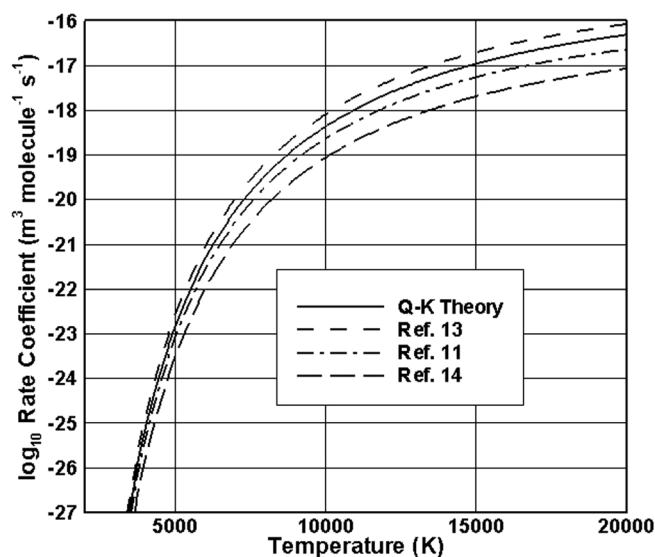
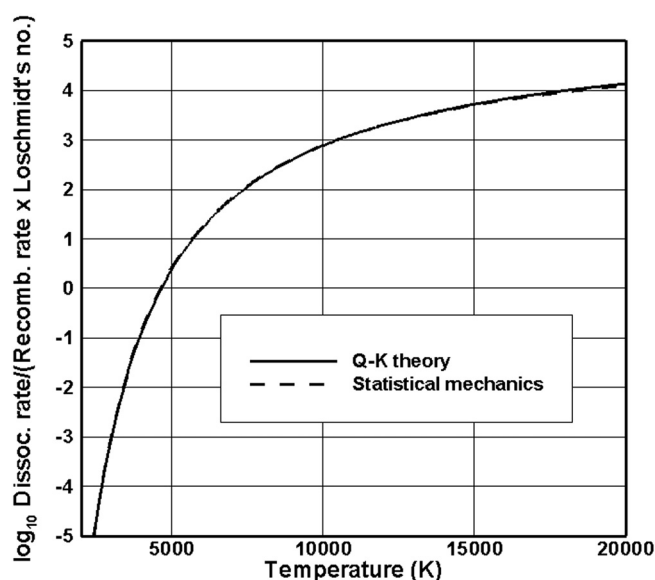


FIG. 2. Dissociation rate coefficient for $\text{N}_2 + \text{N}_2 \rightarrow \text{N} + \text{N} + \text{N}_2$.

FIG. 3. Dissociation rate coefficient for $\text{O}_2 + \text{O} \rightarrow \text{O} + \text{O} + \text{O}$.

The Q-K curve in Fig. 5 employs the ternary collision volume $0.04 V_{\text{ref}}(T/\Theta_v)^{-1.3}$ and the electronic partition functions have been included in the evaluation of the equilibrium constant from statistical mechanics. The ratio $V_{\text{coll}}/V_{\text{ref}}$ is plotted in Fig. 6 for the recombination reactions in the four reaction pairs that are the subject of Figs. 1–4. Results are also shown for the volumes that would be calculated if the electronic partition functions were not included. The particular reaction that is associated with the individual curves is immaterial and the important result is that the electronic partition functions reduce the ternary collision volume, and therefore the recombination rate, by a factor of approximately fifty.

The treatment of recombination reactions in the earlier version¹ of the Q-K model set the ternary collision volume to the volume of the sphere with radius equal to the sum of the three molecular radii, but employed the temperature-dependent VHS radii rather than the fixed reference radii. This volume is shown in Fig. 6 for a gas with viscosity pro-

FIG. 4. Dissociation rate coefficient for $\text{N}_2 + \text{N} \rightarrow \text{N} + \text{N} + \text{N}$.FIG. 5. The normalized equilibrium constant for $\text{O}_2 + \text{O}_2 \rightarrow \text{O} + \text{O} + \text{O}_2$.

portional to temperature to the power 0.75. The assumption was found to be reasonable in the earlier paper only because the electronic partition functions were neglected in that paper.

Because the energy in the electronic states below the ionization limit is almost universally neglected in hypersonic flow studies, the large effect of the electronic partition functions is a matter of concern. It is therefore desirable to compare the Q-K recombination rate coefficients with any available data. It is now a standard practice to specify only the forward rate and use the equilibrium constant to deduce the reverse rates. This applies to the references that have been employed for the comparisons of dissociation rates, but the older “consensus” rates of Bortner¹⁵ list recombination rates that may be based on measurements. The Q-K result for the recombination of oxygen, with an oxygen molecule as the third body, is compared with the Bortner rate in Fig. 7.

