

# Chemical Reactions in DSMC

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**Abstract.** DSMC simulations of chemically reacting gas flows have generally employed procedures that convert the macroscopic chemical rate equations to reaction cross-sections at the microscopic level. They therefore depend on the availability of experimental data that has been fitted to equations of the Arrhenius form. This paper presents a physical model for dissociation and recombination reactions and a phenomenological model for exchange and chain reactions. These are based on the vibrational states of the colliding molecules and do not require any experimentally-based data. The simplicity of the models allows the corresponding rate equations to be written down and, while these are not required for the implementation of the models, they facilitate their validation. The model is applied to a typical hypersonic atmospheric entry problem and the results are compared with the corresponding results from the traditional method. It is also used to investigate both spontaneous and forced ignition as well as the structure of a deflagration wave in an oxygen-hydrogen mixture.

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## INTRODUCTION

The initial development of any DSMC procedure generally makes reference to classical theory and, in the case of chemical reactions, the well established but largely superseded "collision theory" was the obvious starting point. Collision theory was adapted to convert the temperature-dependent continuum rate equations to collision energy-dependent reactive cross-sections. The rate equations were the same as those used in continuum CFD studies and this ensured that the DSMC results merged smoothly with the continuum results at low Knudsen numbers. While these comparisons verified the coding, validation was not possible until comparisons were made [1] with the detailed heat transfer measurements from the early Space Shuttle flights. A similar approach has been adopted in most DSMC codes and it is now generally called the total collision energy or TCE method.

The TCE approach [2] satisfies the basic DSMC requirement that procedures must not be dependent on any macroscopic gas property, but has the disadvantage that the underlying theory assumes an equilibrium distribution function. Moreover, it was noted in this reference that, if Arrhenius rate equations are specified for both forward and reverse equations, equilibrium will be obtained for only a narrow range of temperatures. An "equilibrium collision theory" was therefore proposed that relates the forward and reverse rates through the equilibrium constant. Reference [2] also outlined phenomenological procedures that predict the reactive cross-sections and rate equations for dissociation and endothermic exchange reactions. These procedures were subsequently applied to the re-entry problem and, even though they made no use of rate equations, they were found [3] to produce results that were in close agreement with those from the TCE method.

None of the above procedures made direct reference to the vibrational excitation and were implemented in programs that employed the cumbersome classical vibrational model. The introduction of the quantum vibrational model [4] opened the way for the development of procedures that are incomparably closer to the real physics. For example, there was no longer any need for dissociation rate data because it occurs naturally when the post-collision vibrational level is that for dissociation. The earlier [2] predictive procedure for the endothermic exchange reactions was readily converted to one that is also based on the vibrational levels. The equilibrium constant based on the appropriate collision temperature can then be used to derive steric factors for the reverse exothermic reactions. No reference is made to the macroscopic gas properties and all reaction probabilities are based on the vibrational state of the colliding molecules. The new model is called the "quantum-kinetic" or Q-K model.

The simplicity of the collision-based Q-K criteria for the occurrence of endothermic reactions allows the corresponding rate equations to be written down for an equilibrium gas. This permits the analytical determination of the steric factors for the exothermic reactions. It also allows the Q-K rate equations to be compared with experimentally based reaction rates and, if there are significant discrepancies, an empirical adjustment factor may be brought into the Q-K criteria. The initial presentation of the approach in reference [5] showed good agreement for real air reactions and reference [6] refined and extended the comparisons to cover several chain branching reactions in the hydrogen-oxygen system and the ionization of helium.

## THE QUANTUM-KINETIC CHEMISTRY MODEL

### Dissociation

Consider the serial application [2] of the quantum Larsen-Borgnakke model [4] to a vibrational mode 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  $E_C$ . In order to obtain equipartition of the vibrational energy, the collision temperature that is implicit in the Larsen-Borgnakke procedure must be [5] quantized by truncating the collision energy to that of the highest vibrational level with energy below  $E_C$ . This led to the definition of the “quantized collision temperature”

$$T_{QC} = i_{max} \Theta_v / (7/2 - \omega), \text{ where } i_{max} = \lfloor E_C / (k \Theta_v) \rfloor. \quad (1)$$

$\Theta_v$  is the characteristic vibrational temperature,  $\omega$  is the temperature exponent in the viscosity coefficient and  $k$  is the Boltzmann constant.

