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TECHNICAL NOTE 4144

EFFECT OF OXYGEN RECOMBINATION ON ONE-DIMENSIONAL FLOW AT HIGH MACH NUMBERS

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January 1958

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Page 15, line 2 should read:

"be this efficiency factor. Then $k_R(T) = \text{const}\ \eta(T)T$, or"

Page 20, equation (21) should read:

$$k_R(T) = \frac{50}{\sqrt{T}} \times 10^{-32} \left(\frac{\text{molecules}}{\text{cm}^3}\right)^{-2} \text{sec}^{-1}$$

Note: The value of the constant $k_R(T)$ used in this Technical Note is $\frac{125}{\sqrt{T}} \times 10^{-32}$. Replacing this value by $\frac{50}{\sqrt{T}} \times 10^{-32}$ in evaluating relaxation times would modify figure 8: The shaded portion of the figure would be uniformly displaced upward by a factor of 2.5. Also the effect on the values of $(\tau p)_{O_2\ \text{reaction}}$ given on page 32 is to multiply all of them by 2.5.

Page 22, the definition of f_i should read:

$$f_i = \frac{\text{number of moles of species i}}{\text{total number of moles in cold air}} = \frac{n_i}{\sum_k n_k{}^o}$$

Page 25, line 12 from the bottom should read:

"Equations (26) and (27) were used with $\overline{M} = 28.8$, $\overline{f} = 0.22$, and"

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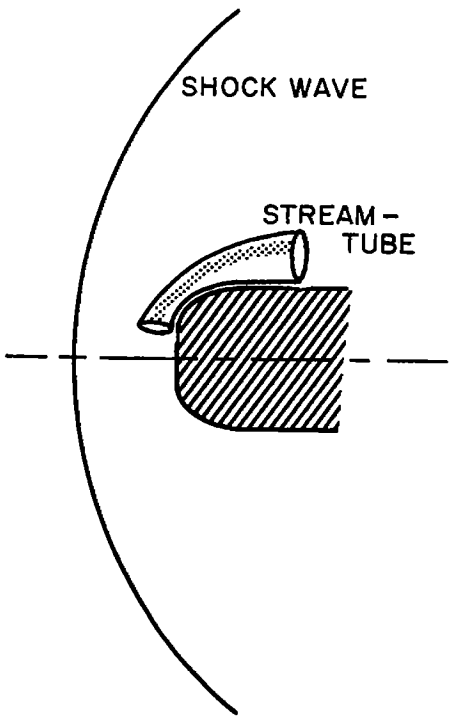
SUMMARY

A theoretical analysis of air flow in a channel in which oxygen dissociation and recombination occur has been made. The channel is viewed as a streamtube in the flow around a blunt body. The analysis is begun with the writing of the differential equation which gives the concentration of atomic oxygen as a function of distance along the channel. The differential equation involves the reaction rate constant for the oxygen recombination reaction. This rate constant is evaluated theoretically from a formula due to Wigner, which yields a different result from simple collision theory. The equation for the atomic oxygen concentration thus obtained is solved together with the flow equations. The equations may be solved by ordinary hand-computation procedures. An example is worked out to show the variation of the flow in a certain streamtube and its dependence on whether the oxygen reaction is "frozen," "in local equilibrium," or proceeding at the finite rate indicated by the theory. The concept of a local relaxation length is employed. From inspection of the flow equations and the behavior of the cumulative lag of the chemical reaction it is possible to judge without detailed numerical calculations whether changing one of the flow parameters brings the system closer to the "chemical equilibrium" or "frozen reaction" limit.

An investigation is made of the comparative relaxation times of the oxygen dissociation-recombination reaction in relation to molecular vibrations. A reason for interest in this is that it has usually been assumed that vibrational relaxation occurs fast relative to chemical relaxation and therefore may be regarded as being in equilibrium. The present analysis indicates that it is not generally true that the vibrational relaxation times are short compared to the time characteristic of the chemical reaction. In this connection the generalization of the concept of chemical equilibrium constant is introduced for the case that the molecular vibrations are not in equilibrium. Some values of the relaxation times are calculated and presented. A method is given to estimate the effect of vibrational lag when the vibrational relaxation times are relatively long.

INTRODUCTION

In the temperature range between 4500° K and 7000° K and at densities lying somewhere between 0.1 normal atmospheric density and 10 times the normal density of the atmosphere, the oxygen of the air is largely in nascent form, while the nitrogen is mostly in diatomic form (see, e.g., ref. 1). This is the state of the air after it has come to chemical equilibrium behind a strong shock wave (Mach numbers 10 to 20, depending on the density of the cold air).



If subsequently this hot air flows around a blunt object, it will expand and cool and the oxygen atoms will recombine. The recombination process is exothermic, giving off 5.12 electron volts for every pair of oxygen atoms that recombine. Thus the reaction is a source of heat and will retard the cooling of the air. In this paper we study the effect of the oxygen recombination on the flow. Because of the difficulties involved in solving the flow around a blunt body even without chemical reaction, we focus attention on a single streamtube of the flow. Such a streamtube is approximated by the one-dimensional flow in a channel of variable cross section. The cross section of the flow at first decreases, reaching a minimum which corresponds essentially to the sonic line, and then increases again (see sketch).

The content of the present study is indicated by the following outline: First a differential equation is derived, whose solution gives the fraction of the oxygen dissociated as a function of position in the channel. The formal solution is written down, but its numerical evaluation requires knowledge of the oxygen recombination rate constant and the value of the local pressures and temperatures. The rate constant is then discussed in the light of theory and experiment. Then the one-dimensional flow equations with chemical reaction and variable specific heat are given; a numerical method of solution of the flow equations is suggested. The three cases, zero reaction rate, infinite reaction rate, and the finite rate corresponding to the actual rate constant, are distinguished and compared in a numerical example. Lastly the assumption of local vibrational equilibrium is examined; some comparisons are made between vibrational relaxation times and chemical relaxation times and their practical and theoretical significance appraised.

SYMBOLS

A	cross-sectional area
A_{min}	cross-sectional area at throat of channel
a	constant length in the Morse potential
a_{OM}	sum of the collision radii in collision between oxygen atom and third particle
$B, B_x, B(y)$	dimensionless parameter, defined by equation (12)
C	number of oxygen atoms, free or combined, per unit mass of fluid
D	dissociation energy of molecule
E	energy
e	base of natural logarithm
$F^{\dagger}$	statistical factor on which the recombination rate depends according to the Eyring theory
f	partition function
g	function related to enthalpy, defined by equation (28)
$\frac{g_s}{\sum_i g_i}$	fraction of states in oxygen-oxygen ground state to be counted as attractive
h	Planck's constant
H	enthalpy per unit mass
k	Boltzmann constant
k_D	dissociation rate constant
k_R	recombination rate constant
K_e	equilibrium constant
l	length
L	length of channel

m	mass of an atom; mass-flow rate through channel; also a constant
$\overline{M}$	mean molecular weight
$\overline{M}_{At}$	mean atomic weight
N_2	nitrogen
NO	nitric oxide
n_{Av}	Avogadro's number
n_{O_2}	number of particles of O_2 per unit volume
n_M	number of particles of M per unit volume
n_O	number of free oxygen atoms per unit volume
O	oxygen atom
O_2	oxygen molecule
p	pressure
P	net number of O atoms liberated per sec per unit volume
R_o	constant length in the formula for the Morse potential
r	distance between two oxygen atoms
$S, S(y), S_x$	dimensionless measure, $\int_0^y \frac{dy}{\lambda_\infty(y)}$
t	time, sec
T	absolute temperature, °K
u	flow velocity
v	relative velocity of two colliding oxygen atoms
$V(r)$	interaction potential between two oxygen atoms
x	fraction of oxygen atoms which are free, $\frac{n_O}{2n_{O_2}+n_O}$
x_o	initial value of x
x_e	value of x corresponding to local chemical equilibrium
y	distance along the flow

ϵ_v	average vibrational energy per diatomic molecule
$\Gamma(r)$	efficiency of a triple collision in producing recombination
ζ	ratio of change in vibrational energy to change in chemical energy, if vibrations are in equilibrium
$\eta(T)$	average efficiency of triple collisions in producing recombination
λ	relaxation length for chemical reaction defined by equation (7)
ν	vibrational frequency of diatomic molecule
ρ	density
σ	constant
τ	relaxation time of the chemical reaction

Subscripts

at	units of atmospheric pressure
o	initial value
sl	sea level
v	vibrational
∞	case of infinite rates of reaction (Thus λ_∞ is an approximate value of λ where all the variables on the right-hand side of equation (8) are replaced by the infinite rate values.)

Superscript

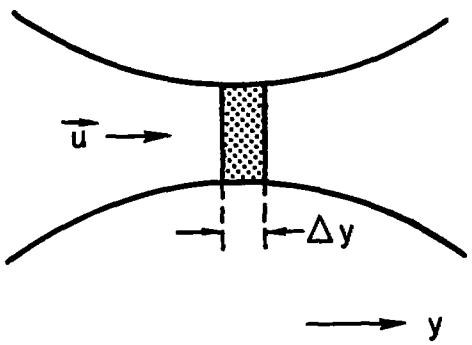
o	cold air

EQUATION FOR THE FRACTION OF OXYGEN IN ATOMIC FORM

As hot gas with partially dissociated oxygen enters a convergent-divergent channel, the cooling of the gas and the oxygen recombination reaction will proceed, causing a continuous variation of the fraction

of the oxygen which is dissociated. The purpose of this section is to derive and solve the equation expressing this variation. The flow treated is steady and one-dimensional. Catalytic reactions at surfaces are not considered. The solution obtained will depend on the value of the reaction rate constant, which will be treated separately in a later section.

Derivation of Equation



Since the flow is assumed steady, so that the condition at any one station is independent of time, we can write a time-independent conservation equation for free oxygen atoms. Let P equal the net number of oxygen atoms liberated per unit volume and unit time. Then

$$PA\Delta y = \oint n_O \vec{u} \cdot \vec{dS} \tag{1}$$

simply states that the number of O atoms liberated per second in the volume element indicated in the sketch must equal the flux of free oxygen atoms across its surfaces. Here A is the cross-sectional area of the channel, $\vec{dS}$ an element of surface, $\vec{u}$ the local velocity of the fluid, and n_O the number of free oxygen atoms per unit volume. If the flow is one-dimensional, we have

$$\oint n_O \vec{u} \cdot \vec{dS} = \frac{d}{dy}(n_O uA)\Delta y$$

Defining $x = n_O/(2n_{O_2}+n_O)$ = mass ratio of the oxygen in free form to the oxygen in either the form O or O_2 (mass fraction of oxygen in atomic form), we can write $n_O = C\rho x$, where C is a constant equal to the number of oxygen atoms, either in the form O or O_2, per unit mass of fluid. Then equation (1) becomes:

$$\frac{dx}{dy} = \frac{A}{mC} P = \frac{P}{\rho uC} \tag{2}$$

where $m = \rho uA$ is the mass flow rate through the channel, a constant.

Now P must be expressed in terms of the chemical rate constant and the concentration of the reactants. In order to dissociate, the

oxygen molecule must collide with another particle which is energetic enough to break up the oxygen molecule. The dissociation reaction can thus be written as:

$$O_2+M \xrightarrow{k_D} 2\ O+M$$

where M is the "other" atom or molecule, which activates the oxygen. The rate of reaction will then be proportional to the number of collisions between O_2 and M, so that one can write[1]

$$\left.\frac{dn_O}{dt}\right)_{diss} = \text{rate of dissociation} = k_D(T)n_{O_2}n_M \tag{3}$$

where k_D is the dissociation rate constant, a function of temperature only.

The inverse process, the recombination of two oxygen atoms, can only occur if some means is available to carry away the energy that the two separate atoms must lose to form a stable diatomic molecule. Two mechanisms for carrying away the energy are conceivable, a three-body collision and radiation. The probability that this energy is given off by radiation is, however, negligibly small: Radiative (dipole) transition can occur only if one of the oxygen atoms is in the excited ^1D state, so the fraction of double collisions leading to combination is $10^{-5}\,\frac{5}{9}\,e^{\frac{-23,000}{T}}\,Z$. Here the 10^{-5} factor is the usual ratio of duration of collision to the time required for radiation; the factor $\frac{5}{9}\,e^{\frac{-23,000}{T}}$ is the probability that one of the two atoms is in the ^1D state; Z is a number much less than unity which gives the probability that the molecular state arising from this collision decays to the stable ground state of oxygen. The fraction of collisions where a third body is present is found from elementary kinetic theory to be of the order of $5\times10^{-4}\,p_{at}$; thus at atmospheric pressure and 5000° K a triple collision is $10^4/Z$ more likely than a radiative collision. A general discussion of this point is given in reference 3, pages 400 to 402.

In the case of a triple collision, the third particle takes up the excess energy and momentum. Thus the reaction is $O + O + M \xrightarrow{k_R} O_2 + M$, and

[1]The implicit assumption is that the time between collisions (or more precisely, the correlation time) is long compared with the time it takes the O_2 molecule to break up once it is activated. The latter time may be of the order of one period of vibration of the molecule or 2×10^{-14} sec, while the correlation time is larger than $\sqrt{\frac{T}{300}}\,\frac{10^{-10}}{p_{at}}$ sec. So we expect equation (3) to be valid for most cases of practical interest (see ref. 2).

$$-\left.\frac{dn_O}{dt}\right)_{rec} = \text{rate of recombination} = k_R(T)n_O{}^2n_M \tag{4}$$

The form (4) of the rate law states the rate is proportional to the number of collisions between three bodies, two of which are oxygen atoms. As will be discussed in detail later (p. 17), $k_R(T)$ has different values for different third bodies; thus when dealing with a gas mixture such as air, the right-hand side of equation (4) should be a sum of terms over different species (M_1, M_2, ...) in the gas. However at the present state of knowledge of the rate constant this appears to be an overrefinement, and the form (4) will be used. This form of the law has been verified experimentally for the recombination of like atoms in an inert gas atmosphere at room temperature and near atmospheric pressure (refs. 4, 5, and 6).

According to all theories of reaction rates the rate constants k_R and k_D depend only on temperature, and do not depend on whether or not chemical equilibrium exists. They are related through the equilibrium constant $K_e(T) = k_D(T)/k_R(T)$. The equilibrium constant is a known function of temperature that can be calculated accurately from statistical mechanics; it permits us to eliminate either k_R or k_D from the equations. In the following analysis k_D has been eliminated rather than k_R.

