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Vibrational Nonequilibrium Effects on Diatomic Dissociation Rates

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The collision-induced dissociation rate of diatomic molecules from a ladder of rotational and anharmonic vibrational states is developed, and the correction for vibrational nonequilibrium is considered. The result is similar to an analytic correction derived by Hammerling et al.[13] for harmonic oscillators. An empirical correction algorithm suggested by Park[6,14] gives similar results when vibrational temperature is comparable to kinetic temperature but underestimates the dissociation rate when vibrational temperature is small compared with the kinetic temperature. This algorithm uses an effective temperature in the experimentally determined Arrhenius expression for the rate coefficient, which is a weighted average of the vibrational and kinetic temperature, whereas theory indicates that kinetic temperature only should appear in the exponential term of the Arrhenius expression. Nevertheless, an effective temperature can always be found that will numerically duplicate the proper rate coefficient at any given condition, but a constant weighting factor cannot be expected to provide this. However, the algorithm can be adjusted to give reasonable results over a range of conditions if the geometric weighting factor is taken to be a simple linear function of the ratio of vibrational to kinetic temperature in the gas.

Nomenclature

C/T^d = pre-exponential term in Arrhenius rate coefficient
D = dissociation energy
E = collision energy
E^* = activation energy from ground state
E_i = internal energy of state i
f = exponent for weighting vibrational and kinetic temperatures
g_i = degeneracy of state i
$\hbar$ = Planck constant/2π
k = Boltzmann constant
n = total density of gas particles
n_i = density of gas particles in state i
P = total probability of reaction due to collision
Q = total partition function
Q_v = vibrational partition function
q = probability of no transition at potential crossing
r = distance between colliding gas particles
r_0 = radius of reaction surface
S = reaction cross section
S_0 = reference ground state cross section
s = collision symmetry number
T = kinetic temperature
T_a = effective temperature in rate coefficient expression
T_v = vibrational temperature
T^* = fictitious temperature $TT_v/(T - T_v)$
$\bar{u}$ = mean collision velocity at infinite separation
x = dimensionless collision energy E/kT
x^* = dimensionless activation energy for ground state, E^*/kT
x_i^* = dimensionless activation energy for state i, $(E^* - E_i)/kT$
y = dimensionless collision energy above threshold, $x - x^*$
κ = total reaction rate coefficient
κ_i = reaction rate coefficient for state i
κ_{eq} = equilibrium dissociation rate coefficient
κ_{neq} = dissociation rate coefficient for nonequilibrium
ω = vibrational frequency, 2π

Introduction

COMPUTATIONAL fluid dynamics (CFD) methods of obtaining solutions to flow about aerospace vehicles have been very successful,[1,2] even at speeds where the fluid medium becomes a complex mixture of chemically reacting species. If the chemical rate coefficients are known, the gas properties in each volume element of the flow are obtained as functions of time by numerical integration of the flow equations (conservation of mass, momentum, and energy and obedience to the equation of state) and the chemical rate equations. The primary constraints are the following: 1) the algorithm for calculating the chemical specie concentrations must be simple and rapid if a complex flow is to be mapped in a reasonable time, and 2) the rate coefficients may need to be extrapolated beyond the range of measurement and to highly nonequilibrium conditions that are unmeasured.

Endothermic rate coefficients are uniformly fit to a simple Arrhenius function that is convenient to use in CFD computations,

$$\kappa = \frac{C}{T^d} e^{-E^*/kT} \tag{1}$$

where d is a constant exponent that accounts for the temperature dependence of the collision velocity and the reaction cross section, and C is a constant proportional to the size of that cross section. The activation energy E^* is usually chosen to be the heat of reaction and the exponent d the value that then best fits the slope of the experimental Arrhenius plot ($\ell n\, \kappa$ vs $1/T$). The constant C establishes the magnitude of the rate coefficient that agrees with experimental results for the given choice of d. Generally d is found to be the order of unity.

There is no doubt that the Arrhenius function can be fit to experimental data very well. However, measured coefficients are not generally available for the nonequilibrium conditions that must be considered in aerodynamic problems. It is the purpose of this paper to examine approximations for the effect of vibrational nonequilibrium on dissociation of diatomic molecules such as N_2, O_2, and NO.