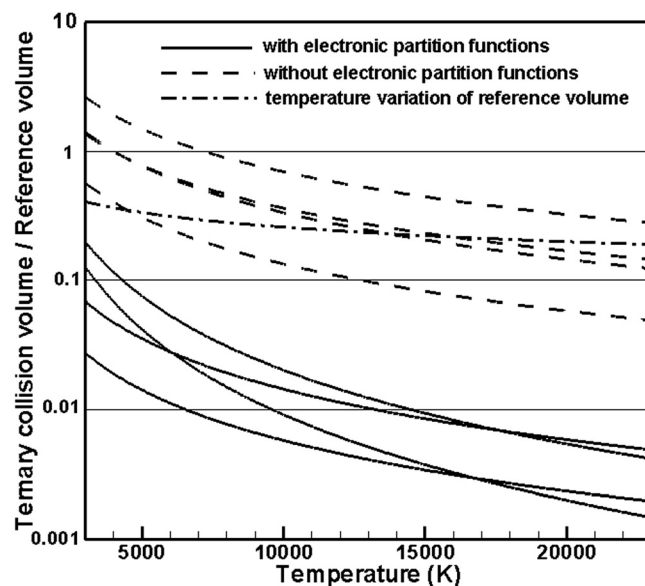
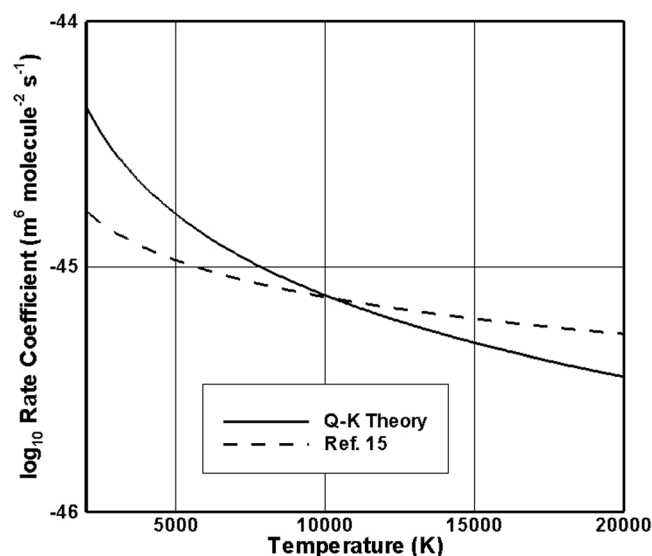
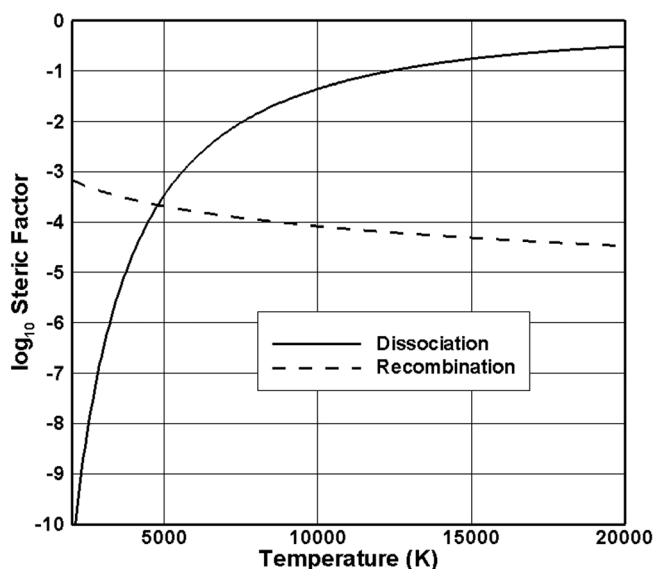
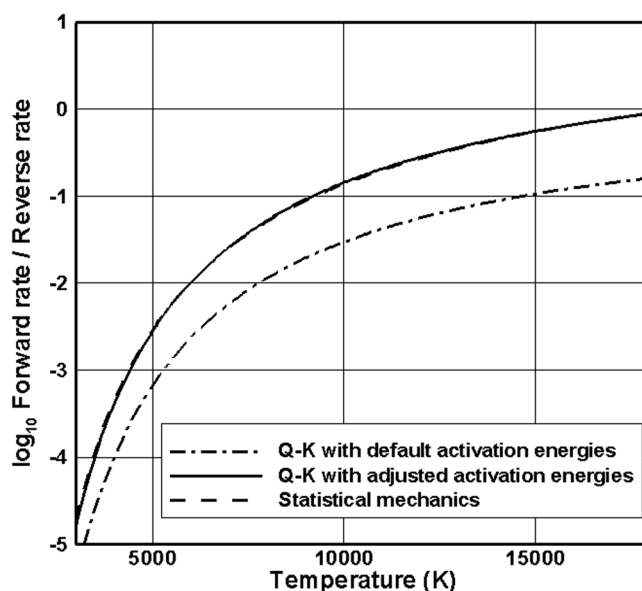