The condition for dissociation of the molecule AB in the reaction  $AB+T \rightarrow A+B+T$  is then

$$i_{max} > \Theta_d / \Theta_v, \quad (2)$$

where  $\Theta_d$  is the characteristic dissociation temperature. This condition is applied in the DSMC collision routine prior to the Larsen-Borgnakke selection of a post-collision vibrational state. This is because there is a continuum (i.e. an infinite number) of levels beyond the dissociation limit so that, with the vibrational collision number set to unity [5] at the dissociation limit and with  $E_C$  as the measure of collision energy, dissociation occurs whenever it is energetically possible. Note that the Larsen-Borgnakke selection process is an even choice from the available states and the transition from a finite to an infinite number of states at the dissociation limit would lead to a discontinuity if the vibrational collision number was not unity at this limit.

The corresponding rate coefficient in an equilibrium VHS gas with  $j$  vibrational modes at temperature  $T$  is

$$k_f(T) = R_{coll}^{AB,T} \sum_1^j \Upsilon(i_{max})^{AB,T}. \quad (3)$$

The collision rate parameter  $R_{coll}^{AB,T}$  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

$$R_{coll}^{AB,T} = (2\pi)^{1/2} / \varepsilon (r_{ref}^{AB} + r_{ref}^T)^2 (T / T_{ref})^{1-\omega^{AB,T}} (2kT_{ref} / m_r^{AB,T})^{1/2}, \quad (4)$$

where  $r_{ref}$  is the molecular radius a temperature  $T_{ref}$ ,  $m_r$  is the reduced mass and  $\varepsilon$  is a symmetry factor equal to 1 for like molecules and 2 for unlike molecules. The parameter  $\Upsilon(i_{max})^{AB,T}$  is the fraction of collisions between AB and T that have sufficient energy to meet the condition in Eq. (2). For an equilibrium VHS gas,

$$\Upsilon(i_{max})^{AB,T} = \sum_{i=0}^{i_{max}-1} \{ Q[(5/2 - \omega^{AB,T}), ((i_{max} - i) \Theta_v^{AB})] \exp(-i \Theta_v^{AB} / T) \} / z_v^s(T)^{AB}. \quad (5)$$

$Q(a, x) = \Gamma(a, x) / \Gamma(a)$  is a form of the incomplete Gamma function and  $z_v^s(T) = 1 / [1 - \exp(-\Theta_v / T)]$  is the vibrational partition function for the appropriate single mode in the harmonic oscillator model. As noted earlier, while this rate equation is not required for the implementation of the Q-K model in DSMC programs, it allows comparisons with the rate equations based on experiment. The resulting agreement for dissociation is so close [5],[6] that Eq. (2) can be regarded as a good physical model rather than just a viable phenomenological model.

## Recombination

The total collision cross-section in a VHS gas is defined as the area of a circle with radius equal to the sum of the radii of the two colliding molecules. A three-body collision volume may be defined as the sphere with radius equal to the sum of the radii of the three colliding molecules. While this lacks the physical justification of the cross-section definition, it is readily evaluated in a DSMC calculation and is the simplest reasonable approximation. For a collision in a gas with a degree of dissociation  $\alpha$ , the mean collision volume is

$$V_{coll} = [4\pi/(3(1+\alpha))] \{ (1-\alpha)(r^A + r^B + r^{AB})^3 + \alpha[(2r^A + r^B)^3 + (2r^B + r^A)^3] \} . \quad (6)$$

where  $r^M$  is the VHS molecular radius of molecule  $M$  in that collision.

The probability of recombination in a collision between species  $A$  and  $B$  is

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

where  $n$  is the number density and  $S$  is the steric factor. The corresponding rate equation is

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

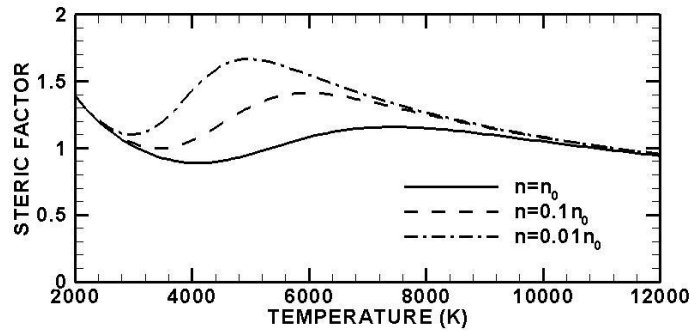
The equilibrium constant is given by  $k_f(T)/k_r(T)$  and this may be equated to the equilibrium constant from statistical mechanics in order to obtain the following expression for the steric factor in a diatomic gas.

