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Nonequilibrium Effects in Supersonic - Nozzle Flows

by J. Gordon Hall and Charles E. Treanor

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NONEQUILIBRIUM EFFECTS IN SUPERSONIC-NOZZLE FLOWS

by

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SUMMARY

Nonequilibrium effects in supersonic-nozzle flows are important in various technical applications such as propulsion, hypersonic wind-tunnel testing, and simulation of streamtube flows occurring about a body in flight. This report discusses such effects with emphasis on surveying the research of recent years. The scope is limited to homogeneous gas-phase nozzle flows only, and to departures from thermochemical equilibrium arising from collisional relaxation of internal degrees of molecular excitation and from chemical reaction, including ionization. Translational-rotational equilibrium is assumed. Nonequilibrium phenomena due to classical viscous effects, condensation, rarefied gas-dynamic effects, radiation, and translational energy difference between free electrons and heavy particles are not discussed.

The first half of the report provides a background on the high-temperature phenomena considered, and covers equilibrium properties of gases and the basic nonequilibrium rate processes involving vibration and electronic excitation, chemical reactions of neutral species, and ionization. The last half of the report discusses the nonequilibrium effects arising from these rate processes in nozzle flow expansions. Emphasis is on diatomic gases and air, but complex mixtures for propulsion applications are also discussed. Bibliographies are included on related nonequilibrium flows, as well as on nozzle flows,

The review indicates great progress over the past decade in increased knowledge and understanding of nonequilibrium nozzle flows of technical interest. An important contribution has been made by numerical studies using high speed machine computers. However, much remains to be done as regards more certain and complete mathematical description of various physical-chemical rate processes which are important. In general, much more emphasis is now needed on basic studies, particularly on experimentation, if a significant rate of progress is to be maintained.

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RESUME

Les effets de non équilibre dans les écoulements de tuyères supersoniques sont importants dans différentes applications techniques, telles que la propulsion, les essais en soufflerie hypersonique, et la simulation des écoulements en tubes de courant qui se produisent autour d'un corps en vol. Le présent rapport étudie ces effets en tenant compte en particulier des recherches effectuées au cours de ces dernières années. Il se borne à n'examiner que les écoulements de tuyère homogènes de phase gazeuse, et les cas de non équilibre thermo-chimique dû à la détente de collision de degrés internes de l'excitation moléculaire et aux réactions chimiques, y compris l'ionisation. L'équilibre de translation et de rotation est supposé. Les phénomènes de non équilibre ayant pour origine les effets visqueux classiques, la condensation, les effets gaso-dynamiques raréfiés, le rayonnement et la différence d'énergie de translation entre les électrons libres et les particules lourdes ne sont pas traités.

La première partie du rapport, qui sert de fond pour les phénomènes étudiés, porte sur les propriétés en équilibre des gaz et les procédés fondamentaux de vitesse des réactions en non équilibre impliquant l'excitation due à des vibrations et électronique, des réactions chimiques des espèces neutres, et l'ionisation. La deuxième partie étudie les effets de non équilibre dus à ces procédés de vitesse dans des dilatations d'écoulements de tuyère. On examine surtout les gaz diatomiques et l'air, mais étudie également des mélanges complexes pour des applications à la propulsion. L'Agardographie comporte des références bibliographiques sur des écoulements en non équilibre correspondants, ainsi que sur les écoulements de tuyère.

La présente étude indique les progrès importants réalisés au cours de ces dernières dix années, et qui se traduisent par des connaissances et une compréhension améliorées des écoulements de tuyère dans des conditions de non équilibre présentant un interêt technique. Des études numériques effectuées à l'aide de calculateurs à grande vitesse ont permis d'y apporter une contribution importante. Néanmoins il reste beaucoup à faire en ce qui concerne une description plus certaine et plus complète de différents procédés de vitesse physico-chimiques qui sont importants. D'une façon générale, il faudra mettre beaucoup plus d'accent sur des études de base, en particulier sur des expérimentations, si l'on veut qu'une cadence d'avancement importante soit maintenue.

CONTENTS

NOTATION

a	sound speed; also $\tan\theta$, where θ = asymptotic half angle of nozzle
A	parameter in inter-particle potential; also cross-section area of nozzle
C'	constant in rate equation for Lighthill gas
D	dissociation energy per mole
D_0	dissociation energy per molecule, D/N_0
e_v	vibrational energy per unit mass of mixture
ϵ_j	energy of level j
h	enthalpy per unit mass of mixture; also Planck constant
k	specific reaction rate coefficient; also Boltzmann constant
K	equilibrium constant
l	$= L/a$, where $a = \tan\theta$
L	radius of nozzle throat
m	mass of an atom or molecule; also mass flow through nozzle
M	Mach number; also any species of mixture
n, N	number of particles per unit volume
N_0	number of particles per mole (6.03×10^{23})
p	gas pressure
R, R_e	intra-nuclear coordinate
R_0	universal gas constant
Re_x	free-stream unit Reynolds number
S	entropy per unit mass of mixture
t	time
T	temperature
u	gas velocity

U_∞	test-flow velocity in hypersonic wind tunnel
V	intermolecular potential
x	distance along nozzle from throat
α	mass fraction of gas in dissociated form
γ	mass concentration of species, moles/gram of mixture; also vibrational non-equilibrium parameter
ρ	gas density, mass per unit volume of mixture
ν	characteristic frequency of molecule
τ	relaxation time
μ	molecular weight
θ	half angle of conical portion of nozzle

Subscripts

i	denotes reaction i
j	denotes species j
o	denotes reservoir or stagnation condition
EQ	denotes equilibrium state
v	denotes vibrational mode
F, R	denotes forward or reverse specific rate coefficients

SECTION 1

INTRODUCTION

Over the past decade a great amount of research has been devoted to high-temperature, physical-chemical phenomena of interest in technical gasdynamics. Much of this effort has centered on nonequilibrium phenomena occurring in shock waves. However, considerable attention has also been devoted to another elementary flow of equal technical importance, namely, expansion flow as typified by flow in a supersonic nozzle. The purpose of this report is to discuss nonequilibrium phenomena in such expansion flows with emphasis on surveying the research results of recent years.

Nonequilibrium effects in nozzle flows have long been of interest in the propulsion field because of the thrust loss resulting from chemical freezing, or recombination lag, occurring in the nozzle expansion process. For example, some of the earliest theoretical studies of chemical nonequilibrium effects in nozzle flows were done around 1947 by Penner, Altman, and co-workers[1,2] in connection with rocket nozzle performance. In recent years the problem of chemical freezing in propulsive nozzles has assumed greater importance with the development of higher-performance chemical rockets, such as hydrogen-fluorine system, and the interest in development of advanced hypersonic ram jet systems[3,4].

Nozzle-flow nonequilibrium is also of much concern in connection with hypersonic wind-tunnel testing. Current test devices such as arc jets and shock tunnels utilize nozzle expansions of air from initial high-temperature conditions where the air may be highly dissociated. Usually some degree of freezing occurs in the nozzle expansion, which produces a test airflow not in an equilibrium state[5,6]. Most often this is undesirable as it complicates interpretation of test data and can prevent proper simulation.

Still a further significance of nonequilibrium nozzle flows is that the thermo-gasdynamic environment is representative of that occurring along certain streamtubes undergoing expansion about a body in hypersonic flight. Thus nozzle-flow experiments provide a means of simulating such streamtube flows directly in order to study nonequilibrium phenomena in a gasdynamic environment appropriate to the flight situation. The importance of the gasdynamic environment in this respect is emphasized by recent research results on vibrational relaxation (discussed in Section 4.3) which indicate important basic differences in vibrational behavior between shock-wave and expansion-flow environments.

Even the limitation of subject to nonequilibrium effects in nozzle expansion flows still leaves a very broad range of specific phenomena which could be discussed. The present scope is arbitrarily limited to consideration of homogeneous gas-phase flows only, and to departures from the thermochemical equilibrium arising from the collisional relaxation of internal degrees of molecular excitation and from chemical reaction, including ionization. However, translational and rotational degrees of freedom are assumed to be in local (Maxwell-Boltzmann) equilibrium. Thus only inviscid nozzle flows in the gas-phase continuum regime are considered, and nonequilibrium phenomena associated with classical viscous effects, condensation, rarefied gasdynamic effects, radiation, and energy balance between free electrons and heavy particles are not discussed.

The organization of the material covered is as follows. Section 2 reviews the methods available for calculating the equilibrium properties of gases at high temperatures. Section 3 discusses the basic rate processes of interest, which concern vibration and electronic excitation, chemical reactions and neutral species, and ionization. Finally, Section 4 considers nonequilibrium effects arising from such rate processes in nozzle flow expansions. While the emphasis is placed on flows of diatomic gases and air, nozzle flows of complex mixtures of interest in propulsion applications are also discussed.

For each section, the pertinent auxiliary material of tables, figures, and a combined bibliography and reference list are located at the end of the section. The combined bibliography and reference lists are organized under several appropriate subheadings as a convenience for bibliographic usage. Although plane shock-wave flows, and two- or three-dimensional inviscid flows are generally not discussed, bibliographies covering nonequilibrium effects in these two classes of flows are included as Appendices A and B.

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SECTION 2

REVIEW OF THERMODYNAMICS AND STATISTICAL MECHANICS OF GASES

There are several separate aspects of high-temperature gas-flow problems that require the accurate description of the thermodynamic state of the gas and which require a detailed knowledge of its molecular and atomic structure. Foremost is the proper description of the internal energy of the gas under these conditions where the assumption of a constant specific heat can no longer be used. This assumption begins to fail appreciably for air at about 1000°K, when vibrational motion of the oxygen molecule becomes important. At higher temperatures, when molecular dissociation and ionization become involved, these chemical reactions supply the primary contributions to the internal energy (Figure 2-1). A similar motivation is the effect the chemical reactions have on the equation of state of the gas simply because of the change in the total number of particles (i.e. the number of moles of gas). Of further importance is the increase of chemical activity of the air due to the atomic gases that are present, and the increase in electrical conductivity from the free electrons that are produced. At very high temperatures the transfer of energy by radiative processes can be important, and can be calculated only with detailed knowledge of the population of the many excited states of the atomic and molecular constituents. For all of these reasons it was early realized that hypersonic flight would require a thorough understanding of the physical structure of the air molecules and the chemistry of their behavior at high temperatures. The resulting investigations have provided tables, graphs and computer programs to describe these equilibrium, high-temperature properties of air. The use of the shock tube to study the chemistry of other gases and the importance of ablative chemistry during reentry has motivated the calculation of high-temperature properties for a variety of gas mixtures.

The development of a consistent description of the macroscopic properties of gases from the microscopic view of atomic and molecular collisions is given in texts[1,2] on statistical mechanics. Furthermore, this development is presented within the context of the application of the final formulas to gasdynamic problems in several texts[3-6] and reports[7,8]. Within the present section it will not be attempted to repeat these derivations, but instead the concepts will be summarized very briefly in presenting the basic formulas. A more detailed discussion is then presented of the real-gas properties that have been obtained from these relations for various gas mixtures - in particular for air - and the magnitude and importance of various real-gas effects.

2.1 Equilibrium Equations for a Reacting Gas

For a given gaseous system, the equilibrium number of particles in each energy state (of molecules, atoms and ions) is determined by the number of stationary states each species possesses, the energy required to occupy each state, and the energy available to the system. As long as the density of the gas is not so great that intermolecular forces play a significant role, these properties are sufficient for the equilibrium description and are summarized for each species by the partition function[1]

$$Q_j = \left(\frac{2\pi m_j kT}{h^2}\right)^{3/2} \sum_n g_{jn} e^{-\epsilon_{jn}/kT} , \qquad (2\text{-}1)$$

where the quantities ϵ_{jn} are the energies of the stationary states of species j , corresponding to various internal potential and kinetic energies. The sum is taken over all energy levels (n), and the terms g_{jn} (the degeneracy) give the number of states with the same energy ϵ_{jn} . Each term is weighted according to the factor $e^{-\epsilon_{jn}/kT}$, proportional to the equilibrium population in that state when the energy available to the system is described by a temperature T . Then, if the energy levels and degeneracies are known for a given species, the partition function for that species can be calculated as a function of temperature. With the molecular mas m_j in grams, Boltzmann's constant k in ergs/$^{\circ}$K and Planck's constant h in erg secs, Q has units of cm^{-3}.

The fact that the energy ϵ_{jn} of any state can be written as a sum of rotational, vibrational and electronic energy permits the partition for any species to be written as a product of the separate functions for each of these degrees of freedom. The rotational partition function is given accurately as

$$Q_{rot} = \frac{T}{\sigma\theta_n} , \qquad (2\text{-}2)$$

where θ_n is the characteristic temperature for rotation for the molecule, equal to the rotational energy constant B divided by the Boltzmann constant. σ is a symmetry factor that is equal to 2 for a homonuclear diatomic molecule, 1 for a hetronuclear molecule. The vibrational partition function is given, in the simple harmonic oscillator approximation, as

$$Q_{vib.} = \frac{1}{1 - e^{-\theta_v/T}} , \qquad (2\text{-}3)$$

where θ_v is the characteristic temperature for vibration for the molecule. More accurate expressions for the vibrational-rotational partition function, taking into account the non-constant energy-level spacing of the vibrator and the coupling between rotation and vibration, are used in the tables that have been prepared for various gases. No approximate formulas are available for the electronic partition functions, so that these sums must be performed numerically.

For any chemical reaction that can occur, the species which are involved will equilibrate in a fixed proportion determined by their partition function and the energy of the chemical reaction. Thus, using the notation of Reference 3, a chemical reaction (reaction i) is specified by the equation

$$\sum_{j=1}^{s} \nu'_{ij} M_j \rightleftarrows \sum_{j=1}^{s} \nu''_{ij} M_j ; \qquad i = 1, 2, \ldots n , \qquad (2\text{-}4)$$

where there are s species and r reactions. The stoichiometric coefficients ν'_{ij} are the number of molecules of M_j on the lefthand side of the i^{th} reaction and ν''_{ij} the number on the righthand side. Then when equilibrium is attained at a given density ρ , the species concentration (γ_j in moles/gm) is given by a set of coupled algebraic equations

$$\prod_{j=1}^{s} \gamma_j^{(\nu''_{ij}-\nu'_{ij})} = \rho^{-\sum_{j=1}^{s}(\nu''_{ij}-\nu'_{ij})} K_i \; ; \qquad i = 1, 2, \ldots n \tag{2-5}$$

and by equations which describe the conservation of the nuclei of the various species and the conservation of electrical charge. The quantities K_i are the equilibrium constants, and can be calculated for any temperature from a knowledge of the appropriate partition functions through the relation

$$K_i = (R_0 T)^{-\sum_{j=1}^{s}(\nu''_{ij}-\nu'_{ij})} e^{-\sum_{j=1}^{s}(\nu''_{ij}-\nu'_{ij})\frac{D_j}{T}} \prod_{j=1}^{s}\left(\frac{Q_j}{N_0}\right)^{\nu''_{ij}-\nu'_{ij}} . \tag{2-6}$$

In this equation R_0 is the universal gas constant and N_0 is Avagadro's number. The number of species which must be included in any particular calculation will depend on the temperature range involved. For temperatures beyond about 10,000°K, multiply-ionized species can be present in appreciable quantities, and the number of equations used must be increased accordingly. Whatever the order of complexity that is required, the solution of this set of simultaneous equations permits calculation of the chemical composition of the high-temperature gas. The thermodynamic properties of the gas can then be determined by combining the expressions for the properties of the separate species in terms of their partition functions, weighted according to their abundance. The main expressions of interest for gas dynamic calculations are the equation of state and the expression for the enthalpy of the gas, which are as follows:

$$\frac{p}{p_0} = \frac{\rho}{\rho_0}\frac{T}{T_0} z \tag{2-7}$$

$$h = RT\left\{\sum_i \gamma_j T\left(\frac{\partial \log_e Q_j}{\partial T}\right)_\rho + \frac{z}{M_0}\right\} . \tag{2-8}$$

The compressibility factor z is equal to the ratio of the total number of particles to the original number. For the derivation of these and other thermodynamic expressions, reference is again made to texts, such as References 1 and 4.

2.2 Numerical Equilibrium Calculations for Gases, Especially Air

Equilibrium equations as described in the previous sections have been solved for a large number of gas mixtures, and results have been published in tabular, graphic, and curve-fit forms. The strong interest in air in the temperature range associated with ICBM reentry led to the publication of several sets of tables for oxygen, nitrogen and air. In these, equilibrium constants and gas compositions have been tabulated or graphed for various air-species reactions, using these ideal-gas assumptions for the component species. The results differ slightly depending on the method used in approximating the vibrational states, on the exact values used for the energy levels, and on the number of energy states used in the calculations of the partition functions. The effects of vibration-rotation corrections and effects of the use of slightly different spectroscopic constants are compared by Allison[26] for air and for CO_2-N_2-A_r mixtures. The most important experimental parameters that are required are the heats of formation D_j , the dissociation and ionization energies of the component species. These values have been accurately measured for the components of high-temperature air and many other gases[9,10,11].

The question of the total number of levels to use in Equation (2-1) involves the difficulty that there are an infinite number of bound states near the ionization energy, so that the sum in fact diverges. Different criteria for terminating the sum are used in different calculations[14,15,16] and the problem is discussed in some detail in Reference 6. At temperatures in the reentry range all these methods give the same results for the partition functions, and at higher temperatures they give different results only for species which are almost completely ionized[16] and therefore present in the mixture in very small abundance.

The neglect of interparticle forces (i.e., use of the ideal-gas assumption for the component species) leads to errors in the calculations at high densities. In addition to the usual virial-coefficient corrections[19,17], long-range coulombic forces become important at the high temperatures where appreciable ionization takes place[18,27]. The compressibility factor, z given in Equation (2-7), is no longer equal to the relative increase in the number of moles of gas, but includes the effects of these intermolecular forces. For nitrogen[18] at 2000°K and 10 times normal density, z is increased by 3%, and at 100 times normal, by 15%. At 15,000°K the effect is a 20% increase at 100 times normal density. Another effect of these forces is to slightly decrease the amount of dissociation and ionization, so that at some conditions of high temperature and intermediate density the effect can be to actually decrease the value of z .