FIG. 6. Ternary collision volumes calculated with and without the inclusion of the electronic partition functions in the equilibrium constant.

FIG. 7. Recombination rate coefficient for $\text{O} + \text{O} + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2$.

The agreement is satisfactory and similar results are obtained for the other recombination reactions. However, it is probable that the Bortner rates are not based on experiment but are also based on the accepted dissociation rates and the equilibrium constant that includes the electronic contribution to the partition functions.

Because of the high activation energies, thermal dissociation is non-existent at room temperature. However, there are other processes that lead to the production of radicals and recombination rates can be measured at room temperatures. The Chemistry WebBook (www.nist.gov) that is published on-line by the National Institute of Standards and Technology lists seven measured values of the rate coefficient for the recombination of oxygen at 300 K. In base SI units, these range from 7×10^{-46} to 2.2×10^{-44} with an average value of 7.2×10^{-45} . The value predicted by the Q-K model at 300 K is 3.6×10^{-44} . Because atomic oxygen has two low-lying electronic levels at 229 K and 326 K, the electronic partition

FIG. 8. Q-K steric factors for $\text{O}_2 + \text{O}_2 \leftrightarrow \text{O} + \text{O} + \text{O}_2$.FIG. 9. The forward to reverse rate ratio for $\text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N}$.

functions are important at room temperature and there would be worse agreement if they were not included.

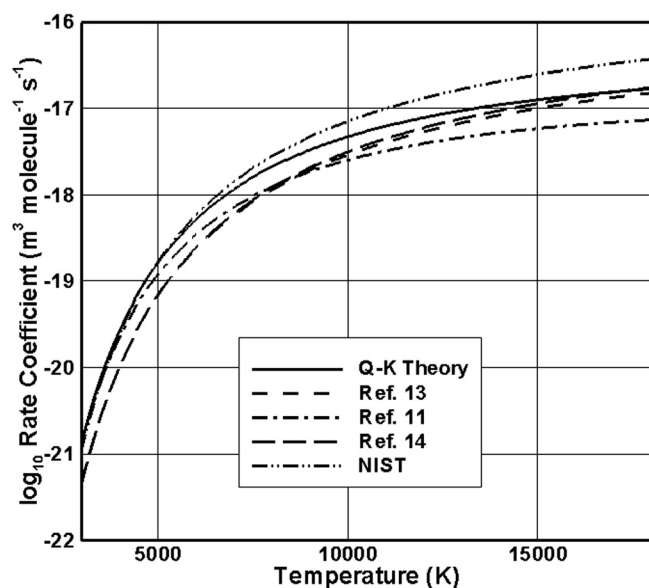
The modified steric factor is here equal to the rate coefficient divided by the collision rate parameter. Figure 8 shows the Q-K steric factors for oxygen dissociation and recombination in a collision with molecular oxygen. The steric factor for recombination is directly proportional to the number density and the plotted result is for standard sea level density.