Reaction Rate Theory

The rate coefficient for chemical reaction is rigorously the reaction cross section S averaged over the distribution of collision energies.[3] Generally this distribution becomes Boltzmann

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like within a few collisions, so the rate coefficient for a given pair of collision partners can be accurately expressed

$$\kappa = \frac{\bar{u}}{s} \int_0^\infty S(x) x e^{-x}\, dx \tag{2}$$

where the symmetry number s is unity for like species in collision and 2 for dissimilar species. For endothermic reaction the cross section is zero up to a threshold x^*, rises steeply at higher collision energies up to some maximum of the order of the total scattering cross section (about 10^{-15} cm^2 for atmospheric gas molecules), and then decays again at much higher collision energy. Changing the variable of integration to $y = x - x^*$, the collision energy excess to the threshold value,

$$\kappa = \left[\frac{\bar{u}}{s} \int_0^\infty S(y)(x^* + y) e^{-y}\, dy \right] e^{-x^*} \tag{3}$$

This is the familiar Arrhenius form with the pre-exponential factor being the expression in parenthesis. This factor cannot rigorously be the simple single term function of T as given in Eq. (1) over the entire range of temperature, for in the limits of very low and very high temperature compared with E^*/k the pre-exponential becomes

$$\lim_{kT/E^* \to 0} (C/T^d) = \frac{\bar{u} x^*}{s} \int_0^\infty S(y) e^{-y}\, dy \tag{4a}$$

$$\lim_{kT/E^* \to \infty} (C/T^d) = \frac{\bar{u}}{s} \int_0^\infty S(y) y e^{-y}\, dy \tag{4b}$$

According to the analyses by Landau[4] and Zener,[5] transitions occur within a narrow range of internuclear distance about some value r_0 where the potentials of the reactants and products either cross or come very close. Collision partners that are energetic enough to reach the reaction surface will cross that surface twice: once approaching the collision event and again while receding. If q is the probability that transition does not occur during a single crossing, the total transition probability P is

$$P = 2q(1 - q) \tag{5}$$

In addition to the transition probability, the cross section must account for the fact that only a fraction $(1 - E^*/E)$ of the collisions that initially approach within the cross section πr_0^2 will actually reach the reaction surface, due to the deflection produced by the repulsion. This factor follows from conservation of angular momentum and is independent of the exact shape of the repulsive potential.[3] The total cross section can then be expressed

$$S(E) = 2\pi r_0^2 (1 - E^*/E) q (1 - q) \tag{6}$$

The problem is that reactive cross sections are not generally available from experimental observation, and theory is incomplete at best. Landau[4] and Zener[5] use some judicious quantum approximations in arriving at an exponential expression for the factor q in Eq. (5) that provides the expected shape of the reactive cross section, but the potential matrix elements required in their formula are not usually known. Park[6] finds that an empirical function $(\ln E/E^*)/(E/E^*)$ roughly duplicates the shape of some measured ionization cross sections due to electron impact.[7,8] Hansen[9] uses an empirical function for collision-induced dissociation that has an adjustable slope of $\ln(S)$ vs $(E - E^*)$ near threshold, which is the most critical part of the cross section at low temperature at least:

$$\begin{gathered} q = (1 - E^*/E)^m \\ S = 2\pi r_0^2 (1 - E^*/E)^{m+1} [1 - (1 - E^*/E)^m] \end{gathered} \tag{7}$$

The coefficient m is expected to be about unity, if ionization cross sections produced by heavy particle impact between neutrals is any indication.[10,11] Varying m between 1 and 2 was found to give about the same functional trend for diatomic dissociation rates,[9] and the quantitative result could be adjusted to agree with experiment with modest changes in the constant r_0. No doubt any one of these cross sections that peaks at about the correct collision energy and has the required slope near threshold would give similar results. Fortunately, for the purpose of evaluating a correction for the effect of vibrational nonequilibrium on dissociation rate, the uncertainties tend to cancel in the ratio of nonequilibrium to equilibrium rates.

