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THE FLOW OF A DISSOCIATING GAS AROUND AND BEHIND A BLUNT HYPersonic BODY (U)

Andrew G. Hammitt
MAY 25, 1982

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Prepared for
AFBMD AIR R&D COMMAND
Inglewood, California

SPACE TECHNOLOGY LABORATORIES, INC.
A SUBSIDIARY OF THOMPSON RAMO WOOLBRIDGE INC.
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA
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ABSTRACT

A study of dissociation reaction of a diatomic gas has been performed for the pressure history, a pressure rise and subsequent decay, common to hypersonic flow about a body. For this simplified case, several interesting phenomena which occur have been explored. A characteristic reaction time has been identified; the areas in which dissociation or recombination is the faster reaction have been specified; the areas in which equilibrium isentropic expansion leads to dissociation or recombination are found; the relative importance of the irreversibility associated with nonequilibrium relaxation has been defined.
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<th>Definition</th>
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<tr>
<td>A</td>
<td>Dissociation reaction rate constant</td>
</tr>
<tr>
<td>B</td>
<td>Recombination reaction rate constant</td>
</tr>
<tr>
<td>C_v</td>
<td>Specific heat at constant volume</td>
</tr>
<tr>
<td>k_d</td>
<td>Dissociation reaction rate</td>
</tr>
<tr>
<td>k_r</td>
<td>Recombination reaction rate</td>
</tr>
<tr>
<td>M</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>N</td>
<td>Reacting species</td>
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<td>p</td>
<td>Pressure</td>
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<tr>
<td>q</td>
<td>Velocity</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>X</td>
<td>Nonreacting species</td>
</tr>
<tr>
<td>a</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>θ</td>
<td>Characteristic temperature</td>
</tr>
<tr>
<td>τ</td>
<td>Characteristic reaction time</td>
</tr>
<tr>
<td>ω</td>
<td>Temperature exponent in reaction rate equation</td>
</tr>
</tbody>
</table>

Subscript
- **eq.** Equilibrium
- **f** Final
- **i** Initial
- **∞** Undisturbed free stream

Superscript
- **-** Average
- **(N)** Mole concentration
1. INTRODUCTION

The flow about a body moving at supersonic speed is characterized by a pressure rise through a bow shock wave and an expansion about and behind the body to ambient pressure. The details of the pressure pattern depend on the exact body shape but the basic compression and expansion features are always present.

At hypersonic speeds, where the kinetic energy of the flow relative to the body is of the order of the dissociation energy of the air molecules, such reactions can be expected to take place. For a pure diatomic gas, such as nitrogen, only the dissociation reaction will take place while air will undergo several reactions involving both oxygen and nitrogen. All these reactions proceed at a finite rate so that, depending on the size of the body, the ambient density, and other characteristic parameters, the chemical reactions may stay essentially in equilibrium with the pressure changes or may badly lag behind the pressure changes. In some cases the chemical reaction are so slow that they may be considered frozen to the scale of the body, but if the condition continues long enough they will eventually approach equilibrium. A nonequilibrium condition may only be considered frozen with respect to some particular scale. In many cases, flow field parameters, such as velocity and pressure, can be considerably effected by nonequilibrium chemical reactions so that both the flow field and chemical equations must be solved simultaneously.

In this report, a diatomic gas subject to a pressure rise and decay separated by a region of uniform pressure is considered to bring out, at least qualitatively, the interesting phenomena. The rate of the chemical reactions taking place are considered in order to specify the characteristic times and the parameters that control these times. The general flow field is examined to discover other interesting phenomena which are then considered in some detail. The pressure rise and decay are both considered to be discontinuous step functions and the chemical reactions are considered to occur under conditions of constant pressure. The time for
chemical reactions to occur under these idealized conditions can be used to determine the relative speed of the reactions compared with the actual rate of change of the pressure.