B. Exchange reactions

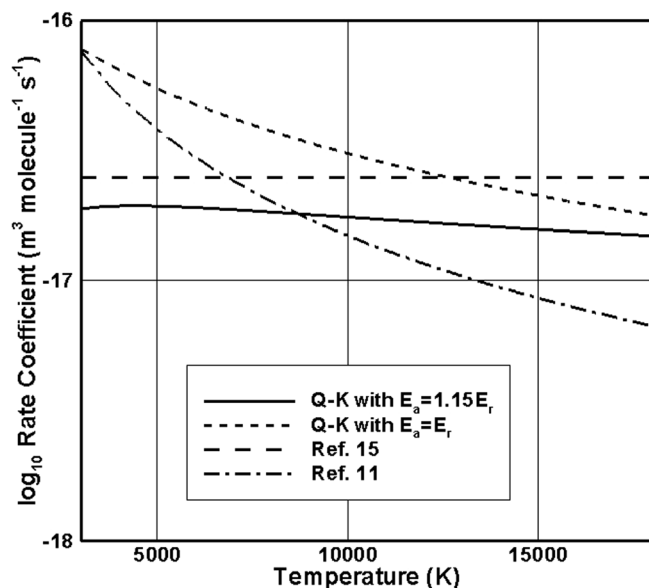
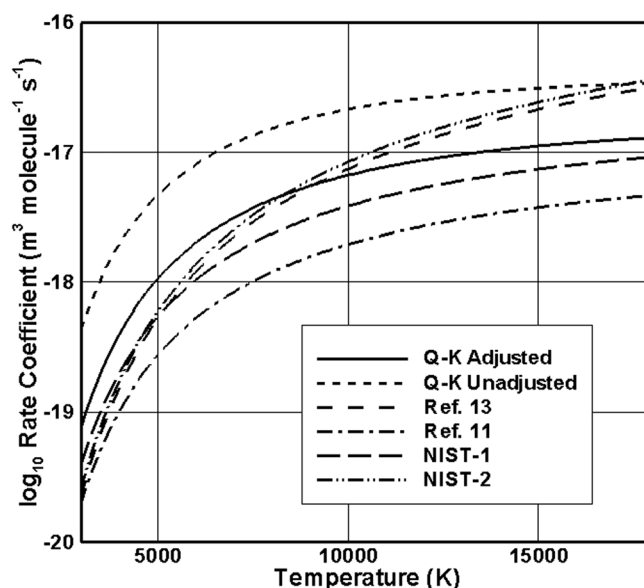
There are two pairs of exchange reactions that involve the formation and destruction of nitric oxide. First consider $\text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N}$ in which NO is formed by the forward or endothermic reaction. The rates are first calculated from Eqs. (14) and (15) with the default activation energies equal to the heat of reaction E_r for the forward reaction and zero for the reverse reactions. The resulting ratio of the forward rate to the reverse rate is shown in Fig. 9 by the dashed-dotted curve and can be compared with the dashed curve for the equilibrium constant from statistical mechanics. The default Q-K ratio is lower by a factor of about eight and, to bring the two curves into agreement, the reverse rate can be reduced by setting a finite activation energy for the reverse reaction. The solid curve shows the Q-K ratio for a reverse activation energy $E_a = 0.0068 (T/273)^{1.145} E_r$. The ratio of this activation energy to the heat of reaction ranges from 0.11 at 3000 K to 0.85 at the 18 000 K.

The activation energy for the forward reaction remains equal to the heat of reaction and Fig. 10 shows that the Q-K rate coefficient for this reaction is in good agreement with the generally accepted rates. The NIST results for this reaction show little scatter and the plotted rate is typical. However, these rates are for temperatures up to about 3000 K so that the anomalously high rates at the high temperatures should be disregarded.

As with recombination, the rates for the reverse reactions that are listed by Bortner¹⁵ provide a further test of the

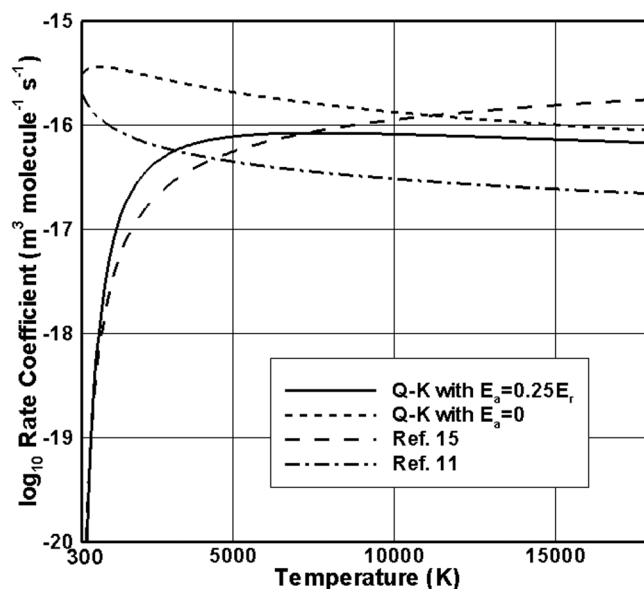
FIG. 10. Forward rate coefficient for $\text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N}$.