Effects of Excited States on Dissociation

If dissociation is assumed to occur only from the ground state and the constants C and d of the Arrhenius function, Eq. (1), are adjusted to agree with measured dissociation rate data, the temperature dependence of the pre-exponential term T^{-d} does not agree with the pre-exponential term of Eq. (3) for any realistic shape of the cross section; moreover, the constant C requires cross sections that are two or three orders of magnitude greater than reasonable. The explanation for this discrepancy is that dissociation does not occur from the ground state to any appreciable extent but from a ladder of excited rotational and vibrational states. The rate coefficient is the sum of rates from all of these states[9]

$$\kappa = \sum_{i=1}^{i_m} \kappa_i \frac{n_i}{n} = \frac{1}{Q} \sum_{i=1}^{i_m} \kappa_i g_i e^{-E_i/kT} \tag{8}$$

The summations are truncated at some maximum level i_m to account for the fact that reactions are never observed under full equilibrium conditions but only when the forward and reverse rates are out of balance. The dissociation rates measured in shock tubes, for example, are essentially one way rates observed when the reassociation reaction is negligible. Keck and Carrier[12] observed that these measured rates are the total rates taking place from a pseudo-steady distribution that is Boltzmann like in the lower levels but is depleted in upper levels as given by solutions to the master equations. Hansen[3]

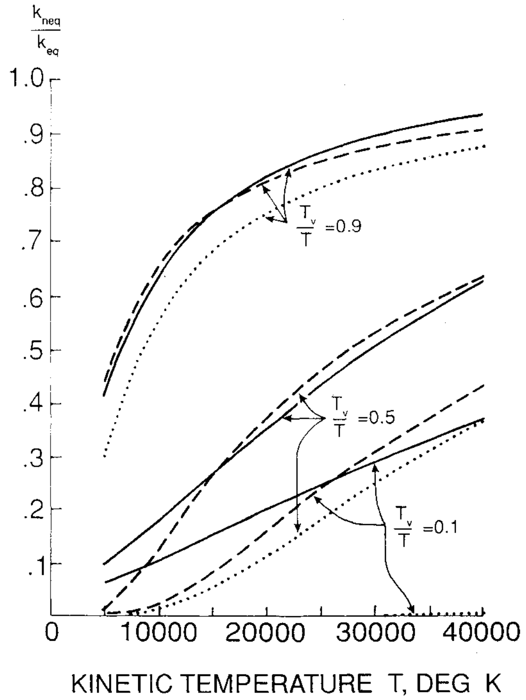

Fig. 1 Effect of nonequilibrium vibrations on N_2 dissociation: ——, Eq. (14); ----, Eq. (15); $T_a = (TT_v)^{0.5}$.

found that forward rates from distributions given by the master equations could be numerically duplicated reasonably well by truncating the Boltzmann distribution at a level that changes with temperature, occurring about kT below the dissociation limit. This was done to get better correspondence between theory and experiment in the absolute rates,[9] though that is not so important for the present purposes as the ratio of nonequilibrium to equilibrium rate is found to be very insensitive to the exact cutoff used. In fact, almost the same ratio is obtained when distributions complete to the dissociation limit are used.

If all of the rate coefficients κ_i are Arrhenius functions like Eq. (2),

$$\kappa = \frac{\bar{u}S_0}{Q}\, e^{-x^*} \sum_{i=1}^{i_m} g_i \int_{x_i^*}^{\infty} \frac{S_i}{S_0}\, x e^{-x}\, dx \tag{9}$$

where S_0 is a reference cross section the order of the total scattering cross section. The lower limit of the integral is the dimensionless activation energy for the state i. The experimental Arrhenius pre-exponential term

$$\frac{C}{T^d} = \frac{\bar{u}S_0}{Q} \sum_{i=1}^{i_m} g_i \int_{x_i^*}^{\infty} \frac{S_i(x)}{S_0}\, x e^{-x}\, dx \tag{10}$$

is then consistent with a reasonable size cross section S_0 the order of 10^{-16} cm^2 and with an exponent d the order of unity,[9] as observed experimentally.