$$S = \frac{\varepsilon}{(1+\alpha)R_{coll}^{A,B}} \left[ \frac{1-\alpha}{2} R_{coll}^{AB,AB} \Upsilon(i_{max})^{AB,AB} + \alpha(R_{coll}^{AB,A} \Upsilon(i_{max})^{AB,A} + R_{coll}^{AB,B} \Upsilon(i_{max})^{AB,B}) \right] \times \quad (9)$$

$$\times \frac{h^3}{(2\pi kT)^{3/2}} \left( \frac{m^{AB}}{m^A m^B} \right)^{3/2} \left( \frac{T}{\varepsilon' \Theta_r} \right)^{AB} \exp\left( \frac{\Theta_d}{T} \right) / V_{coll},$$

where  $h$  is the Planck constant and  $\Theta_r$  is the characteristic rotational temperature. The rotational partition function has been written here in the diatomic form  $z_r(T) = T / (\varepsilon' \Theta_r)$  where  $\varepsilon'$  is equal to the number of rotational orientations of  $AB$  that are indistinguishable. Statistical mechanics can also be used to derive the following expression for the equilibrium degree of dissociation, so that the steric factor becomes a function of temperature and the undissociated ( $\alpha = 0$ ) number density  $n$  which can be normalized by the standard number density  $n_0$ .

$$\alpha^2 / (1-\alpha) = (2/n) [\pi(m^A m^B / m^{AB}) kT / h^2]^{3/2} (\varepsilon' \Theta_r^{AB} / T) [1 - \exp(-\Theta_v^{AB} / T)] \exp(-\Theta_d^{AB} / T). \quad (10)$$



**FIGURE 1.** The steric factor based on the combination of equations (9) and (10) for the recombination of oxygen.

While a steric factor cannot exceed unity, the above analysis employs the approximate collision volume of equation (6) and the high temperature approximations to the partition functions. Moreover, because there is no data, estimated values are employed for some physical properties of the dissociated radicals and reasonable variations to these estimates can lead to variations in the steric factor that are greater than those in Figure 1. Similar results are obtained for other diatomic molecules and the steric factor  $S$  is best set to unity in equation (7). Therefore, the Q-K criterion for recombination is that it occurs in every collision that can be regarded as a three-body collision.

## Endothermic 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 reaction  $A + B \rightarrow C + D$  with activation energy  $E_a$  and in which A and C are the molecules that split. The phenomenological DSMC condition is that the reaction occurs if the vibrational level  $i$  in any mode of molecule A after a trial Larsen-Borgnakke redistribution of the sum of the relative translational energy and the vibrational energy of A is equal to a particular level  $i_a$  with energy above the activation energy. i.e.

$$i_a = \left\lceil E_a / (k\theta_v^A) \right\rceil + i_c, \quad (11)$$

where  $i_c$  is either zero or a small positive integer that allows an empirical adjustment of the resulting rate coefficient. The correction would be based on comparisons with any reliable measured rate coefficients or would be made to reduce any unphysical steric factors for the corresponding exothermic reaction that exceed unity. The trial redistribution is made to avoid an unphysical depletion of the  $i_a$  level during the calculation.

The rate coefficient that is set by this condition is simply the product of the collision rate parameter and the fractional sums of the probabilities of these levels in the Boltzmann distribution. For  $j$  relevant vibrational modes,

$$k_f(T) = R_{coll}^{A,B} \sum_1^j \left\{ \exp(-i_a \theta_v^A / T) / z_v^s(T)^A \right\}. \quad (12)$$

A number of rate coefficients based on this equation with  $i_c$  set to zero have been compared [5],[6] with the accepted coefficients that are based on experiment. The agreement is generally good and, should it be unsatisfactory, the results can be brought into close agreement by the setting of the appropriate value of  $i_c$ . Note that all the computational results in this paper have been obtained with  $i_c$  set to zero.

## Exothermic Exchange and Chain Reactions

Define a steric factor  $S$  as a function of the collision temperature  $T_C$  based on the energy  $E_C$  that is here the sum of the relative translational energy and all the internal energies of both molecules. The reaction then occurs with probability

$$P_{reaction} = S(T_C)$$

$$\text{where } T_C = (E_C / k) / \left( 5/2 - \omega^{A,B} + \zeta_r^A / 2 + \zeta_r^B / 2 + \sum_1^j i^A \ln(1 + 1/i^A) + \sum_1^j i^B \ln(1 + 1/i^B) \right). \quad (13)$$

$\zeta_r$  is the number of rotational degrees of freedom. While a term in the expression for the effective vibrational degrees of freedom becomes singular for the ground state, the mathematical limit of the expression is then zero.