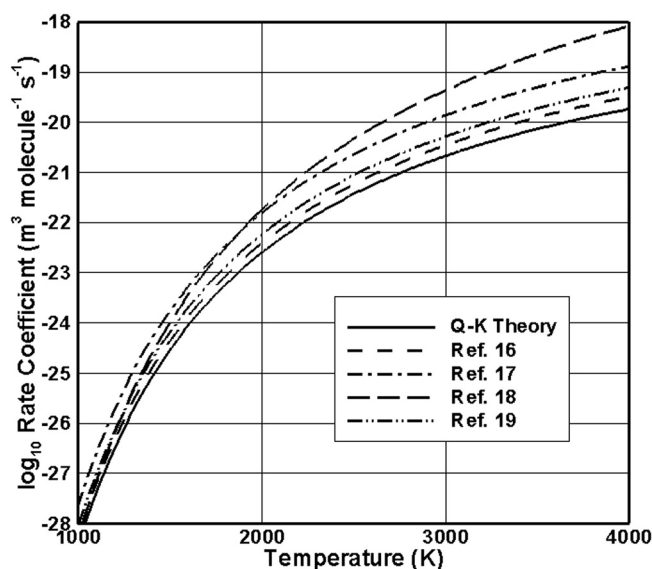
Q-K procedure for exchange reactions. Table II of Boyd¹¹ also includes values for the reverse rates for exchange reactions and Fig. 11 presents a comparison of the reverse rates with the Q-K results. The agreement with the default $E_a = E_r$ for the forward reaction is satisfactory, but all 31 entries in the NIST database have rates that are either independent of temperature or increase with temperature. Most of these are for temperatures around 300 K, but those for a temperature range that reaches 3000 K average just over 2×10^{-17} . The Q-K rates match this behavior only if there is physically real increase in the activation energy for the forward reaction, and as shown in Fig. 11, the Q-K result for a 15% increase in the forward activation energy leads to good agreement with Ref. 15 and the NIST database. This leads to a decrease in the forward rate that is plotted in Fig. 10, but the curve remains within the bounds of uncertainty.

FIG. 11. Reverse rate coefficient for $\text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N}$.FIG. 12. Forward rate coefficient for $\text{NO} + \text{O} \leftrightarrow \text{O}_2 + \text{N}$.

In the case of the other exchange reaction $\text{NO} + \text{O} \leftrightarrow \text{O}_2 + \text{N}$, the ratio of the forward to reverse reaction rates based on the default or unadjusted activation energies is higher than the equilibrium constant from statistical mechanics. This means that the activation energy of the forward reaction must be increased to values above the heat of reaction in order to reduce the forward rate coefficient. The required increase ranged from 33% at 3000 K to 43% at 18 000 K. Figure 12 shows that adjusted forward rate coefficient is in closer agreement with the generally accepted rates and also with two rate coefficients that are most representative of the NIST database.

The rate coefficient in Ref. 11 has zero activation energy for the reverse reaction and Fig. 13 shows that the shape of the rate coefficient curve is similar to the Q-K result with the default activation energy. On the other hand, that from

FIG. 13. Reverse rate coefficient for $\text{NO} + \text{O} \leftrightarrow \text{O}_2 + \text{N}$.

FIG. 14. Rate coefficient for $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$.

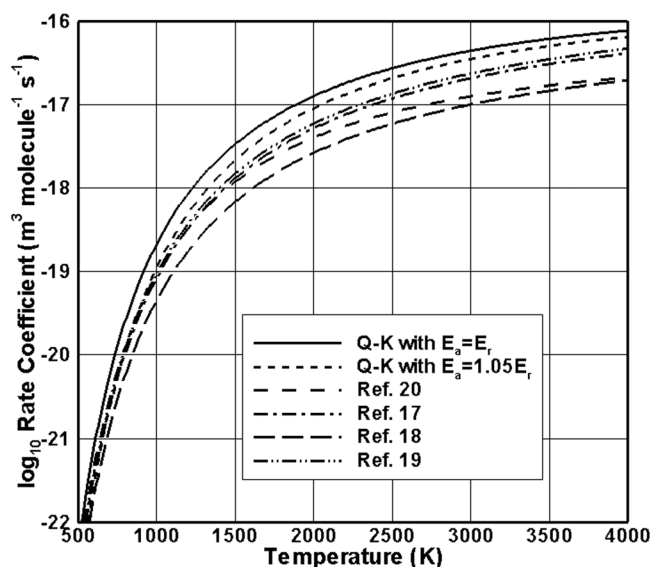
Ref. 15 has an activation energy that is almost 25% above the heat of reaction. The rates in the NIST database support this result in that they predominantly have similar activation energies and the values at 300 K are below 1×10^{-20} . An energy barrier equal to 25% of the heat of reaction was therefore applied to the Q-K model. This requires an increase to the activation energy that had already been applied to the forward reaction in order to re-match the rate ratio to equilibrium constant. The consequent reduction in the adjusted Q-K rate coefficient in Fig. 12 brings it close to the “NIST-1” curve and into even better agreement with the accepted rates.