The final calculation of the thermodynamic properties of a gas from equations such as (2-7) and (2-8) are relatively simple once the concentrations γ_j have been obtained. To obtain equations for the specific heats and the speed of sound requires that a second derivative of the partition functions be obtained, and the resulting formulas are lengthy, but tractable[15,16]. The equilibrium speed of sound for air is tabulated in References 15 and 28 and given graphically in the Mollier chart which accompanies Reference 23. References 24 and 25 contain these properties for oxygen and nitrogen. A Mollier diagram which includes the effect of second virial coefficients is given in Reference 29.

2.3 Methods for Equilibrium Calculations

The use of tables of thermodynamic properties provides obvious limitations in performing gas-dynamic calculations. To circumvent this difficulty it is possible to use a simplified analytic model which applies to a dissociating diatomic gas, or, in machine calculations, to use a sub-routine capable of producing the thermodynamic properties of very complicated gas mixtures.

2.3.1 Ideal Dissociating Gas

The equations for a reacting gas simplify considerably for the special case of a dissociating diatomic gas[4]. They can be simplified still further by the approximation due to Lighthill[30] that, over a broad range of temperatures, the vibrational partition function can be taken as proportional to the square root of the temperature, or

$$Q_{vib} = \frac{1}{1 - e^{-\theta_v/T}} \simeq CT^{1/2} . \qquad (2\text{-}9)$$

This is equivalent to the assumption that the vibrational mode is "half-excited", so that it contributes ½RT to the enthalpy per mole. An approximation to the equilibrium constants, Equation (2-6), can be written as

$$K_i = C_i T^{\eta_i} e^{-D_i'/kT} , \qquad (2\text{-}10)$$

where D_i' is the energy of the reaction, given in the notation of Equation (2-6) as

$$D_i' = \sum_{j=1}^{s} (\nu_{ij}'' - \nu_{ij}) D_j . \qquad (2\text{-}11)$$

The values of the constants C, η and D for the equilibrium constants for high temperature air have been given by Wray[27,4]. With the final assumption that the electronic partition function can be taken as a constant equal to the degeneracy of the ground electronic state, the equilibrium equations can be written in a much simplified form that still retain the important physical features of the dissociating gasdynamics. For this reason the Lighthill model has been used in many analytic approaches to real-gas problems.

2.3.2 Methods for Sub-Routine Use with Other Calculations

Because of the great calculation speed now available with digital computing machines, it is possible to solve numerical gasdynamic problems using sub-routines to calculate real-gas properties within the flow. Several such programs have been published in detail[31-34].

In some of the programs the enthalpy for each species is calculated by a curve-fit formula which is a polynomial in the temperature[31-33], rather than by calculating the derivatives of the partition function, as indicated in Equation (2-8). The data for the curve-fit can be obtained from the JANAF tables[10] for many chemical species. The conversion of the JANAF data for thermo-fit purposes is described in Reference 33. Other of the programs use approximate formulas for the internal partition functions and calculate the enthalpy directly. These calculations are then used as the starting point to solve for the equilibrium conditions[35,36].

Graphs of the thermodynamic properties of air and some other species are available for graphical solution of shock-wave[37] or expanding-flow[23] problems.

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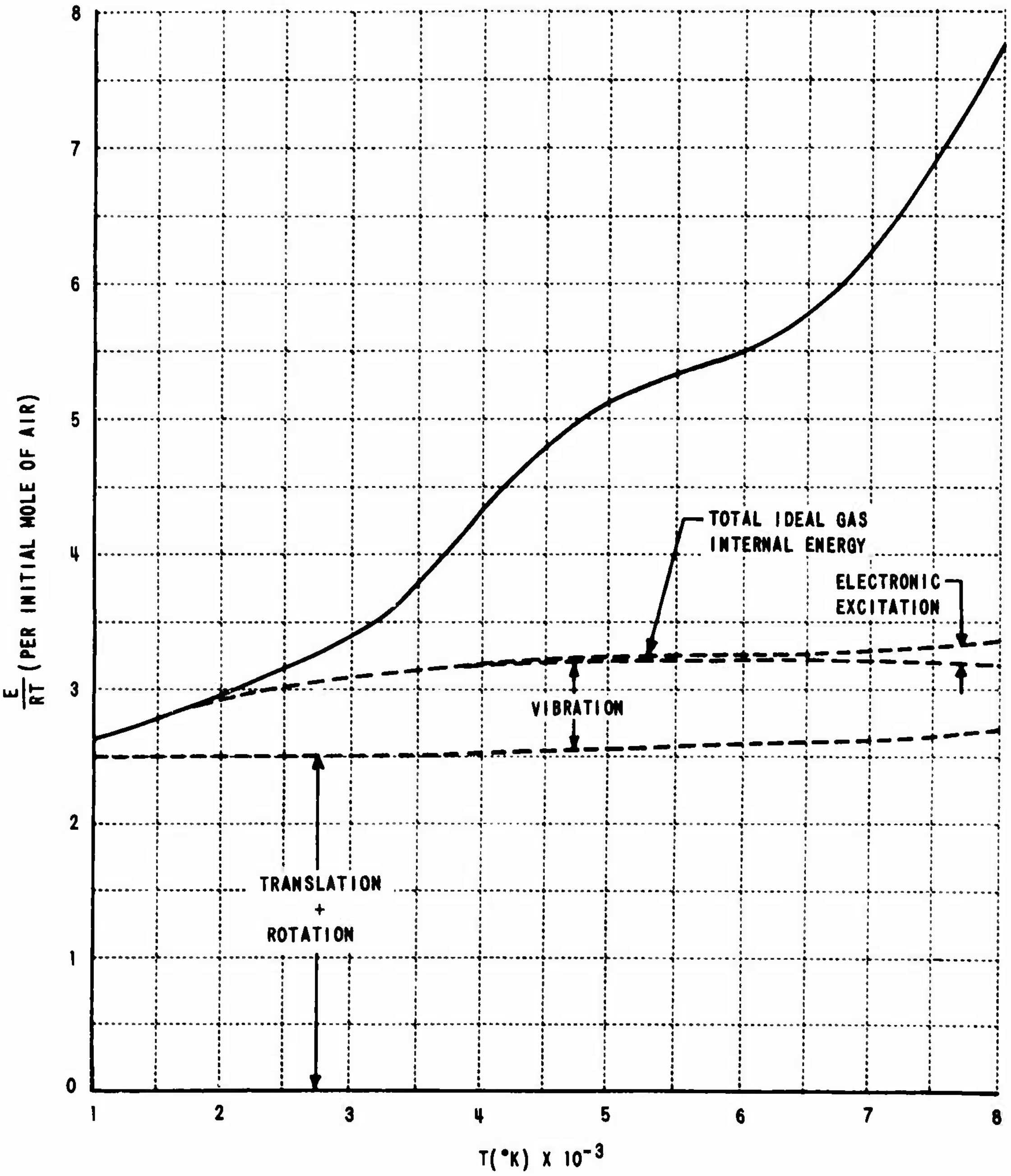

Fig. 2-1 Internal energy of air $(\rho/\rho_{STP}) = 1$

SECTION 3

BASIC NONEQUILIBRIUM RATE PROCESSES

The conventional treatment of aerodynamic problems requires the assumption that the air can be treated as a continuum, and that the state parameters vary continuously from point to point, or from time to time. It is understood, of course, that the air is composed of molecules with a distribution of velocities, and that collisions among these molecules are the *sine qua non* which change the density and temperature and other state parameters of the gas. The assumption of a continuum is the assumption that on any scale of distance or time in which there is an appreciable change in the state parameters, many of these collisions occur, so that for most of the molecules a Boltzmann distribution of velocities is always present and the state parameters can be defined at each point in the flow. The number of collisions required for this local equilibration of translational motion to be established cannot be specified exactly, but some number less than ten would suffice, since the transfer of translational energy among the molecules is an efficient process. The use of the equilibrium relations discussed in Section 2 requires a further assumption, and that is that so many of these collisions occur that *all* important chemical processes reach an equilibrium distribution. This might easily require 10^6 or more collisions, since the occurrence of many chemical processes upon collision requires special conditions - either a very energetic collision, or some special geometry of the impact, or a sequence of several processes occurring on different collisions. Thus, there are many aerodynamic problems of interest where the first assumption is satisfied, so that the flow can be treated as a continuum and a local value of the temperature can be defined, but the second assumption is violated, so that equilibrium relations among the state parameters cannot be used. It is the purpose of this section to describe the "slow" physical processes which occur, to formulate the nonequilibrium equations to be used under these conditions in place of the equilibrium thermodynamic relations, and to indicate their general importance in aerodynamic problems.

The internal motions of a molecule can be described in terms of rotation and vibration of the nuclei and orbital motion of the electrons. Extreme excitation of rotation and vibration leads to separation of the nuclei, or dissociation, while extreme excitation of the electronic motion results in ionization. Upon the collision of some atoms and molecules the interchange of nuclei occurs, i.e., there is a chemical reaction. The energies that are involved with the various processes (for air) and therefore the temperature ranges where they are of interest, have been discussed in Section 2. These same processes are now to be discussed again, this time with a view to the rate at which they approach equilibrium in a given physical situation - that is, the average number of collisions required for each process to obtain its equilibrium value.

On every collision there is a transfer of momentum between the colliding particles, and this transfer is really what is meant by a collision. Except in a case where the masses of the colliding particles are very different (such as an electron-atom collision), this momentum transfer is accompanied by appreciable energy transfer. As mentioned before, only a few collisions are required, on the average, to establish a Boltzmann distribution of translational motion at a new temperature when the overall translational energy of the gas is changed. As noted in the Introduction, the present scope is limited to those flows where the translational motion remains in a local equilibrium as the state properties of the flow change. The reader who wishes to investigate the problem of translational nonequilibrium is referred to Chapters IX and X of Reference 1, and the many references given therein.

Since translational equilibration is all that is required before a temperature and pressure can be defined in the usual way, the equation of state relating p , ρ , and T (Equation (2-7)) can be applied at all points in the gas under consideration.

3.1 Relaxation of Internal Modes

The adjustment of the rotational and vibrational energies of molecular nucleii, and the adjustment of orbital energies of the electrons of either atoms or molecules, will be considered in this section. The relaxation of a single mode can never be considered completely apart from the other motions since energy is transferred between modes, very often with high efficiency. As one mode approaches equilibrium it affects the energy distribution in a second mode, and this energy distribution affects the rate at which the first process proceeds. The two modes are coupled. However, under many conditions a useful separation can be made according to the characteristic times for equilibration of the separate modes. The translational and rotational relaxations are by far the fastest. The next most rapid may be the exchange of vibrational energy among molecules, both between different vibrational states of a given molecular species and between different molecules. Next is vibrational relaxation where the energy is transferred from translational motion, and often at the same rate (or faster) is the excitation of the high electronic states. The processes requiring the longest time to equilibrate are dissociation and ionization, and these are treated separately in Section 3.2.

The rotational motion of the gas is known to be coupled very closely to the translational motion, and to adjust with almost equal rapidity to a Boltzmann distribution at the temperature defined by the translational motion[1]. It is not surprising that this adjustment is rapid, since the energy spacing of the rotational levels is small, and energy can be passed from translation to rotation in small increments. Thus, almost any collision is capable of this energy transfer, and it is a common assumption that the rotational motion relaxes as rapidly as the translational motion, so that the two modes remain in local equilibrium at all times. Experimental[24, 25] and theoretical values of the rotational collision number range from about 4 collisions (at room temperature) to about 10 collisions (at 1500°K) for oxygen and nitrogen, and are less for polar gases[29]. The assumption will be made here that the translational and rotational motions cannot be effectively separated. The treatment of this problem is surveyed in Reference 2. The high temperature conditions, where rotational relaxation occurs on the same time scale as vibrational relaxation, electronic excitation, and dissociation is illustrated in Reference 30.

3.1.1 Vibrational Relaxation

The vibrational motion of molecules adjusts relatively slowly to an equilibrium distribution when the translational and rotational motions of the molecule are disturbed.

The time required for this adjustment can easily be of the order of the flow time in aerodynamic problems, since 10^4 to 10^7 collisions can be required[3] for the adjustment of the vibrational energy. At final equilibrium of diatomic molecules, this vibrational motion may contain as much as 2/7 of the total energy of the molecules; thus, the question of whether or not this energy has been absorbed cannoted be neglected, and the correct evaluation of the rate of vibrational equilibration is necessary for the description of air flows which reach temperatures greater than about 1500°K. In this section the experimental and theoretical treatments of vibrational relaxation for diatomic molecules are described. Much of this treatment applies as well to more complicated molecules with more than one vibrational mode, but the discussion is limited to diatoms.

The reason for the slow adjustment of vibrational motion is, basically, that the natural period of vibration of a molecule is short in comparison with the time required for most molecular impacts to occur. During the impact, both atoms of the molecule experience similar forces during the collision - the atom nearer to the impact particle being acted on directly, and the farther atom being acted on through the "spring" forces of the molecule. Since the spring is relatively stiff, the contraction of the spring can follow the motion of the impacting particle adiabatically, and as the particle slowly recedes the spring can return slowly to its original length, without being left with any residual vibrational energy. Thus, although there may be a transfer of translational energy between the incident particle and the molecule (as there would be between two colliding atoms), there is no transfer of energy from translation to vibration. Only in an unusually energetic collision does one atom of the molecule gain considerable velocity relative to the other, resulting in a net transfer of vibrational energy to the molecule. Thus, vibrational energy is transferred only by the very energetic collisions, and it follows that on the average, a large number of collisions is required for the transfer of a small amount of vibrational energy. Molecules with greater spring constants (higher natural frequencies) require more collisions for vibrational equilibration. As a corollary it follows that at higher temperatures, where there are more highly energetic collisions, the efficiency of energy transfer to vibration will increase.

The analytical description of relaxation of any process in a gas wherein a local translational velocity distribution can be defined, can be conveniently divided into two quite separate problems, and this separation has been used in the presentation which follows for vibrational relaxation. The first has to do with the mechanical problem already discussed, determining the amount of vibrational energy transferred in a single collision for which the initial conditions are defined. These transfer rates can then be averaged over all collision angles and over the Maxwellian distribution of translational velocities that are assumed to exist in the gas, to obtain the average rate of energy transfer to a molecule with a given initial vibrational energy as a function of the temperature of the gas. Given these rates, the second problem is to describe the time history of the distribution of vibrational energy during the relaxation process. Each of these problems has received a great deal of attention, and each has been solved with certain restrictive approximations. These solutions have provided the framework within which it has been possible to order and compare experimental results, and to perform calculations for conditions similar to those that have been tested by experiment. However, the approximations limit the credibility with which the theory can be applied to cases where experimental verification is not available, or where the experiments are difficult to interpret.

The approximate theories have been described in several texts[1-4] and so will be presented only in summary fashion here. The basic material that is discussed here in more detail has to do with limitations of the approximations involved and the possibility of extension beyond these approximations. Thus the emphasis here is, in a somewhat unbalanced measure, on the restrictive applicability of the theory and the care with which it must be applied to aerodynamic problems where direct experimental measurements are not available.

Vibrational energy transfer in collision

The collision of two molecules or of a molecule and an atom is a many-body problem involving all the electrons of the colliding partners, as well as their nuclei. As such, the problem is not tractable, either classically or quantum mechanically, and no discussion of the difficulties will be given here. Instead the problem is at first simplified by neglecting the kinetics of the electron motion, and replacing the electrons with a potential field dependent only on the separations of the various nuclei. This (Born-Oppenheimer) separation of the electron and nuclear motions has good theoretical and experimental justification, and cannot be considered a serious limitation of vibrational energy-transfer calculations. However, it must be recognized that because of this extreme simplification, empiricism enters the problem at a very early stage; a mathematical form of the potential must be chosen, and the parameters which enter the form must be determined from experiment.

The portion of the potential associated with the intra-nuclear coordinate R can be obtained with good accuracy, because of the mass of experimental data available in the form of molecular spectra. There are several standard analytic forms that are employed for this potential, the most familiar probably being the Morse potential

$$V = D_0 \left[1 - e^{-\beta(R-R_e)} \right]^2 , \qquad (3\text{-}1)$$

which has two parameters, D_0 and β. These can be related, for example, to the two experimental data of the dissociation energy (D_0) and the vibrational frequency of the molecule

$$\nu = \frac{1}{2\pi} \sqrt{\left(\frac{2D_0\beta^2}{m} \right)} . \qquad (3\text{-}2)$$

The equilibrium value of the intranuclear separation, R_e, does not enter into the collision problem. An important feature of all such potentials is that, for $R - R_e$ small, they reduce to the simple-harmonic potential. For example, Equation (3-1) is written in this limit as

$$V = D_0\beta^2(R - R_e)^2 \qquad (3\text{-}3)$$

and many of the calculations discussed later are made within this approximation.

The potential describing the interaction of the incident atom, a distance r from one of the molecular nuclei, is usually taken as a simple repulsive exponential[31-34]

$$V = Ae^{-\alpha r} = E_0 e^{-\alpha(r-r_1)} . \qquad (3\text{-}4)$$

The two forms are equivalent, but the second illustrates that, in an end-on collision with initial kinetic energy E_0, the turn-around point will be at $r = r_1$. The exponential form is much more tractable in collision calculations than the more detailed potentials which include the effects of long-range attractive forces and it is the short-range repulsive forces which determine the rate of energy transfer. Values of A and α can be obtained from scattering experiments or from virial-coefficient data. In Reference 33, α is obtained for various collision partners from tabulated values of the constants for the more common Lennard-Jones potential by equating the expressions for dV/dr at $r = r_1$, for the two potentials. The result can be written approximately as[33]

$$\alpha \simeq (17.5)/r_0 , \tag{3-5}$$

where r_0 is the constant appearing in the Lennard-Jones potential

$$V = 4\epsilon \left\{ \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6} \right\} . \tag{3-6}$$

The problem of a monatomic species colliding with a diatom can now be formulated in terms of these potentials. The general formalism is reviewed by Takayanagi[6], including reference to other intermolecular potentials. For the case where the velocity vectors are in the plane of the three particles, numerical solutions have been obtained by Benson and Berend[27]. For an analytic solution, however, a much more drastic simplification is required. The problem is solved for the very special case of end-on collisions and thus rotational excitation is excluded from the start. The mechanical problem is then a function of the two coordinates given in Equations (3-1) and (3-4), the distance R between the molecular nucleii, and the distance r from the closer nucleus of the molecule to the incoming nucleus.