The rate coefficient for the reverse reaction is then

$$k_r(T) = R_{coll}^{C,D} S(T_C). \quad (14)$$

The equilibrium constant based on Eqns. (12) and (14) may be equated to that from statistical mechanics to give

$$S(T_C) = \frac{k_f(T_C)}{R_{coll}^{CD}} \left( \frac{m^A m^B}{m^C m^D} \right)^{3/2} \frac{z_r(T_C)^A z_v(T_C)^A z_r(T_C)^B z_v(T_C)^B}{z_r(T_C)^C z_v(T_C)^C z_r(T_C)^D z_v(T_C)^D} \exp[E_a / (kT_C)]. \quad (15)$$

$z_r$  is the rotational partition function and the overall vibrational partition function  $z_v$  is the product of the functions for each mode. The activation energy for the reverse reaction is assumed to be zero. Unlike the other DSMC conditions, the evaluation of equation (15) is computationally intensive. However, when the overall computation time is compared with that for a constant steric factor, the penalty has proved to be less than one percent in the worst case. Should it be necessary to include the electronic partition functions, a table look-up might be preferable.

## APPLICATION TO AN ATMOSPHERIC ENTRY PROBLEM

A one-dimensional calculation has been made for the flow along the stagnation streamline of a blunt body moving with a speed of 7.5 km/sec in the atmosphere at an altitude of 85 km. The shock stand-off distance is stabilized at 0.32 m through the uniform removal of molecules from the streamline between the rear of the shock wave and the surface. Mass conservation is achieved by setting the mass flux of removed molecules equal to the mass flux of molecules that enter the streamline at 0.7 m from the surface. It has been shown [2] that momentum and energy are also conserved if the removal probability of the molecules is independent of their velocity component along the streamline, but proportional to the square of their velocity component normal to the streamline.

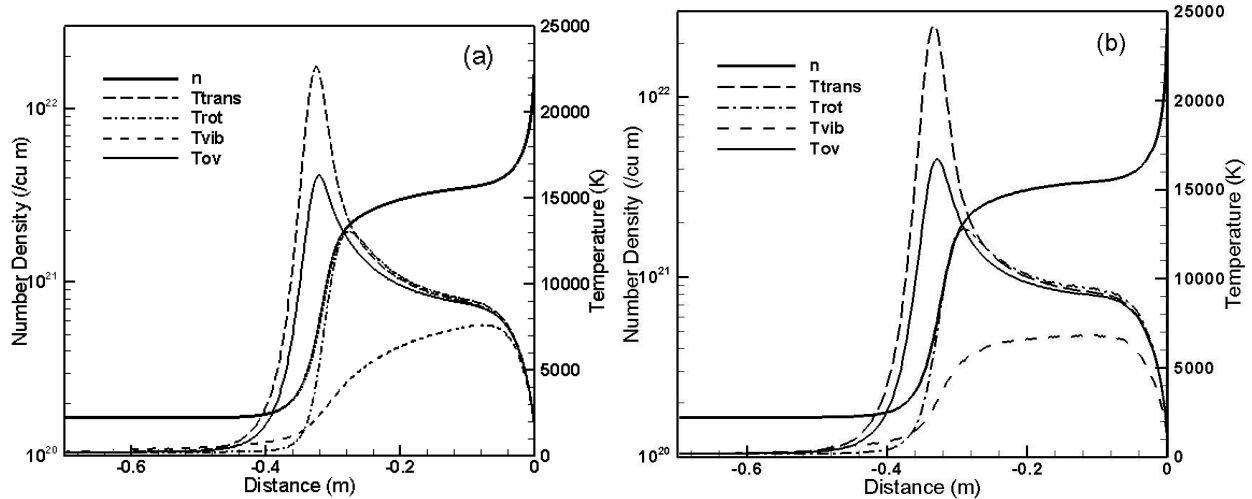


FIGURE 2. The number density and temperature profiles along the streamline for (a) the Q-K model and (b) the TCE model.

The density profiles in Figure 2 are almost identical and the only significant difference between the temperature profiles is that the vibrational mode comes to equilibrium more quickly with the Q-K model. With regard to the composition profiles in Figure 3, there is less NO when the Q-K model is employed. There is one exothermic exchange reaction that depletes NO and one that enhances it. The rate equations for the reaction that enhances NO are in good agreement and the difference is caused by a much higher Q-K rate for the reaction that depletes NO.

The number flux, pressure and heat transfer coefficients at the stagnation point all agree to well within one percent.