2. REACTION RATE ANALYSIS

The dissociation reaction for a diatomic gas can be written

\[ N_2 + X \rightleftharpoons N + N + X \]  

(1)

The rate equation for this reaction is

\[ \frac{d(N)}{dt} = 2 k_d (N_2)(X) - 2 k_r (N)^2 (X) \]  

(2)

If \( a \) is the mass fraction of \( N \) then

\[ (N) = \frac{\rho a}{M_N}, \quad (N_2) = \frac{\rho (1-a)}{M_{N_2}}, \quad (X) = \frac{\rho}{M_N} \]  

(3a)

where

\[ \frac{1}{M} = \frac{a}{M_N} + \frac{1-a}{M_{N_2}} \]  

(3b)

\( M \) being an average molecular weight. Using the perfect gas relation

\[ \frac{\rho}{M} = \frac{p}{RT} \]  

(4a)

where \( R \) is the universal gas constant. Applying relation (3b)

\[ \frac{\rho}{M_N} = \frac{2}{1 + a} \frac{p}{RT} \]  

(4b)

since \( M_{N_2} = 2 M_N \). Substituting relations (3) and (4) into (2) the rate relations can be written in terms of mole fractions, pressure, and temperature.

\[ \frac{d\alpha}{dt} = (1 - a) \frac{p}{RT} k_d - \frac{4a^2}{1+a} \left( \frac{p}{RT} \right)^2 k_r \]  

(5)
For many diatomic gases

\[ k_d = AT^{-\omega} I^{-\theta/T}, \quad k_r = BT^{-\omega} \]  \hspace{1cm} (6)

For oxygen and nitrogen there is fairly general agreement on the values of the constants in these equations. Values of these constants which seem best based on a current survey of the literature are

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>( \omega )</th>
<th>( \theta )</th>
</tr>
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<tbody>
<tr>
<td>Oxygen</td>
<td>1(10^{20}) cm^3/mole sec</td>
<td>5(10^{18}) cm^6/mole^2 sec K^{-\omega}</td>
<td>1.5</td>
<td>58,600^oK</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>6(10^{20})</td>
<td>3(10^{19})</td>
<td>1.5</td>
<td>113,260^oK</td>
</tr>
</tbody>
</table>

These are the numerical constants which will be used where required in this report. If these expressions for \( k_d \) and \( k_r \) are substituted into the rate equation

\[ \frac{da}{dt} = (1 - a) \frac{A}{RT} \frac{I^{-\theta/T}}{1 + a} - 4a^2 \frac{BP^2}{RT^2} \]  \hspace{1cm} (7)

Equilibrium conditions occur when \( da/dt = 0 \)

\[ \frac{a^2}{1 - a^2} = \frac{A}{4B} \frac{RT}{P} I^{-\theta/T} \]  \hspace{1cm} (8)

or

\[ \frac{a^2}{1 - a} = \frac{A}{4B} \frac{1}{P} I^{-\theta/T} \]

Equation (8) is consistent with Lighthill's equilibrium equation for an ideal dissociating gas (1) and Equation (7) with Freeman's dissociation rate law (2) In these references the term \( A/4B \) is called a characteristic density.
The next step in considering Equation (7) will be to attempt to find a characteristic time of reaction so that the speed of reaction may be easily estimated. It is also useful to consider which parameters effect the relative speed of the dissociation and recombination reactions. A simple answer to this question based on the fact that the dissociation reaction, the process of the molecules breaking up into atoms, requires a two-body collision and the recombination reaction requires a three-body collision is not sufficient. While the two molecule collision may seem more probable, this does not mean that the dissociation rate is the more rapid. At equilibrium dissociation and recombination are proceeding in equal rate. The effective dissociation or recombination rate is the rate at which the concentrations proceed towards equilibrium if the initial condition is not an equilibrium one. This rate is the difference between the dissociation and recombination rate which is zero at equilibrium. A first approximation to both the effective dissociation and recombination rate can be obtained by considering the rate of change of the effective rate, with species concentration for an adiabatic change at constant pressure, evaluated at equilibrium concentration. In this approximation, the effective recombination and dissociation rates are the same at equal changes of species concentrations from the equilibrium but in opposite directions. In order to distinguish which of these is the fastest, the next higher derivative of the rate of change of effective rate with concentration must be considered.