Since the net number of atoms liberated, P, is the balance between those freed by dissociation and the number of free atoms bound through recombination, one obtains with the help of equations (3) and (4) upon eliminating k_D:

$$P = k_R n_M(n_{O_2}K_e - n_O{}^2) \tag{5}$$

We can write equation (5) in terms of x, the fraction of oxygen atoms which are free, and x_e, the "local equilibrium value" of x. In other words, x_e is that value of x for which $[n_{O_2}K_e(T) - n_O{}^2] = 0$. Then, noting that $K_e = 2C\rho x_e{}^2/(1-x_e)$, one finds:

$$P = -k_R(T)C^2\rho^2 n_M\left(\frac{x_e}{1-x_e} + x\right)(x-x_e) \tag{6}$$

Putting equation (6) into equation (2) gives

$$\frac{dx}{dy} = \frac{-(x-x_e)}{\lambda} \tag{7}$$

with

$$\frac{1}{\lambda} = \frac{k_R(T)C\rho n_M}{u}\left(\frac{x_e}{1-x_e} + x\right) \tag{8}$$

Equations (7) and (8) give the gradient of the quantity x at every point in the channel, and the integral of equation (7) gives the value of x at any point y. Equations (7) and (8) are valid no matter how far the deviation from chemical equilibrium and regardless of whether recombination or dissociation is the dominant process.

Physical Interpretation and "Local Relaxation Length"

The quantity λ defined through equations (7) and (8) is called the "local relaxation length" of the reaction, and the time $\tau = \lambda/u$ is the corresponding relaxation time.

In the special case that $1/\lambda$ and x_e are approximately constant throughout the flow region of interest, the integration of equation (7) yields an exponential decay to equilibrium:

$$x(y) - x_e = [x(0)-x_e]e^{-\frac{y}{\lambda}} \tag{9}$$

Here λ is seen to be the distance required to reduce the deviation of x from its equilibrium value to one eth of what it is initially. Practically, λ and x_e may be regarded as constant only when the density, temperature, and velocity vary slowly. In addition, λ has some dependence on the deviation from local equilibrium, as can be seen by writing equation (8) in the form

$$\frac{1}{\lambda} = \frac{k_R(T)C\rho n_M}{u}\left[\left(\frac{x_e}{1-x_e} + x_e\right) + (x-x_e)\right]$$

where it must be remembered that the number of third particles, n_M, will usually have a linear dependence on $(x-x_e) + x_e$. The dependence of $1/\lambda$ on $(x-x_e)$ can always be safely neglected when $(x-x_e)/x_e$ is small compared to unity.

Generally the physical situation is quite different from that described by equation (9) because the temperature and density may vary rapidly along the streamtube. Thus, for example, if the flow begins (at $y = 0$) in chemical equilibrium, but the parameters of the flow (ρ,T,u) vary continuously and rapidly along the streamtube, then the system, unable to keep up, will lag further and further behind as the flow proceeds. In this case, the deviation from equilibrium may increase rather than decrease with distance. Generally the tendency to lag behind equilibrium and the tendency to decay to local equilibrium exponentially

are operating simultaneously. Thus the qualitative behavior of the system (whether it stays closer to the infinite rate case or is nearer to the frozen case) is generally not determined by the magnitude of the relaxation length alone, but also by the magnitude of the gradient of x_e and the gradient of λ. These gradients can be expressed in terms of the gradients of temperature, density, and velocity. It is the relative magnitude of these gradients to the relaxation length that matters. Whenever throughout the flow $\lambda << L_e$, where L_e is the length within which x_e changes by a factor of the order of one eth, the flow may be regarded as being in chemical equilibrium in the region of length L_e. Deviations from equilibrium can be neglected in a channel of length L if everywhere $\lambda << L, L_e$. On the other hand the flow is locally frozen when $\lambda/L_e >> 1$; it can be treated as frozen throughout a channel, if everywhere $\lambda/L >> 1$. The more precise and complete criteria come from solving the differential equation for x. This will now be done.

Solution of the Differential Equation

Equation (7) together with equation (8) expresses the conservation of oxygen atoms. In principle these equations should be solved simultaneously with the other equations (such as mass and energy conservation) which the channel flow must satisfy. Although such a solution will be very tedious, it is always possible by numerical means if the function $k_R(T)$ is known.

However, an approximation to the solution is obtained by an iteration procedure which begins either with frozen flow or equilibrium flow. Here we shall for the sake of being definite deal only with the procedure beginning with chemical equilibrium. In this procedure one evaluates the factor $1/\lambda$ at the values ρ_∞, T_∞, u_∞, and x_∞ corresponding to the case of the reaction always being in equilibrium during the flow (infinite rate). Similarly x_e can be replaced by x_∞ in equation (7). The distinction between x_e and x_∞ is a subtle one: x_e is the equilibrium fraction of free oxygen atoms for the temperature distribution existing in the channel whatever the reaction rate; x_∞ is the special value of x_e when the reaction rate is infinite. By this replacement it becomes unnecessary to solve equations (7) and (8) simultaneously with the other equations describing the flow, but one may first solve the flow for local chemical equilibrium, ignoring equation (7), and then use the result to evaluate equation (8) and integrate equation (7). Let us call the approximate solution obtained thusly $x^{(1)}$. Then the error in x introduced by this approximation can be shown to be

$$x - x^{(1)} = \sum_{n=0}^{\infty} \left(-\lambda \frac{d}{dy}\right)^n \delta(y)$$

where

$$\delta(y) \equiv (x_e - x_\infty) + \frac{\lambda - \lambda_\infty}{\lambda_\infty}\left[x^{(1)} - x_\infty\right]$$

is the error in first order. An upper limit to δ may be calculated by evaluating x_e and λ at the temperature and density corresponding to chemically frozen flow.

In the present approximation (i.e., replacing x by $x^{(1)}$) equation (7) is linear and the formal solution can be written immediately. This solution, which is the exact solution of the equation,

$$\frac{dx^{(1)}}{dy} = \frac{-\left[x^{(1)} - x_\infty\right]}{\lambda_\infty}$$

is (see Appendix A):

$$x^{(1)}(y) = x_\infty(y) + e^{-S(y)}\left[x(0) - x_\infty(0)\right] + e^{-S(y)} \int_{x_\infty(y)}^{x_\infty(0)} e^{S^*} dx_\infty' \tag{10}$$

where the quantity $S(y)$ is defined by $S(y) \equiv \int_0^y \frac{dy'}{\lambda_\infty(y')}$, and S^* is the function of x_∞ which at every point is numerically equal to $S(y)$. If one inverts the function $x_\infty(y)$ to obtain $y(x_\infty)$, then $S^*(x_\infty) = S[y(x_\infty)]$.

The last term in equation (10) vanishes when temperature and density (and therefore x_∞) are constant along the flow. In this case it is seen that only the exponential decay term remains. On the other hand, if the fluid is in chemical equilibrium initially, the middle term vanishes leaving

$$x^{(1)}(y) = x_\infty(y) + e^{-S} \int_{x_\infty(y)}^{x_\infty(0)} e^{S^*} dx_\infty' \tag{11}$$

The solution (10), which is constructed to be most accurate for near equilibrium flow, is seen to be exact also in the opposite limit of frozen flow ($S = 0$). In practice δ and its derivatives are expected to be sufficiently small so that (10) will always be a fair approximation.

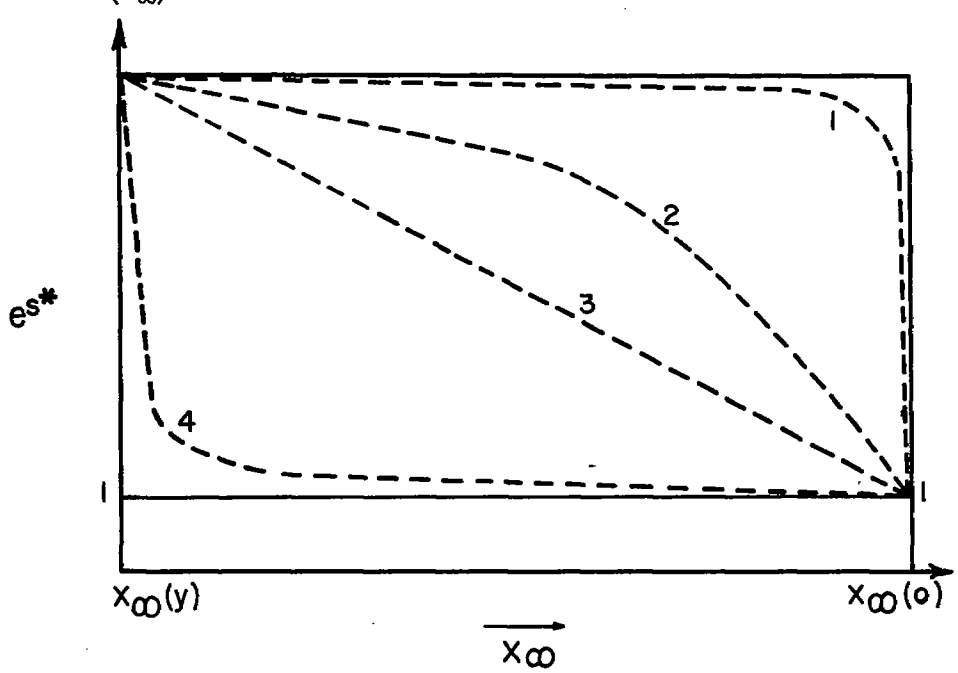
Measure for Proximity to the "Frozen Flow" or "Equilibrium Flow" Limits

The location of the solution relative to the two limiting cases ("frozen" and "local equilibrium") is with the help of equation (10) given by:

$$B(y) = \left|\frac{x(y)-x_\infty(y)}{x(0)-x_\infty(y)}\right| \approx \left|\frac{e^{-S}}{x(0)-x_\infty(y)}\left[x(0)-x_\infty(0)+\int_{x_\infty(y)}^{x_\infty(0)} e^{S^*}dx_\infty\right]\right| \qquad (12)$$

Now $B = 0$ means the reaction occurs at an infinite rate, and $B = 1$ shows the reaction is frozen. It seems from equation (12) that one has to evaluate $x^{(1)}(y)$ completely in order to see whether B is closer to zero or to unity. However, for some applications this is not necessary: If $S(y) \ll 1$, it follows from equation (12) that $B(y)$ is near unity. This is a precise statement of the fact that if the relaxation length is long compared with the dimensions of interest, then the zero-rate approximation is valid.

Another special application is to the flow leading from the region near the stagnation point of a blunt body around the edges to the sides of the body. In this case the reaction is expected to be in equilibrium at the initial point, taken in the stagnation region. Then it is clear from equation (12) that B has the property $e^{-S} \leq B \leq 1$. Further $B(y)$ can be given a simple geometric interpretation: It is the ratio of the two areas $\int_{x_\infty(y)}^{x(0)} e^{S^*}dx_\infty$ and $e^S[x(0)-x_\infty(y)]$. As is to be expected from the earlier discussion, the value of B depends on the shape of the function $S^*(x_\infty)$.



In the illustrative sketch above, the area of the rectangle enclosed by the heavy solid line represents $e^{S^*}[x(0)-x_\infty]$, and the total area under one of the alternative dotted lines (which represent different functions S^*) is $\int_{x_\infty(y)}^{x_\infty(0)} e^{S^*}dx_\infty$. The extreme shapes 4 and 1 clearly correspond to B approaching e^{-S} and unity, respectively. For any convex shape such as 2, as well as for the straight line 3, one has $1/2 < B < 1$. In the last section use will be made of equation (12) to discuss the effect of body size and density on the solution.

The quantity B does not tell us whether both limiting cases are a good approximation or if they are both poor - it only tells of their relative merit. A more complete specification of the situation is obtained if the two parameters

$$\Delta_\infty = \frac{x(y)-x_\infty(y)}{x_\infty(y)}, \quad \Delta_0 = \frac{x(0)-x(y)}{x(0)} \tag{13}$$

are employed. They represent the percent deviation from each of the limiting curves. They are related to B through:

$$B = \left[1 + \frac{x(0)\Delta_0}{x_\infty\Delta_\infty}\right]^{-1} \tag{14}$$

THE RECOMBINATION RATE CONSTANT

This section is concerned with a detailed evaluation of knowledge concerning the recombination rate constant, a parameter upon which the flow depends. The reader who is not concerned with this aspect of the problem is invited to skip to page 21.

At present there are no direct measurements available from which one can obtain the oxygen recombination rate $k_R(T)$, for the temperatures of interest. However, considerable careful work (refs. 4, 5, and 6) has been done in measuring the rates of recombination of other diatomic gases (I_2, Br_2) at room temperature in the presence of an inert gas. Recently a few results (refs. 7, 8, and 9) have been published for I_2 and Br_2 at temperatures between 1000° K and 2700° K in a shock tube. It was found that the recombination rate for these halogens is smaller at high temperatures than at low temperatures.[2]

[2]After the calculations in the present paper were made, a shock-tube experiment using air was reported (ref. 10). The author (S. Feldman) interprets the experiment to yield a lower limit for the recombination rates, which are about ten times larger than the rates given by equation (21).

In order to interpolate or extrapolate from experimental results for one temperature to different temperatures or to a different diatomic gas or to different inert gases, a theory and some understanding of the mechanism of reaction is necessary. No altogether satisfactory theory for the oxygen recombination rate constant exists. There are, however, at least three methods available for estimating a rate constant from theoretical considerations. The three methods are (1) application of collision theory of chemical reactions, (2) application of the general theory of "absolute" reaction rates due to Eyring and co-workers (hereafter simply referred to as the "Eyring theory"), and (3) a method developed by E. Wigner specifically for the combination reaction. Since each of the three theories can make a contribution to our understanding of the reaction, some comments are made about each approach; we finally use Wigner's theory to obtain a numerical value for the rate constant. Attention will be focussed on the temperature dependence of the rate constant, because predictions based on the three theories give essentially different temperature dependencies if the usual approximations are made in applying the theories. This is graphically illustrated in figure 1. The graph will be further discussed at the end of this section. The disagreement between the theories may be due to the nature of the approximations made; it is possible that the rigorous calculation by Eyring theory, and further refinement of collision theory, would yield results in agreement with an exact calculation by Wigner's theory.

Collision Theory

The basic idea of collision theory (refs. 2, 6, and 11) is to count the number of recombinations by counting the number of triple collisions. Some arbitrariness comes in defining the effective radii of the colliding particles. This is resolved by approximating the atoms by hard spheres whose effective radii are taken to be the range of the interatomic forces. Experimental data such as viscosity measurements or spectroscopic measurements are often used to determine these radii (see ref. 12). Sometimes experimental results are used to determine an efficiency factor, that is, the number of reactions per triple collision. This adds another element of incompleteness to the theory. The advantage of collision theory is the simplicity and easy visualization of the concepts employed.

If the duration of the collision is assumed to be inversely proportional to the relative velocity of the atoms before collision, then a rate constant of the form $k_R(T) = \text{const}\sqrt{T}$ is obtained. On the other hand, if this duration is assumed to be a function of only the interaction of the two atoms, one obtains $k_R(T) = \text{const}\ T$. But no matter which way the duration is calculated, if the efficiency factor is regarded as a constant, the rate constant increases with temperature and disagrees with the iodine and bromine experiments.