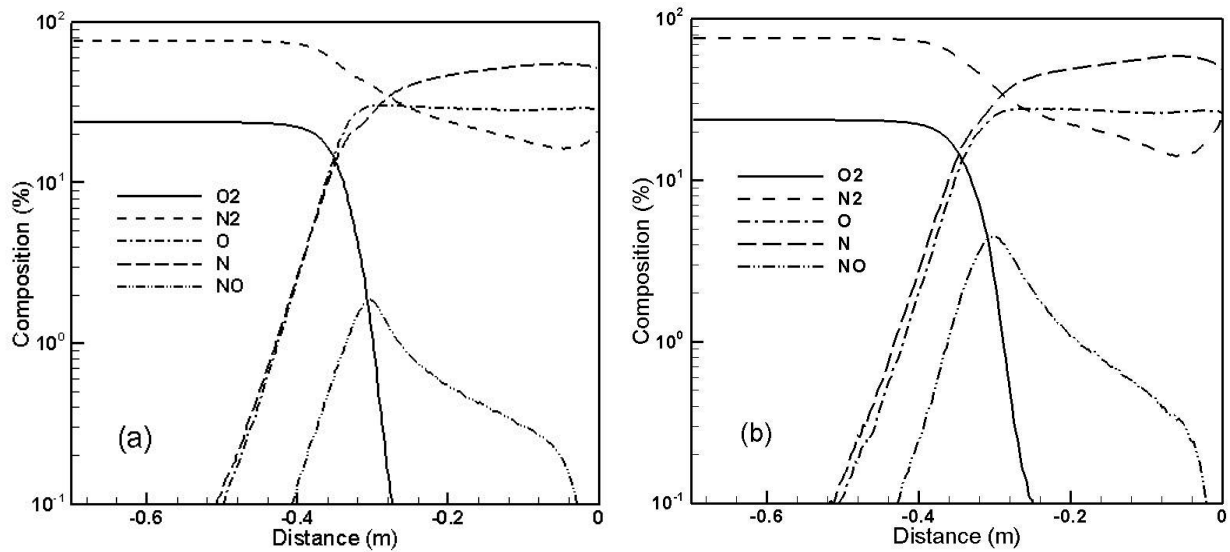
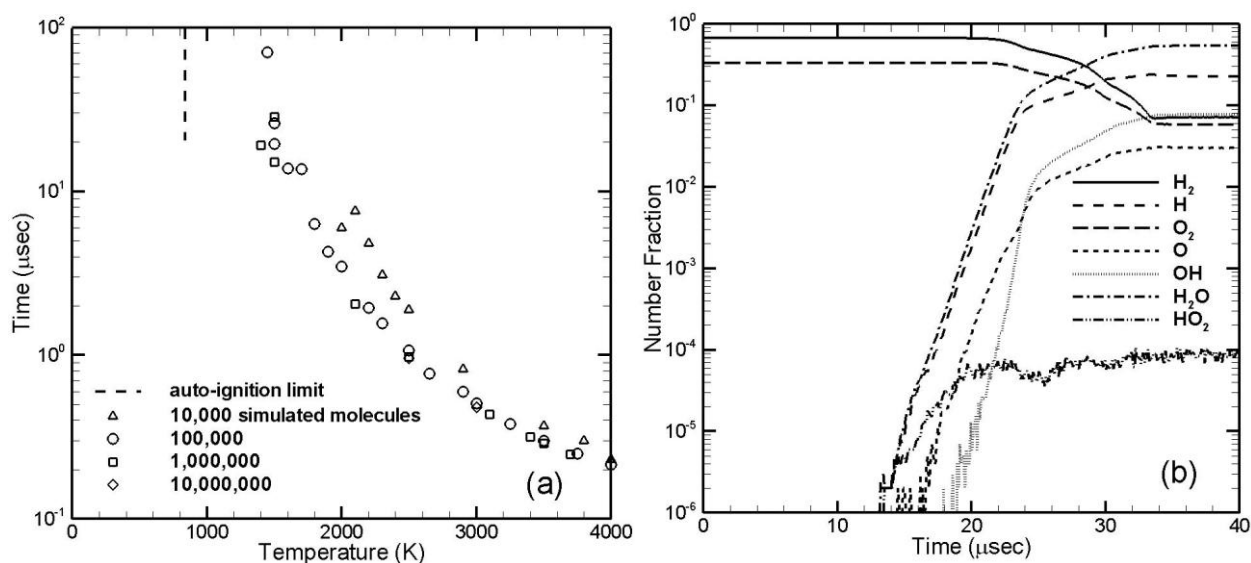


FIGURE 3. The chemical composition of the gas along the streamline for (a) the Q-K model and (b) the TCE model.