The first approximation to the rate may be written

\[
\frac{\text{d}a}{\text{d}t} = - (a - a_{eq}) \left[ \frac{\text{d}}{\text{d}a} \left( \frac{\text{d}a}{\text{d}t} \right) \right]_{eq}
\]

which is the first term of a Taylor series developed about \( a_{eq} \). A characteristic time \( \tau \) can now be defined as

\[
\frac{1}{\tau} = - \left[ \frac{\text{d}}{\text{d}a} \left( \frac{\text{d}a}{\text{d}t} \right) \right]_{eq}
\]

and Equation (9) can be integrated to give
\[
\frac{t_f - t}{\tau} = \ln \frac{a - a_{eq}}{a - a_{eq}}
\]  
(10)

where \(a\) is the initial composition and \(a_{eq}\) the final composition.

This relation shows that near equilibrium, where this first order logarithmic term predominates, all reactions should follow a straight line on a semi-log plot using the coordinates of Equation (10). To determine how well the actual reaction follows this line at large deviations from the equilibrium concentrations, Equation (7) will be integrated for different initial conditions.

\(\tau\) can be related to the other variables by differentiating Equation (7) and evaluating at equilibrium conditions.

\[
\frac{1}{\tau} = \left[ -\frac{d}{da} \left( \frac{da}{dt} \right) \right]_{eq} = \left\{ \frac{4a^2}{1 + a} \frac{BP^2}{R^2 \theta^2} \theta^2 + \omega \left( \frac{2(1 + a - \alpha^2)}{a(1 - \alpha^2)} - (1 + \frac{\theta}{T}) \frac{1}{T} \frac{dT}{da} \right) \right\}_{eq}
\]  
(11)

If equation (11) for \(1/\tau\) is used to nondimensionalize Equation (7), the result is

\[
\frac{da}{d(t/\tau)} = \frac{AR\theta}{BP} (1 - a) \left( \frac{\theta}{T} \right)^{1+\omega} - \frac{4a^2}{1 + a} \left( \frac{\theta}{T} \right)^{2+\omega}
\]

\[
\left\{ \frac{2(1 + a - \alpha^2)}{a(1 - \alpha^2)} - (1 + \frac{\theta}{T}) \frac{1}{T} \frac{dT}{da} \right\}_{eq}
\]  
(12)

This expression can be integrated if \(T\) is known as a function of \(a\). The relation

\[
\frac{T}{\theta} = \left( \frac{h}{C_v} \theta - \frac{AR}{C_v} \left( \frac{1}{1 + (1 + a) \frac{R}{C_v}} \right) \right)
\]  
(13)

can be obtained by expression enthalpy as a function of temperature and composition and then solving for the temperature. For the case of inviscid constant pressure reaction \(h\) is a constant along a stream line and Equation (13) may be differentiated to give
Equations (13) and (14) may be used in the integration of Equation (12) to give

$$-\frac{1}{T} \frac{dT}{da} = \frac{R}{C_V} + \frac{R}{C_V} \frac{h}{C_V \theta} - \frac{aR}{C_V} \frac{1}{1 + (1 + a) \frac{R}{C_V}}$$

(14)

Equations (13) and (14) may be used in the integration of Equation (12) to give

$$\frac{t_f - t}{\tau} = \left\{ \frac{4a^2}{1 + a} \left( \frac{\theta}{T} \right)^{2+\omega} \left\{ \frac{2(1 + a - a^2)}{a(1 - a^2)} - (1 + \theta) \left( \frac{1}{T} \frac{dT}{da} \right) \right\} \right\}_{eq}

\int_a^{\theta_f} \frac{AR\theta}{BP} \left( 1 - a \right) \left( \frac{\theta}{T} \right)^{1+\omega} \frac{da}{\theta - \theta / T} - \frac{4a^2}{1 + a} \left( \frac{\theta}{T} \right)^{2+\omega}

(15)

The indicated integration of Equation (15) has been carried out numerically for \( R/C_V = 1/3, \ \omega = 1.5, \ AR\theta/Bp = 10^6, 10^8, 10^{10}, \) and \( h/C_V \theta \) between 0.1 and 0.5. \( R/C_V = 1/3 \) is the value suggested by Lighthill and probably the best compromise if the variation of vibrational specific heat with temperature is not considered. The quantity \( AR\theta/B \) has units of pressure and varies with the gas considered. For oxygen it is \( 2.4 \times 10^7 \) atm and for nitrogen it is \( 4.7 \times 10^7 \) atm so the chosen values are in the range of practical interest for these gases. The results of this integration are shown in Figure 1a, b, c plotted to the coordinates suggested by Equation (10).