It is clear that once this simplification is made the mechanical problem becomes immensely easier. Using a potential which is a sum of Equations (3-3) and (3-4), that is, the end-on collision of an atom with a simple-harmonic oscillator, the problem has been solved classically[26, 35], quantum-mechanically[32, 33], and semi-classically[36]. Each of these different methods contain some further approximation which limits its range of applicability, as discussed briefly below. However, for conditions where these ranges overlap, the different methods give essentially the same answer for the probability of energy transfer in a collision of given velocity and molecular parameters, and the reasons for this are discussed in References 35, 37 and 38. Whether the exponential repulsion of Equation (3-4) is used or a linearized form is employed has little effect on the result for nitrogen up to incident velocities of 9×10^5 cm/sec (and thus for temperatures of 10,000°K). This is demonstrated in Reference 38 by comparison of the solution with a linear potential (for which an exact solution to the semi-classical problem can be obtained) with the numerical solution for an exponential intranuclear potential[39]. A recent numerical quantum-mechanical calculation[40] of this problem gives results which are in some disagreement with these earlier calculations, and this discrepancy has not yet been explained. The use of an infinite-step potential in place of Equation (3-4) results in a considerably different result, as demonstrated in References 40 and 41. This disagreement would be expected, in view of the qualitatively different results obtained in classical mechanical problems when impulsive collisions are considered.

The most radical (and most fruitful) further simplification that can be made in the quantum-mechanical problem is the application of first-order perturbation theory, in which case the results are much more easily formulated. The general conclusions that can be drawn from this collision model (simple harmonic oscillator, end-on collision, transition probabilities much less than 1) are[42, 3]

1. The probability that in a collision a molecule in the first vibrational state will make a transition to the ground vibrational state, giving up energy $h\nu$ to translation is given by

$$p_{10} \sim e^{-4\pi^2\nu/v\alpha} . \tag{3-7}$$

2. The probability that in a collision a molecule in state $r + 1$ will make a transition to state r is related to p_{10} by

$$p_{r+1,r} = (r + 1)p_{10} . \tag{3-8}$$

3. Transitions occur only between adjacent levels

$$p_{i,j} = 0 \quad \text{for} \quad i \neq j \pm 1 . \tag{3-9}$$

If first-order perturbation theory is not used, but instead the semi-classical method is employed[35-37], each of these conclusions is modified. For very high-energy collisions (in nitrogen negligible below 5000°K) the value of p_{10} given in Equation (3-7) approaches and exceeds 1, so that the true value is less than this, and in addition multiple-jump transition probabilities are not zero. These effects compensate in such a way that the rate of *energy absorption* in transitions from the ground state can still be correctly calculated[37, 38] from Equations (3-7) and (3-9). The results that have been obtained for $p_{r,0}$ by different methods are compared in Figure 3-1 for the case of collisions of two nitrogen molecules. A three-dimensional solution has been obtained[34] for the collision problem using a quantum-mechanical perturbation theory (method of partial waves) in which the potential is nearly spherical, but the spherical form is multiplied by a term which depends on the oscillator coordinate. The result is very similar to the corresponding one-dimensional calculation[33]. A classical two-dimensional calculation[28], including effects of rotational energy transfer, demonstrates that rotational motion can be effectively transferred to vibration.

The calculation for a Morse internuclear potential - this is, using Equation (3-1) instead of Equation (3-3) presents several difficulties that are not resolved[43, 44]. The spacing between the vibrational energy states decreases for higher energy states, and the probability of a transition between these states increases because of the smaller energy required in the transition (see Equation (3-7)) and because the matrix elements for a Morse oscillator increase rapidly[45]. It has been shown[46] that if α (in Equation (3-4)) is equal to β (in Equation (3-1)(Ref. 1)), Equation (3-9) is correct within the limits of first-order perturbation theory. In summary, Equations (3-7) and (3-9) may be reasonably accurate for the end-on collision at moderate velocity of a Morse oscillator, but Equation (3-8) is completely incorrect. For very high-velocity collisions, Equations (3-7) and (3-9) must be modified as well[38, 39].

In addition to the transfer of energy between vibrational and translational motion, it is also of interest to consider the transfer of vibrational energy between molecules with similar vibrational energy spacings. This resonant, or near-resonant, exchange of vibrational energy can occur with high probability ($\sim 10^{-1}$), providing that the energy defect for the transition is small. A review of available data for transitions of this type important in the CO_2-N_2 laser has recently been published[47]. The methods of calculation and the potentials involved are similar to those previously described. Both classical and quantum mechanical approaches have been used[4, 33, 50].

Master equations for the time-history of the vibrational energy

When the rates for vibrational energy transfer in specific collisions have been determined, there remains the problem of describing the change of the vibrational energy of the gas when the translational energy undergoes a change. The molecules are first grouped according to their vibrational energy state, and then a differential equation (a rate equation) is written for the rate of change of molecules in a given energy state (say the r^{th}) due to collisions of all the molecules. Thus, the expression for the transition probability $p_{r+1,r}$, as given by Equations (3-7) and (3-8), must be averaged over all velocities, weighted according to the velocities that occur in a Boltzmann distribution of translational motion at a temperature T. The rate constants derived in this way are then functions of the temperature rather than the velocity of any given collision. The differential equation utilizing this rate constant contains a separate term for each type of molecular pair that can collide which will result in the production (or destruction) of a molecule in the r^{th} state, with the other molecule having the choice of remaining in its original state or making a transition to another state. If the gas being considered is a mixture of gases A, B, C, etc, the equation is further complicated by the requirement of keeping account of the species involved in the collision. We begin by writing this equation in some detail, after which it will be simplified by various approximations so as to obtain a solution.

Consider a mixture of diatomic gases A and B, and consider transitions where only one-quantum transitions are involved, consistent with Equation (3-9). The differential equation for the number density of molecules of Type A in the r^{th} state is then

$$
\begin{aligned}
\frac{dn_r}{dt} = {} & P_{r+1,r}\left[n_{r+1}n - e^{-(\epsilon_{r+1}-\epsilon_r)/kT}n_r n\right] - P_{r,r-1}\left[n_r n - e^{-(\epsilon_r-\epsilon_{r-1})/kT}n_{r-1}n\right] + \\
& + \sum_s P^{s-1,s}_{r+1,r}\left[n_{r+1}n_{s-1} - e^{-(\epsilon_{r+1}+\epsilon_{s-1}+\epsilon_r-\epsilon_s)/kT}n_r n_s\right] - \\
& - \sum_s P^{s,s+1}_{r,r-1}\left[n_r n_s - e^{-(\epsilon_r+\epsilon_s-\epsilon_{s+1}-\epsilon_{r-1})/kT}n_{r-1}n_{s+1}\right] + \\
& + Q_{r+1}\left[n_{r+1}N - e^{-(\epsilon_{r+1}-\epsilon_r)/kT}n_r N\right] - Q_{r,r-1}\left[n_r N - e^{-(\epsilon_r-\epsilon_{r-1})/kT}n_{r-1}N\right] + \\
& + \sum_R Q^{R-1,R}_{r+1,r}\left[n_{r+1}N_{R-1} - e^{-(\epsilon_{r+1}+\epsilon_{R-1}-\epsilon_r-\epsilon_R)/kT}n_r N_R\right] - \\
& - \sum_R Q^{R,R+1}_{r,r-1}\left[n_r N_R - e^{-(\epsilon_r+\epsilon_R-\epsilon_{R+1}-\epsilon_{r+1})/kT}n_{r-1}N_{R+1}\right] . \qquad (3\text{-}10)
\end{aligned}
$$

A term such as $P^{s-1,s}_{r+1,r}\, n_{r+1} n_{s-1}$ describes the rate at which molecules enter the r^{th} state from the $(r + 1)$ state, due to collisions of molecules in the $(s - 1)$ state with A-type molecules in the $(r + 1)$ state, where the same collision provides a transfer of the molecule in the $(s - 1)$ state into the (s) state. Capital letters refer to the second-type molecule. The equation includes the substitution of the detailed-balance relation, namely, that

$$P^{s,s-1}_{r,r+1} = e^{-(\epsilon_{r+1}+\epsilon_{s-1}-\epsilon_r-\epsilon_s)/kT} P^{s-1,s}_{r+1,r} . \qquad (3\text{-}11)$$

In writing this relation, and in writing the rate constants as a function of the translational temperature alone, there is the assumption that all other modes of excitation are in equilibrium at the translational temperature. If this were not the case then more terms would be required in Equation (3-10) accounting for the exchange of vibrational energy with the other modes, and a separate detailed-balance relation would be required for each of these separate reactions. With gases at moderate temperatures, where a clear-cut distinction can be made between translational-rotational relaxation time and vibrational relaxation time, this restriction is not a serious one. At higher temperature, where dissociation and chemical reactions are involved, as discussed previously this separation becomes more difficult, and a complete description cannot be obtained without taking these other nonequilibrium effects into account.

Vibrational relaxation of a dilute mixture of molecules and atoms

A great simplification of Equation (3-10) is obtained in treating the very special case of vibrational relaxation of a diatomic molecule in a very dilute mixture with a monotomic species. If A is the diatom and B is the monatom, we can consider a mixture so dilute that molecule-molecule collisions can be neglected, and Equation (3-10) simplifies to

$$\frac{dn_r}{dt} = Q_{r+1,r}N\left[n_{r+1} - e^{-(\epsilon_{r+1}-\epsilon_r)/kT} n_r\right] - Q_{r,r-1}N\left[n_r - e^{-(\epsilon_r-\epsilon_{r-1})/kT} n_{r-1}\right] . \qquad (3\text{-}12)$$

The next step in the solution requires the specification of the dependence of the rate constants $Q_{r+1,r}$ on the energy states $r + 1$ and r . As discussed in the previous section, this dependence can be obtained for the case where the molecule is properly described as a simple-harmonic oscillator by averaging Equations (3-7) and (3-8) over a Boltzmann velocity distribution, resulting in[3,42]

$$Q_{10} \sim e^{-(54\pi^4\nu^2\tilde{m}/kT)^{1/3}} , \qquad (3\text{-}13)$$

$$Q_{r+1,r} = (r + 1)Q_{10} , \qquad (3\text{-}14)$$

where $\tilde{m}$ is the reduced mass of the system, given for an incoming particle A striking a molecule B-C , as

$$\tilde{m} = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} .$$

Using Equation (3-14), the first-moment equation can be obtained[42] from Equation (3-12) by multiplying both sides of the equation by r (and by $h\nu/\rho$) and summing over all values of r . There results

$$\frac{de_v}{dt} = \frac{e_{v\,EQ} - e_v}{\tau_v} , \tag{3-15}$$

where e_v is the vibrational energy per unit mass of gas related to n_r by

$$e_v = \frac{h\nu}{\rho} \sum_{r=0}^{\infty} r n_r \tag{3-16}$$

with ρ equal to the density of the gas. $e_{v\,EQ}$ is the vibrational energy per unit mass that would be contained by the gas if it were at equilibrium at the local temperature T . τ_v is a relaxation time that is related to Q_{10} through

$$\tau_v = \frac{1}{Q_{10}(1 - e^{-\omega/kT})} . \tag{3-17}$$

These extremely simple equations have found widespread use in spite of the limitations required for their derivation.

A detailed solution of Equations (3-12) to (3-14) has been given[51] for the case where T is constant during the relaxation. This limitation is consistent with the previous assumption that the diatomic species is strongly diluted with a monatomic species. If the gas starts in an initial Boltzmann distribution at temperature T_0 , its distribution can be described at any latter time by[51]

$$n_r = n_0 e^{-\epsilon_r/kT_v} = n_0 e^{-rh\nu/kT_v} , \tag{3-18}$$

where T_v is a time-dependent parameter that starts at a value T_0 and approaches a value T as the relaxation proceeds. That Equation (3-18) is a solution of Equations (3-12) to (3-14) can be demonstrated by direct substitution. Thus, the vibrational population remains in a Boltzmann-like distribution throughout the relaxation, and T_v is referred to as the vibrational temperature. It is related to the vibrational energy per gram by the usual formula for the energy of a system of simple-harmonic oscillators, viz.,

$$e_v = \frac{n}{\rho} \frac{h\nu}{e^{h\nu/kT_v} - 1} . \tag{3-19}$$

The departure of real molecular oscillators from the simple-harmonic model has an important effect on Equation (3-14) for the transition probabilities of the higher-level transitions, as previously described. For many cases of aerodynamic interest, almost all of the vibrational energy is contained in the first few energy states, so that this change in transition probability for higher states has little effect[52] on the validity of Equations (3-13), (3-15) and (3-17). However, Equation (3-18) must be applied with considerable caution for higher states, and in problems of rapidly expanding flows this can affect the validity of Equations (3-15) and (3-17).

Comparison of experimental results with the predictions of Equations (3-13), (3-15), (3-17), and (3-18) is given in Section 4.3.

Vibrational relaxation of a pure gas

To describe the vibrational relaxation of a pure gas it is necessary to include terms from Equation (3-10) that describe both the transformation of translational energy to vibration, and the exchange of vibrational energy between molecules in a collision. Equation (3-10) can then be written

$$\frac{dn_r}{dt} = P_{r+1,r}\left[n_{r+1}n - e^{-(\epsilon_{r+1}-\epsilon_r)/kT}n_r n\right] - P_{r,r-1}\left[n_r n - e^{-(\epsilon_r-\epsilon_{r-1})/kT}n_{r-1}n\right] +$$

$$+\sum_s P^{s-1,s}_{r+1,r}\left[n_{r+1}n_{s-1} - e^{-(\epsilon_{r+1}+\epsilon_{s-1}-\epsilon_r-\epsilon_s)/kT}n_r n_s\right] -$$

$$-\sum_s P^{s,s-1}_{r,r-1}\left[n_r n_s - e^{-(\epsilon_r+\epsilon_s-\epsilon_{s+1}-\epsilon_{r-1})/kT}n_{s+1}n_{r-1}\right]. \tag{3-20}$$

A unique feature of this equation which aids in its approximate solution is that terms $\sum_s P^{s,s+1}_{r+1,r}\, n_{r+1}n_s$ are much larger than the terms $P_{r+1,r}\, n\, n_{r+1}$. That is, there is a much higher probability, in a collision, that a vibrational quantum will be exchanged between the colliding molecules than there is that the vibrational energy will be transferred to translational motion. One molecule makes a transition to the next lower vibrational state, while the other molecule makes a transition to the next higher state. Transitions of this type do not change the total number of vibrational quanta in the gas, defined (per unit mass) by

$$\mho = \frac{1}{\rho}\,\Sigma r n_r\,, \tag{3-21}$$

but they do rearrange the quanta among the vibrational states. These rapid exchange collisions attempt to establish a local-equilibrium distribution of molecules in the vibrational states which will make the brackets in the last two lines of Equation (3-20) separately equal to zero for a given number of vibrational quanta. It can be seen by direct substitution in Equation (3-20) that this is accomplished by the distribution[53,54]

$$n_r = n_0 e^{-\gamma r} e^{-\epsilon_r/kT}\,, \tag{3-22}$$

where γ is determined by the total number of quanta available, evaluated by substituting (3-22) into (3-21). Equation (3-22) reduces to a Boltzmann-like distribution at a temperature T_v for a simple harmonic oscillator so that within this approximation the exchange of vibrational quanta does not affect relaxation, and Equations (3-15) to (3-17) should apply[55,56]. For an anharmonic oscillator, the departure from a Boltzmann-like distribution depends on the number of vibrational quanta contained by the gas relative to the equilibrium number at the translational temperature T . If the number of quanta is less than the equilibrium number (as during vibrational excitation), the upper states are underpopulated, and if the number of quanta is greater than the equilibrium number (as during vibrational deexcitation) the upper states are overpopulated.

For the topmost quantum numbers the distribution given by Equation (3-22) becomes invalid because the assumption that vibration-vibration exchange is much more rapid than vibration-translation energy transfer becomes incorrect for two reasons; these states are very far from resonance with the lower, more densely populated states, thus decreasing the probability of vibrational exchange, and, in addition, the probability of transfer of energy from vibration to translation increases to an appreciably greater value in the highest states because of the closer spacing of the levels.

With these restrictions in mind, a differential equation for the time history of $\mathcal{U}$ can be obtained by multiplying Equation (3-20) by r/ρ and summing over all states. The terms involving exchange do not contribute to the sum, since these exchanges of vibrational quanta do not affect the total number of quanta. The result is[54, 57]

$$\frac{d\mathcal{U}}{dt} = \frac{n}{\rho}\sum_r P_{r+1,r}\left[n_{r+1} - e^{-(\epsilon_{r+1}-\epsilon_r)/kT} n_r\right] - n\sum_r P_{r,r-1}\left[n_r - e^{-(\epsilon_r-\epsilon_{r-1})/kT} n_{r-1}\right]. \tag{3-23}$$

This equation, along with the distribution given by Equation (3-22) provides a closed set which, in principle, determines $\mathcal{U}$ (or γ) as a function of time. The solution requires, however, a knowledge of all the values of $P_{r+1,r}$, and these are not known with any certainty. In addition, the restrictions at high quantum number on the distribution given by Equation (3-22) become important in problems involving low translational temperatures and high vibrational energies. Some attempts at the solution of Equation (3-23) are given in References 54, 57, 58, 52, and 56. The general conclusions obtained there are that vibrational excitation of a pure gas, where the molecules are described as anharmonic oscillators with rapid vibrational exchange, can be adequately described by assuming a Boltzmann-like distribution during excitation and employing the Landau-Teller model. However, during deexcitation, the overpopulation of upper vibrational levels by exchange effects could increase the rate at which quanta are lost, and it is suggested that this may provide the reason for the observed rapid vibrational deexcitation in nozzle flows (see discussions in Section 4.3). The conditions under which vibrational exchange may enhance vibrational deexcitation are given in References 54 and 57 as:

1. The translational temperature must be less than the characteristic vibrational temperature of the gas to ensure that the vibrational exchange mechanism is dominant.
2. The initial vibrational temperature must be at least a considerable fraction of the characteristic vibrational temperature if there is to be any significant influence of the excited vibrational states.
3. The ratio of the initial vibrational temperature to the translational temperature must be considerably greater than one, for the anharmonicity of oxygen or nitrogen, so that Equation (3-20) represents a large departure from a Boltzmann-like distribution.