Effect of Vibrational Nonequilibrium on Dissociation of Diatomics

The functional form of the summation over states in Eq. (9) or Eq. (10) is found to be rather insensitive to the actual distribution of states over energy as long as these are scattered more or less uniformly across the spectrum.[9] A random distribution would probably give about the same functional relation. Thus a fair approximation is obtained if the rotations are all assumed to be in the same level and the summation is over vibrational states only. If these states are populated in a Boltzmann distribution characterized by the vibrational temperature T_v, Eq. (9) becomes

$$\kappa = \frac{\bar{u}S_0}{Q}\, e^{-x^*} \sum_{v} e^{-E_v/kT^*} \int_{x_v^*}^{\infty} \frac{S_i(x)}{S_0}\, x e^{-x}\, dx \tag{11}$$

where the fictitious temperature T^* is given by

$$\frac{1}{T^*} = \frac{1}{T_v} - \frac{1}{T} \tag{12}$$

and the sum is over all vibrational quantum states v with the vibrational energy E_v up to the maximum level with energy close to $(D - kT)$. The lower limits of the integrals are the dimensionless activation energies $x_v^* = (D - E_v)/kT$.

The ratio of the rate coefficient for vibrational nonequilibrium to the equilibrium value can then be expressed

$$\frac{\kappa_{\text{neq}}}{\kappa_{\text{eq}}} \approx \frac{Q(T)}{Q(T_v)} \frac{\sum_v F_v e^{-E_v/kT^*}}{\sum_v F_v} \tag{13}$$

where F_v denotes the integral factors of Eq. (11). As noted earlier, the summations were found to be rather independent of the actual distribution of states, and so a harmonic oscillator distribution gives somewhat the same result as the more realistic Morse oscillator distribution with about double the number of vibrational states per unit of vibrational energy in the upper levels.[9] The factors F_v that contribute most are relatively constant near their maximum; if these factors are replaced by an effective average value and pulled out of the summations, and the summations are then performed over a harmonic oscillator ladder of vibrational levels, Eq. (13) becomes the same as derived by Hammerling et al.[13] for dissociation of harmonic oscillators in the ground rotational level

$$\frac{\kappa_{\text{neq}}}{\kappa_{\text{eq}}} \approx \frac{\hbar\omega}{D} \frac{1 - e^{-\hbar\omega/kT_v}}{1 - e^{\hbar\omega/kT}} \frac{1 - e^{-D/kT^*}}{1 - e^{-\hbar\omega/kT^*}} \tag{14}$$

except that they use an effective number of levels N in place of the ratio $D/\hbar\omega$. At extremely high temperatures this correction can exceed unity even though T_v is much less than T. This unrealistic result occurs merely because the harmonic oscillator partition functions become infinite at high temperatures instead of approaching a finite limit as they should. The discrepancy disappears if the partition function sums are terminated at the dissociation limit; this introduces an additional factor $(1 - e^{-D/kT})/(1 - e^{-D/kT_v})$ in Eq. (14):

$$\frac{\kappa_{\text{neq}}}{\kappa_{\text{eq}}} \approx \frac{\hbar\omega}{D} \frac{1 - e^{-\hbar\omega/kT_v}}{1 - e^{-\hbar\omega/kT}} \frac{1 - e^{-D/kT}}{1 - e^{-D/kT_v}} \frac{1 - e^{-D/kT^*}}{1 - e^{-\hbar\omega/kT^*}} \tag{14a}$$

However, this additional factor is unnecessary except at temperatures the order of D/k.

For many practical purposes Eq. (14) should be an adequate correction to the dissociation rate coefficient when vibrational nonequilibrium occurs. It gives somewhat the same results as the presumably more complete calculation based on a complete ladder of rotational and anharmonic vibrational states.[9] However, Eq. (14) is more cumbersome than desired for a fast CFD subroutine. A yet simpler empirical method suggested by Park[6,14] has been widely used; he realized that the rate should decrease substantially when the vibrational temperature is less than the kinetic temperature and proposed that the effective temperature in the experimentally determined Arrhenius expression should be replaced by an effective mean temperature $T_a = T^f T_v^{1-f}$, where the exponent f is somewhere between 0.5 and 0.7. This does indeed roughly approximate the more detailed corrections of Eqs. (13) or (14), provided that T_v is within about $T/2$. However, the Arrhenius rate is so very sensitive to the exponential term that this expedient will far underestimate the correction when the vibrational temperature