A serious shortcoming in the collision theory formulation lies in the neglect of the fact that the efficiency of a triple collision in

leading to chemical reaction is a function of temperature. Let $\eta(T)$ be this efficiency factor. Then $k_R(T) = \text{const}\ \eta(T);\ T$ or $k_R(T) = \text{const}\ \eta(T)\sqrt{T}$. It is of interest to get some idea as to the direction and the extent by which the introduction of $\eta(T)$ modifies the rate constant, so a very crude estimate of the efficiency of a triple collision is made in Appendix B. The efficiency factor is found to be the position average of $\Gamma(r)$ where:

$$\Gamma(r) = 1 - e^{-\frac{V(r)}{kT}}\left\{1 + \frac{V(r)}{kT} + \frac{1}{2}\left[\frac{V(r)}{kT}\right]^2\right\} \tag{15}$$

Here $V(r)$ is the value of the interaction potential between the two oxygen atoms at the point (r) where the triple collision is taking place. The dependence of Γ on $1/T$ is very strong when $V/kT << 1$ (when Γ is close to zero), and becomes weaker as V/kT (and Γ) increases. The limiting forms are:

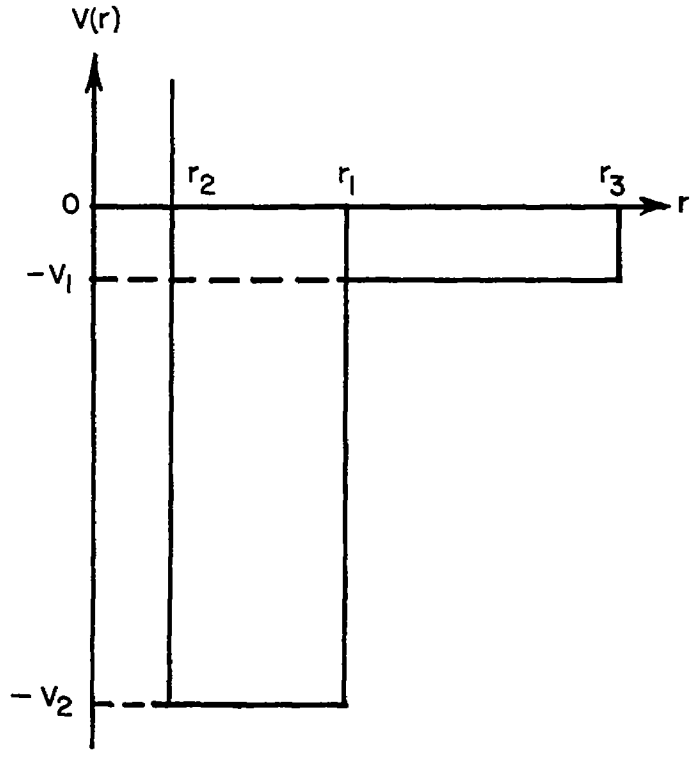
$$\Gamma = \Gamma_1(r) = \frac{1}{6}\left(\frac{V}{kT}\right)^3 ; \quad \frac{V}{kT} << 1 \tag{16a}$$

$$\Gamma = \Gamma_2(r) = 1 - \frac{1}{2}\left(\frac{V}{kT}\right)^2 e^{-\frac{V}{kT}} \approx 1 ; \quad \frac{V}{kT} >> 1 \tag{16b}$$

Formula (16a) applies for large r where the potential between the two oxygen atoms is very weak, and (16b) applies whenever the triple collision occurs within the central part of the Morse curve. The value of $\eta(T)$ is the appropriate average over the quantum mechanical states of the two oxygen atoms of:

$$\frac{\int_{V<0} \Gamma(r)\ \frac{r^2}{v(r)}\ dr}{\int_{V<0} r^2\ \frac{dr}{v(r)}} \tag{17}$$

In the averaging process, equation (17), each volume element is regarded an equally likely site for a triple collision, except for a factor $dr/v(r)$ which measures the time spent in the region dr during a collision. Note that for equation (16a) the multiplicative factor r^2/v is relatively large and for equation (16b) it is relatively small. The different states to be summed over arise from different relative orientations of the angular momentum vector, which are possible between two atoms in their ^3P state.



Since $\eta(T)$ is an average of $\Gamma(r)$, it will always decrease with increasing temperature because $\Gamma(r)$ does. Just how rapidly it decreases will depend on the detailed shape of the potential. To illustrate these remarks consider the simple potential shown in the sketch; there Γ_1 and Γ_2 are independent of r. If $V_2/kT >> 1$, and $V_1/kT << 1$, then by the averaging procedure of equation (17)

$$\eta(T) = (1-\alpha)\Gamma_1 + \alpha\Gamma_2 \approx \frac{1-\alpha}{6}\left(\frac{V_1}{kT}\right)^3 + \alpha$$

where

$$\alpha \approx \left[1 + \sqrt{\frac{V_2}{kT}}\,\frac{\left(r_3\right)^3 - r_1^3}{r_1^3 - r_2^3}\right]^{-1}$$

leading to

$$k_R(T) \cong \text{const}\left[\frac{1-\alpha}{6}\left(\frac{V_1}{kT}\right)^3 + \alpha\right]\sqrt{T} \tag{18}$$

Equation (18) indicates that the efficiency factor could modify the simple collision theory sufficiently to change a rate constant with a positive square root temperature variation to one which decreases with increasing temperature, but in any case the modification will be in that direction.

A further small effect arises from the fact that at low temperatures the effective collision diameter on which the constant in equation (18) depends is not quite constant. It is shown in Appendix B that a factor proportional to $T^{-\frac{1}{2}}$ is introduced into the recombination rate at low temperature on that account. Thus also this factor tends to reduce the positive temperature coefficient which simple collision theory would predict. Another approximation of collision theory (not further analyzed here) is to replace the duration of the collision by some average value, not taking into account the relative angular momentum of the two atoms.

A collision type theory which attempts to take these various effects into account properly would require an integration over two velocities, two impact parameters, and one spatial angle. The region of integration would again be given by equation (B1). No such integration will be attempted here but, as will be seen later on, Wigner's theory does in effect just that, although using a language rather different from collision theory.

Eyring Theory

The approach used by the Eyring theory (see refs. 13, 14, and 15) is to diagram the total potential energy of the three atoms as a function of their relative positions. The diagram takes the form of an irregular surface similar to a system of mountains and valleys; the initial relative position and velocity together with the interatomic forces cause the three atoms, represented by a point on the diagram, to move in a certain way. If the appropriate coordinate system is used, the motion of this point is identical with that of a mass point rolling around under the action of gravity without friction in the corresponding mountain range. The combined state (O_2) is represented by a certain valley, which is usually reached via a mountain pass. When the three atoms are in the particular relative position to each other, which is represented in the diagram by a point in the neighborhood of this mountain pass, the group of atoms is referred to as an "activated complex"; before two oxygen atoms can combine, they must be part of an activated complex.

According to the theory the rate constant is then seen as the product of a statistical factor F^{+} giving the concentration of the activated complex, and the transmission coefficient κ giving the probability that the activated complex will decay into the combined molecule plus third particle, $k_R(T) = \kappa F^{+}$. The activated complex is defined only for reactions requiring the addition of an activation energy; thus for two oxygen atoms which approach head-on, it cannot be defined because the potential energy curve has no maximum so that there is no activation energy required. However, generally two colliding oxygen atoms will have some relative angular momentum, and hence a centrifugal potential which yields a slight maximum in the potential energy curve. This fact permits the calculation of the recombination rate within the framework of the Eyring theory. We shall not attempt the complicated task of calculating the transmission coefficient for the oxygen recombination reaction. However, some rather general observations can be made from Eyring's theory about the relative behavior of different third bodies:

1. An inert third body is much less effective (κ much smaller) in bringing about recombination than a third particle, such as an oxygen atom, which can form a chemical bond with one of the reacting atoms.

2. The statistical factor F^{+} has a different temperature dependence for different third bodies. If the third body is a

hard sphere $F^{+} \sim \sqrt{T}$, the collision theory result; but if there exists any - however slight - attractive force between the third atom and the reacting atom, then the temperature dependence lies between $F^{+} \sim T$ and $F^{+} \sim (T)^{3/2}$ at the temperatures of aerodynamic interest. If the third body is a diatomic molecule, such as O_2 or N_2, then the temperature dependence lies between $F^{+} \sim (T)^{2}$ and $F^{+} \sim (T)^{5/2}$. The reason for these differences is that F^{+} is proportional to the partition function of the activated complex; in the hard sphere case the activated complex is just a diatomic molecule, in the active atom case it is a triatomic molecule, and if the third body is diatomic, the complex consists of four atoms. The more atoms the complex involves, the larger the number of internal degrees of freedom and the sharper the dependence of the partition function on temperature.

3. One cannot assert that the recombination rate constant will have a temperature dependence identical with that of F^{+} because κ may vary with temperature. However, one does not expect the variation of κ with T to be so different for different third bodies as to wash out altogether the differences in temperature dependence due to differences in $F^{+}(T)$, nor would it be expected that κ decreases sufficiently rapidly as T increases to produce a rate constant with a negative temperature coefficient when the third body is a diatomic molecule.

Wigner's Theory

Wigner (refs. 16 and 17) regards the three particles needed for a recombination as a member of a canonical ensemble (each member is three such point particles in a box, see ref. 18), and represents it as a point in (twelve-dimensional) phase space, where the 12 dimensions are the relative positions and momenta of the three particles. A certain region of this phase space represents the combined state, while the rest of the space represents the separated state. He then asks (and answers) the question: If initially the system is in an uncombined state, what is the probability that after a time t it will be in the region representing the combined state? He assumes that the particles follow the classical laws of mechanics and their interaction potential is a function of their relative position <u>only</u>, having no explicit time dependence (adiabatic hypothesis). These same assumptions also appear in the Eyring theory. For more detailed discussion of the assumptions underlying the theory and their validity see references 16, 17, and 19. For the case in which the third body is an inert atom, so that its interaction with the oxygen is that of a hard sphere, he obtains an especially simple upper limit for the rate constant:

$$k_R = \frac{g_s}{\sum_i g_i} \frac{2\pi^2 a_{OM}}{\sqrt{\pi m k T}} \int_{V<0} dr(r^3+2a_{OM}r^2)V(r) \tag{19}$$

where r is the distance between the oxygen atoms, a_{OM} is the sum of the collision radii for interaction between the oxygen and the third body, and $V(r)$ is the interaction potential between the two oxygen atoms. The fraction $g_s/\sum_i g_i$ is required to include the fact that the interaction between two oxygen atoms in their ground state depends on the relative orientation of their angular momenta. If several attractive states exist as is the case for oxygen (see, e.g., ref. 3), the really correct procedure would be to add several terms of the form (19), one for each attractive state. But without considering the detailed shape of each of these potentials, one can estimate $g_s/\sum_i g_i$ on the basis of the formal Wigner-Witmer rules (ref. 3). It is noted that the values of g_i are constants and depend neither on temperature nor on the nature of the third body.

The only dependence of equation (19) on the nature of the third body is through the a_{OM}; the rate is larger, the bigger the inert atom. This is in quantitive agreement with experiments on I_2 and Br_2 in different rare gas atmospheres at room temperature. Further equation (19) predicts a temperature dependence for the upper limit $k_R(T) \sim (T)^{-\frac{1}{2}}$. That it is only an upper limit arises in the following way: In Wigner's derivation of the rate constant, it is necessary to define the region of phase space corresponding to the combined state not only for the case that the third body is far away, but also while all three are in collision. Wigner shows that the correct definition of the latter region is the one which makes the rate constant a minimum, subject to the boundary condition that it reduces to the correct region when the third body is far away. Not having any simple procedure for obtaining the shape of this region, Wigner uses a simple and reasonable formula for the shape of the region; this will generally give too large a value for the rate constant. Moreover, the error introduced by using the wrong region increases with increasing temperature; consequently, it is expected that k_R decreases more rapidly as the temperature increases than equation (19) predicts (i.e., more rapidly than $1/\sqrt{T}$).

For the present purpose, equation (19) will be used with $a_{OM} = 2.60$ A and a Morse potential function for V corresponding to the $^3\Sigma_g^-$ (ground) state of O_2:

$$V(r) = D\left[e^{-\frac{2(r-R_o)}{a}} - 2e^{-\frac{(r-R_o)}{a}}\right] \tag{20}$$

with

$$a = 0.373 \text{ A}, \quad R_o = 1.20 \text{ A}, \quad D = 5.12 \text{ e.v.} = 59{,}000^\circ \text{ K}$$

The fraction $g_s/\sum g_i$ is estimated from the Wigner-Witmer rules to be 1/10. As was mentioned earlier, such an estimate involves some uncertainty.

The resulting rate constant is, if the third body is inert,

$$k_R(T) = \frac{125}{\sqrt{T}} \times 10^{-32} \left(\frac{\text{molecules}}{\text{cm}^3}\right)^{-2} \text{sec}^{-1} \tag{21}$$

The corresponding relaxation times for various temperatures and densities, which will be discussed in a later section, are shown in figure 8.

Comparative Discussion of the Three Theories

From collision theory a mechanical model or picture of the reaction is obtained, but the theory is, in some respects, too incomplete, and in practice, requires the use of experimental data for application.

From Eyring's theory some information is gained about relative rates with different third bodies. The difficulty in applying the Eyring theory to the present problem lies in the difficulty of calculating the transmission coefficient. The probability that the activated state leads to reaction is the probability that the particles end up not only in a certain relative position (the two O atoms together), but also with certain relative momenta (the third particle carrying off most of the kinetic energy). For this reason Eyring's use of a potential energy diagram in configuration space is not the most natural way to proceed, but rather the use of phase space is indicated where momenta and coordinates enter in symmetrical fashion. Also the use of the concept of activated complex seems not really suited to the present problem, which involves practically no activation energy.

Wigner, by working in phase space and avoiding the introduction of any activated complex, can express the rate constant in terms of an integral, which he evaluates for the case that the third body is a hard sphere. The resulting rate constant varies as $T^{-\frac{1}{2}}$; the fact that the rate decreases as T increases is at least in qualitative agreement with the aforementioned I_2 and Br_2 experiments, although the data is best fitted by a $T^{-\frac{3}{2}}$ dependence. The modifications of this $T^{-\frac{1}{2}}$ law which would result if the third body were a diatomic molecule rather than a hard sphere are not clear from Wigner's integrals. The earlier discussion, in terms of Eyring's activated complex, suggests that a less negative or perhaps even a positive temperature coefficient would result. In the present analysis we shall make the simplest assumption, namely that all third bodies act as hard spheres, rather than assuming an activated complex.

These arguments led the author to select for use in this analysis the theory of Wigner. The reasons for this choice are:

1. Of the three methods his is the most naturally suited to the problem.

2. The integrals obtained can actually be carried out, at least for a hard sphere third body.

3. What experimental evidence there is, supports a negative temperature coefficient, and Wigner's rate constant gives a negative temperature coefficient, at least for a hard sphere third body.