These conditions are considered conservative, in the sense that the non-Boltzmann effect may also become noticeable for conditions closer to equilibrium.

Numerical solutions for Equations (3-20) are given for 12- level and 24- level molecules in Reference 59, with assumed values for $P^{s,s+1}_{r+1,r}$ and $P_{r+1,r}$. These solutions demonstrate the time dependence of the vibrational-energy distribution during the high-speed vibrational-exchange relaxation.

Vibrational relaxation of a mixture of gases

In the relaxation of two or more diatomic or polyatomic gases, exchange processes between nearly resonant modes can be of primary importance[60, 61]. Measurements of the simultaneous relaxation of N_2 and NO is interpreted in terms of the relative importance of vibrational exchange and vibration-translation transitions in Reference 60. An effective relaxation time is determined from the separate relaxation rates[4].

The equations and concepts discussed in the previous section can be applied to such mixtures of gases with the same type of restrictions and limitations as given for the case of a pure gas. In the case of two near-resonant gases, the full equation given as Equation (3-10) applies. The steady-state distributions established by exchange[53, 54], as given in Equation (3-22), applies to both gases with the same value of γ in the two distributions. Thus, we can write

$$\left.\begin{aligned} n_r &= n_0 e^{-\gamma r} e^{-\epsilon_r/kT} \\ N_R &= N_0 e^{-\gamma R} e^{-\epsilon_R/kT} \ . \end{aligned}\right\} \qquad (3\text{-}24)$$

That these relations reduce all the exchange terms in Equation (3-10) to zero can be seen by direct substitution. As for a single gas, the simple-harmonic-oscillator approximation yields a Boltzmann-like distribution with some vibrational temperature T_v . However, for gases with different fundamental frequencies their vibrational temperatures will not be equal. These distributions are discussed further in References 53 and 54. The numerical calculation of the time dependence of these distributions is described in Reference 62.

3.1.2 Electronic Excitation

The orbital motion of electrons in atoms and molecules contributes a relatively small amount to the total energy of a high-temperature gas. This is demonstrated for air in Figure 2-1. The importance of the electronic excitation is not related to the total energy that resides there at any one time, but rather to the many ways this energy can be transferred within the gas. It is closely coupled with vibrational excitation in molecules, it is an intermediary step in the ionization process, and it is the starting point for the radiative process. The fact that the radiative intensity is proportional to the population of the excited electronic states has made it important to understand this excitation process in correlating the observed radiation from high-speed vehicles with the physical description of their flight trajectory.

The experimental observation of excited electronic states is accomplished directly by observation of the light emitted from these states. However, the amount of data available for electronic excitation rates in the high-temperature range is much less than that previously discussed for vibrational excitation. The chief reason for this is that the temperature range of interest is typically much higher, so that the excitation processes occur more rapidly and are less accessible to shock-tube instrumentation.

The theoretical interpretation of the experimental results is also much more difficult than for the vibrational relaxation case. There is no simplification available for low-lying electronic states parallel to the simple-harmonic-oscillator approximation for vibrational states. In addition there are many vibrational states with lower energy than even the low-lying electronic states, and so coupling with these and other electronic states must be considered in the excitation process. Finally, chemical reactions, particularly dissociation and ionization, occur in the temperature range where electronic excitation is observed and are necessarily involved in the interpretation of the experimental results.

Several recent reviews of electronic excitation rates are available[7,8]. In these reviews it is emphasized that high-temperature-rate data for the excitation of electronic states of atoms and molecules by heavy-particle impact are relatively few, and that the excitation processes pertinent to flight problems are complicated and not well understood. Much of the available information about molecular electronic excitation comes from fluorescence and electron-bombardment experiments performed at room temperature, and cannot reliably be extrapolated to high temperature conditions. The data on excitation by impact of free electrons[7,9] are obtained with molecules at room temperature, and thus apply to low-lying rotational and vibrational states.

The limited information available from shock-tube experiments provides very little guidance for predictions of electronic excitation in air[63,64], although for pure nitrogen sufficiently detailed experiments have been performed to correlate them with a simple model for excitation of the A and B states of N_2 by N_2 and N collisions[65,66]. Similar detailed spectroscopic investigations[67] for shock-heated CO_2 involve too many unknown chemical reactions to permit evaluation of mechanisms or rates for excitation of electronic states.

Chemical excitation of electronic states has long been a subject of fundamental interest in flame spectroscopy[10,68] and other experimental investigations[69,70], and has found recent application to chemical lasers[71]. Some application has been made to reentry physics problems in connection with radiation from the flow field of blunt hypersonic reentry vehicles[72].

3.2 Chemical Reactions

Processes which involve a change in chemical structure of the molecules of the gas usually occur at a rate much slower than those involving only internal readjustments. The reactions must continue until an equilibrium distribution as described by Equations (2-5) is reached, and this equilibration requires the production of the new species in all its permitted equilibrium energy states. These products will be produced with various efficiencies from the many permitted states of the parent species. The kinetics of attaining these final states can involve a complicated route through many intermediate states, including some whose equilibrium population is so small that the states can be neglected in equilibrium calculations. Thus a complete mathematical description of chemical reactions would take sets of equations much more complicated than Equations (3-10) that were used to describe vibrational relaxation.

It is fortunate for the subject of chemical kinetics that it is not necessary to include all the intermediate steps in the description of a chemical process. Often only the starting and ending species need be included. In fact much of the experimental and theoretical work in chemical kinetics is directed toward finding the minimum mathematical complexity to describe the observed species production. It must be understood, however, that the application of the chemical rates and mechanisms to environments much different from those where experiments were performed requires caution.

The basic equations of chemical reactions in flow systems were summarized in 1955 by S.S.Penner[11] and they have since been discussed in several aeronautical texts[1,5]. No attempt is made here to repeat the derivations of the basic equations, but as with the basic equations of Section 2 they are discussed briefly and presented for reference later. Several items of special interest are discussed in more detail.

3.2.1 Reaction Rate Equations

Continuing with the notation of Reference 11, a chemical reaction is described by

$$\sum_{j=1}^{s} \nu_j' M_j \underset{k_{Ri}}{\overset{k_{Fi}}{\rightleftarrows}} \sum_{j=1}^{s} \nu_j'' M_j \,, \qquad i = 1, 2, \ldots r \tag{3-25}$$

where the quantities k_{Fi} and k_{Ri} are the forward and reverse rate constants for the i reaction and are taken to be functions only of the translational temperature of the gas. The general differential equation to describe the rate of production of species j is

$$\frac{d\gamma_j}{dt} = \frac{1}{\rho} \sum_{i=1}^{r} (\nu_{ij}'' - \nu_{ij}') \left[k_{Fi} \rho^{\nu_i'} \prod_{\alpha=1}^{s} \gamma_\alpha^{\nu_{i\alpha}'} - k_{Ri} \rho^{\nu_i''} \prod_{\alpha=1}^{s} \gamma_\alpha^{\nu_{i\alpha}''} \right], \tag{3-26}$$

where $\nu_i' \equiv \sum_{\alpha=1}^{s} \nu_{i\alpha}'$ and $\nu_i'' \equiv \sum_{\alpha=1}^{s} \nu_{i\alpha}''$.

There is in these equations the implication that the collision of the molecules on the left-hand side of Equation (3-25) will result in the products on the right-hand side, the probability of the reaction being related to the rate constant k_{Fi} . The reaction does not, of course, occur in a one-step process, but instead the molecules absorb rotational and vibrational energy in a series of collisions, and finally the excited molecules are involved in a sufficiently energetic collision for the reaction to occur. Likewise, the inverse reaction occurs in a large number of separate steps. However, a description that is adequate for most purposes can be formulated by ignoring the intermediate steps.

Under the assumption that Equations (3-25) and (3-26) properly describe the physical processes, the equilibrium constants K_i discussed in Section 2, can be related to the forward and reverse rate constants. In equilibrium $(d\gamma_j/dt) = 0$ and from the principle of detailed balance, each of the terms in the sum on the right-hand side of Equation (3-26) equals zero. It follows that

$$\frac{k_{Fi}}{k_{Ri}} = \rho^{(\nu_i'' - \nu_i')} \prod_{\alpha=1}^{s} \gamma_\alpha^{(\nu_{i\alpha}'' - \nu_{i\alpha}')} = K_i \,. \tag{3-27}$$

The accuracy of this relation when the details of intermediate steps in the reaction are included will be discussed later.

Machine programs have been written for the simultaneous solution of Equations (3-26) and the flow-field equations for a variety of flow situations, such as normal shock waves, quasi-one-dimensional expansions, external flows including boundary layer effects and ablation effects, and wake flows. These various programs will not be discussed here, but references are given in the Appendices. Some discussion of expansion-flow calculations is given in Section 4. For normal-shock flows a large number (~ 50) of chemical reactions can be included with only moderate calculation time required. However, for more complicated flow situations the calculation time can increase rapidly, so that the amount of chemistry which can be included must be reduced.

The temperature dependence of the forward and reverse rate constants is a prime consideration of experimental and theoretical investigation. For the atomic recombination reaction to occur, there is no appreciable activation energy required. A reaction of this type (which we write as a reverse reaction) then has very little temperature dependence, and can be described as

$$k_{Ri} = C_{Ri} T^{\eta_{Ri}} , \qquad (3\text{-}28)$$

where η_i is a small constant. The forward rate constant is related through Equation (3-27). Within the approximation of Equation (2-10) for K, k_{Fi} is then of the form

$$k_{Fi} = C_{Fi} T^{\eta_{fi}} e^{-D_i/kT} . \qquad (3\text{-}29)$$

Suitable constants for these relations for air reactions are given in Reference 1.

3.2.2 Dissociation

The application of Equations (3-25) and (3-26) to the dissociation of a symmetric diatomic molecule provides a simple example which has been studied extensively and which involves several of the problems associated with high-temperature-air chemistry. Equation (3-25) becomes

$$\left.\begin{array}{l} A_2 + A_2 \underset{k_{R1}}{\overset{k_{F1}}{\rightleftarrows}} A_2 + 2A \\[2ex] A_2 + A \underset{k_{R2}}{\overset{k_{F2}}{\rightleftarrows}} 3A \end{array}\right\} \qquad (3\text{-}30)$$

and Equation (3-26) is

$$\rho \frac{d\gamma_{Az}}{dt} = (-k_{F1}\gamma_{A2}^2 + k_{R1}\gamma_{A2}\gamma_A^2) + (-k_{F2}\gamma_{A2}\gamma_A + k_{R2}\gamma_A^3) \qquad (3\text{-}31)$$

These equations have been used to analyze shock-tube experiments for pure O_2 (Ref.73) and N_2 (Ref.74) as well as many other gases[12]. The assumption that the rate constants can be taken as functions of temperature, independent of the state of internal excitation, is open to question on any time scale of order of the internal relaxation times, as discussed below.

For the calculation of gas flows where an appreciable dissociation occurs, the temperature changes considerably, due to the energy required for the dissociation, so that the rate constants change during the dissociation. For a tractable analysis of aerodynamic problems without use of large machine programs, some simplification of Equation (3-31) is required. These can be obtained by applying the approximations introduced by Lighthill for the ideal dissociating gas.

Ideal dissociating gas

The approximations for an ideal dissociating gas, discussed in Section 2, were formulated by Freeman[75] to describe the kinetics of dissociation. He included the approximation to the rate constants given by Equations (3-28) and (3-29), and further neglected the change in dissociation rate associated with the different rate constants for atomic and molecular collisions. This latter simplification is obviously a poor one if the degree of dissociation is large. Changing variables to the mass fraction of dissociated atoms

$$\alpha = \gamma_A M_A \, , \tag{3-32}$$

where M_A is the atomic weight of A, the conservation of mass gives

$$\gamma_{A2}(2M_A) = (1-\alpha) \, .$$

The approximations then reduce Equation (3-31) to

$$\frac{d\alpha}{dt} = C'T^{-s}\rho\left[(1-\alpha)\,e^{-D/R_0T} - \frac{\rho}{\rho_D}\,\alpha^2\right] , \tag{3-33}$$

where ρ_D is a constant that enters from the Lighthill approximation to the partition functions and C' and s are related to C_f and η_f of Equation (3-29). This formulation was used by Freeman[75] to discuss dissociation in shock waves, and by Bray[76] to discuss recombination in expanding flows. It has since been used by several authors to investigate the magnitude of dissociation effects in diatomic gas flows, but is not suitable for careful interpretation of experiments.

Vibrational-dissociation coupling

The dissociation of a diatomic molecule by collision with an inert atom provides the simplest dissociation reaction, both from a theoretical and experimental point of view. For example, a small amount of oxygen in a large amount of argon can be studied in a shock tube over a large temperature range[77]. Theoretically, there is no need to consider temperature changes during the reaction, and vibrational-exchange reactions and dissociation by impact with the small amounts of O_2 or O in the experiment are negligible. Then in the analysis of this reaction it is feasible to consider the details of the vibrational excitation of the molecule as the intermediate process by which the molecule proceeds to dissociation. This effect is of special importance in applying recombination rates to problems of expanding flows, where the recombination rate to be used is determined from the measured dissociation rate and the equilibrium constant, through Equation (3-27).

For the dissociation of a small amount of O_2 in Ar, Equation (3-26) is

$$\frac{1}{\rho}\frac{d\gamma_{O_2}}{dt} = -k_F\gamma_{O_2}\gamma_{Ar} + k_R\gamma_O^2\gamma_{Ar} \, . \tag{3-34}$$

However, if each vibrational level of the molecule is considered as a separate species, with concentration γ_{O_2v} in the v vibrational level, then a chemical equation of this type can be written for each level, along with terms to describe the change in population of the v level due to transitions from other vibrational levels. The resulting equations are

$$\frac{1}{\rho}\frac{d\gamma_{O_2v}}{dt} = Q_{v+1,v}\gamma_{Ar}\left[\gamma_{O_2v+1} - e^{-(\epsilon_{v+1}-\epsilon_v)/kT}\gamma_{O_2v}\right] -$$

$$- Q_{v,v-1}\gamma_{Ar}\left[\gamma_{O_2v} - e^{-(\epsilon_v-\epsilon_{v-1})/kT}\gamma_{O_2,v-1}\right] - k_{Fv}\gamma_{O_2v}\gamma_{Ar} + k_{Rv}\gamma_O^2\gamma_{Ar}\,, \quad v = 0,1,2\ldots \quad (3\text{-}35)$$

where k_{Fv} and k_{Rv} are the forward and reverse rates for dissociation from the vibrational level v , and the remaining terms are the same as given in Equation (3-12) for vibrational relaxation.

These equations contain two approximations that limit their validity. One is that the translational and rotational distributions are in Boltzmann distribution at temperature T , and are unaffected by the dissociation process, leading to rate constants in Equation (3-35) that depend only on T . In particular, the forward and reverse rates for dissociation from the v level are taken as related through detailed balance as

$$\frac{k_{Fv}}{k_{Rv}} = K_{O_2}Q_{vib}e^{\epsilon_v/kT}\,. \quad (3\text{-}36)$$

The second is that only one-quantum vibrational transitions are included, whereas multiquantum transitions certainly occur at higher vibrational levels. These approximations are included to simplify the description, and with the idea that to some extent the values of the rate constants could be modified to compensate for these effects.

The equation to replace (3-34) is obtained by summing Equation (3-35) over all vibrational states v . The sums for internal excitation are then equal to zero, and there results

$$\frac{1}{\rho}\frac{d\gamma_{O_2}}{dt} = -\gamma_{Ar}\sum_v k_{Fv}\gamma_{O_2v} + \gamma_{Ar}\gamma_O^2\sum_v k_{Rv}\,. \quad (3\text{-}37)$$

If a Boltzmann distribution at temperature T is assumed for the vibrational distribution, Equation (3-34) is obtained directly. This distribution is not correct, however, because the finite rate of vibrational relaxation and the dissociation process both affect the distribution, which must be obtained by solving Equation (3-35).

There are three separate regions of time that can be discussed in terms of Equation (3-35). The first is during the early portion of the dissociation (or recombination) process, at times less than the vibrational relaxation time. For dissociation immediately behind a shock wave, there are essentially no molecules in upper vibrational states (from which most dissociation normally occurs) so that essentially no dissociation can occur until a time of order of the vibrational relaxation time (the induction time). Somewhat after this time the collisional excitation of vibrational states reaches a steady state with dissociational destruction of these states, and a distribution is established which persists as long as recombination $(\gamma_{Ar}\gamma_{O}^{2}k_{Rv})$ is unimportant. In this steady-state distribution the upper vibrational levels are underpopulated, so that the dissociation rate is suppressed. Finally, when enough atoms are produced to make recombination important, the vibrational populations approach their final, Boltzmann distribution. A similar sequence can be described for a recombination experiment. Consider an experiment[78] where an ozone-argon mixture is shock-heated to moderate temperature. The ozone quickly dissociates to O_2 and O. Most of the O atoms must then recombine to form the final equilibrium mixture. At very short times the atoms recombine quickly to populate the upper vibrational states. At longer times the steady state is reached where upper vibrational levels are overpopulated, and recombination to upper states, vibrational deexcitation of these states, and thermal redissociation of these states are balanced. The net effect (due to the redissociation) is a depression of the observed recombination rate. The third region is again the final, Boltzmann state.

One question that can then be asked of Equation (3-35) is under what conditions will the steady-state dissociation rate and the steady-state recombination rate be related by the equilibrium constant as in Equation (3-27). This question has been addressed in many theoretical papers[79,84]. It has been demonstrated by Snider[80], in agreement with Rice's original discussion[79], that the forward and reverse rates measured within the steady-state region are depressed by the same factor, so that their ratio is still equal to the equilibrium constant. Detailed consideration[84] of the region of applicability of this statement shows that it applies to the conditions of the O_2 - Ar shocktube experiments. Other types of reactions, where Equation (3-27) can be applied, are discussed in Reference 83, and it is clear from that discussion that considerable caution must be used in relating forward and reverse rate constants for more complicated reactions. Very few experimental results are available where both the forward and reverse rates have been measured.

The complete solution of Equations (3-35) requires a statement of all the values of the rate constants ($Q_{v+1,v}$ and k_{Fv}). This has been accomplished for the steady-state region using various approximations for these rates[85,86]. In Reference 85 both classical and quantum mechanical models are investigated, and the equations for the classical model, similar to Equation (3-35), are reduced to a diffusion-equation form. The calculation of rate constants from a classical model is discussed in Reference 87 and in other papers referenced there.