The purpose of this plot is to compare the prediction of the simple logarithmic Equation (10) with the exact solution given by Equation (15). The departure of the curves, Equation (15), for the various values of the parameters from the straight line, Equation (10), shows the difference between these two relations. Before comparing in more detail an explanation of the integration of Equation (15) is needed. Since the time to reach equilibrium is infinite, as shown by either Equation (10) or (15), the time to reach some final composition, near equilibrium, must be
considered. For this calculation, \( a_i \) is taken as far from equilibrium as possible; \( a_i = 0 \) for all dissociating cases and \( a_i = 1 \) for all recombination cases except those cases for which \( h/C_\gamma \theta \) is too low to provide enough energy for complete dissociation. For these cases \( a_i \) is taken as that value which gives \( T = 0 \). The \( a_i \) values for these various curves are listed in Table 1. The final value of \( a \) considered, \( a_f \), is defined so that \( a_f = a_{eq} \pm 5 \) percent of \( a_i - a_{eq} \).

Figure 1 demonstrates several interesting features. First, the line of Equation (10) generally falls between the dissociation and recombination curves for any given set of conditions. It eliminates the variation caused by the changing parameters and leaves only the variation between the dissociation and recombination curves. Although the factor \( \tau \) does not bring all the curves together it would appear to be as useful a single parameter as can be expected for correlating all these curves. Actually, knowledge of the value of \( \tau \) allows one to estimate the reaction time only within a factor of 10. For the larger values of \( AR0/Bp \) the curves depart from the logarithmic part much sooner but the recombination rate follows the logarithmic curve closer than the dissociation curve.

More accurate values of the time for any given reaction may be found by using the appropriate value of \( AR0/Bp \) to give the time between any two values of \( a \). The correct value of \( a_f \) for which the curve are drawn must be used in making the computation.

In Figure 1, all of the curves show a higher dissociation rate than recombination except the one for \( h/C_\gamma \theta = 0.1 \) and \( AR0/Bp = 10^6 \). The suggested conclusion is that for the value of parameters of most practical interest for oxygen and nitrogen, dissociation is always faster but that the opposite condition may occur at values of \( AR0/Bp \) lower than \( 10^6 \). The relative speed of the processes will be considered in more detail later.

The range of variation of the parameter \( \tau \) is shown in Figure 2 for the same range as the parameters considered in Figure 1. \( \tau \) varies between \( 10^7 \) and \( 10^{14} \) over this range. The spread of a factor 10 in \( \left( t_f - t \right)/\tau \)
shown in Figure 1 is only a small part of the total change in reaction rate
and most of the change is accounted for by the characteristic time \( \tau \). The
value of \( A^2/B\theta \omega \) is about \( 3.2 \times 10^{14} \) sec\(^{-1}\) for \( N_2 \) and \( 1.4 \times 10^{14} \) sec\(^{-1}\) for
\( O_2 \) so \( \tau \) varies from the order of 1 sec for \( AR\theta/Bp = 10^{10} \) to the order
of \( 10^{-7} \) for \( AR\theta/Bp = 10^6 \).

An examination of the relative effective rates of dissociation and
recombination can best be made by considering the second derivative of
Equation (7). A positive value of this derivative would mean that the
dissociation rate would become larger than the recombination rate for
small departures from equilibrium and a negative value would mean the
opposite. If this derivative is taken and evaluated at equilibrium it is

\[
\frac{d^2}{da} \left[ \frac{d a}{d (\frac{t}{\tau})} \right]_{eq} = \left( \frac{4a^2}{1 + a} \right) \frac{B \theta P^2}{R^2 T^2 + \omega} \left[ \frac{2(1 + a - a^2)}{a(1 - a)^2} - \left( \frac{1 + \theta \gamma}{T} \right)^2 \frac{d T}{d a} \right]_{eq}
\]

\[
+ \frac{2(1 + a - a^2)}{a(1 - a)^2} \left( \frac{1 - 2a}{1 + a - a^2} = \frac{1 - 3a^2}{a(1 - a)^2} \right)
\]

\[
+ \frac{\theta \gamma}{T} \left( \frac{1}{T} \frac{d T}{d a} \right)_{eq} \left( 1 + \frac{\theta \gamma}{T} \right) \frac{d T}{d a} \left( \frac{1}{T} \frac{d T}{d a} \right)_{eq}
\]