This concludes the critical evaluation of the three theories. It is of interest to look again at the graphical presentation (fig. 1) in the light of the above discussion because some more definite statements can be made: For oxygen in an inert gas presumably curve ① is close to the correct form and ② is a bad approximation. For oxygen in an atmosphere of N_2 the curve is expected to have a shape intermediate between ① and ③. The absolute value of curve ① is obtained from equation (21). No absolute values for the curves ② and ③ are calculated; they are arbitrarily taken to agree with ① at 1000° K, permitting a comparison of the temperature dependence. These curves and their uncertainty serve to point up the need for further experimental measurements of the rate constants.

FLOW WITH CHEMICAL REACTION

The Equations

Before one can integrate equation (7) the results (21) for the recombination rate constant must be inserted into equation (8) and λ must be expressed in terms of x and A, rather than temperature (T), density (ρ), and velocity (u). There is then obtained the following equation for x in terms of A, for any specified channel shape $A(y)$:

$$\frac{dx}{dA} = -\frac{dy}{dA}\frac{x-x_e}{\lambda} \tag{22}$$

This equation is to be solved simultaneously with the remaining flow equations to describe the flow completely. There are six variables: x_e, x, T, ρ, p, and u; hence, five additional equations are needed. These are given below. The equations allow for chemical reaction and variable specific heat but neglect transport phenomena:

$$\rho u A = m \qquad \text{(mass conservation)} \tag{23}$$

$$u\,du + \frac{dp}{\rho} = 0 \qquad \text{(momentum conservation)} \tag{24}$$

$$u\,du + dH = 0 \qquad \text{(energy conservation)} \tag{25}$$

$$\frac{p}{\rho} = (1+\bar{f}x)\frac{RT}{\bar{M}} \qquad \text{(equation of state)} \tag{26}$$

$$K_e(T) = 2C\rho\frac{x_e^2}{1-x_e} \tag{27}$$

The quantities $\bar{M}$ and $\bar{f}$ are defined by

$$\bar{M} = \sum_i f_i M_i \; ; \quad \bar{f} = f_{O_2} + \frac{1}{2} f_O$$

where

$$f_i = \frac{\text{number of moles of series } i}{\text{total number of moles in cold air}} = \frac{n_i}{\sum_k n_k{}^o}$$

and M_i is the molecular weight of each species. For oxygen in an inert gas, $\bar{M}$, $\bar{f}$, and C are constant. However, for air both C and $\bar{f}$ depend on the concentration of NO and thus are functions of temperature, but $C/\bar{f}$ is independent of the variable concentration of NO. The equilibrium constant $K_e(T)$ and the enthalpy H are computed from statistical mechanics; these functions have been tabulated by various authors (see refs. 1, 20, 21, 22, 23, and 24).

Method of Solution

Rather than attempting to solve all six equations ((22) to (27)) simultaneously, one can simplify the calculation by dealing with the frozen flow or equilibrium flow limit, depending on which is expected to be nearer to the case of interest, and then correcting for the finite rate case:

For the frozen flow limit, one obtains the result by solving simultaneously the four equations ((23) through (26)) using $x = x_o = \text{const}$ in equation (26). This differs from the well-known one-dimensional flow without reaction only in that care must be taken in evaluating the enthalpy H. The enthalpy at any point is obtained by adding to the initial enthalpy the change in enthalpy of each constituent due to the change of temperature, but not adding enthalpy change due to a heat of reaction, since no reaction is permitted. (See, e.g., the tables of refs. 21 and 22.) Then equations (27) and (22) can be solved in that order. Of the six variables, only x is sensitive to changes in the shape of the channel. If a higher approximation to the flow is desired, one then inserts the $x(A)$ obtained from equation (22) into equation (26)

and, keeping p/ρ fixed, which is essentially equivalent to ignoring corrections to the enthalpy, obtains a new temperature at every point.

In the other extreme case, equilibrium flow, one solves equations (23) to (27) simultaneously, replacing x in equation (26) by x_∞. The solution (11) for (22) can then be employed. If a higher approximation to the flow is desired, one inserts the resulting $x(A)$ - rather than x_∞ - into equation (26) and obtains a new $T(A)$.

It is interesting to note that in both limiting cases, the properties of the flow (p, ρ, T, u) are a unique function of the cross-sectional area A, regardless of how slowly or rapidly the cross section varies along the channel. However, the corrections to the flow in the finite rate case are not unique functions of A, but through equation (22) depend on the channel shape, dA/dy; so for a finite reaction rate the flow is different for a channel which contracts (or expands) very suddenly to a certain cross section than for one which contracts (expands) slowly to the same cross section. This dependence on the linear distance arises because a characteristic length, the relaxation length, has entered into the problem.

The simultaneous solution of equations (23) through (27) needed for the equilibrium flow is accomplished as follows: In analogy to the case of constant specific heat we introduce into equation (25) instead of H, the variable g defined by:[3]

$$H = \frac{g}{g-1}\frac{p}{\rho} \tag{28}$$

In general, g does not represent the ratio of specific heats. We then eliminate x_e from equations (26) and (27) and u from equations (24) and (25). There are then obtained two equations involving only p, T, and ρ and one can find $p(\rho)$ and $T(\rho)$ from them numerically. The equations are

$$\frac{\overline{M}p}{\rho RT} - 1 = \overline{f}\,\frac{Q}{2}\left(\sqrt{1 + \frac{4}{Q}} - 1\right); \qquad Q \equiv \frac{K_e(T)}{2C\rho} \tag{29}$$

$$\frac{p}{p_o} = \frac{g-1}{(g-1)_o}\, e^{\int_{\rho_o}^{\rho} \frac{g}{\rho'}\, d\rho'} \tag{30}$$

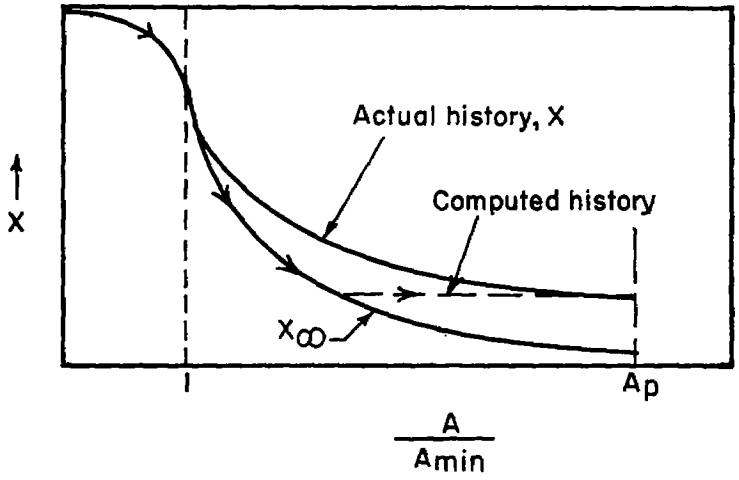
[3]This is the γ' used by Gilmore, reference 1. He gives some numerical values for air.

Whenever g is constant along the path, equation (30) represents a polytrope:

$$\frac{p}{p_o} = \left(\frac{\rho}{\rho_o}\right)^g \tag{30a}$$

Usually g is a slowly varying function, and equation (30a) is a useful first approximation. The procedure used in the present calculation was to obtain the first $p(\rho)$ from equation (30a), and to introduce this result into equation (29) to find $T(\rho)$. Then if it was found that $g(\rho,T)$ did indeed vary along the path, we fitted the slowly varying function $g(\rho)$ by a linear or quadratic function, thus avoiding numerical integration of equation (30). This procedure converges very rapidly. Once $p(\rho)$ and $T(\rho)$ are known, one readily obtains without further iteration $u(\rho)$, $\rho(A)$, etc., from equations (23) and (24). In numerical evaluation the most inconvenient feature of this method is that in equation (29) on the left-hand side one is subtracting two large numbers from each other to obtain a relatively small one and thereby losing some accuracy. On the other hand a helpful feature is that the slopes of the right-hand side of equation (29), plotted as a function of T, and that of the left-hand side are very different.

As was noted in an earlier paragraph, it has up to now been assumed that the change in enthalpy dH in equation (25) is the same for flow with finite reaction as for the limiting case (equilibrium or frozen) on which the calculation is based. Now we show how the variation in dH may be evaluated. The enthalpy H (or the function g in eq. (30)) must be recalculated with the new $x(A)$ and $T(A)$. This correction will have some (however small) effect on all the flow variables. In computing the enthalpy, it must be remembered that H depends on T, ρ, and x. This contrasts with the equilibrium situation, in which H depends only on T and ρ. To compute H for air with the help of available tables, it is useful to replace the actual history of the system by a different history, as is indicated in the accompanying sketch. This is permissible because H



To find H or g at the point A_p, the history is taken to follow either the equilibrium curve or a (horizontal) line on which no reaction is taking place.

is a point function of T and x, and so it is independent of the history of the gas expressed in terms of these three variables. With this modification of the enthalpy determined, we repeat the solution and by this iteration obtain the correction to the flow variables.

The enthalpy correction tends to be small not only because it is proportional to $[x^{(1)}-x_\infty]$, but also because it is due to two partially cancelling effects: A change in T and a change in x in the opposite direction. These changes have opposite signs because ρ is kept fixed. The resulting corrections to the other flow variables for a given correction to H are smaller the higher the temperature and flow velocity.

The modification of the flow variables due to the correction of the enthalpy was found to be negligibly small in the example which follows.

Example

As a numerical example the following initial conditions were taken for the channel flow:

$$\frac{p_o}{p_{sl}} = 7.80 \ , \qquad \frac{u_o}{a_1} = 1.47$$

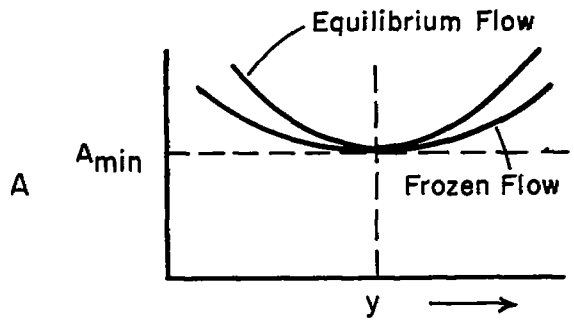
$$\frac{\rho_o}{\rho_{sl}} = 0.336 \ , \qquad T_o = 5300^\circ \text{ K}$$

where p_{sl} and ρ_{sl} are the standard pressure and density at sea level and a_1 is the free-stream velocity of sound at an altitude of 25 km. These initial conditions correspond to the conditions of air having come to thermodynamic equilibrium behind a normal shock wave of Mach 14.7 at an altitude of 25 km. For the finite rate case, the length of the channel was taken to be 2.5 meters.

Equations (26) and (27) were used with $\overline{M} = 28.8$, $\overline{f} = 0.000765$, and $C = 0.22\ n_{Av}/\overline{M}_{At}$. Thus the concentration of NO is neglected. For the rate constant equation (21) was used; the linearized version of the rate equation (7) was assumed so that the solution (10) could be employed. In figures 2 through 6 the results are plotted as a function of cross-sectional area. This area has to decrease sufficiently from its initial value so that the flow can reach sonic velocities; after that point the cross section increases again.

It is seen from the graphs that for the frozen case (zero rate), the contraction of the streamtube at the throat is much less than for the infinite rate case. This shows that the oxygen reaction can change the shape of streamtubes in the flow. The effect reflects the relatively

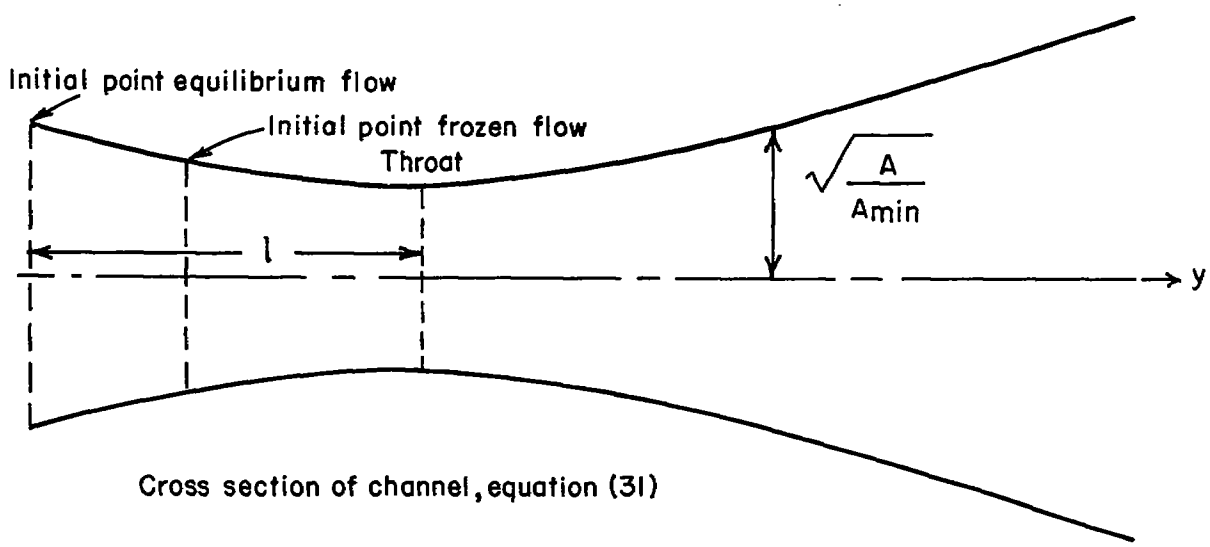
large equilibrium flow velocity at the throat compared to the slower frozen flow velocity. In the equilibrium case the enthalpy change between the initial point and the throat is comparatively large, being due to both thermal and chemical changes; the large enthalpy change requires a large increase in velocity, hence the greater contraction of the streamtube in equilibrium flow (see sketch).



In addition, the temperature, density, pressure, and velocity are shown in the figures to be lower for frozen flow than for equilibrium flow when the flow is supersonic and when the area ratios are the same. Of course the variable x, the mass fraction of free oxygen, is always greater in the frozen case (x_0) than in the equilibrium case (x_∞).

The initial values of ρ, u, T, p, and x are taken to be the same for the zero rate and equilibrium case. From figures 3 and 4 it is seen that for both limiting cases the density falls below the free-stream value long before the pressure does. Although the curves for equilibrium and frozen flow appear to be very close to each other for both pressure and density, it must be remembered that their absolute values are small when A/A_{min} is large and, consequently, the percent difference between the two cases may be considerable. In figures 2 through 6 all the curves have an infinite slope at the throat. This does not mean that the gradients are especially large in that neighborhood because $dA/dy = 0$ when $A = A_{min}$, and for any realistic streamtube dA/dy is very small in the neighborhood of A_{min}. To compute x(A) (fig. 6) a particular shape had to be considered (see sketch):

$$A/A_{min} = 1.00 + 19.00 \tanh 0.0586 \, (y/l)^2 , \quad l = 75 \text{ cm} \tag{31}$$



Cross section of channel, equation (31)

This shape has the property that for distances far from the throat ($|y| >> l$), the cross-sectional area approaches the constant value $A = 20\ A_{min}$. The value of $B(y)$ turns out to be practically zero for small y and increases with increasing y. Its value for $y = 230$ cm is only 0.20. Thus in this example $x(y)$ stays relatively close to $x_\infty(y)$, as is also seen in figure 6. The first-order correction to T is shown in figure 2. The enthalpy corrections (for T, ρ, p) discussed in the preceding section were found to be small, leading to practically no change from the infinite rate case.