The induction time for O_2 dissociation behind strong shocks in O_2 - Ar mixtures has been measured[77] over the temperature range of 5,500-18,000°K. The measurements show that the induction time is of the order of the vibrational relaxation time, and appears to increase more rapidly than the vibrational relaxation time at lower temperatures. The experimental method (measurement of O_2 ultraviolet absorption) did not permit measurements at temperatures below 5500°K. However, experiments employing the resonance-absorption of atomic oxygen[88] are now being performed to extend this information to the lower-temperature range. The theoretical problem of relating the induction time to the relaxation rates is given in Reference 89.

In shock-waves at very high temperature the times for vibrational and dissociational relaxation become comparable, and the separation into specific time regions is no longer possible. High-temperature experiments where these regions are obviously mixed are described in References 90 and 91. There are no theoretical treatments available for flows under these conditions, but basic work on the excitation and dissociation from high-energy collisions is a subject of continuing study[92,93].

Normal-shock coupled vibration-dissociation

For treatment of shock calculations for conditions where vibration and dissociation are coupled, a simplified interpretation of Equation (3-37) was given in References 94-96. It was assumed that the solution of Equation (3-35) for γ_{O_2v} could be represented by a Boltzmann-like distribution at an unknown temperature T_v. The value of T_v was determined from a vibrational energy relaxation equation which included terms[95,96] to account for the loss of vibrational energy due to dissociation. The reverse rate constant for recombination to the vibrational level was taken to have the form[96]

$$k_{rv} = C(U)e^{\epsilon_v/kU} , \qquad (3\text{-}38)$$

where U was an adjustable parameter. The reverse rate was related to the forward rate through Equation (3-36). The parameter kU was taken as 1/6 of the dissociation energy. Calculations with this model[96] succeeded in duplicating the induction time of the O_2 – Ar experiments[77] and resulted in a steady-state vibrational temperature considerably below the translational temperature, thus depressing the dissociation rate constant, as would be expected. However, the assumption concerning the vibrational temperature cannot be justified, and numerical calculations[97,98] show that the upper levels are more severely depleted than this assumption would imply.

3.2.3 Other Chemical Reactions

The shock tube has now become a standard method of studying high-temperature chemical reactions and has been applied to a wide variety of problems. This research during the past several years has been comprehensively reviewed by Bauer[12], and the wide range of chemical kinetic studies being pursued with the shock tube is clearly demonstrated. A review of the very recent chemical kinetic work is given in Reference 13. The many reactions of both clean-air and carbon chemistry involved with reentry ablation problems are reviewed by Heicklen in Reference 14. The remarks presented in the present section will be concerned specifically with the nitric oxide reactions in air, in order to illustrate the level of complication for a two-gas mixture.

The primary chemical processes in shock-heated air other than the dissociation reactions, are those resulting in production of nitric oxide. They were studied by Glick, Klein and Squire[99] in the chemical shock tube, where air was heated to high temperature by a shock wave and then cooled rapidly after a fixed length of time by an expansion wave. Subsequent analysis of the gas in the shock tube permitted evaluation of the mechanisms and rate constant. It was concluded that the mechanism was the one previously proposed by Zel'dovich[100], namely

$$(1) \quad O_2 + M \rightleftarrows 2O + M$$

$$(2) \quad O + N_2 \rightleftarrows NO + N$$

$$(3) \quad N + O_2 \rightleftarrows NO + O .$$

Thus the first oxygen atoms are produced[101] by dissociation of O_2, and then two "shuffle" reactions become active in producing NO. The importance of these shuffle reactions in expanding-flow chemistry is discussed in Section 4.3. In shock-heated flows the high speed of reactions (2) and (3) results in a large production of NO, in an attempt to bring the NO into local equilibrium with the O_2 and N_2 concentrations. When the O_2 later dissociates, the NO concentration decreases. Such NO overshoots were predicted by Duff and Davidson[102], and by Lin and Teare[103], and have been observed in shock-tube flows.

Recent experiments[104] indicate that it may be possible to investigate the NO-producing reactions in as much detail as has been obtained for dissociation reactions. Camac and Feinberg[104] have observed induction times in the formation of nitric oxide in air, and have correlated this with N_2 vibrational relaxation times. They suggest that the vibrational excitation of the nitrogen may be a prerequisite for reaction (2). Again, sensitive experiments to determine atomic oxygen production[88] would add considerably to the total knowledge about this reaction.

The formation of NO from the reaction

$$(4) \quad N_2 + O_2 \rightarrow 2NO$$

was not observed in the work reported in Reference 104, leading to the conclusion that this rate is at least 10 times slower than previously reported. The reverse reaction had previously been measured[105,15], using NO-absorbtivity measurements to determine the rate at which NO was destroyed behind a shock wave in pure NO. In Reference 104 it was determined that this rapid NO destruction was caused by the reaction

$$(5) \quad 2NO \rightarrow N_2O + O$$

rather than the inverse of reaction (4). They conclude that reaction (4) is usually unimportant for air kinetics. This simplification, along with chemical experiments in expanding flows (Section 4) may permit more detailed understanding of the shuffle reactions.

These recent considerations of the nitric oxide reactions constitute the major changes in the knowledge of measured reaction rates for neutral pure-air chemistry since the review presented by Wray[15] in 1962. The more recent data on N_2 dissociation rates should also be noted[74].

3.2.4 Ionization

The problems of ionizing and deionizing reactions in air have received a considerable amount of attention because of their connection with upper-atmospheric phenomena and with nuclear reactions, as well as their importance in reentry phenomena. The well known communications black-out during reentry results from a high density of free electrons in the vehicle flowfield, and free electrons in the trail of reentering missiles provide the reflecting material for radar returns. Thus, there has been a broad interest in the identification of ionic reactions and the measurement of rate constants over a range of temperatures from atmospheric up to many times that associated with reentry. The massive literature available on this subject is under constant review. There is presented here a brief summary of the review articles that are currently available, with emphasis on those directed toward aerodynamic problems.

The simplest models of high-temperature air flows use a single ionizing reaction[1,15]:

$$N + O \rightleftarrows NO^{+} + e .$$

For a good description of atmospheric reentry, however, a host of other reactions must be considered. For example, the forebody flow of an Apollo vehicle can be divided into four separate regions[106], with each region corresponding to a different type of ionizing reaction. For each type of reaction, many separate reactions must be considered. In References 16 and 106 this problem is reviewed for Apollo-reentry flows for pure-air reactions.

For missile reentry, the review of gas phase chemistry by Heicklen[14] includes some discussion of ion-producing reactions. The subject of pure-air ion chemistry is reviewed within the context of wake flows by Sutton[107] and the requirement of properly identifying the dominant ionic reactions is clearly demonstrated.

General reviews of both theory and experiment are given in several texts[9,17,18] and special publications[19]. Experimental data for electron-impact ionization was reviewed by Kieffer and Dunn[20] and a comprehensive bibliography of both theoretical and experimental results was recently prepared by Kieffer[21]. A current bibliography of electron swarm data is also available[22]. The recent publication of the NASA Reaction Rate Handbook[23] provides a summary with emphasis on the ion chemistry of high-altitude nuclear bursts.

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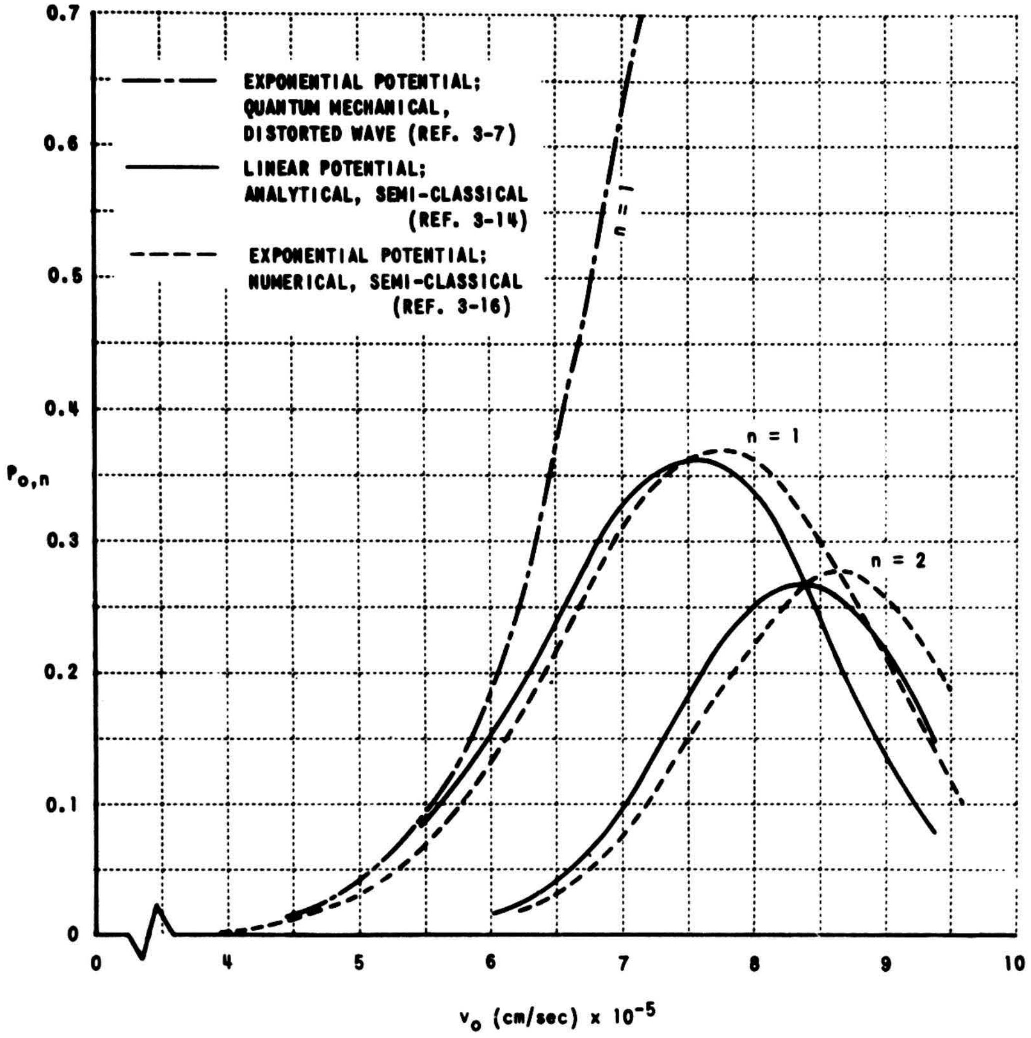

Fig. 3-1 Calculated vibrational transition probabilities for nitrogen

SECTION 4

NONEQUILIBRIUM FLOWS IN SUPERSONIC NOZZLES

The classical convergent-divergent de Laval nozzle accelerates gas from subsonic to supersonic velocities with attendant conversion of internal or thermal energy to the kinetic energy of bulk motion. The isentropic expansion of a perfect gas in such a nozzle is a familiar flow example discussed in all textbooks on gasdynamics (e.g. Liepmann and Roshko[1]). As the usual analysis based on pseudo-one-dimensional, inviscid flow shows, local sonic or critical flow conditions are attained at the minimum cross-section area, or throat, of the nozzle. Downstream of the throat the gas pressure, density, and temperature decrease very rapidly, while the gas velocity increases; typical maximum cooling rates might be in the range 10^5 to 10^6 °K/sec. For large expansions (large ratio of nozzle exit area to throat area) the exit flow Mach number becomes hypersonic, and the exit values of p, ρ, and T are very much less than the pre-expansion nozzle reservoir values.

The typical situation of present interest is where the inlet or reservoir gas is in thermal-chemical equilibrium prior to expansion. It turns out that over a wide range of reservoir conditions and nozzle scale of practical interest, the rate or relaxation processes discussed in Section 3 have characteristic times of the same order of magnitude as, or larger than, particle residence or flow times in the nozzle. As a consequence, departures from equilibrium in practice can be quite large. If sufficient energy is involved, the relaxing mode can interact strongly with the local thermo-gasdynamic state of the nozzle flow. Typically, energy is withheld or "frozen" in the relaxing mode during expansion (e.g. lagging atom recombination) with a consequent reduction of nozzle flow pressure, velocity, and temperature below the corresponding equilibrium flow values.

The discussion will be limited to nonequilibrium effects in such nozzle flows involving either the vibrational, chemical, or ionization relaxation processes discussed in Section 3. While departures from local equilibrium in translational as well as rotational degrees of freedom have been observed in steady expansion flows[13-16] significant nonequilibrium effects in these degrees mainly occur at lower densities than of concern here.

The pseudo-one-dimensional formulation of the inviscid, nonequilibrium nozzle-flow problem will be briefly outlined first, and some general features of the solution and aspects of numerical integration of the governing equations will be discussed. Subsequent sections then discuss some particular theoretical and experimental results for nonequilibrium nozzle flows involving dissociation, vibration, and reacting gas mixtures. Previous review articles pertinent to the scope of the present discussion include the excellent review papers by Bray[8]; Penner, Porter, and Kushida[9]; and Olson[10, 11].

4.1 Pseudo-One-Dimensional Formulation and Methods of Solution

Most analyses of nonequilibrium effects in steady supersonic nozzle flows have been simplified by assuming the flow to be pseudo-one-dimensional as well as inviscid, adiabatic, and shock free. The one-dimensional flow approximation assumes that all flow quantities depend only on axial distance x along the nozzle; gradients and velocity components normal to x are neglected. This approximation is valid provided the nozzle expansion angle is sufficiently small. The pseudo-one-dimensional flow approximation is certainly adequate for revealing basic effects, and is not inconsistent with the limited state of knowledge concerning typical nonequilibrium rate processes of interest. Even disregarding two-dimensional effects and considering only the simplest rate processes, such as dissociation-recombination of a diatomic gas, analysis of the problem is still far from trivial*.

From pseudo-one dimensional flow, the fluid-dynamic equations for inviscid steady flow simplify to

$$\rho u A = m = \text{constant} \tag{4-1}$$

$$\rho u \frac{du}{dx} + \frac{dp}{dx} = 0 \tag{4-2}$$

$$h + \frac{u^2}{2} = h_0 = \text{constant} . \tag{4-3}$$

These equations express conservation of mass, momentum, and energy, respectively. The quantity A is the local cross-section area of the nozzle, assumed to be a prescribed function of distance x .

If we regard p , ρ , T , and u as the primary thermodynamic dependent variables of interest, then three additional relations are needed to complete the formulation. These are: (i) the thermodynamic equation of state for ideal-gas mixtures, i.e. $p = \rho R_0 T \sum_{j=1}^{s} \gamma_j$; (ii) a caloric equation of state expressing the specific enthalpy h in terms of the translational temperature T and the nonequilibrium variables considered, e.g. vibrational energy e_{vj} or species mass concentrations γ_j ; and (iii) the appropriate system of rate equations and element conservation equations expressing the rates of change of the nonequilibrium variables. The particular expressions for h and typical rate equations for vibrational or chemical nonequilibrium have been given in Sections 2 and 3.

The necessary boundary conditions can take various forms depending on the particular problem or nozzle geometry considered. For initially supersonic flow expanding in a continuously diverging nozzle, the initial state may be specified. The case of supercritical flow through a converging-diverging nozzle is somewhat more difficult as regards boundary conditions. Commonly in this case the thermodynamic state of the

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* Consideration of two-dimensional effects in nonequilibrium nozzle flows may be found in References 119-122.

gas effectively far upstream of the nozzle throat is specified, i.e. the equilibrium reservoir or stagnation conditions, denoted by p_0 , ρ_0 , and T_0 , say, corresponding to the gas initially at rest. In addition, for supercritical flow a boundary condition must be applied at the throat to fix or determine the nozzle mass flow m (Equation (4-1)) as the maximum or critical value. The problem is thus a two-point boundary value one. In general, the throat boundary condition equates the local flow velocity to the appropriate local sound speed, as further discussed below.

Because actual reaction rates are finite and streamwise gradients exist, the accelerating flow from an equilibrium reservoir must progressively depart from equilibrium, as is evident from the rate equations of Section 3. As previously mentioned, the effect of nonequilibrium is to reduce the pressure, temperature, and velocity from equilibrium values, whereas the local density is increased. Because of the normal decrease of gas density and temperature with flow acceleration, the local reaction rates typically decrease strongly (or local relaxation lengths increase strongly) as the gas expands down the nozzle. This quenching effect becomes particularly strong immediately downstream of the throat where streamwise gradients are large. As a consequence of departure from equilibrium together with quenching, the expanding flow typically undergoes a transition from equilibrium to frozen conditions. The location of this transition in the nozzle depends on nozzle geometry and reservoir pressure, as well as on other parameters. Of course, the maintaining of equilibrium flow is favored by large scale and high pressures. Over a wide range of nozzle scale and reservoir pressures of practical interest, significant departures from equilibrium flow occur only downstream of the nozzle throat.

It is often useful to have the limiting solutions for equilibrium and frozen nozzle flows, corresponding to infinite and zero reaction rates, respectively, for comparison with experiment or corresponding nonequilibrium (finite-rate) solutions. The calculation of these two limiting cases is relatively straightforward as both limiting flows are isentropic[4], and their solution involves only algebraic equations. Thus Equation (4-2) may be replaced in both cases by the appropriate entropy relation $S(\rho, T, \gamma_j) = S_0$ = constant . The rate equations may be replaced by the corresponding equilibrium Law of Mass Action in the equilibrium case, and by the conditions of constant vibrational energies or species mass concentrations in the frozen case. The throat boundary condition to determine the critical mass flow equates the flow velocity at the geometric throat to the local equilibrium sound speed $a_{e\star}$ for equilibrium flow and to the local frozen sound speed $a_{F\star}$ for frozen flow. Because of the limiting nature of both flows, i.e. infinite or zero reaction rates, both solutions depend only on the local nozzle area ratio $A/A_\star$ ($A_\star$ = throat area) for given reservoir conditions, and not on the nozzle shape or scale. Whereas the (completely) frozen solution is further independent of the reservoir state (e.g. when normalized as p/p_0, etc.), this is not so for the equilibrium solution. Detailed discussion of a calculation method for equilibrium and frozen nozzle flows is given by Vincenti and Kruger[4]. Specific solutions for such nozzle flows of air are given in References 94-96.