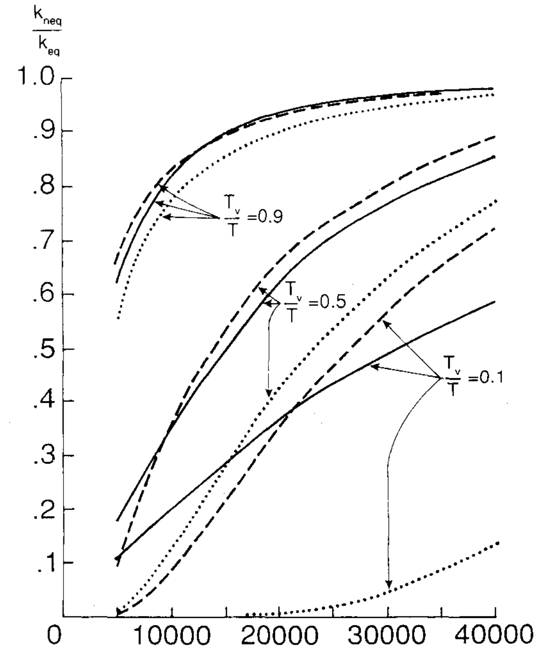

Fig. 2 Effect of nonequilibrium vibrations on O_2 dissociation: ——, Eq. (14); ----, Eq. (15); $T_a = (TT_v)^{0.5}$.

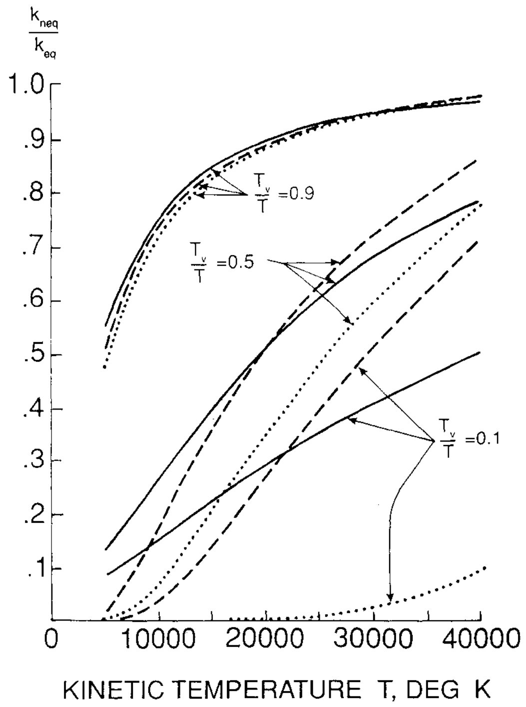

Fig. 3 Effect of nonequilibrium vibrations on NO dissociation: ——, Eq. (14); ----, Eq. (15); $T_a = (TT_v)^{0.5}$.

is much less than half the kinetic temperature. The temperature in the exponent of the Arrhenius expression should rigorously be the kinetic temperature only, and the vibrational temperature can merely modify the pre-exponential term. However that may be, one can always find an effective temperature T_a that will agree with exact theory or experiment, but then it is only realistic to expect that the weighting factor f will be variable.

Corrections to the dissociation rate coefficient provided by Eq. (14a) were assumed to be valid, and values of the coefficient f were determined that produced agreement between this relation and the empirical effective temperature method:

$$\frac{\kappa_{\mathrm{neq}}}{\kappa_{\mathrm{eq}}} = \left(\frac{T}{T_a}\right)^d e^{-D(1 - T/T_a)/kT} \tag{15}$$

$$T_a = T^f T_v^{1-f}$$

As a first approximation, the coefficient f was found to be approximately a linear function of the ratio of vibrational to kinetic temperature and relatively insensitive to the level of the kinetic temperature. For N_2 dissociation with $d = 0.5$

$$f \approx 0.90 - 0.30(T_v/T) \tag{15a}$$

and for O_2 dissociation with $d = 1.0$

$$f \approx 0.85 - 0.25(T_v/T) \tag{15b}$$

whereas for NO dissociation with $d = 1.5$

$$f \approx 0.80 - 0.30(T_v/T) \tag{15c}$$

Values of the coefficient d are those suggested by Blottner[15] in his review of experimental data for these dissociation reactions.