The comment made earlier about the lag of the reaction being cumulative can be examined from this example and, for this purpose, figure 7 has been prepared. Even though the concentration of atomic oxygen lies relatively close to the infinite rate case, this figure shows that the percent deviation becomes progressively larger as the flow proceeds.

Having considered a specific example, it is of interest to consider the effect of varying the parameters of the problem. One would intuitively expect that an increase of initial density would cause the reaction to stay still closer to chemical equilibrium (decrease the value of B), because a higher density means more collisions and therefore faster reactions. Also one would expect that decreasing the length scale of the channel would cause the reaction to stay closer to the frozen limit (increasing the value B). Both these expectations are borne out by the equations. (Qualitatively this can be seen from equations (8) and (12) alone; quantitatively density and distance must also be traced through the whole set of equations (23) to (27).) These facts show that one can simulate the chemical aspects of the flow at high altitude flight by using a small model at higher densities.

WHEN CAN VIBRATIONAL RELAXATION BE IGNORED

In the foregoing analysis the contribution of molecular vibrations to the internal energy of the gas has been included. However, it has been implicitly assumed that the equilibrium distribution of energy between vibrations and other degrees of freedom exists at all times. This assumption is investigated in the present section. Most of the results obtained apply to channel flow generally; but some are applicable only to a channel flow where initially thermodynamic equilibrium exists; still others apply to the situation immediately behind a shock wave, before the gas has come to thermodynamic equilibrium. Whenever a result does not apply generally, the particular situation to which it does apply will be stated.

Two Alternative Conditions Permitting the Neglect of Vibrational Relaxation

In order to find the circumstances under which vibrational equilibrium can be assumed without introducing any significant errors, it is useful to define (see Bethe and Teller, ref. 21) a relaxation length for vibration, λ_V, which is the distance over which an initial deviation of the vibrational energy of the system from its equilibrium value will be reduced to one eth if the temperature of the gas does not change. This quantity is the exact analog to the chemical relaxation length λ defined in equations (7) and (8); λ gives the distance over which an initial deviation in x from its equilibrium value will be reduced to one eth, if the density and temperature of the gas remain constant.

With this definition one can state in a quantitative way that vibrational equilibrium can always be assumed, if the vibrational relaxation happens sufficiently fast. Roughly, "sufficiently fast" means:

$$\frac{\tau_V}{\tau} = \frac{\lambda_V}{\lambda} << 1, \quad \frac{\lambda_V}{L_V} << 1 \text{ everywhere} \tag{32}$$

Here L_V is the distance over which the equilibrium vibrational energy changes to one eth of its original value. If in (32), much less than is replaced by much greater than, one has a sufficient condition permitting one to regard the vibrations as frozen. The more precise conditions, including cumulative effect, will not be discussed because for the present purpose only simple estimates based on (32) are required. These cumulative effects are analogous to those discussed in connection with chemical relaxation. The first of the conditions (32), $\tau_V/\tau << 1$, states that the time scale of vibrational relaxation is so short compared to the chemical relaxation that, when initially both are out of equilibrium, the vibrations will already be adjusted before the chemical concentrations change significantly. The second statement says that vibrations will stay near equilibrium if the equilibrium position does not move away faster than the system's rate of approach to equilibrium.

Short relaxation times for vibrations provide a sufficient condition permitting the neglect of the effects of relaxation; but it is not a necessary condition. This becomes clear if one considers low temperatures where vibrational relaxation times become very long; yet one can usually regard the flow as being in vibrational equilibrium simply because the fraction of the molecular energy tied up in vibrations is so minute, that whether vibrations relax rapidly or slowly will have no significant effect on the flow. Thus there exists a different, also sufficient but not necessary, condition allowing the neglect of vibrational relaxation which expresses the requirement that the amount of energy tied up in vibrations is sufficiently small:

$$\frac{\Delta E_V}{\Delta H} << 1 \tag{33}$$

Here ΔE_V is the change of vibrational energy for the case of vanishing vibrational relaxation time. The quantities ΔE_V and ΔH are the changes of E_V and H along a streamtube. When the condition (33) is satisfied, it is quite inconsequential whether the vibrations are treated as frozen or as being in equilibrium. (The basis for the condition (33) is given in Appendix C.)

In the remainder of this section these two conditions, (32) and (33), are discussed in further detail; numerical estimates are made of the required quantities and applied to practical situations.

The useful concept of "vibrational temperature" will be employed. It is defined in the following way:

When there exists thermodynamic equilibrium, the vibrational energy per diatomic molecule is related to the temperature by

$$\epsilon_V(T) = \frac{h\nu}{e^{h\nu/kT}-1}$$

where h is Planck's constant and ν is the vibrational frequency of the molecule. In a nonequilibrium situation this relation between vibrational energy and temperature will not hold, but one can always find a number T_V such that

$$\epsilon_V = \frac{h\nu}{e^{h\nu/kT_V}-1}$$

It has been shown by Rubin, Shuler, and Montroll (refs. 25 and 26) that for all the cases of interest here,[4] the vibrational energy will be divided among the molecules according to a Boltzmann distribution, where T_V plays the role of the temperature. Thus during the time when vibrational relaxation is occurring, the gas is correctly regarded as two systems (vibrations and the other degrees of freedom) in contact, each having a different temperature (T_V and T, respectively); T_V is called the vibrational temperature.

[4]More exactly, the situation considered by these authors is that of a system of harmonic oscillators which initially have a Boltzmann distribution corresponding to a temperature T_0, and which are contained in an excess of inert gas acting as a heat reservoir of temperature T. It is then proved that as time proceeds the system of oscillators continues to have a Boltzmann distribution, the temperature of which is the T_V defined above. The coupling between the chemical reaction and vibrations may cause deviations from the Boltzmann distribution.

Numerical Values of Relaxation Times

In the considerations concerning chemical relaxation behind shock waves, it was assumed by earlier authors (refs. 12 and 21) that the vibrational relaxation times are short compared to chemical relaxation times. Recent experimental evidence (refs. 10, 27, and 28), however, seems to indicate that at high Mach numbers chemical equilibrium of oxygen is achieved before the vibrations have become active, so that condition (32) is not satisfied.

Perhaps an intuitive reason for the earlier assumption is that an energy exchange between molecules sufficient to cause dissociation is much less likely than the small energy exchange required to produce vibrational excitation, and thus the time of relaxation must be longer. Here it must be remembered that the transition probability from O_2 molecule plus M to two O atoms plus M is proportional to the density of final states, and this density is large for three free atoms, whose energies and momenta are not quantized. Furthermore, to achieve a vibrational state with energy $nh\nu$ from the ground state, it requires n collisions, each of which must transfer a quantum $h\nu$ of energy to the molecule in question; it requires more such collisions if the molecule loses some of its vibrational energy in between. However, dissociation may occur in one step, although its probability is expected to be higher if the molecule is in a high vibrational state already (see refs. 27 and 29).

Numerical values for vibrational relaxation times were calculated by using the harmonic oscillator model (following Bethe and Teller) for vibrations, and the transition probabilities based on the rather satisfactory theory of Schwartz and Herzfeld (refs. 30 and 31). Blackman's experimental data were used to estimate collision diameters (see ref. 32).

To make some numerical estimates of chemical relaxation times in air, equation (8) is used together with the recombination rate constant given by equation (21). Above 6000° K it is found that the chemical relaxation times are the same immediately behind the shock wave ($x = 0$, dissociation) and during the subsequent expansion process ($x \gtrsim x_e$, recombination). At the lower temperatures there is some dependence on x. Thus for 5000° K and lower temperatures two values are given, the value for $x = 0$ and the one for $x = x_e$, the latter being put in parentheses. The chemical relaxation times are also expected to be different if the vibrations are frozen in instead of being in equilibrium. Both cases are tabulated in adjacent columns below and shown in figure 8.

T, °K	ρ	$(\tau p)_{O_2}$ chemical reaction		$(\tau p)_{O_2}$ vibrations	$(\tau p)_{N_2}$ vibrations
		Vibrations frozen at $T_v << 2300°$ K	Vibrations active		
3,000	10	7.7 (3.7)	8.1 (4.1)	1.2	40
3,000	.01	330 (125)	330 (125)	1.2	40
4,000	10	.90 (.45)	1.38 (.69)	.29	16.5
4,000	.01	12 (10)	25 (20)	.29	16.5
5,000	10	.27 (.18)	.45 (.30)	.17	5.6
5,000	.01	.45	1.25	.17	5.6
7,000	10	.015	.056	.15	2.2
7,000	.01	.019	.071	.15	2.2
12,000	10	.0012	.0071	.11	.57
12,000	.01	.0012	.0071	.11	.57

Note: The units for τp are microsecond atmospheres. The unit of ρ is normal atmospheric density. The quantity $(\tau p)_{vibrations}$ is independent of density or pressure, and $(\tau p)_{chemical\ reaction}$ also becomes insensitive to changes in density and pressure at the higher temperatures.

The chemical relaxation time depends on the equilibrium constant through x_e and equation (27). The frozen relaxation times were calculated with the help of a generalization for vibrational nonequilibrium of the usual concept of an equilibrium constant of the $O_2 \rightarrow 2\ O$ reaction. By definition the equilibrium constant is a ratio of concentrations or the corresponding partition functions. When the distribution over vibrational states is that corresponding to a temperature T_v rather than T, but that over other states is that corresponding to a temperature T, the natural generalization for $K_e(T)$ is:

$$K_e(T,T_v) = \frac{n_O{}^2}{n_{O_2}} = K_e(T)\ \frac{f_v(T)}{f_v(T_v)} \tag{34}$$

where $f_v(T)$ is the vibrational partition function corresponding to the temperature T:

$$f_v(T) = \left(1-e^{-h\nu/kT}\right)^{-1}$$

For vibrational equilibrium $T_v = T$, while for frozen vibrations $h\nu/kT_v >> 1$ and $f_v(T_v) = 1$. For oxygen $h\nu/k = 2300°$ K is the critical temperature, so that a vibrational temperature near ordinary room temperature leads to $f_v(T_v) = 1$. The evaluation of τ for the frozen-vibrations case also requires that some assumption be made regarding the

dependence of the recombination rate constant on T_V. The simplest, and not too unreasonable, assumption[5] is made that k_R is independent of T_V. Wigner's formula (21) is used throughout.

In figure 8 the relaxation times are plotted as a function of temperature. The nearly horizontal regions into which vibrational relaxation times fall are shaded in to point up how chemical relaxation times (based on Wigner's theory) vary in relation to the vibrations. It is seen from this figure or the table that at temperatures in the neighborhood of 5000° K, the vibrational and chemical relaxation times are of the same order of magnitude, but that at higher temperatures the chemical relaxation times are relatively much shorter, and at lower temperatures they become longer than the vibrational relaxation times. In symbols:

$$\tau/\tau_V \sim 1 \text{ , when } T \approx 5000^\circ \text{ K}$$

$$\tau/\tau_V \ll 1 \text{ , when } T \gtrsim 7000^\circ \text{ K}$$

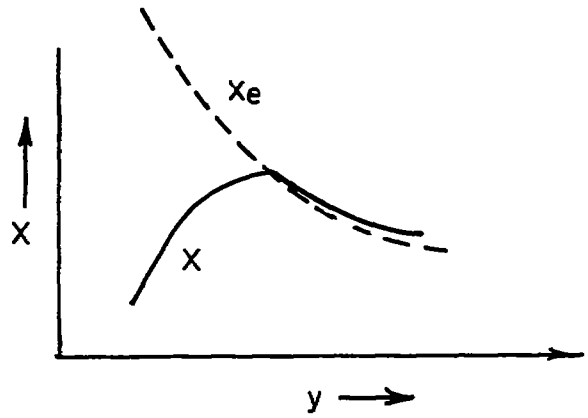
If the collision theory recombination rate used by Wood (ref. 12) is employed, one obtains still shorter chemical relaxation times. The region in which the two relaxation times are of the same order of magnitude is of special interest: It suggests the possibility of studying the coupling of the two processes. This coupling between the two simultaneous processes is sensitive to some details of the reaction mechanism, which otherwise would elude observation. For this reason further study of this coupling is considered to be of interest.

The relative numerical values of τ and τ_V have some implications for the flow immediately behind a strong shock, as well as for the flow of air around the corner of a rapidly moving blunt body. We consider the former case first.

Behind shock waves the above result, that at higher temperatures chemical relaxation times are shorter than vibrational relaxation times, appears to be borne out by the unpublished results of Resler's experiments with shock tubes (ref. 28) and also in line with corresponding experimental results for the dissociation of nitrogen obtained by the use of strong shock waves (refs. 27 and 29). Both the vibrational and chemical relaxation produce rapid cooling of the (translational temperature of the) gas and consequently a rapidly sinking equilibrium value for the degree of dissociation x_e and an increasing chemical relaxation time. As is suggested in the sketch, it is possible that x does not increase monatonically behind the shock wave but reaches a maximum and then decreases. This occurs as follows: At first the rate of approach to chemical equilibrium (eq. (7)) is rapid because it is proportional to $(x-x_e)$ and because the temperature is high. As the reaction absorbs some of the thermal energy, the quantities x and x_e approach each other.

[5]The only such dependence on T_V would arise if the third body in a triple collision were a molecule and its internal motion made it a better or worse energy absorber.

If the vibrational relaxation time is relatively long, the vibrations will absorb thermal (i.e., random translational and rotational) energy, even after x and x_e are very close to each other, and cause a continuing temperature decrease and decrease of x_e. This permits the two curves $x(y)$ and $x_e(y)$ to intersect with a resulting maximum in $x(y)$. The experiments of Resler indicate such a maximum.



Now in the expansion process, such as the channel flow considered here (see also ref. 8), the situation differs from the flow behind the shock in that vibrations are initially overexcited and the gas overdissociated, while the other extreme occurs immediately behind the shock. In the analysis of this expansion in the earlier part of this paper it was assumed that the vibrations are in equilibrium throughout the flow. Yet, since τ_V is not small compared to τ, clearly the condition (32) is <u>not</u> satisfied. The justification for neglecting vibrational relaxation must then be based on the condition (33) that the vibrational energy is sufficiently small.

Application of the Sufficiently Small Vibrational Energy Condition

In Appendix C it is shown that a practically equivalent way of stating the condition (33), that the change of vibrational energy be small compared to the change in enthalpy, is:

$$\eta \equiv \left| \frac{\Delta\epsilon_V}{\frac{7}{2} k\Delta T + \frac{D}{5} \Delta x} \right| << 1 \tag{35}$$

This condition states that the change of vibrational energy is small compared to other changes in the enthalpy.