In contrast to the equilibrium or frozen flow cases where the solution at any point depends only on the overall area change involved, the solution for nonequilibrium or finite-rate nozzle flow depends at any point on the entire history of the flow up to that point. In particular, the nonequilibrium flow solution at any point depends on the preceding history of the nozzle shape as well as on the area change itself. Typically in the nonequilibrium case the governing differential equations, i.e. the fluid dynamic and coupled nonlinear rate equations, are intractable analytically, and a solution must therefore be obtained by numerical or step-by-step forward integration. Beginning with the development of exact numerical methods and solutions for nonequilibrium nozzle flows of diatomic gases[17, 18, 21], much effort has been devoted to the successful development of high-speed computing machine methods for calculation of nonequilibrium nozzle flows involving complex systems of coupled reactions[67-79].

The numerical integration of the nonequilibrium nozzle flow equations encounters a basic difficulty when the starting point is an equilibrium state upstream of the throat and the nozzle geometry is specified. This difficulty is the resulting two-point boundary-value problem. The critical mass flow m, which is determined by a boundary condition at the throat region equating the local flow velocity to the local frozen sound speed, cannot be determined *a priori* since the flow in the throat region depends on the entire preceding flow history. A further complication is the fact that under nonequilibrium conditions the sonic condition $u = a_F$ for supercritical flow does not in general occur at the geometric nozzle throat but an unknown distance downstream of that point.

To illustrate the foregoing remarks, consider the familiar relation

$$\frac{1}{u}\frac{du}{dx} = \frac{(1/A)dA/dx}{\dfrac{u^2}{(dp/dx)/(d\rho/dx)} - 1} , \tag{4-4}$$

which is readily derived from Equations (4-1) and (4-2). As for the case of perfect gas flow, this relation states that at the geometric throat, $(dA/dx) = 0$, the flow velocity must equal $[(dp/dx)/(d\rho/dx)]^{\frac{1}{2}}$ if the flow is to be continuously accelerating, i.e. $du/dx \neq 0$. For the equilibrium or frozen flow limits, we have $[(dp/dx)/(d\rho/dx)]^{\frac{1}{2}}$ equal to a_e or a_F, respectively. However, for nonequilibrium flow the quantity $(dp/dx)/(d\rho/dx)$ is not particularly useful since it is no longer a function of the thermodynamic state only, but depends on the particular flow history involved. An alternative relation to Equation (4-4) may be obtained from Equations (4-1) to (4-3) by considering the enthalpy h as a function of p, ρ, and α, say, considering the example of a dissociating diatomic gas. This relation is[4]

$$\frac{1}{u}\frac{du}{dx} = \frac{\dfrac{1}{A}\dfrac{dA}{dx} - \dfrac{h_\alpha}{\rho h_\rho}\dfrac{d\alpha}{dx}}{\dfrac{u^2}{a_F^2} - 1} , \tag{4-5}$$

where $h_\alpha = (\partial h/\partial\alpha)_{p,\rho}$ etc., and a_F is the frozen sound speed defined by

$$\left(\frac{\partial p}{\partial \rho}\right)^{\frac{1}{2}} = \left(\frac{\rho h_\rho}{1 - \rho h_p}\right)^{\frac{1}{2}} .$$

In general, the quantity $(h_\alpha/\rho h_\rho)(d\alpha/dx)$ in Equation (4-5) is positive. Thus the numerator of the right side will vanish only downstream of the throat where dA/dx is positive. At that point then, the condition $u = a_F$ must simultaneously apply (to make the denominator vanish) if the flow is to be supercritical. In practice, it is usually found that the point where $u = a_F$ is displaced only a small distance downstream of the geometric throat.

The simplest solution of the difficulty of the unknown critical mass flow is to determine its value by trial and error. That is, the solution is computed to the throat using successive guesses for the mass flow until supercritical flow downstream of the throat is obtained. The initial guess is guided by the equilibrium and frozen limits which do not differ greatly and which are less and greater, respectively, than the desired value. This approach has been used by Bray[17], and by Hall and Russo[18], and a systematic refinement is discussed by Emanuel[70]. Another solution to the difficulty, described by Eschenroeder, Boyer, and Hall[67], involves an inverse method. In this approach the starting point is the density distribution corresponding to equilibrium flow in the subsonic region of the given nozzle. A perturbation procedure, including perturbation of the nozzle geometry, then provides an exact nonequilibrium flow for a corresponding new nozzle geometry (subsonic) matching this density distribution. Because of the general insensitivity of flow density to nonequilibrium, the new subsonic nozzle geometry closely matches that originally given.

A second difficulty encountered in numerically solving the nonequilibrium nozzle flow is that of starting the integration of the rate equations from an initial equilibrium state wherein the initial gradients of γ_j and e_{vj} given by the rate equations are identically zero. As pointed out by Bloom and Ting[9], the initial departure from equilibrium is mathematically a singular perturbation behavior, analogous, for example, to the fluid dynamic boundary layer. Starting methods used to overcome this difficulty include asymptotic expansions[17,18], linear perturbation about the corresponding equilibrium flow[67,71], and direct starting from equilibrium with the nonlinear rate equations[68].

Apart from the special problem in starting the integration from an initial equilibrium state, it may be noted that the usual numerical methods for integration of the exact nonlinear rate equations, such as the fourth-order Runge-Kutta scheme, for example, generally encounter a serious instability problem for near equilibrium flow conditions. In order to maintain stability near equilibrium, the integration step size must be kept very small. Thus the overall computing time can become unreasonably long if an appreciable region of near equilibrium flow is involved. The underlying reasons for this behavior are discussed in Reference 69. In the past few years, methods for overcoming this problem have been developed by several authors[73-77].

In spite of these difficulties, machine methods for computing nonequilibrium nozzle flows with complex systems of coupled reactions have rapidly been brought to a state of considerable efficiency and precision. Unfortunately, knowledge of pertinent reaction mechanisms and rates has not advanced at a similar pace. Currently, uncertainties in the fundamental kinetics often place a serious limitation on the significance of numerical solutions.

4.2 Dissociation Nonequilibrium in Nozzle Flows of Diatomic Gases

This section discusses an important example of chemical nonequilibrium in steady nozzle flow involving a single dominant reaction, namely, that of symmetrical diatomic gas which undergoes dissociation and recombination by two- and three-body collision processes, respectively, during the flow expansion. The appropriate type of rate equation for this example can be taken as that for the Lighthill ideal dissociating gas discussed in Section 3, i.e.

$$\frac{D\alpha}{Dt} = u\frac{d\alpha}{dx} = C'\rho T^{-s}\left\{(1-\alpha)e^{-D/R_0T} - \frac{\rho}{\rho_D}\alpha^2\right\}. \tag{4-6}$$

In terms of a local equilibrium value of α equal to α_e, defined in terms of density and temperature by the relation

$$\frac{\alpha_e^2}{1-\alpha_e} = \frac{\rho_D}{\rho}e^{-D/R_0T},$$

Equation (4-6) can be written

$$u\frac{d\alpha}{dx} = \frac{C'\rho^2T^{-s}}{\rho_D}\left\{\frac{1-\alpha}{1-\alpha_e}\alpha_e^2 - \alpha^2\right\}.$$

For $\alpha \ll 1$, this becomes

$$u\frac{d\alpha}{dx} = \frac{C'\rho^2T^{-s}}{\rho_D}\left\{\alpha_e^2 - \alpha^2\right\}. \tag{4-7}$$

Rate equations of the general form of Equations (4-6) or (4-7) can also describe nonequilibrium ionization where electron-ion recombination occurs by either a two- or three-body collision process without an energy of activation. In this case α represents the degree of ionization and D is the ionization energy per mole.

4.2.1 Numerical Solutions

Some of the earliest theoretical studies of nozzle-flow nonequilibrium governed by a single chemical reaction were done by Penner and his co-workers around 1947 (see References 2 and 9 for surveys). One of the first numerical solutions was obtained by Krieger[20] for the finite-rate dissociation and recombination of hydrogen in a rocket nozzle flow. Numerical solutions for hypersonic nozzle flows of dissociating diatomic gases were obtained by Bray[17] for the Lighthill gas and by Hall and Russo[18] for oxygen. The case of nonequilibrium ionization was studied by Smith[66], Eschenroeder[61], and Rosner[62]. More recently, comprehensive analytical treatments of nozzle-flow nonequilibrium for the Lighthill gas have been given by Blythe[22] and by Cheng and Lee[23, 24].

As previously mentioned, the numerical solutions for monotonically diverging nozzles typically exhibit the characteristic feature of the "freezing-out" of the atom mass fraction α, and thus the energy in dissociation, at sufficiently large area or distance down the nozzle. Illustrative results for the hypersonic nozzle flow of dissociated oxygen, taken from Reference 18, are shown in Figures 4-1 to 4-5. These figures show the computed variation of α, T, p, u, and ρ with nozzle area ratio A/A_* for the equilibrium reservoir condition $T_0 = 5900^\circ K$, $p_0 = 82$ atm. At this reservoir condition the oxygen is about 69% dissociated ($\alpha_0 = 0.6931$). The nozzle geometry for these calculations was axisymmetric of the form $(A/A_*) = 1 + (ax/L)^2$, with a throat radius $L = 0.5$ mm and asymptotic half-cone angle $\tan^{-1}\alpha = 7.5^{\circ}$ for large ax/L. The oxygen molecule was assumed to be a harmonic oscillator, in vibrational equilibrium throughout the expansion. The dissociation rate equation for α was of the general form of Equation (4-6); rate constant data from the shock tube studies of Byron[26] were used in the calculations.

Several distinct regions may be identified in the variation of α as typified by Figure 4-1. Following departure from the equilibrium reservoir state, near equilibrium conditions are maintained initially, in this case until some distance downstream of the throat. A rather rapid departure from equilibrium then occurs over a limited transition region. Downstream of this region, α approaches asymptotically a constant frozen value*. The temperature (Fig. 4-2) is strongly affected by freezing in this case because of the significant fraction of the total enthalpy frozen in dissociation. When the transition to frozen dissociation commences, the temperature decreases rapidly from the equilibrium limit as the heat release from recombination decreases. The static pressure (Fig. 4-3) is not as strongly affected, but the reduction in pressure below the corresponding equilibrium limit becomes quite large at large area ratios. The velocity and density (Figs. 4-4, 4-5) are least affected by freezing, and are decreased and increased, respectively, relative to equilibrium by roughly similar amounts since the mass flow is only weakly affected by nonequilibrium.

The frozen degree of dissociation is decreased by an increase in reservoir density ρ_0, recombination rate constant k_R, or nozzle scale L/a, and by a decrease in reservoir temperature T_0. The numerical studies cited show that the effects of ρ_0 and T_0 in this respect are much stronger than of k_R or L/a. The strong effect of density level is due to the dependence of α_0 on ρ_0 as well as the dependence of $D\alpha/Dt$ on ρ^2. Typically, a change of a factor of two or three in k_R or L/a has little effect on the frozen dissociation level (k_R and L/a enter the nondimensional rate equation as a product). Also, the dissociation is only weakly affected by the exact temperature dependence of k_R, i.e. by weather s has the value 0, 1, or 2, for example, in the relation $k_R \alpha T^{-s}$ assumed.

4.2.2 Approximate Methods of Solution

Approximate methods for the analysis of dissociating nozzle flows have been developed by various authors, for example by Penner[2], Bray[17] and Hall and Russo[18], as well as by others. The method due to Bray for determining the approximate freezing point and frozen dissociation level in terms of a corresponding equilibrium solution will be briefly discussed since it has been widely used in recent years. The method of Reference 18 is essentially similar, and Penner has discussed the similarity of his criterion for near-equilibrium flow to Bray's method[9].

Bray's procedure is based on the following observations concerning the rate equation (Equation (4-6)) expressed as

$$\frac{D\alpha}{Dt} = R_D - R_R ,$$

where R_D and R_R are the rates of dissociation and recombination, respectively. Upstream of the transition region where freezing commences, the flow is close to

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* Under certain conditions to be discussed, freezing at a nonzero value of α may not occur.

equilibrium and R_D and R_R are large and very nearly equal. In this near-equilibrium region, $D\alpha/Dt$ is small compared with either R_D or R_R. Once appreciable departure from equilibrium has occurred, R_D rapidly becomes very small because of the exponential Arrhenius factor e^{-D/R_0T}. Downstream of the transition region, where the flow tends toward a frozen state, R_D is much smaller than R_R and $D\alpha/Dt \simeq R_R \gg R_D$. Thus in the change from near-equilibrium to near-frozen flow, R_D varies from $\gg D\alpha/Dt$ to $\ll D\alpha/Dt$. At some point in the transition region, $D\alpha/Dt$ must therefore be of the same order as R_D. Bray[17] postulates a narrow transition region, or sudden freezing, with the freezing point located where the relation

$$\left(\frac{D\alpha}{Dt}\right)_e = K(R_D)_e \tag{4-8}$$

is satisfied. Here K is a constant of order unity (set equal to 1 by Bray) and the subscript e indicates evaluation from the equilibrium-flow solution. The approximate solution obtained thus consists of an equilibrium-flow solution upstream of the freezing point and a frozen-flow solution downstream.

Since this approximate solution consists of two isentropic branches, it neglects the increase in entropy which occurs in the actual nonequilibrium flow. However, the entropy rise which occurs in such nonequilibrium expansions is generally very small compared with the reservoir entropy itself, as discussed in detail by Eschenroeder[27]. As a further extension of the sudden freezing approximation, Bray[28] showed that the gas properties at the freezing point (α_F, T_F, h_F etc.) depend only on the reservoir entropy S_0 (and not also on h_0, for example) for a particular nozzle geometry. Thus within the accuracy of the sudden freezing concept, nonequilibrium flows in a given nozzle may be represented as isentropes on a Mollier-type diagram of h versus S_0. This usefulness of the reservoir entropy as a correlating parameter for nonequilibrium nozzle flows extends to more complex chemistry, as discussed in Section 4.4 in connection with nozzle flows of air.

Comparisons made by various authors (e.g. References 17, 18, 29) of the approximate, sudden freezing solution with exact numerical solutions show the sudden freezing approximation to be surprisingly accurate over a wide range of conditions despite its empirical nature (see Figure 4-1). Typically, the sudden freeze approximation predicts the frozen dissociation level to within a few percent. Several authors have improved on this simple sudden-freeze solution by taking account of the variation of α in the asymptotic recombination region downstream of the freezing point. This was done by Smith[21], Eschenroeder[61], and Rosner[62] for the case of weak ionization decoupled from the gasdynamic behavior (where the rate equation is of the general form of Equation (4-7) and by Eschenroeder[27] for atom recombination. These authors obtained improved asymptotic solutions by solving the equation $D\alpha/Dt \simeq -R_R$ applying in the near-frozen, recombination region and matching to the equilibrium solution at the freezing point determined by Equation (4-8).

4.2.3 Analytical Treatments

As distinct from numerical or semi-empirical treatments, rigorous analytical treatments of nozzle-flow nonequilibrium governed by the nonlinear Lighthill-gas rate (Equation (4-6)) have been given by Blythe[22] and by Cheng and Lee[23,24]. Blythe, who also treats separately the linear rate equation for vibrational relaxation (see Section 4.3), considers the case of very small dissociation such that the appropriate (nonlinear) rate equation is Equation (4-7) which is assumed to be completely uncoupled from the fluid dynamic equations. Blythe's analysis of this limiting case reveals three basic regions to the flow structure. As evidenced in the numerical studies of previous workers, these are: an upstream near-equilibrium region, a rather narrow transition region where rapid large departure from equilibrium occurs, and a downstream asymptotic region of near-frozen flow where recombination dominates. Correctly matched analytic solutions to these three regions are obtained. Blythe shows that the simple sudden-freeze solution discussed here is mathematically incorrect in the limiting case of weak dissociation. The error is primarily in using the wrong asymptotic solution downstream of the freezing point (i.e. completely frozen flow) rather than in matching this solution directly to the equilibrium solution (i.e. without the transition region rigorously required). In this respect, the asymptotic recombination solutions of References 21, 27, 61, and 62, which are also matched directly to the equilibrium solution, are a better approximation than the sudden freeze model.

The assumption that the rate equation (Equation (4-7)) can be uncoupled from the remaining gasdynamic equation limits α in practice to exceedingly small values. For negligible coupling, the energy in dissociation (αD per mole, say) must be a completely negligible part of the enthalpy. Any effect on temperature due to dissociation can have a very strong effect on $D\alpha/Dt$ due to the dissociation term in the rate equation containing the exponential factor e^{-D/R_0T}. Cheng and Lee[23] show that the completely uncoupled case applies only for $\alpha_{FP} << \epsilon^2$, where subscript FP denotes values at the freezing point given by Equation (4-8) and the quantity $\epsilon = (R_0T_{FP}/D)$ is assumed $<< 1$. Under the assumption of small ϵ, these authors define two basic flow regimes in terms of the ratio α_{FP}/ϵ, which is roughly the ratio of the energy in dissociation to that in the translational degrees of freedom. For regime I defined by $\alpha_{FP}/\epsilon \leqslant O(\epsilon)$, the gasdynamics are only weakly influenced by the chemistry, whereas for the regime II defined by $(\alpha_{FP}/\epsilon) \geqslant O(\epsilon)$, the gasdynamics are strongly influenced. In regime I the analysis of Reference 23 reveals the three basic flow regions found by Blythe. However, in regime II the analysis reveals four distinct flow regions: upstream equilibrium, incipient transition, rapid transition, and downstream recombination[23].