## SPONTANEOUS COMBUSTION IN AN OXYGEN-HYDROGEN MIXTURE

A stoichiometric mixture of hydrogen and oxygen at a number density of  $10^{24} \text{ m}^{-3}$  is known [7] to auto-ignite at temperatures above about 840 K. The initiating reaction (if reactions involving hydrogen peroxide are ignored) is the  $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$  reaction that leads to the formation of the hydroperoxyl radical. This is an endothermic reaction and an  $\text{H}_2$  molecule must be in the fifth vibrational level for the reaction to meet the reaction condition of Equation (11). The probability of a hydrogen molecule being in this level in an equilibrium gas at 840 K is only  $1.84 \times 10^{-16}$ . The TCE steric factor that corresponds to the continuum rate equation for this reaction at 840 K is similarly small. While spontaneous combustion near the auto-ignition limit cannot be modeled with the number of simulated molecules that can be used in practical DSMC calculations, ignition occurs readily at higher temperatures.

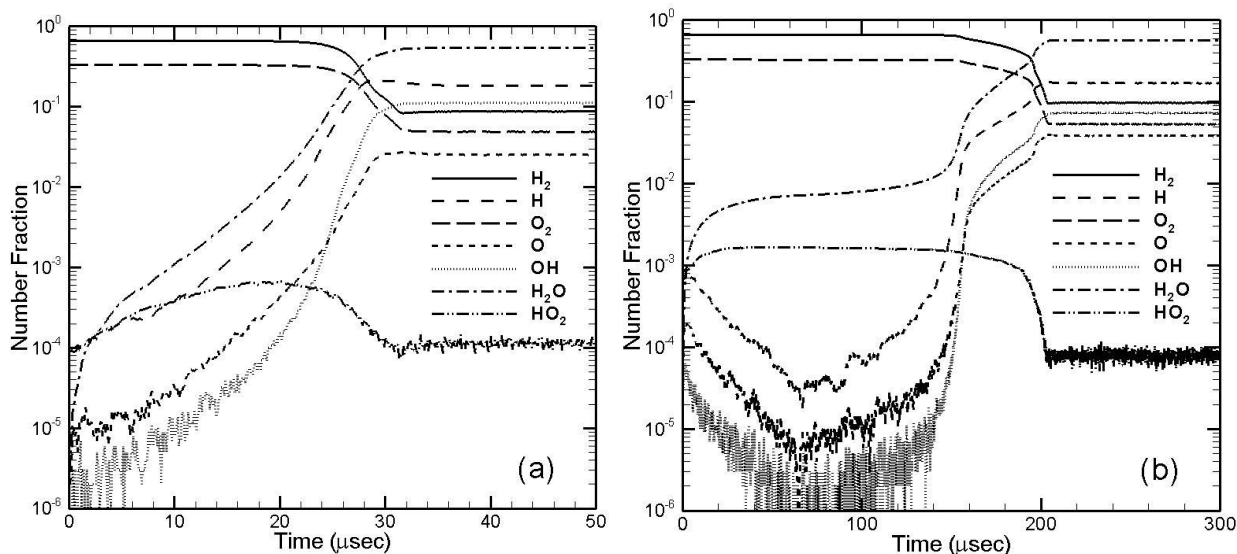


**FIGURE 4.** (a) The time to reach an  $\text{H}_2\text{O}$  number fraction of 0.3 in the spontaneous ignition of a stoichiometric mixture of hydrogen and oxygen at an initial number density of  $1 \times 10^{24} \text{ m}^{-3}$  and (b) the time history of the number fractions at an initial temperature of 1,500 K in a calculation employing the Q-K method with 1,000,000 initial simulated molecules.

The results from homogeneous gas DSMC calculations for the auto-ignition delay time were found to be almost independent of the ratio of simulated to real molecules as long as the number of simulated molecules exceeds 100,000. Auto-ignition was not obtained in calculations with 1,000,000 simulated molecules below a temperature of 1,400 K. The probability of finding a hydrogen molecule in vibrational level 5 at this temperature is only  $2.76 \times 10^{-10}$ , but each hydrogen molecule undergoes many thousands of collisions during the delay. The ignition delay is known to be many milliseconds at the 840 K limit, and the results in Figure 4(a) are consistent with this. A log plot of the delay times against the inverse of the temperature fall on a straight line and this is consistent with measured delay times. The equilibrium concentrations in Figure 4(b) are in reasonable agreement with theory [7].