For the special case of flow <u>immediately behind a shock wave</u>, the vibrational energy is initially zero, so that $\Delta\epsilon_V = \epsilon_V$ is the total energy per molecule received by the vibrational mode. From the analysis of Bethe and Teller it is known that the temperature behind a shock decreases, giving energy to the vibrations and the reaction. This exchange of energy would make $\eta = 1$, so that condition (35) is certainly not fulfilled. Actually η is usually even larger than unity because the slowing down of the flow behind the shock front reduces the decrease in thermal energy (ΔT) which would otherwise occur.

It is quite different in the one-dimensional channel flow in which one has vibrational equilibrium initially. In this case $\Delta\epsilon_v \approx k\Delta T_v \leqq k\Delta T$. The equality pertains when there is no vibrational lag, so that $\Delta T_v = \Delta T$. For oxygen $D/5k \approx 12{,}000^\circ$ K; the condition (35) becomes

$$\frac{1}{\eta} = \frac{7}{2} + 12{,}000\,\frac{\Delta x}{\Delta T} >> 1$$

In the particular example shown in figures 2 through 7, one sees from the graphs that $\Delta x/\Delta T \sim 1/5000^\circ$ K; hence $1/\eta \sim 5$ and the condition (35) is fairly well satisfied.

A simple estimate of the enthalpy in this example indicates that the failure to consider finite vibrational relaxation times causes one to overestimate the changes in enthalpy by about 1 or 2 percent. From equation (25) it then follows that the flow velocity changes a little more slowly than in the equilibrium case; the corresponding changes in the other flow variables can be easily obtained from equations (23) to (27). The changes are so small that they could hardly show up on figures 2 through 7.

CONCLUDING REMARKS

In conclusion we summarize the status of the problem of one-dimensional channel flow in the presence of recombination and dissociation.

In principle, one only has to know the rate constant $k_R(T)$, and one can, by numerical means, integrate forward the exact rate equation together with the flow equation, and all variables of interest will be given by the solution (see eqs. (22) to (27)). If another reaction is occurring simultaneously, another variable will be introduced, analogous to the mass fraction of oxygen in atomic form used for the dissociation-recombination reaction, and an additional equation must be considered.

The simultaneous numerical evaluation of the flow and the rate of reaction is not necessary if the deviation from local chemical equilibrium is not large. In this case one can compute the relaxation length (see eq. (8)) from the infinite rate approximation for the flow; then the solution for the mass fraction of oxygen dissociated takes on a relatively simple form, permitting numerical evaluation of the lag of atomic oxygen concentration behind equilibrium. This lag leads to readily computed modifications of the flow variables. One can express the amount of lag in terms of a parameter, whose numerical value identifies a flow which is essentially frozen or essentially in equilibrium. The chemical aspect of flow around a large body at low densities may be simulated by increasing density and decreasing size.

In particular it is noted that the shape of streamtubes, for given initial conditions, will be a function of the amount of lag behind chemical equilibrium. When the equations are applied to flow similar to that in a streamtube beginning near the stagnation region of a bluff body and leading around the body, it becomes apparent that the contraction of the streamtube in the sonic region is considerably greater when the reaction rate is very fast than when it is very slow.

In experiments involving flow, the rate constant $k_R(T)$ is not observed directly, but rather the relaxation length. This length depends not only on the temperature but also on local density, flow velocity, and extent of dissociation. Thus it requires a measurement of several quantities to determine the function $k_R(T)$ at one temperature. Until further experimental data become available, however, Wigner's theory of the recombination process is regarded as the best basis for estimating a rate constant. Collision theory fails to consider some important physical features of the recombination process. The Eyring theory contributes information about the relative reaction rates for oxygen in an inert gas atmosphere compared to oxygen in an atmosphere of nitrogen molecules.

It is not generally permissible to regard the vibrational relaxation as fast compared to chemical relaxation. In fact the present calculations indicate that at high temperatures the rate of dissociation adjustment of oxygen is greater than the rate of vibrational adjustment. However, even when vibrational relaxation is relatively slow, it may turn out to be entirely negligible because the energy involved in vibrations is small. The study of the coupling of the two relaxation times, when they are of the same order of magnitude, holds promise in yielding information about the reaction mechanism.

Ames Aeronautical Laboratory
National Advisory Committee for Aeronautics
Moffett Field, Calif., Sept. 10, 1957

APPENDIX A

THE SOLUTION OF EQUATION (7)

To prove that equation (10) in the text,

$$x(y) = x_\infty(y) + e^{-S(y)}[x(0)-x_\infty(y)] + e^{-S(y)}\int_{x_\infty(y)}^{x_\infty(0)} e^{S^*}dx_\infty'$$

is the solution of the linearized form of equation (7):

The standard form of the solution of the linear first-order equation (7) is

$$x(y) = e^{-S(y)}\left[\int_0^y \frac{x_\infty}{\lambda_\infty} e^{S(y')}dy' + x(0)\right] \tag{A1}$$

From the definition of S, one has

$$\int_0^y \frac{x_\infty}{\lambda_\infty} e^{S(y')}dy' = \int_0^y x_\infty \frac{dS}{dy'} e^S dy' = \int_{x_\infty(0)}^{x_\infty(y)} x_\infty' e^{S^*} \frac{dS^*}{dx_\infty'} dx_\infty'$$

$$= \int_{x_\infty(0)}^{x_\infty(y)} \left[\frac{d}{dx_\infty}(x_\infty e^{S^*}) - e^{S^*}\right] dx_\infty' = e^S x_\infty - x_\infty(0) + \int_{x_\infty(y)}^{x_\infty(0)} e^{S^*}dx_\infty'$$

Putting this result into equation (A1) gives equation (10).

APPENDIX B

CORRECTIONS TO COLLISION THEORY

The efficiency of a triple collision, Γ, is not, in general, a constant. A crude estimate of this quantity (ignoring the steric factor) might be made as follows: A triple collision is successful if the initial velocities of the three particles are such as to lead to a final state in which the two oxygen atoms are bound:

$$\frac{1}{2}\left(\frac{m_o}{2}\right) v'^2_{relative} < V(r) \tag{B1}$$

The prime indicates final velocities. This condition on the velocities depends on r, the distance of the two oxygen atoms when the triple collision is occurring. To simplify things we note $\overline{v^2_{relative}} = 2\overline{v_1^2}$ and replace (B1) by:

$$\frac{1}{2} m_o v_1'^2 < V(r) \tag{B2}$$

The proposed model for the recombination process is then as follows: Oxygen atoms 1 and 3 are in collision (i.e., they are within a diameter of each other). A foreign atom, 2, collides with 1 and reduces its velocity so as to satisfy (B2). We ask what fraction of triple collisions satisfy (B2).

When it enters the potential field, particle 1 will increase its kinetic energy by the amount V so the number which "while in collision" have a velocity squared between $v_1^2 + 2V/m_1$ and $v_1^2 + 2V/m_1 + dv_1^2$ is:

$$f\left(\frac{m_1}{2} v_1^2 + V\right) dv_1^2 = \left(\frac{m_1}{2\pi kT}\right)^{3/2} e^{-\frac{m_1 v_1^2}{2kT}} \frac{v_1}{2} dv_1^2$$

At any one time the number in collision in a given velocity range is proportional to the duration of collision which varies as $1/\sqrt{v_1^2 + 2V/m} \cong 1/v_1$. This approximation is evidently best when $V/kT << 1$. If the center of mass of 1 and 2 is assumed at rest then the relative frequency of triple collision of different velocities $\vec{v_3}$ is $(m_3/2\pi kT)\,|v_3|\,e^{-m_3 v_3^2/2kT}\,d\vec{v_3}$. So finally we have for the average effectiveness of a triple collision:

$$\Gamma(r) \cong \frac{\iint_{v_1'^2 < \frac{2V}{m_1}} v_3 e^{-\frac{m_3 v_3^2}{2kT} - \frac{m_1 v_1^2}{2kT}} d\vec{v_3}\, dv_1^2}{\iint_{\text{all velocities}} v_3 e^{-\frac{m_3 v_3^2}{2kT} - \frac{m_1 v_1^2}{2kT}} d\vec{v_3}\, dv_1^2}$$

For simplicity we take $m_1 = m_2 = m$, and then $v_1'^2 + v_3'^2 = \left(v_1^2 + \frac{2V}{m}\right) + v_3^2$. To avoid the integration over angles we simply take $v_1'^2 \cong \frac{1}{2}\left[\left(v_1^2 + \frac{2V}{m}\right) + v_3^2\right]$. Then the integrations are elementary giving:

$$\Gamma(r) = 1 - e^{-\frac{V}{kT}}\left[1 + \frac{V}{kT} + \frac{1}{2}\left(\frac{V}{kT}\right)^2\right] \tag{B3}$$

When even in the tail of the potential V/kT is greater than or of the order of unity, the effective size of the molecule decreases with rising temperature, because collisions taking place in the long Van der Waal tail of the potential curve will make an important contribution to the total number of successful reactions. To make some estimate of this effect, we note from equation (B3) that Γ is a decreasing function as $|V(r)|$ decreases. Now let us count only those triple collisions occurring within a radius such that on the average (over velocity) they have at least a probability $\Gamma[V(r)/kT] = 1/n$ of succeeding. For example, let us choose n such that in the region of interest, Γ can be approximated by some power law with an exponent s. Noting that the form of the potential for large r is $V(r) = -c/r^6$, giving a maximum

$$r = r_{max} \sim \left(\frac{1}{n}\right)^{1/s}\left(\frac{c}{kT}\right)^{1/6}$$

then the diameter $\sim r_{max} \sim (c/kT)^{1/6}$. As the diameter enters into the expression for k_R cubed, the effect of an increasing diameter is to introduce a factor $\sqrt{c/kT}$.

APPENDIX C

ANALYSIS OF CONDITION (33) FOR NEGLECTING VIBRATIONAL RELAXATION

Generally one must look at all the flow equations, (22) to (27), to see the effect of vibrational disequilibrium. In a formal way these equations are unchanged, although an equation for the rate of change of vibrational energy (E_V) would have to be added. However the internal energy and thus the enthalpy H (eq. (25)) become a function of the amount of vibrational energy E_V and similarly the equilibrium constant K_e (eq. (27)) will now depend both on T and E_V, and finally the chemical relaxation length λ (eq. (22)) will depend on E_V.

It is stated in the text that if the condition $\Delta E_V/\Delta H << 1$ (eq. (33)) is satisfied, the effects of vibrational disequilibrium are unimportant. The quantity ΔE_V is the change of vibrational energy assuming no vibrational lag, thus giving an upper limit to the change in E_V. We wish to show how this condition assures that neither H nor K_e nor λ is importantly modified:

That the modification of H is negligible is explicit in the condition (33) and needs no further discussion. The necessary modification of K_e is expressed by equation (34) (i.e., $K_e(T)$ is replaced by $K_e(T, T_V)$). These two numbers are significantly different only when $f_V(T_V)$ and $f_V(T)$ are very different and, consequently, ΔE_V is large and the inequality (33) cannot be fulfilled. (When one has a large temperature gradient, ΔH can become quite large, but ΔE_V will increase proportionally.)

From equations (27) and (8) it is seen that the inverse chemical relaxation length is approximately linear in K_e and also depends on ρ, T, and u. The modifications required of ρ, T, and u to account for vibrational lag can be shown to be proportional to the modification in H. Thus if condition (33) is satisfied, neither K_e nor ρ, T, or u are much changed due to the finite vibrational relaxation time, and therefore $1/\lambda$ is not much changed either.

Having pointed out that (33) is indeed a sufficient condition, we now show that condition (35) is practically equivalent to (33): For a dissociating diatomic gas A_2 of molecular weight M_{A_2} of which a fraction $\chi \equiv n_A/n_A+2n_{A_2}$ is in atomic form, the internal energy consists of random translational motion $[E_T = 3/2\ RT/M_{A_2}(1+\chi)]$, rotational energy $[E_R = RT/M_{A_2}(1-\chi)]$, vibrational energy $[E_V = N/M_{A_2}(1-\chi)\epsilon]$, energy due to dissociation $[E_D = (ND/M_{A_2})\chi]$, and electronic energy E_{el}. One then obtains the following expression for the enthalpy per unit mass H by making use of the equation of state of the gas:

$$\left.\begin{aligned} H &= E + \frac{p}{\rho} \\ &= E_T + E_R + E_v + E_D + E_{el} + (1+x)\frac{RT}{M_{A_2}} \\ &= \frac{N}{M_{A_2}}(1-x)\epsilon_v + \frac{RT}{M_{A_2}}\left(\frac{7+3x}{2}\right) + \frac{ND}{M_{A_2}}x + E_{el} \end{aligned}\right\} \quad (C1)$$

The expression (C1) does <u>not</u> assume either chemical or vibrational equilibrium. We make one simplifying assumption, namely, that changes in electronic excitation do not occur. This is certainly a good approximation at low temperatures, but the assumption must be dropped at very high temperatures. The characteristic temperatures (which appear in the Boltzmann factor) are 22,710° K and 27,610° K for atomic oxygen and nitrogen, respectively, while for molecular oxygen and nitrogen they are 11,340° K and 71,580° K. For air, if the nitrogen is undissociated but a fraction x of the oxygen is dissociated, then

$$x \approx \left(1 + \frac{n_{N_2}}{n_{O_2} + \frac{n_O}{2}}\right)x \approx 5x$$

Now we have from equation (C1)

$$\frac{\Delta E_v}{\Delta H} \approx \frac{1}{1 + \dfrac{\frac{7}{2}k\Delta T + \frac{D}{5}\Delta x}{\Delta\epsilon_v}} \qquad (C2)$$

It is evident from equation (C2) that the condition $\Delta E_v/\Delta H << 1$ is equivalent to $\left|\dfrac{\Delta\epsilon_v}{\frac{7}{2}k\Delta T + \frac{D}{5}\Delta x}\right| << 1$. This is the condition (35) that was to be derived.