Cheng and Lee mainly treat régime II and obtain analytical solutions for the four flow regions by means of matched asymptotic expansions in the small parameter ϵ. They also assess the validity of previous approximate methods. In contrast to regime I, the simple sudden freeze solution of Equation (4-8) is shown to be valid and quite accurate for velocity in regime II, and also valid for the frozen dissociation level if $(\alpha_{FP}/\epsilon) >> 1$, provided the dissociation level does ultimately freeze. However, the sudden freeze solution for temperature is not rigorously valid, although the numerical error may typically be small. The authors[23] also determine the conditions for which the asymptotic downstream flow will freeze (i.e. conditions for which $\lim_{x\to\infty} \alpha = \alpha_\infty \neq 0$) for nozzle geometries of the form $A \propto x^{2m}$. For example, it is shown that the dissociation level will freeze ($\alpha_\infty \neq 0$) if $m > 1/4$, and will be "self limiting" ($\alpha_\infty = 0$) if $m < 1/4$, provided $|s| < 1$. Here s is the exponent for the inverse temperature dependence of k_R. For $s > 1$, the dissociation will freeze for $m > 3/\{2(7-s)\}$ and will be self limiting for $m < 1/4$. Subsequent to their initial study, Cheng and Lee have further generalized their analysis to include nozzle geometries of arbitrarily diverging shape[24].

4.2.4 *Experimental Studies*

Despite this extensive amount of theoretical study, and the pressing need for more precise chemical kinetic data in nozzle-flow environments, nonequilibrium nozzle flows involving a single dominant reaction have received rather limited experimental study. The lack of experiment is due in part to the difficulty of creating well understood flows with significant dissociation of diatomic gases as oxygen and nitrogen, as well as the generally difficult diagnostic problem involved in determining local chemical composition.

One of the earliest definitive nozzle-flow experiments involving a single reaction for dissociation and three-body recombination was done by Wegener[30-32] for the reaction

$$N_2 + N_2O_4 \rightleftarrows N_2 + 2NO_2 \ ,$$

which involves the dissociation of nitrogen tetroxide. The experiments were done in a carefully designed, closely one-dimensional supersonic nozzle. Small concentrations of N_2O_4 were used in a large excess of inert N_2 carrier gas. The rate constants for this reaction are well known in the temperature range of the experiments (about 250 to 400°K). The local NO_2 concentration along the nozzle was determined by measuring the absorption of blue light (4300 Å) to which N_2 and N_2O_4 are transparent. Appreciable departures from equilibrium composition were observed. Wegener's results generally confirm the theoretical expectations, and show good qualitative agreement with the simple sudden freeze model. Further experimental results obtained for the same chemical system, but in a strongly two-dimensional nozzle, are reported by Zupnik *et al.*[119].

Additional experimental studies of single-reaction chemistry in nozzle flows have included, for example, studies of dissociated nitrogen flows by nozzle static pressure measurements (Nagamatsu and Sheer[33]); dissociated oxygen flows by ultraviolet light absorption measurement of O_2 (Wilson[34]) and by catalytic-probe heat-transfer measurement of O (Reddy[35]; Bartz[132]); dissociated hydrogen flows by static pressure measurements (Widawsky, Oswalt, and Harp[36]; Russo, Hall, and Lordi[37]); and ionized air flows, where the dissociative-recombination reaction $NO^+ + e^- \rightleftarrows N + O$ dominates, by microwave interferometer measurements of electron density (Eschenroeder *et al.*[63]). Generally speaking, all such experiments have given results which agree qualitatively, at least, with the theoretical predictions based on available kinetic data and the flow models discussed. What few recombination rate data have been determined directly in these experiments do not contradict the usual assumption that $k_D/k_R = K_e(T)$ under nonequilibrium conditions. However, in most cases the precision of the recombination rate constant determination is too low to provide an accurate assessment of this relation. In particular, static pressure measurement, although perhaps the easiest type of measurement to make, is inherently a difficult approach to rate constant determination because of the relative insensitivity of pressure to nonequilibrium effects. Improved diagnostic methods are needed to exploit nozzle flows as a chemical kinetic tool with the precision desired.

4.3 Vibrational Nonequilibrium in Nozzle Flows of Diatomic Gases

In the preceding discussion of nozzle-flow nonequilibrium involving dissociation and recombination, the question of simultaneous vibrational nonequilibrium was not considered. The Lighthill gas model effectively assumes that vibration is always excited to one-half the classical equipartition value; the oxygen nozzle-flow solutions discussed were obtained assuming vibrational equilibrium. As discussed in Section 3, the coupled effects of nonequilibrium vibration and dissociation are a matter of current research. Simple models for such coupling in nozzle flows have been considered recently by several authors (e.g. Bray and Pratt[38], and Tirumalesa[40]). However, because of the lack of a firmly established theoretical model of coupling useful for flowfield analysis, most calculations of chemically reacting nozzle flows have assumed either vibrational equilibrium or else a vibrational relaxation process uncoupled from dissociation.

The present section will be limited to discussion of the simplest example of vibrational nonequilibrium in nozzle expansions, namely that where chemical change does not occur so that vibrational relaxation is the only rate process involved. An important example is the expansion of a diatomic gas from initial nozzle reservoir conditions of equilibrium state such that vibration is excited but dissociation is negligible. Such reservoir conditions are employed, for example, in lower-temperature operation of hot-shot and shock tunnels, and in steady-state heated nitrogen tunnels. Of course, the energy in vibrational excitation never becomes nearly as large a fraction of the total enthalpy as does the energy in dissociation at higher temperatures. Nevertheless, the vibrational energy is not negligible, being approximately 10% of the total internal energy in air at 2000°K for example. This amount of internal energy is enough to produce nontrivial gasdynamic effects if appreciable departure from equilibrium nozzle flow occurs. Thus vibrational nonequilibrium can produce effects of some importance on nozzle test-flow conditions in these types of wind-tunnel facilities.

4.3.1 Analysis for Harmonic Oscillator Model

As discussed previously in Section 3, the simplest equation which approximately describes the exchange of energy between vibrational and translational degrees of freedom in a pure undissociated diatomic gas is the linear equation due to Landau and Teller:

$$\frac{De_v}{Dt} = \frac{e_{v\,EQ} - e_v}{\tau_v} . \tag{4-9}$$

Here e_v is the vibrational energy per unit mass of gas and $e_{v\,EQ}$ is the value of e_v when vibration is equilibrated with translation. The quantity τ_v is the relaxation time for vibrational-translational energy exchange; τ_v is inversely proportional to collision frequency (or density) and increases strongly with decreasing translational temperature. As pointed out in Section 3, one of the several key assumptions on which this equation is based is that the molecules behave as simple harmonic oscillators for which the vibrational energy levels are equally spaced. In this case, the exchange of vibrational energy between the vibrational modes of two colliding molecules is a resonance phenomenon which serves only to redistribute vibrational energy without exchange with translational degrees of freedom. If a Boltzmann population of the vibrational energy levels is maintained, as is typically the case for harmonic oscillator molecules, the vibrational mode can be characterized by a vibrational temperature T_v . For the harmonic oscillator model, e_v is then given in terms of T_v by:

$$e_v = \frac{R_0 h\nu}{k\mu_0 (e^{h\nu/kT_v} - 1)} .$$

Despite its simplifying assumptions, Equation (4-9) has been widely used to analyze vibrational relaxation in nozzle flows. Although the equation is linear, numerical solution is still generally necessary for the calculation of nozzle flows, where both density and translational temperature vary strongly. However, because the vibrational energy is typically a rather small fraction of the total enthalpy, Equation (4-9) can often be decoupled from the associated fluid dynamic equations without introducing significant error.

Numerical solutions based on Equation (4-9) have been obtained by several authors for diatomic-gas nozzle flows (e.g. References 41-44). Most of these calculations have used values for the relaxation time τ_v deduced from shock-tube experiments on vibrational relaxation behind plane shock waves. The calculations of Stollery and Smith[42] for vibrational relaxation in conical-nozzle flows of undissociated air give typical results. As the gas expands down the nozzle from the initial equilibrium state, the vibrational temperature T_v decreases more slowly than the rapidly decreasing translational temperature. At some point in the diverging nozzle, depending on the initial reservoir conditions and the nozzle geometry, the vibrational energy (or T_v) freezes or levels off at a constant value higher than the local translational temperature.

This freezing of vibrational energy is analogous to the freezing of molecular dissociation discussed previously. The gasdynamic effects are qualitatively the same as for dissociation freezing, but typically much smaller. Of course, in the case of vibrational relaxation only binary collisions are involved, whereas ternary collisions are also important in chemical nonequilibrium involving three-body recombination. It may be noted that as vibrational relaxation involves only two-body collisions, binary scaling can be applied to solutions of Equation (4-9) for undissociated flows in nozzles of given shape. For the nozzle geometry mentioned in Section 4.2, for example, solutions can thus be correlated or scaled in terms of the parameter ρ_0 (L/a) , where ρ_0 is the initial reservoir density, for a given gas and initial reservoir temperature or enthalpy.

Rigorous analytic treatment of Equation (4-9) for nozzle flows has been given by Blythe[22,47] for the limiting case where the vibrational energy is sufficiently small that Equation (4-9) can be decoupled from the fluid dynamic equations. Blythe's analysis and solutions reveal a gross mathematical similarity to the dissociation freezing pattern, in that three basic regions (as discussed in Section 4.2) characterize the flow structure. However, the detailed asymptotic behavior for vibrational freezing differs from dissociation due to the linearity of Equation (4-9) as opposed to the nonlinearity of Equation (4-6).

As for the case of dissociation freezing in nozzle flows, semi-empirical approximate methods, including similar sudden freeze approximations, have been proposed and used to estimate vibrational freezing from Equation (4-9) (see References 41, 43, 45, 46). Although these methods typically give results which agree quite well with numerical solutions, Blythe[22] shows them to be mathematically incorrect as in the case of weak dissociation freezing discussed in Section 4.2.

4.3.2 Experimental Studies

In contrast to the relative scarcity of experimental data on dissociation nonequilibrium in nozzle flows, considerable effort has been expended in recent years on nozzle-flow experiments involving vibrational relaxation. One reason for this activity is the results of initial experiments by Hurle, Russo, and Hall[48] in 1962-63 to measure vibrational temperature relaxation in nozzle flows of undissociated nitrogen. The vibrational temperatures determined in these experiments showed only qualitative agreement at best with the predictions of Equation (4-9) based on values of τ_v $(= \tau_{vs})$ from shock wave experiments. Quantitatively, the measured values of T_v were considerably lower than predicted, which suggested faster vibrational de-excitation than given by $\tau_v = \tau_{vs}$. These initial experiments stimulated further experimentation (Refs. 51-54, 56-58), and, more recently, theoretical studies concerning effects not included in Equation (4-9), particularly the effects of anharmonicity[59,60].

The experiments of Reference 48 utilized the particular spectrum-line reversal method due to Gaydon and Hurle[5,49] as the diagnostic technique to determine the vibrational temperature of N_2 at different stations along a 15°-conical nozzle driven by a shock tube. The technique involves simultaneous monitoring of the emission and absorption intensities of a suitable spectrum line from a trace species (Na and Cr were used) added to the test gas. Interpretation of a vibrational temperature depends on close equilibration of the electronic transition with the vibrational mode. Typical results from these experiments in the form of T_v/T_0 versus A/A_* are shown in Figure 4-6 for both Na and Cr as the trace additives for line-reversal measurement. The uppermost curve in Figure 4-6 is the prediction of Equation (4-9) with τ_v equal to τ_{vs}, the value deduced from shock-wave experiments. The lowest curve is for complete equilibrium flow, i.e. $\tau_v = 0$. The experimental points are fitted by the curve shown, which is calculated from Equation (4-9) with τ_v equal to $(1/70)\ \tau_{vs}$. Thus the data suggest that the vibrational de-excitation of N_2 in the nozzle flow proceeds much faster than predicted by the Landau-Teller relaxation equation on the basis of the shock-wave relaxation times*.

In view of the unexpected nature of these results, further experimentation, including the use of different diagnostic techniques, has been done on vibrational relaxation in nozzle flows of N_2. In total, these further studies support the results of Reference 48. Further Na line-reversal experiments include studies of the influence of impurities (Russo[51]), and the behavior of dilute N_2-Argon mixtures with attention to the effects of free electrons (Hurle and Russo[52]). Different diagnostic techniques applied include the electron beam method (Petrie[53] and Sebacher[54,55]) where the N_2 is ionized and electronically excited by a narrow beam of electrons passing through the flow field. The vibrational temperature of ground state N_2 is deduced from the ratios of intensities of different vibrational bands in the observed emission spectrum (usually of N_2^+). A different reversal spectroscopic technique has been used recently by Russo[56] wherein CO is added in trace amounts to the N_2 as a thermometric element. Band reversal spectroscopy using the fundamental, infrared vibration-rotation band of CO permits determination of the CO vibrational temperature, from which the coupled vibrational temperature of N_2 can be deduced†.

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* The factor 1/70 is a revision from the earlier value 1/15 given in Reference 48. The value of this factor depends on the reference values chosen for τ_{vs}. The revision to 1/70 from 1/15 is based on what is believed to be a better correlation of data for τ_{vs}, as discussed in Reference 50.

† In addition to these experiments on N_2 vibration in steady expanding flows generated in a nozzle, Holbeche and Woodley[58] have used the Na line reversal method to determine vibrational temperatures in one-dimensional, unsteady expansion flows generated in a shock tube. Their results show a similarly fast relaxation for N_2, but not, however, for CO.

As already noted, the further studies of N_2 vibrational relaxation in nozzle flows generally support the finding of Reference 48 that the effective relaxation time in the nozzle flow is smaller than behind the shock wave at the same translational temperature and density. The nozzle-flow vibrational temperatures measured by the different techniques and experimenters appear to be in good quantitative agreement, as discussed in References 50 and 55*. Based on the experiments of References 48, 53, and 54 and Equation (4-9), Sebacher[55] has deduced an empirical expression for the variation with temperature of the vibrational relaxation time of N_2 in nozzle flows, which is then usable with Equation (4-9) for the purpose of calculations. This expression is

$$\tau_v p = 3 \times 10^{-12} \exp (181\ T^{-1/3}) \text{ atm sec} ,$$

where τ_v is the relaxation time in seconds, and p the local static pressure in atmospheres. Although Equation (4-9) with this expression for τ_v will give predictions for T_v in agreement with the above-mentioned experiments, it must be emphasized that such a procedure is empirical, and without a rational basis at present. As mentioned at the end of this section, recent theoretical studies suggest that anharmonic effects may be partly responsible for the different behavior of N_2 vibrational relaxation in nozzle flow and shock wave environments. Such effects are not included in Equation (4-9).

Similar nozzle-flow experiments with CO, again using the Na line-reversal method to measure vibrational temperatures, were done by Russo and Rich at the Cornell Aeronautical Laboratory[50]. Qualitatively similar results as for N_2 were observed in that the measured vibrational temperatures were closer to equilibrium values than predicted by Equation (4-9) using shock-wave relaxation times. More recently, Russo[57] has repeated this experiment with CO but using the infrared band-reversal method mentioned above to measure T_v. Similar results were obtained as with the Na line-reversal method.

In Reference 48 it was speculated that the apparent faster vibrational relaxation in the N_2 nozzle-flow expansions as compared to shock wave flows was possibly due in part to differing effects of anharmonicity under the different thermo-gasdynamic conditions and initial states of molecular excitation existing in the two environments. In the shock wave flow, where the net relaxation process is excitation, the vibrational temperature is initially much less than the translational temperature. Also, the translational temperature and gas density remain roughly constant through the relaxation process. In the nozzle expansion flow, however, the net relaxation process is de-excitation. In this case the vibrational temperature is initially high, and rapidly becomes substantially higher than the translational temperature as the latter decreases strongly and a vibrational lag develops during flow expansion.

Recent theoretical studies suggest that anharmonic effects may indeed be a factor in the above respect[59, 60]. As discussed in Section 3, with anharmonic oscillators the vibration-vibration exchange process can produce very large departures from a Boltzmann-like population of the vibrational energy levels when the population of the low lying levels exceeds that for equilibrium with the translational temperature. The effect is to overpopulate the higher vibrational levels, and for sufficiently extreme

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* The recent work of Russo[56] using infrared band reversal with CO as a trace additive provides additional data beyond that discussed in References 50 and 55.

conditions, a large population inversion can occur. As vibration-translation energy exchange becomes more efficient at higher vibrational levels, this effect can increase the net rate of vibrational de-excitation. The low vibrational levels can become significantly underpopulated relative to predictions of the linear Landau-Teller relaxation equation. The conditions necessary for anharmonic vibration-vibration exchange to affect significantly the vibrational population, i.e. high vibrational energy and low translational energy, tend to occur in the nozzle expansion-flow environment, but not behind a shock wave. Rich and Rehm[59], and Bray[60] have recently considered theoretically the relaxation of anharmonic oscillator models which exhibit such effects. Bray's[60] work includes calculations of anharmonic relaxation effects for specific comparison with the N_2 nozzle-flow experiments of Reference 48. Although there is necessarily much uncertainty in the basic transition probabilities assumed in the theoretical model, it is encouraging that the calculated results show qualitative agreement with experiment.

4.4 Chemical Nonequilibrium in Nozzle Flows of Coupled-Reaction Gas Mixtures

Sections 4.2 and 4.3 have discussed the simplest examples of nozzle-flow nonequilibrium, involving only single rate processes governing dissociation or vibrational relaxation in diatomic gases. Of course, in technical applications involving nonequilibrium nozzle flows the working fluid is often a multi-species gas mixture involving coupled chemical reactions, rather than a pure diatomic gas. This is the case with high-enthalpy airflows in hypervelocity test facilities, and is typically the case also with nozzle flows of interest in the propulsion field. This section will review briefly some typical studies of such coupled-reaction nozzle flows. The example of high-enthalpy nozzle airflow is emphasized because of its relative importance; some considerations of nonequilibrium effects in hypervelocity wind-tunnel testing are included (Section 4.4.2).

As discussed in Section 4.1, machine computational methods are now fairly well developed for obtaining "exact" numerical solutions to nonequilibrium nozzle flows of complex chemically reacting mixtures. Typically, present machine codes for this purpose are based on the simplifying gasdynamic assumptions of pseudo-one-dimensional and inviscid flow. In particular, the one-dimensional flow assumption does not represent a fundamental limitation, but is more a matter of practical convenience as regards the costs and limitations of present machine computing techniques. It may be noted that what studies have been made of two- or three-dimensional inviscid nozzle flows with nonequilibrium chemistry suggest that departures from a one-dimensional inviscid-core behavior may often be significant, particularly as regards the chemical composition (see, for example, References 119-122). Thus, inclusion of two-dimensional effects in the supersonic inviscid core will likely become more common (for example, using the method of characteristics) as the general capabilities of computing mechines, and also the knowledge of reaction rate-constant data, continue to improve.