Comparisons between the results of Eq. (14), shown as the solid lines, and Eq. (15), shown as the dashed lines, are presented in Fig. 1 for N_2 dissociation, Fig. 2 for O_2 dissociation, and Fig. 3 for NO dissociation. In addition, the dotted curves shown are for the effective temperature $(TT_v)^{0.5}$ first suggested by Park.[14]

When the vibrational temperature is nearly equal to the kinetic temperature, all three algorithms give about the same result as shown for the $T_v/T = 0.9$ curves. However, as T_v decreases to about half the kinetic temperature T, the linearized expressions for the effective temperatures of Eqs. (15a–15c) can only be adjusted to cut through the middle of the presumably more precise results. If vibrational temperature is decreased enough, any constant weighting factor f must eventually underestimate the correct nonequilibrium rate coefficient because of the extreme sensitivity of the exponential term in the Arrhenius expression. For example, at $T_v/T = 0.1$, the effective temperature $(TT_v)^{0.5}$ predicts rate coefficients that are many orders of magnitude smaller than realistic. A larger weighting factor $f = 0.7$ was later used by Sharma et al.,[16] which is somewhat better. However, any constant weighting factor will eventually fail if vibrational temperatures are low enough. Such an approximation might unrealistically introduce a large delay in the onset of dissociation in a cold gas that is shock heated, for example. Fortunately, a rather simple variation of the weighting factor f can mitigate this effect over rather wide ranges of the vibrational and kinetic temperatures. The results of Eq. (15) generally agree within a factor of 2 with Eq. (14), except at very low kinetic temperatures where the dissociation rates are not yet a major factor in the flow relations. At higher temperatures the agreement is about as good as needed for many computations, and further complication of the rate algorithm is to be avoided if possible. At temperatures on the order of D/k, the correction to the rate coefficient approaches unity anyway, since then dissociations excited by the tail of the Boltzmann distribution occur with about equal probability from any of the vibrational levels.

Up to 40,000 K the empirical corrections are somewhat better for N_2 than for the other gases, partly because of the higher dissociation energy for N_2 ($D/k = 113{,}260$ K) that leads to larger dimensionless threshold energies at the temperatures considered, and partly because of the smaller coefficient d in this case.

In some flow domains, conditions in the gas change so rapidly that uncertainties in the nonequilibrium corrections may not always make a large difference in the flow solution. However, where nonequilibrium effects are important, the use of a nonconstant weighting factor f in the effective temperature method can give substantial improvement in the dissociation rate coefficients when vibrational nonequilibrium obtains over a wide range of temperatures.

Concluding Remarks

A reactive cross section theory for collision-induced dissociation of diatomic molecules is used to assess the effect of vibrational nonequilibrium on the dissociation rate from a ladder of rotational-vibrational states. The results are rather similar to a simple analytic correction formula derived by Hammerling et al.[13] for harmonic oscillators dissociating from the ground rotational level.

Although the formula of Hammerling et al.[13] is relatively simple, a still simpler empirical algorithm suggested by Park[6,14] is more useful for CFD calculations because of the speed with which it computes. This algorithm uses an effective temperature in the Arrhenius formula for equilibrium dissociation that is a weighted mean between the kinetic and vibrational temperature of the gas. Theory shows that the correct temperature in the exponential term of the Arrhenius function should be the kinetic temperature, so that any constant weighting of T_v in the effective temperature will eventually fail because of the extreme sensitivity of the exponential term to the temperature used. However, the empirical algorithm can be improved by choosing a variable weighting factor. Though this complicates the algorithm somewhat, the results appear to give a better approximation to the dissociation rate coefficient over a wider range of vibrational nonequilibrium.

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