Boyd¹¹ compared the forward and reverse rates for the exchange reactions in air and concluded that, if both rates are represented by equations with the form of the modified Arrhenius constant, they cannot be consistent with the equilibrium constant. This may or may not be a general result, but Fig. 9 and similar comparisons for the other reactions show that equations of the form of (14) and (15) can be entirely consistent with the equilibrium constant.

V. HYDROGEN-OXYGEN REACTIONS

The Q-K model with the now superseded reverse reaction procedures has been used³ to study both spontaneous and forced ignition as well as the structure of a deflagration wave in an oxygen-hydrogen mixture. The rate coefficients based on the revised procedures are not significantly different from those employed in the earlier paper and may be compared with the Arrhenius rates that have been proposed in Refs. 16–20 and with the rates in the NIST database. The temperature range of interest in combustion applications is much lower than that for the atmospheric re-entry applications in Sec. IV. Also, while the accepted rates for high temperature air have been based largely on measurements in shock tubes, many of the combustion rates involve short lived radicals and some rates are based on the results from transition state theory.

First consider the endothermic chain-initiating reaction $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$ that is the subject of Fig. 14. This

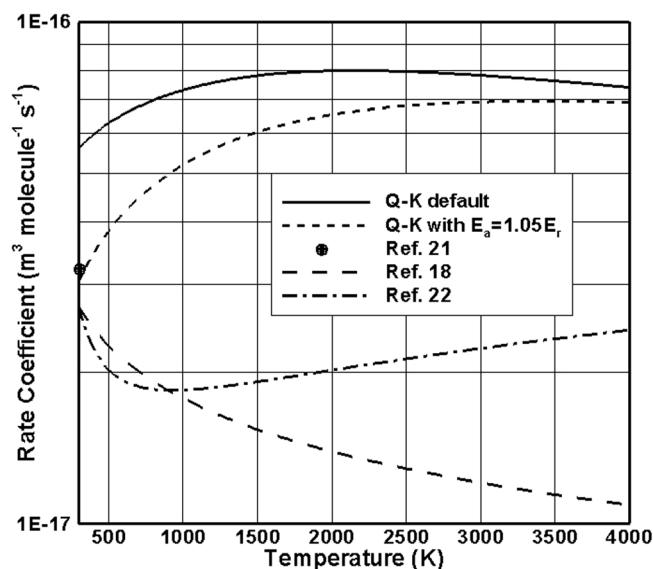
FIG. 15. Rate coefficient for $\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$.

reaction is similar to that shown in Fig. 13 in that the use of the default activation energies leads to a forward to reverse rate ratio that is above that predicted by statistical mechanics. The required upward adjustment of the activation energy of the forward reaction ranges from 15% at 1000 K to 63% at 4000 K. This lowers the Q-K curve from near the top of the quoted range to just below it.

Figure 15 shows a similar comparison for the chain-branching reaction $\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$. The degree of agreement with the accepted hydrogen-oxygen combustion rates is similar to that for the chain-initiating reaction but, because the Q-K curve is above rather than below these rates, it will be bought into better agreement if the activation energy of either the forward or reverse reaction is above the default value. The effect of a forward activation energy that is 5% above the heat of reaction is shown. Any Q-K result that is above an accepted rate can be bought into almost exact agreement with that rate if the increase in activation energy is made temperature dependent. At the same time, the uncertainties in the accepted rates are such that there is generally insufficient justification for doing so on the basis of the forward rate alone. The study of the exchange reactions in air indicated that comparisons of the reverse rates can be more useful than those of the forward reactions and Fig. 16 shows the comparison for the reverse chain-terminating reaction.