## FORCED IGNITION IN AN OXYGEN-HYDROGEN MIXTURE

Figure 5 shows typical ignition processes followed by combustion to an equilibrium composition when a fraction of the molecules are initially set to the fifth vibrational level. The Q-K model was employed and each calculation involved one million initial simulated molecules. Only 500 of these molecules were set to level 5 in case (a) and the energy associated with this degree of non-equilibrium contributes just two degrees Kelvin to the initial temperature of 1200 K. In order to achieve ignition in a gas initially at 900 K, it was necessary to set 5,000 of the one million simulated molecules to vibrational level 5. The corresponding energy contributes 25 K to the initial temperature and, even then, Figure 5(b) shows that the initial concentration of radicals declines for about 70 microseconds. The hydroxyl radical declines to about one part in a million, or an average of just one simulated molecule. At the same time, the concentration of hydroperoxy is maintained at about one part in a thousand and there is a gradual build up of water vapor. This build-up is accompanied by an increase in the gas temperature and, when this reaches about 1200 K, combustion occurs with an induction time that is strongly dependent on the initial gas temperature.

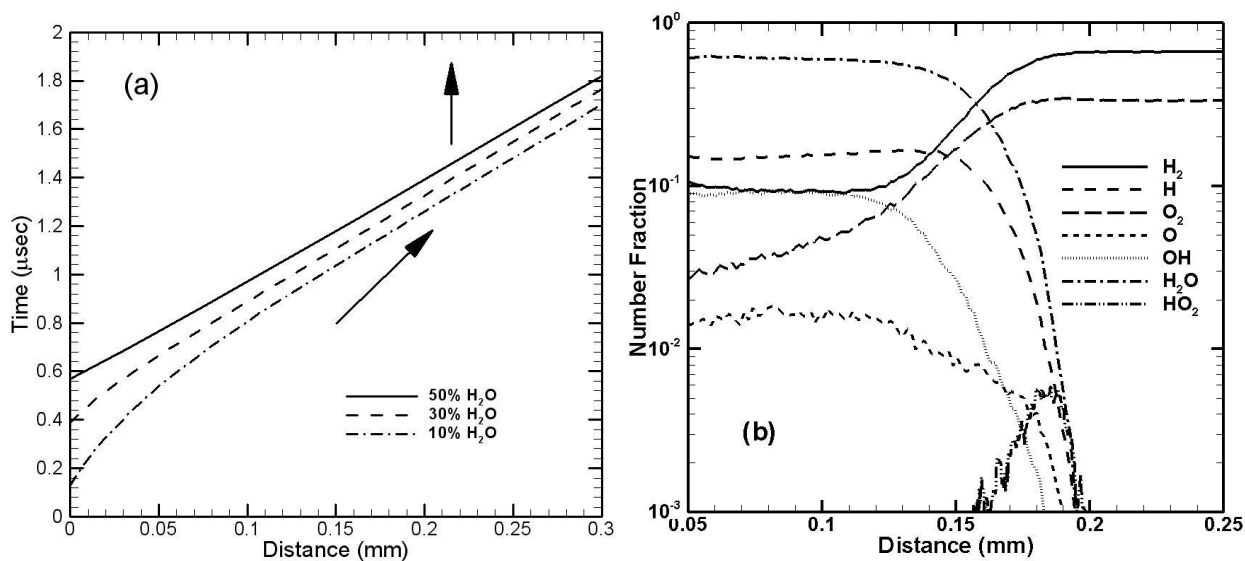


**FIGURE 5.** Constant volume combustion in a homogeneous stoichiometric mixture of hydrogen and oxygen at an initial number density of  $10^{24} \text{ m}^{-3}$  and an initial temperature of (a) 1200 K and (b) 900 K.

At lower initial temperatures or smaller concentrations of initially excited molecules, the water vapor and hydroperoxy concentrations also decline and ignition does not occur. Many similar calculations were made and it was found that, for ignition to occur in a gas at a temperature below 900K, an excessive degree of non-equilibrium is required.

### THE FORMATION OF AND THE STEADY STATE OF A DEFLAGRATION WAVE

A stoichiometric mixture of oxygen and hydrogen at a number density of  $10^{25} \text{ m}^{-3}$  and a temperature of 900 K was ignited at the specularly reflecting end-wall at the lower coordinate by setting one percent of the flow length to  $10^{24} \text{ m}^{-3}$  and 9,000 K. Note that only one part in a thousand of the gas was at the higher temperature and there was no pressure difference between the two regions. Ignition was rapid with the equilibrium burnt gas composition being established at the origin in less than a microsecond and the time associated with the formation of a steady wave was of the order of five microseconds. The thickness of the wave is of approximately 0.1 mm or about 400 mean free paths in the unburned gas.