A calculation of this derivative over the range of parameters being
considered, gives the results shown in Figure 3. This figure shows that
the derivative is positive over most of this range and values down to
\( AR\theta/Bp = 10^4 \) must be considered in order that the derivative is negative
over a large range of \( h/C\gamma \theta \). These lower values of \( AR\theta/Bp \) correspond
to high pressures, about \( 10^4 \) atm for \( N_2 \). While there seems to be no
fundamental reason why dissociation should be faster than recombination,
the parameters for hypersonic flight in air are such that they fall in the
zone where this is the case.
3. DIRECTION OF REACTIONS IN ISENTROPIC FLOW

In general in an adiabatic flow field recombination will occur through an isentropic expansion of the gas. However, it should be recognized that the reaction is not always in this direction, while a decrease in temperature tends to decrease the dissociation, a decrease in density tends to increase it. The expression for a change in entropy as a function of $T$ and $\alpha$ is given by Lighthill

$$dS = \frac{C_v}{RT} dT + \log \left[ \frac{A}{4Bp} \frac{1 - \alpha}{\alpha^2} \right] d\alpha - (1 + \alpha) \frac{d\alpha}{\rho}$$

If the equilibrium expression for $\alpha$ as a function of $p$ and $T$, Equation (8), is used to eliminate $p$ and $dS$ is set equal to zero, then

$$T \frac{d\alpha}{dT} = \frac{(1 + \alpha) \theta/T - \frac{C_v}{R}}{\theta/T + (1 + \alpha)(\frac{2}{\alpha} + \frac{1}{1-\alpha})}$$

The condition for

$$\frac{d\alpha}{dT} = 0 \text{ is } (1 + \alpha) \frac{\theta}{T} = \frac{C_v}{R}$$

For $C_v/R = 3$ a plot of this condition is shown in Figure 4 on the $T$, $\rho$ plane. For all conditions above and to the right of this curve dissociation will occur through an equilibrium isentropic expansion and for cases below and to the left recombination will occur. Almost all cases of practical interest lie below and to the left so that recombination should occur through an isentropic expansion.

4. EFFECT OF CHEMICAL NON-EQUILIBRIUM OF THE FLOW FIELD

The conditions in the flow field cause the chemical reactions to take place as has been illustrated and the chemical reactions have an effect upon the flow field. A chemical reaction requires a driving potential which
generally leads to an irreversible change. In the two limits of equilibrium, no driving potential, and frozen, no reaction, the process is truly reversible. Since an actual case can only approximate these limits, it must always be somewhat irreversible. While a frozen process is reversible while it remains frozen, in certain ways this is an unrealistic case. For instance, an expansion about a body may be frozen and reversible but in the wake of the body the relaxation will eventually take place in an irreversible manner. For the equilibrium case there will be no subsequent relaxation. In this respect the reversible frozen expansion prepared the way for the irreversible relaxation unless there is some intermediate step such as a frozen compression which restores equilibrium conditions reversibly.

In the case of flow about bodies consisting of a rapid pressure rise through a bow shock and then an expansion to ambient, three different chemical rates give the limiting conditions on the wake flow. Rapid chemical rates give equilibrium conditions throughout, intermediate rates give an equilibrium shock and a frozen expansion and relaxation in the wake, and very slow rates give frozen conditions throughout and no need for an eventual relaxation if the temperature behind the expansion is not high enough to cause dissociation. The ratio between the free stream velocity and the wake velocity for nitrogen under these three conditions and several free stream Mach numbers are as follows:

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<tbody>
<tr>
<td>15</td>
<td>0.899</td>
<td>0.765</td>
<td>0.904</td>
</tr>
<tr>
<td>20</td>
<td>0.794</td>
<td>0.656</td>
<td>0.918</td>
</tr>
<tr>
<td>25</td>
<td>0.781</td>
<td>0.583</td>
<td>0.929</td>
</tr>
</tbody>
</table>
The additional decrease in the wake velocity caused by the frozen expansion is of the same order of magnitude as the decrease in velocity caused by the normal shock for the equilibrium case. The irreversibilities associated with the relaxation following the frozen expansion are of about the same order as those introduced by the equilibrium normal shock. In other words, the irreversible chemistry can be as important in producing the inviscid wake as the normal shock. The case of frozen shock frozen expansion gives the highest wake velocities because the irreversibility associated with the frozen shock wave is less than for the equilibrium shock since the modes of energy absorption are reduced and higher temperatures are realized. Since the frozen shock is followed by a frozen expansion there is no irreversible relaxation process.

The fact that the ratio of the wake velocity to the free stream velocity goes up with Mach number for the frozen shock, at first seems surprising. In fact this velocity ratio approaches 1 as Mach number approaches \( \infty \) if the specific heat of the gas remains finite. A velocity ratio of one does not mean that there are no total head losses or that the temperature in the wake is the same as the free stream temperature. As \( M \to \infty \), the velocities relative to the object has become so large that the change in the wake velocity, although it is a large number compared with free stream speed of sound, is negligible compared with the velocity relative to the object.

5. CONCLUSIONS

a. A characteristic time can be derived which specified the reaction rate near equilibrium and gives the correct order of magnitude even far from equilibrium.

b. The speed of the dissociation and recombination reactions are the same near equilibrium and their relative magnitudes far from equilibrium depends on the parameters of the reaction. For the normal aerodynamic range the dissociation is the faster.

c. Nonequilibrium chemical relaxation can introduce irreversibilities of the same order as a normal shock.
Table 1. Conditions for Reaction Rate Curves Shown in Figure 1.

<table>
<thead>
<tr>
<th>$A$</th>
<th>$h/\bar{C}_v$</th>
<th>$a_{eq}$</th>
<th>$a_i$</th>
<th>$a_f$</th>
<th>$a_i$</th>
<th>$a_f$</th>
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<tr>
<td>$10^6$</td>
<td>0.1</td>
<td>0.04502</td>
<td>0</td>
<td>0.04277</td>
<td>0.300</td>
<td>0.05777</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.49628</td>
<td>0</td>
<td>0.4714</td>
<td>0.900</td>
<td>0.51647</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.92309</td>
<td>0</td>
<td>0.87694</td>
<td>1.0</td>
<td>0.9269</td>
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<tr>
<td>$10^8$</td>
<td>0.1</td>
<td>0.08510</td>
<td>0</td>
<td>0.80850</td>
<td>0.300</td>
<td>0.9585</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.59266</td>
<td>0</td>
<td>0.5630</td>
<td>0.900</td>
<td>0.6080</td>
</tr>
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<td></td>
<td>0.5</td>
<td>0.99602</td>
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<td>0.94621</td>
<td>1.0</td>
<td>0.9962</td>
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<td>0.1</td>
<td>0.11900</td>
<td>0</td>
<td>0.11305</td>
<td>0.300</td>
<td>0.1280</td>
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<td>0.9181</td>
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1. Comparison of actual reaction times with those predicted by logarithmic law.

2. Characteristic reaction time as a function of reaction conditions parameters.

3. Second derivative of reaction rate at equilibrium as a function of reaction conditions parameters.

4. Areas of reaction conditions for which dissociation and recombination occur for equilibrium isentropic expansion of a diatomic gas.

Table 1. Conditions for reaction rate curves shown in Figure 1.
Figure 1a. Comparison of Actual Reaction Times with Those Predicted by Logarithmic Law.
Figure 2. Characteristic Reaction Time As A Function Of Reaction Condition Parameters
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A study of dissociation reaction of a diatomic gas has been performed for the pressure history, a pressure rise and subsequent decay, common to hypersonic flow about a body. For this simplified case, several interesting phenomena which occur have been explored. A characteristic reaction time has been identified; the areas in which dissociation or recombination is the faster reaction have been specified; the areas in which equilibrium isentropic expansion leads to dissociation or recombination are found; the relative importance of the irreversibility associated with nonequilibrium relaxation has been defined.