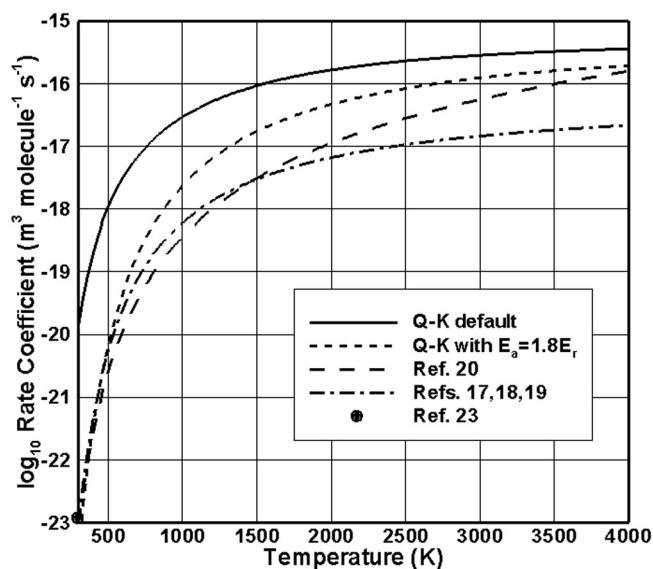
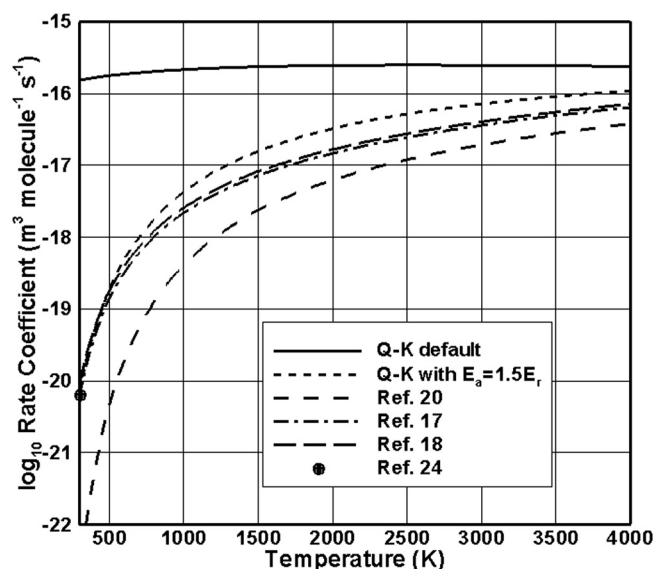
Only one of references that provide tabulated rates for oxygen-hydrogen combustion reactions includes a rate for $\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$. Robertson and Smith²¹ have provided a measured value from laser induced fluorescence at 295 K and Miller and Garrett²² have produced a rate from transition state theory. These are in agreement at room temperature and provide justification for applying the 5% increase in the activation energy for the forward reaction. The 5% increase has little effect at the higher temperature and there would be better overall agreement if the percentage increased with temperature.

The similar chain reaction $\text{H}_2 + \text{O} \leftrightarrow \text{OH} + \text{H}$ has a heat of reaction that is only 37.5% of that for the preceding case and the rates can be expected to be more sensitive to energy

FIG. 16. Rate coefficient for $\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$.

barriers. Figure 17 shows that the tabulated lists of H_2/O_2 combustion rates are in agreement for this reaction and all agree with flash photolysis measurements²³ at room temperature. The “Q-K default” result employs the default activation energies but includes the phenomenological adjustment that is required to bring the forward to reverse rate ratio into agreement with the equilibrium constant. In this case, the activation energy for the reverse reaction had to be increased from zero to $0.09(T/273)E_r$. The Q-K rate is bought into agreement by increasing the activation energy for the forward reaction by 80%. The reverse activation energy has then to be increased to $0.71(T/273)^{0.375}E_r$ in order to maintain detailed balance.

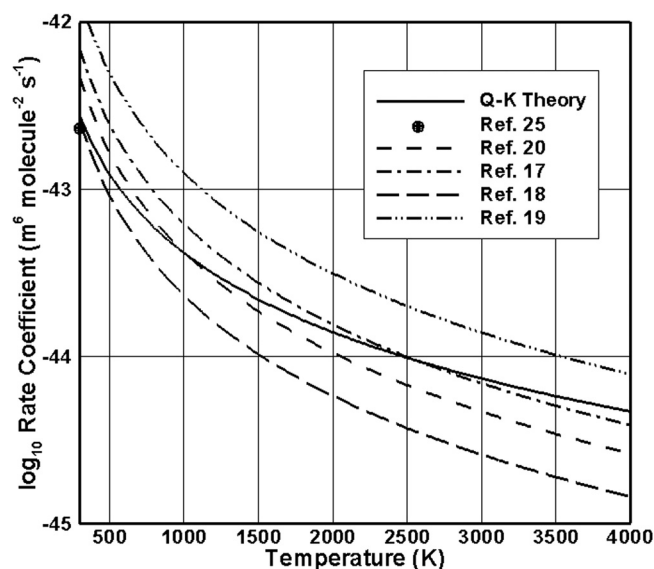
The reaction $\text{H}_2\text{O} + \text{H} \leftrightarrow \text{OH} + \text{H}_2$ is an exchange reaction and it is the reverse reaction that is of greater interest because it is one of the reactions that produce the end-product of the combustion. Figure 18 is for this reaction and