**FIGURE 6.** Contours of constant concentration of  $\text{H}_2\text{O}$  together with the velocity vectors in an  $x$ - $t$  diagram (a) and the spatial distribution of all species at a time of 1.2 microseconds (b).

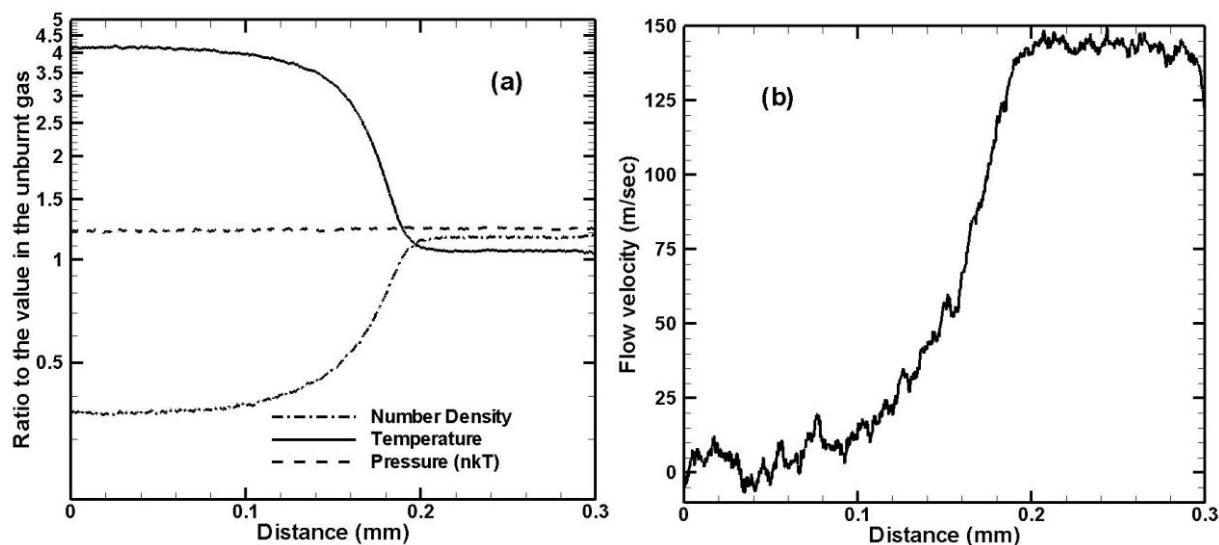


FIGURE 7. The spatial distributions of density, pressure and temperature (a) and velocity (b) at a time of 1.2 microseconds.

The velocity of the flame front is 240 m/s and the pre-compression of the unburnt gas leads to a 20% increase in the undisturbed gas pressure. The velocity due to the pre-compression is approximately 145 m/s so that the velocity of the flame relative to the unburnt gas is about 95 m/s. The combustion takes place at constant pressure.

## CONCLUDING REMARKS

Phenomenological models are not definitive and are always subject to variations that may or may not prove to be advantageous. This paper has employed the equilibrium constant rather than the “detailed balance” procedure [5] to establish the exothermic exchange and chain reaction rates. It is undesirable to base a DSMC procedure on the equilibrium constant even though it employs a collision-based temperature. The recent addition of the correction term  $i_c$  to condition (11) may mean that the “detailed balance” balance procedure has the advantage for combustion as well as re-entry flow applications. The validation of this procedure was based [5] on computational studies and an analytical study is needed to determine whether or not it exactly satisfies the reciprocity principle.

The rate equation of equation (12) for forward (endothermic) exchange and chain reactions has an exponential term that is very close to that in the Arrhenius equation, but the temperature exponent in the pre-exponential term is constrained by the collision rate parameter of equation (4) to be around 0.75. While this may be an unduly severe constraint, the unlimited range of this exponent in the Arrhenius equation allows the specification of unphysical values when experimental results are curve-fitted to this essentially empirical equation in order to obtain the corresponding rate coefficients. The conversion of these rates to steric factors in the TCE method does impose some constraint because the conversion is mathematically impossible [2] for sufficiently large negative exponents. However, many listed rate coefficients specify negative values for the temperature exponent that are well beyond this limit and some indiscriminate Arrhenius curve-fits even lead to negative activation energies!

The TCE and Q-K models can provide equally good results when reliable data is available for the chemical rate coefficients over the full range of temperatures that are encountered in the application. On the other hand, if the rate data is not available or if the application necessitates the extrapolation of the data to temperatures well outside the temperature range of the underlying measurements, the advantages of the Q-K model are overwhelming.

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