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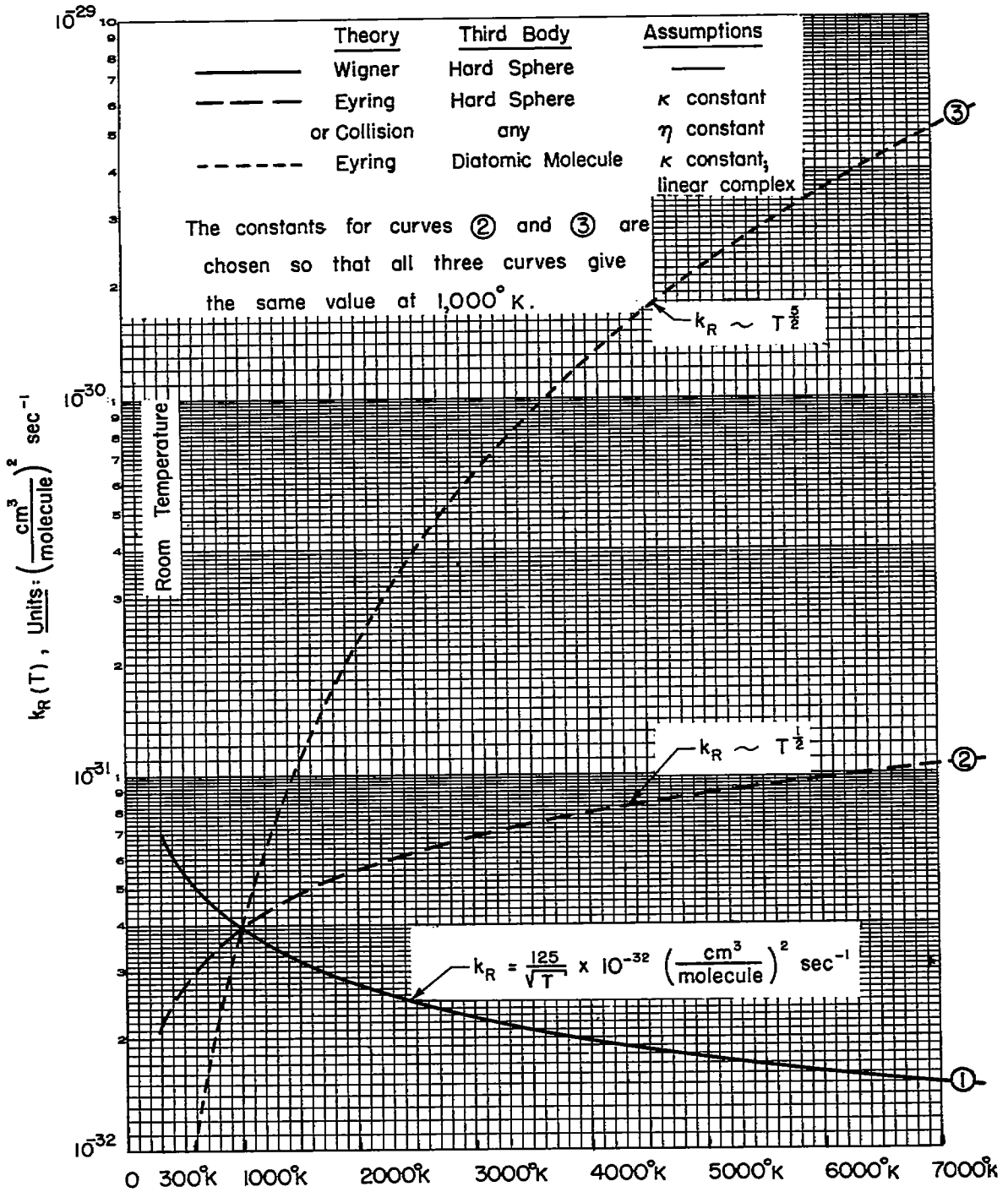

Figure 1.- Temperature dependence of the recombination rate by different theories.

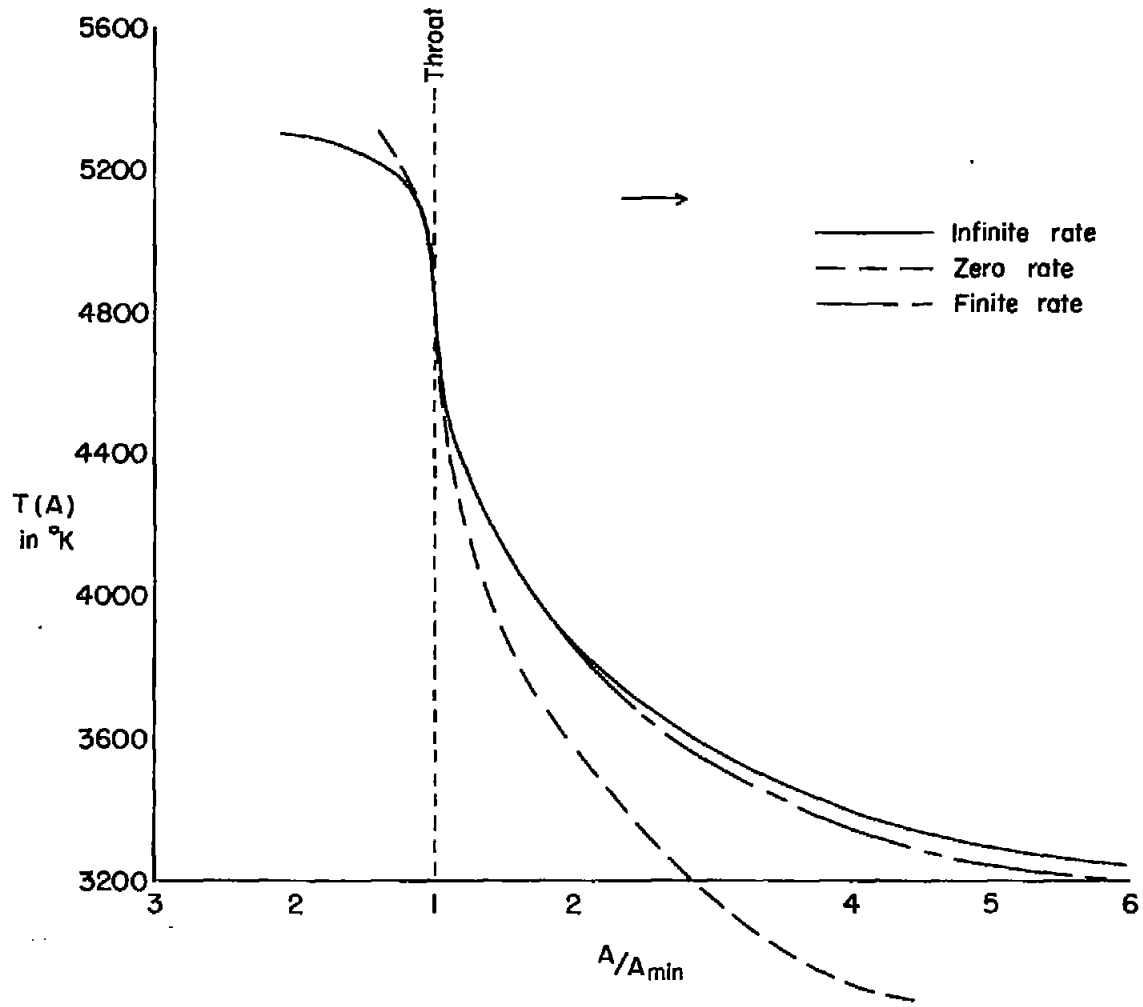

Figure 2.- Temperature variation of air flowing through a converging-diverging channel with oxygen recombination.

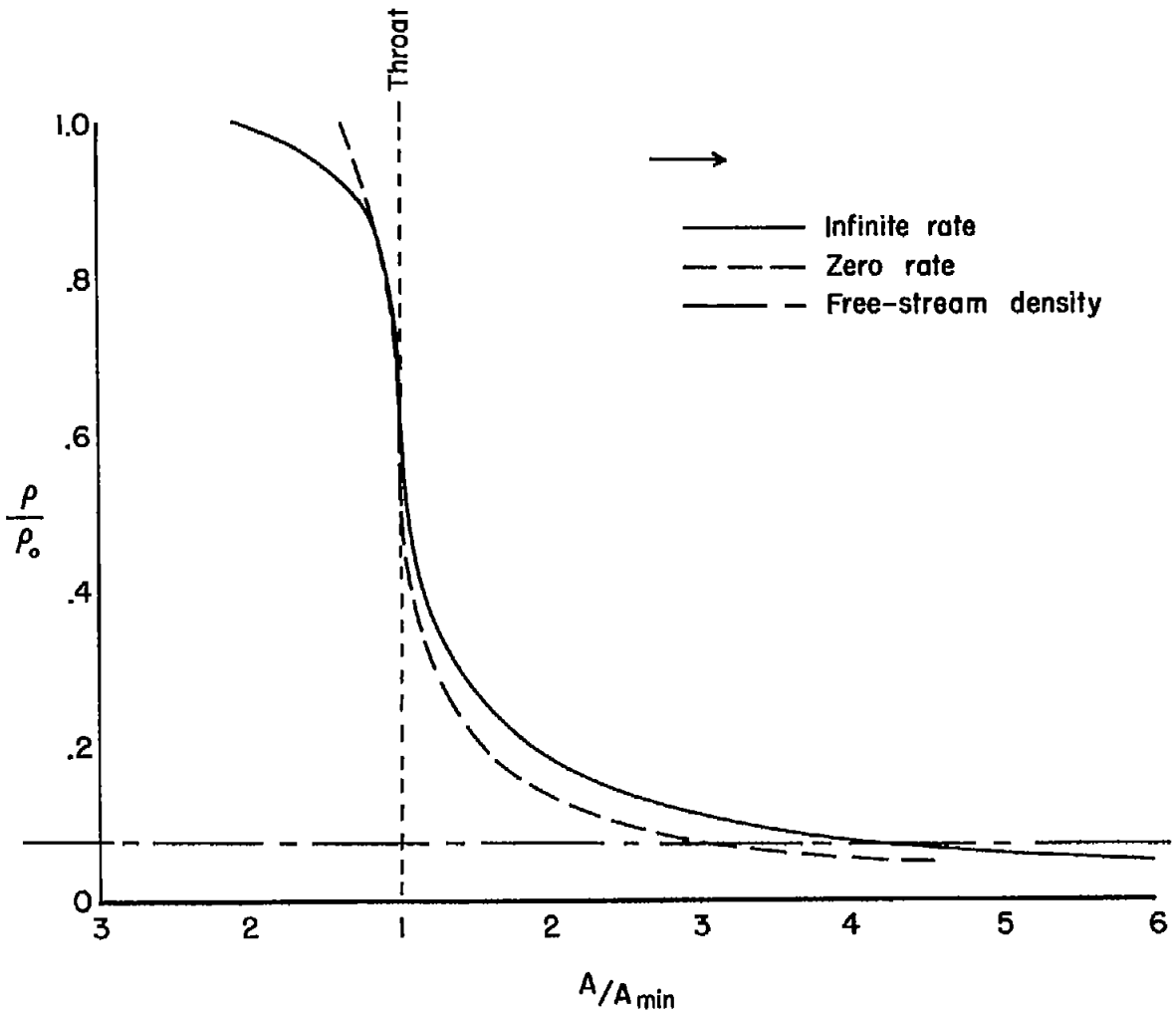

Figure 3.- Density variation of air flowing through a converging-diverging channel with oxygen recombination.

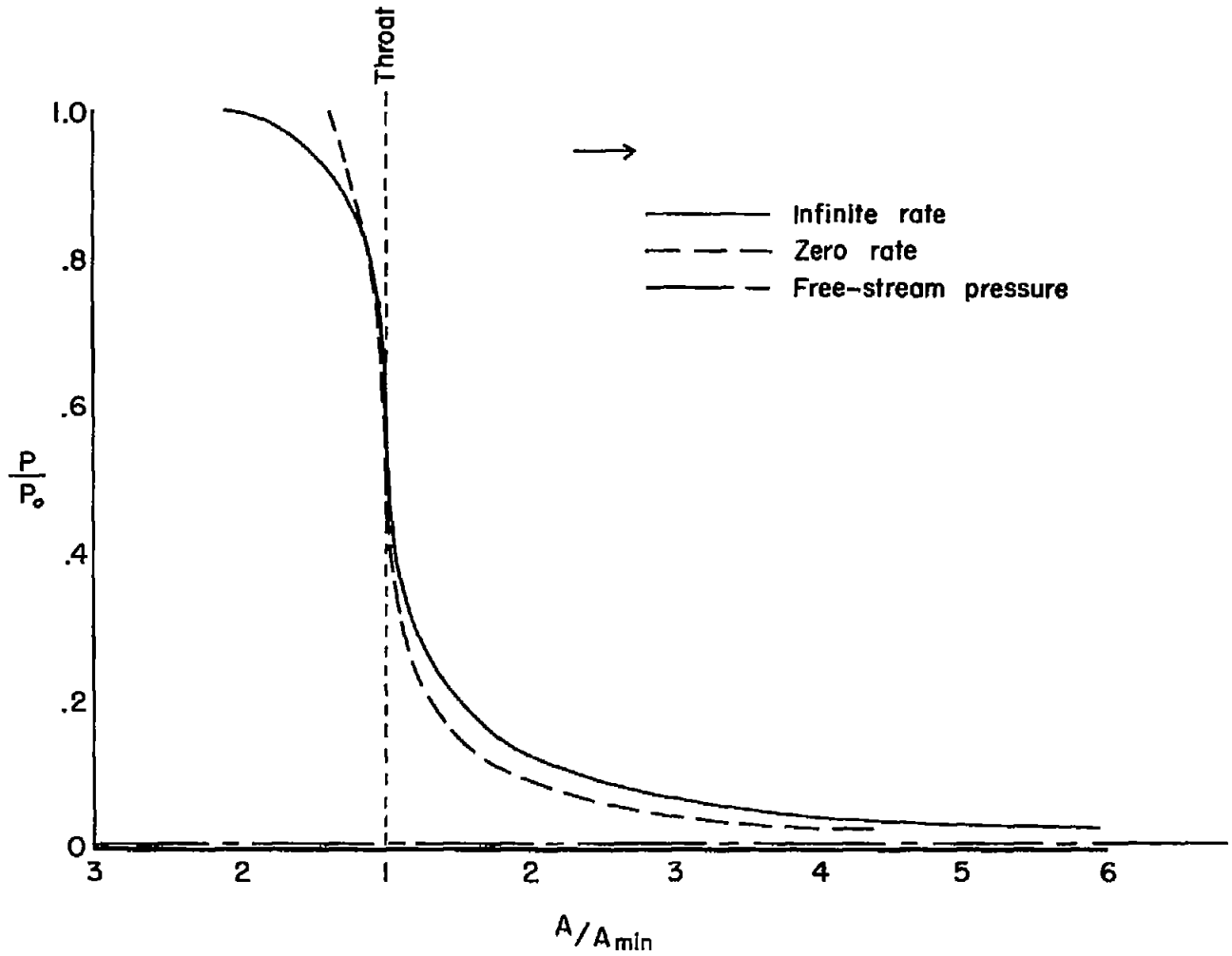

Figure 4.- Pressure variation of air flowing through a converging-diverging channel with oxygen recombination.