FIG. 17. Rate coefficient for $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$.FIG. 18. Rate coefficient for $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$.

the procedures that led to it are completely analogous with those that led to Fig. 16. Even though the plot is for the reverse reaction, the physically realistic activation energy increase that is required to match the rates at room temperature is again applied to the forward reaction. The adjustment in this case is large, but it has physical justification in that the Arrhenius rate equations for this reaction incorporate an activation energy that is similar to that involved in the adjustment. The spot value for the rate coefficient at room temperature is based on an extensive literature review²⁴ that is claimed to be accurate within about 25%.

The Q-K results for the remaining chain and exchange reactions associated with hydrogen-oxygen combustion have a similar relationship to the accepted rate coefficients and can be reconciled in the same way.

While combustion temperatures are generally too low for dissociation, radicals are formed in the chain reactions and recombination reactions must be taken into account. Consider the recombination of a hydroxyl radical and a hydrogen atom to form a water molecule. Because measurements of endothermic reaction rates generally involve a low concentration of reactants in an inert gas, the reaction $\text{OH} + \text{H} + \text{Ar} \rightarrow \text{H}_2\text{O} + \text{Ar}$ is considered as a typical example. The Q-K model for dissociation does not include any adjustable parameters and the ternary collision volume that sets the recombination rate is fully constrained by the equilibrium constant. The rate coefficients for this reaction from the combustion literature all have a temperature exponent of minus two and define an ordered band of values. The Q-K result lies within this band, but the temperature dependence is smaller. The results are supplemented by a direct measurement²⁵ of the rate through a study of the resonance fluorescence from electron beam excitation of the reactants in an argon bath at 300 K. The direct measurements at room temperature are arguably the most reliable of the experimental results and the agreement between these measurements and the Q-K results in Figs. 16–19 provides the strongest validation of the model.

FIG. 19. Rate coefficient for $\text{OH} + \text{H} + \text{Ar} \rightarrow \text{H}_2\text{O} + \text{Ar}$.

VI. CONCLUDING REMARKS

The Q-K model is not intended to compete with the modern theories for gas-phase chemical reactions that provide a much better physical representation of real reactions. These generally involve the study of the reaction trajectory on the potential energy surface, while the Q-K theory can be regarded as a collision theory that provides results that are more accurate than those from the traditional collision theories. A major objective has been to obtain a set of simple procedures that can be applied to each of the millions or billions of the collisions in a DSMC application without the significant increase in the computational requirements that is associated with the existing TCE model. The Q-K rates are brought into near exact agreement with the equilibrium constant of statistical mechanics, but this constant does not have to be calculated within the DSMC implementation. A further advantage of the Q-K procedures over the TCE procedures is that their derivation does not assume equilibrium and they can be applied with greater confidence to reactions that may involve large distortions of the equilibrium distributions. While these are important considerations, the major advantage of the Q-K model is that it does not depend on the availability of rate coefficients that are based primarily on experiment.

While the Q-K procedures do not make use of existing data for the rate coefficients, they are so simple that the corresponding rate equations in an equilibrium gas can be readily derived. The predictions of the Q-K theory can then be compared with the generally accepted rates and these comparisons serve to validate the computational procedures. The comparisons between the Q-K rates and the accepted rates for atmospheric re-entry applications have covered almost all reactions, while those for hydrogen-oxygen combustion have necessarily dealt only with representative cases. All the reactions that are needed for the application of the DSMC method to problems in these areas have been studied and the rates fall either within or only just outside the range of uncertainty in the accepted rates. However, it should be remembered that the Q-K model is phenomenological in nature and

there may be cases in which it leads to rates that are well outside the range of uncertainty of the measured rates. While the Q-K theory involves adjustment processes in order to satisfy detailed balance, it does not contain adjustable parameters and, if there are compelling reasons to bring a Q-K result into agreement with another rate, it would be necessary to apply an empirical correction factor to the reaction probability in the DSMC procedures. At the same time, the Q-K model can be applied with some confidence in DSMC applications that involve reactions with unknown rate equations. Similarly, the analytical expressions for the rate coefficients that correspond to the DSMC procedures may be useful in continuum studies of reacting flows with unknown rates.

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