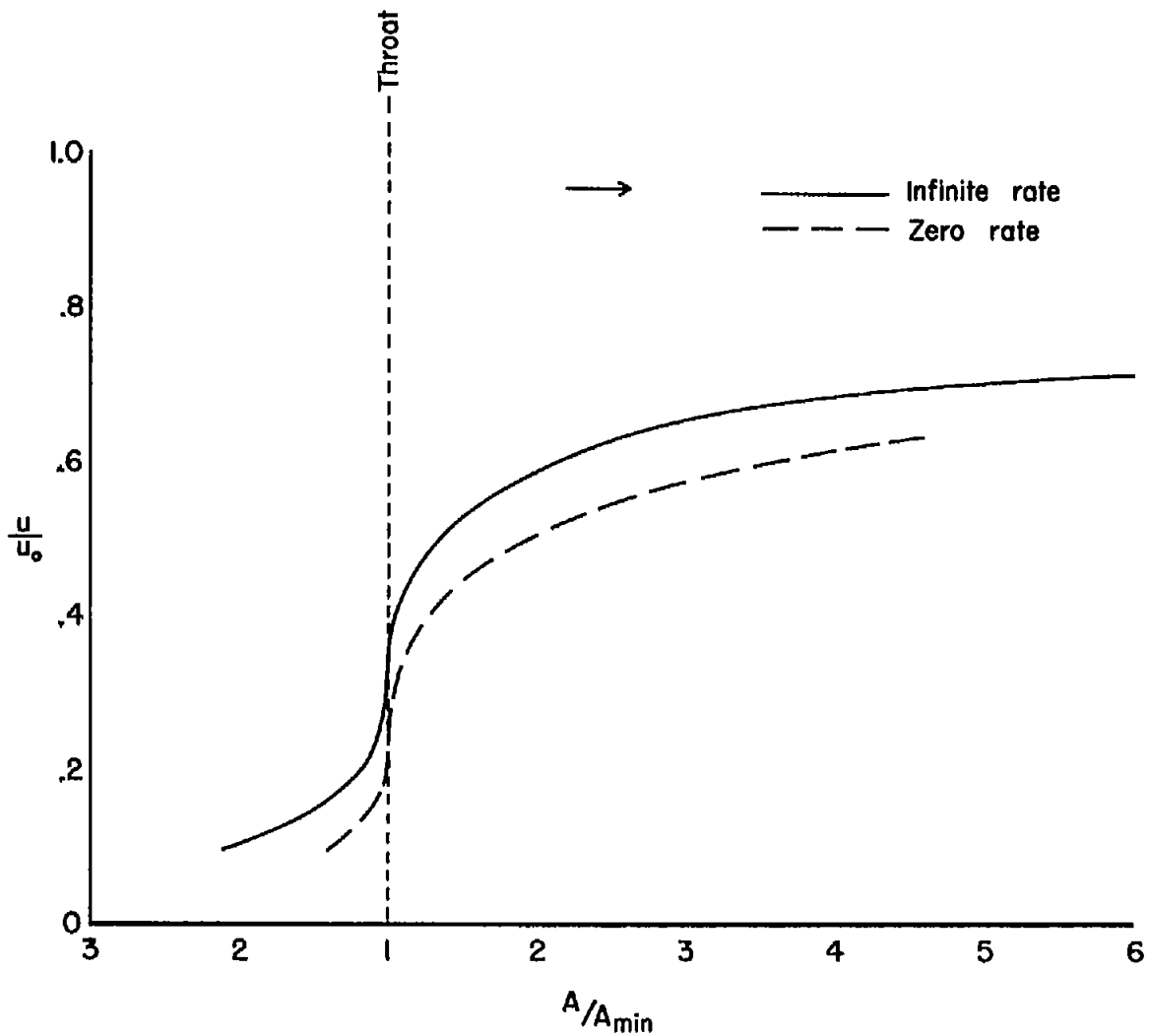

Figure 5.- Velocity variation of air flowing through a converging-diverging channel with oxygen recombination.

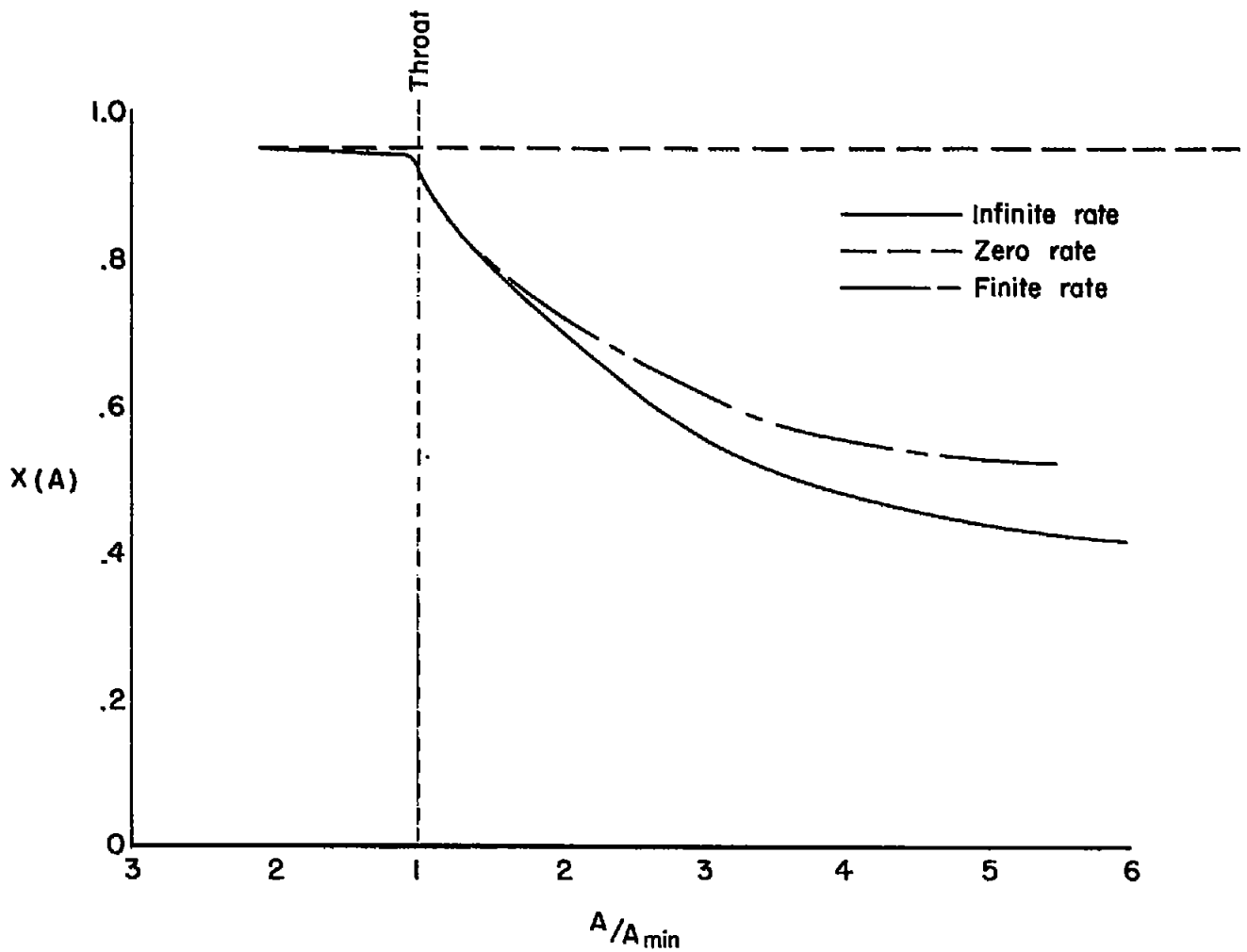

Figure 6.- Degree of oxygen dissociation of air flowing through a converging-diverging channel with the shape given by equation (31).

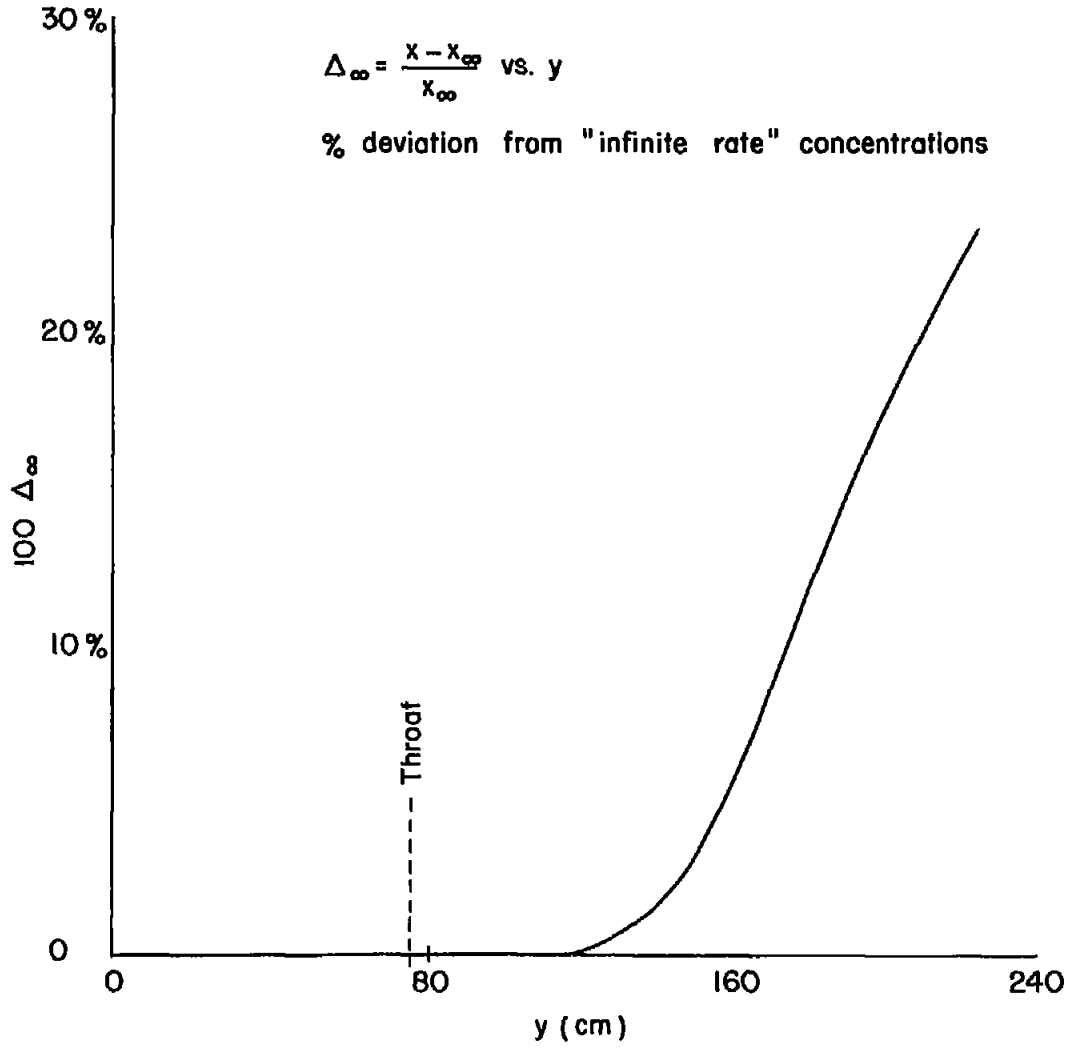

Figure 7.- Lag of degree of oxygen dissociation behind its equilibrium value for air flowing through a converging-diverging nozzle with the shape given by equation (31).

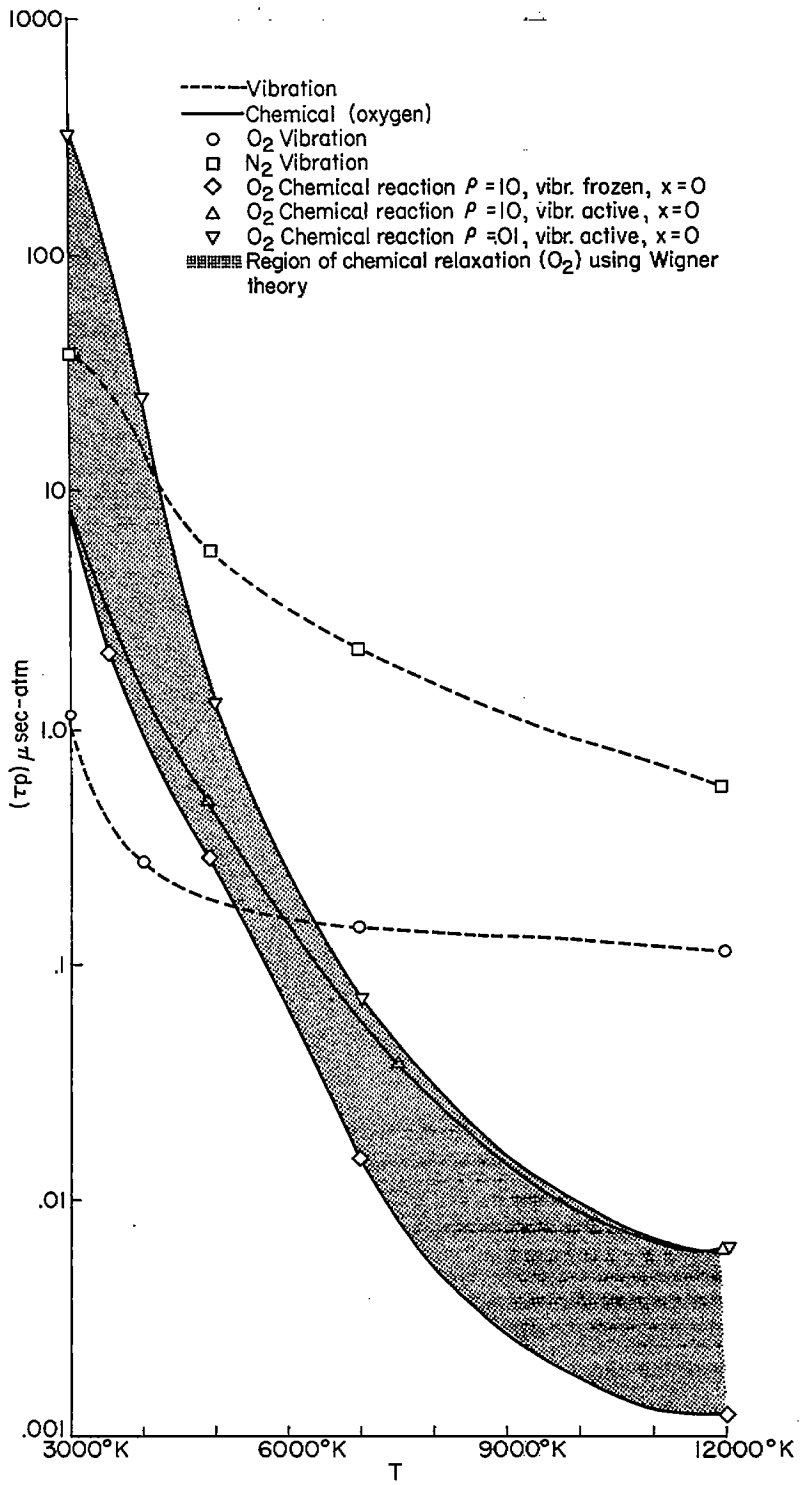

Figure 8.- Relaxation times.