Of course, particularly with complex mixtures the various simplifications and uncertainties in the phenomenological description of the physical-chemical rate processes involved constitute the real limitation of present nozzle-flow machine codes. With complex kinetics, a description of the coupling of chemical reaction rates with internal degrees of excitation is generally not attempted. All internal modes, including vibration, are usually assumed to be in thermal equilibrium with the translational temperature. Thus the forward and reverse specific rate constants of all reactions are related through the equilibrium constants in the usual way. With ionized nozzle flows the problem is further complicated by the effects of Coulomb forces and the possible lack of equilibrium between the light free electrons and the translational energy of the heavy particles. No doubt the mathematical description of the kinetics of complex mixtures will continue to improve as knowledge increases of important elementary reactions and rate constants, as well as of the influence of internal degrees of excitation.

The approximate methods of analysis described in Section 4.2 for dissociating diatomic gases have had some extension to multi-component coupled-reaction nozzle flows, principally for gas mixtures of interest in propulsion applications (e.g. References 8, 78, 81, 83, 84, 88, 89). However, the general applicability of the simple sudden-freeze approximation to complex kinetics systems appears rather limited. Apart from the question of mathematical correctness, which exists even for the pure diatomic gas case (Section 4.2), the detailed manner of application of sudden-freeze criteria becomes quite arbitrary and empirical with complex systems. The basic difficulty is that in a complex kinetics system, neither all species nor reactions "freeze" simultaneously in general. Typically, complex mixtures of interest involve fast bimolecular exchange-type reactions in addition to coupled dissociation-recombination reactions. Such bimolecular reactions do not tend to freeze, and can provide such a fast path for atom removal that atom freezing does not necessarily occur. Wilde[88] gives a brief but informative summary of various approaches taken to apply the simple sudden-freeze concept to complex mixtures. These approaches include applying the sudden-freeze criterion of reactions[8,84] to species[78], and to the average molecular weight of the mixture[83]. Perhaps the main usefulness of approximate methods for complex kinetics at present is where the basic chemical kinetic behavior of the flow is already fairly well known from more exact methods of solution. Certainly where applicable and carefully used, approximate methods can provide worthwhile reductions in computing effort. This is illustrated, for example, by Migdal and Goldford[122] who greatly simplify the analysis of nozzle-flow two-dimensional effects by applying a sudden-freeze criterion along individual streamlines. The streamline gasdynamic histories and geometries are initially determined by the method of characteristics for equilibrium or frozen flow.

4.4.1 Nonequilibrium Nozzle Flows of Propulsion Mixtures

The past five or six years has seen intensive application of the machine codes to study nonequilibrium nozzle flows of complex mixtures specifically of interest in various propulsion applications, as well as of air. Of course, chemical freezing in rocket exhaust nozzles has long been of interest because of the consequent loss in rocket thrust or specific impulse. Usually, however, such effects are not of major importance with solid or liquid propellant rockets of modest performance. The limits of equilibrium and frozen flow might typically give thrust differences of several percent, so that with the characteristically high pressures of rocket chambers and modest nozzle expansion rates, the percentage impulse loss due to nonequilibrium effects tends to be quite small. Nonequilibrium nozzle-flow effects can assume much greater importance with high performance rocket systems and hypersonic ramjet applications[10,11,80]. In the case of the hypersonic ramjet, the net propulsive thrust represents essentially the relatively small difference between the exhaust and inlet momentum fluxes, both of which are large quantities. Thus nonequilibrium effects of a magnitude considered unimportant for rocket performance can be quite important for hypersonic ramjet performance.

A comprehensive review of research in this area up to 1962 is given by Olson[11]. Representative numerical studies of recent years are those of Westenberg and Favin[84], Sarli *et al.*[85], and Wilde[87, 88]. Westenberg and Favin did a comprehensive study of nonequilibrium nozzle flows for two important types of mixtures: one typical of rocket exhaust products, containing H_2, H_2O, CO, CO_2, H, and OH and described kinetically by four elementary reversible reactions; and a second typical of ramjet exhaust products after hydrogen-air combustion, containing H_2, H_2O, O_2, H, OH, and O and described kinetically by eight elementary reversible reactions. Particularly, for the ramjet example, the results demonstrate the importance of bimolecular reactions such as

$$\text{(a)}\quad H_2O + H \rightleftarrows H_2 + OH\,, \qquad \text{(c)}\quad H_2 + O \rightleftarrows OH + H\,,$$

$$\text{(b)}\quad O_2 + H \rightleftarrows OH + O\,, \qquad \text{(d)}\quad H_2O + O \rightleftarrows OH + H\,,$$

which are typically fast compared to the several dissociation-recombination reactions involved.

For the example of H_2-Air combustion, Figure 4-7 shows results from Reference 84 for calculated equilibrium and nonequilibrium distributions of H_2, H, and OH along a 25° conically divergent nozzle. The mixture expands from supersonic, initial equilibrium conditions of 3000°K and 5×10^5 cm/sec velocity at the initial pressures and H_2/air stoichiometric equivalence ratios (E.R.) shown. The departures from equilibrium composition are seen to be substantial. Increased pressure level produces a flow closer to equilibrium, as in the case of the pure diatomic gas. Also, the gas-dynamic consequences of nonequilibrium are similar to the pure diatomic gas case - local pressure, translational temperature, and velocity are reduced below corresponding equilibrium values. The faster than equilibrium rate of decrease of H_2 and OH at low pressure, and the downstream increase in H at high pressure, are interesting features which are due to the dominance of the above bimolecular reactions. As will be discussed, bimolecular reactions play a similarly important role in the case of air, where analogous reactions to (b) and (c) must be considered involving NO.

In the study by Sarli *el al.*[85], machine calculations of a similar nature were done for H_2-air combustion products expanding in a subsonic-entry ramjet exhaust nozzle. In this case the chemical kinetic model also included the bimolecular and dissociation-recombination reactions involving N and NO which had previously been demonstrated to be important in high-temperature pure air expansions[98, 97]. However, in the example considered, the inlet temperature before expansion (about 2800°K) was really not high enough for N and NO to play a significant role. The nozzle entrance conditions in this example were near-equilibrium conditions resulting from a separate machine calculation of the H_2-air combustion process in a subsonic constant-area combustor. The same kinetic system and calculation methods were applied by the authors to estimate the relative importance of thrust losses due to skin friction and chemical nonequilibrium for a simplified supersonic-combustion ramjet configuration employing a conical exhaust nozzle[86]. The results indicate that skin friction losses are dominant, but that for optimum nozzle expansion angles and high thrust levels the nonequilibrium losses are of comparable magnitude at the flight conditions considered (flight Mach number of 15 at 150,000 ft altitude).

Wilde has performed careful numerical studies to assess nozzle-flow nonequilibrium effects for several complex kinetic mixtures which give high rocket impulse. The study of Reference 87 concerns $H_2 - F_2$ mixtures while Reference 88 considers UDMH/N_2H_4 - N_2O_4 and also $CH_2 - O_2$ systems. Particularly in the case of hydrogen-fluorine, the combustion temperature is sufficiently high that appreciable energy can be stored in molecule dissociation prior to flow expansion in the nozzle. Thus the thrust loss from chemical freezing becomes of greater importance with such high performance systems[11]. In both studies, impulse values are calculated using the assumed kinetic models and rate constants for comparison with selected experimental data. For $CH_2 - O_2$, the calculated exhaust temperatures agree well with experimental values reported by Boynton[123] for the RP-1/O_2 (gas) propellant system over a range of oxidizer/fuel ratios giving appreciable nonequilibrium effects. The calculated vacuum impulse exceeds experimental values of Fortini, Hendrix, and Huff[124] obtained for RP-1/O_2 (liquid) by amounts up to five or six percent. This discrepancy in impulse is attributed to unaccounted experimental losses, rather than inadequacy of the chemical kinetic model used in the calculations. In the case of the $H_2 - F_2$ system, the calculated vacuum impulse agrees very closely with experimental data (reported by Olson[11]) at higher chamber pressures for near stoichiometric mixtures, but falls a few percent below experimental values with increased amounts of H_2. At near stoichiometric ratios, the impulse loss due to nonequilibrium effects is about 5 to 6% for a chamber pressure of 20 atm, a conical nozzle half-angle of 15°, an expansion area ratio of 25, and a throat diameter of 10 cm.

Wilde interprets the relatively high experimental values of impulse with hydrogen rich $H_2 - F_2$ mixtures in terms of HF being unusually effective as a catalytic third body in H-atom recombination. On this basis, the three-body recombination rate constant with HF as the third body is interpreted as the order of 1000 times larger than with H_2 as the third body. The author also speculates that the inferred rate enhancement may be due to formation of the stable intermediate species H_2F and a consequent rapid two-body path for H-atom removal, i.e.

$$H + HF \rightleftarrows H_2F$$

$$H + H_2F \rightleftarrows H_2 + HF \ .$$

The interesting possibility of deliberately introducing such two-body chain reactions (as a faster path for atom recombination than three-body reactions) by addition of small amounts of a catalyst body to H_2 has been considered by several investigators (Refs. 92, 93, 125). Nonequilibrium nozzle-flow calculations to assess such possible gas-phase catalysis of H-atom recombination are described in Reference 92 for seeding with carbon, in Reference 93 for seeding with oxygen and oxygen-nitrogen mixtures, and in Reference 87 for seeding with fluorine. In general, the results of these numerical studies suggest that such catalytic seeding of dissociated hydrogen offers only marginal gains in impulse because of the molecular weight penalty that must also be incurred. More definitive theoretical assessment of this technique for reducing nozzle-flow dissociation levels requires more exact rate data for the elementary reactions involved.

Before turning to studies of high-enthalpy airflows, further mention may be made of nozzle-flow experiments with complex mixtures of interest in propulsion systems. In general, the emphasis in such experiments is on measurement of the gross thermo-gasdynamic characteristics as pressure, temperature, and nozzle thrust, for example. Representative studies of recent years include the experiments of Hoglund, Carlson, and Byron[90], on recombination lag in nozzle flows of the RP-1/O_2 (gas) system, the experiments of Lezberg and Franciscus[82] on nozzle flows of hydrogen-air and also methane-air combustion products, and the experiments of Boynton[123] with RP-1/O_2 already mentioned. Typically, the observed departures of the gasdynamic quantities from their equilibrium behavior are predicted fairly well by exact finite-rate calculations, in spite of the considerable complexity of the kinetic models and uncertainties in many of the rate constants involved. While this is encouraging, improved rate constant data are certainly needed, as are additional nozzle-flow experiments wherein species concentrations are also determined. On the difficult matter of determining species concentrations, the recent experiments of Hill, Unger, and Dickens[91] may be noted. These authors used infrared emission and absorption spectroscopy to determine the concentration of CO_2, as well as temperature, in nozzle expansions of solid-propellant combustion products containing CO, CO_2, H_2O, H_2, H, and OH. The concentrations of CO_2 along the nozzle axis determined from the absorption measurements are in good agreement with the authors' calculated results obtained from the kinetic model used by Westenberg and Favin[84].

4.4.2 Nonequilibrium Nozzle Flows of Air

The chemically-active neutral species of importance in dissociated air at high temperatures are usually taken to be N_2, O_2, N, O, and NO (Section 2). This composition neglects more complex molecules, such as high oxides of nitrogen, which are usually unimportant at high temperatures because of their small concentrations. As discussed in Section 3, an important kinetic role is played by NO, although it may only be present in relatively small amounts, through the fast bimolecular exchange or "shuffle" reaction system

1. $O + N_2 \rightleftarrows NO + N$

2. $N + O_2 \rightleftarrows NO + O$.

These reactions, in addition to the dissociation-recombination reactions

3. $O_2 + M \rightleftarrows 2O + M$

4. $N_2 + M \rightleftarrows 2N + M$

5. $NO + M \rightleftarrows N + O + M$

constitute the important elementary reactions governing the neutral species in high-temperature air, as was first demonstrated in the normal shock wave calculations of Duff and Davidson[126], and Lin and Teare[127].

Numerical solutions for nonequilibrium nozzle flows of dissociated air based on the coupled rate equations for the above kinetic model were first obtained by Eschenroeder, Boyer, and Hall[97,98] for a range of conditions of interest in hypersonic shock-tunnel testing. These solutions included equilibrium reservoir temperatures up to 8000°K at reservoir pressures from 10 to 1000 atm; the calculations were subsequently extended by Lordi and Mates[100,101] to 15,000°K and 9000 atm. These studies were essentially limited to determination of neutral species concentrations and the flow variables. For the conditions considered, the energy involved in ionization was sufficiently small that the ionization kinetics could be uncoupled from the fluid dynamic and neutral-species kinetics equations. Corresponding nonequilibrium solutions for the ionized species were subsequently obtained by Eschenroeder[61, 102].

The nozzle-flow solutions for the above kinetics reveal an important role of the bimolecular shuffle reactions 1 and 2 in delaying N-atom freezing. On flow expansion from the nozzle reservoir state, reaction 1, and also reaction 2 at higher temperatures and lower pressures, depart from equilibrium in the direction of N-atom removal because of the corresponding low activation energies. Even at relatively low concentrations of O_2 and NO, these bimolecular paths are much more efficient for recombining N atoms during the flow expansion than the three-body recombination path via reaction 4. As a consequence, the freezing of N atoms can be greatly delayed beyond the point where three-body recombination from reaction 4 has essentially ceased. Practically all N is thereby recombined to N_2 by this bimolecular path in dissociated air expansions from intermediate (100 atm) or higher reservoir pressures. This is in contrast to the very rapid freezing of N which would occur if three-body recombination through reaction 4 were the only path for N-atom removal.

The foregoing remarks are illustrated by Figure 4-8 from Reference 97 which shows (calculated) equilibrium and nonequilibrium species mass concentrations versus nozzle expansion ratio for air initially at 8000°K and 100 atm pressure expanding in a nozzle of geometry stated in Section 4.2 with $L/a = 1$ cm. At these reservoir conditions the nitrogen is appreciably dissociated, and the oxygen essentially completely so. The initial energy in nitrogen dissociation actually exceeds that in oxygen dissociation, being about 25% of the total enthalpy. The mass concentration of O atoms is seen to "freeze" essentially at the nozzle throat. The amount of O actually increases somewhat with flow expansion due to O-atom production via the bimolecular reactions 1 and 2 as three-body recombination of O via reaction 3 ceases. By contrast, the concentration of N drops rapidly with flow expansion due to the bimolecular path for N-atom removal. When N-atom freezing finally sets in, the N-atom concentration is only about 1% of the reservoir value.

Corresponding calculated results from Reference 97 for reservoir pressures of 10 atm and 1000 atm at 8000°K are shown in Figures 4-9 and 4-10, respectively. At low pressures (Fig. 4-9), the initial N-atom concentration is very large. Because of the low-density level not even the fast bimolecular reactions are effective in recombining N atoms in the flow expansion in this case. Hence, freezing of both O and N occurs at near reservoir levels. At high pressures (Fig. 4-10) the N-atom concentration is initially small and energetically unimportant, and is equilibrated during the flow expansion. Three-body recombination is greatly enhanced at this high pressure, and, as a result, O-atom freezing is appreciably delayed. Similar trends with increase in reservoir pressure are shown in the calculations of References 100 and 101 for higher reservoir temperatures.

It may be noted that the calculated entropy changes occurring in these nonequilibrium air expansions are typically a very small fraction of the reservoir entropy; i.e. the expansions are closely isentropic. The use of the reservoir entropy to correlate certain frozen properties of diatomic gas expansions for given nozzle geometry was discussed in Section 4.2. Lordi and Mates[100, 101] confirmed that a similar correlation applied to the exact solutions obtained for air expansions. Figure 4-11 shows such a correlation of the calculated enthalpy frozen in the expansion (h_F) for the range of air reservoir conditions noted and the nozzle geometry previously stated (L/a = 1 cm). The rather marked change in slope at about $S = 2.7$ cal/gm °K is due to the onset of significant freezing of N atoms. At higher values of S , oxygen is essentially all dissociated and frozen. Other nonequilibrium effects as frozen species mass fractions and reductions in pressure and temperature are also correlated by the entropy[100, 101, 104].

Experimental studies of nozzle flows of dissociated air wherein neutral species concentrations were determined appear to be virtually nonexistent to date. However, a number of experimenters have measured gasdynamic quantities, such as pressure, in dissociated nozzle airflows and demonstrated the expected magnitude of departures from calculated equilibrium values. Measurements of axial static pressure distributions have been reported, for example, by Nagamatsu and co-workers[33, 105], by Duffy[106], and by Zonars[107]. In addition to static pressure distributions along the nozzle wall, Zonars also measured the transverse distributions of pitot pressure, stagnation-point heat transfer, and local mass flow at the nozzle exit. Measurements of local molecular speed ratio (proportional to $U\sqrt{(\mu/T)}$, where U is local free-stream velocity, μ is molecular weight, and T is translational temperature) have been made by Vidal, Skinner, and Bartz[108] in shock-tunnel nozzle expansions of dissociated air using small-scale probe techniques which depend on free-molecule heat transfer.

In general, these experimental studies typically show a fairly good agreement between measured quantities and nonequilibrium values calculated on the basis of the chemical kinetic model for air already discussed. Figure 4-12, for example, shows a comparison given by Duffy[106] of measured and predicted axial static pressure distributions in a 30° total angle conical nozzle for air reservoir conditions of 7000°K and 250 lb/in^2 absolute. The experimental pressure data were carefully corrected for boundary-layer and static-pressure probe size effects. The reduction of the measured pressures below equilibrium values is seen to be very large at area ratios exceeding 100. The theoretical pressure distribution shown for nonequilibrium flow, calculated by Lordi[106] for the chemical kinetic model discussed above, is in close agreement with the experimental data. It may be noted that for the conditions of this experiment, the bimolecular exchange reactions previously discussed play an important role in recombining N atoms and thus determining the static pressure. Approximately equal amounts of energy are involved initially, in the reservoir, in oxygen and nitrogen dissociation. Whereas the energy in nitrogen dissociation is substantially recovered during the expansion, that in oxygen dissociation is largely lost due to the freezing of O atoms close to the nozzle throat.

While these experiments do provide at least some confidence as regards the prediction of gasdynamic effects due to nonequilibrium, there is clearly need for a more critical assessment of theoretical predictions by direct measurement of species concentrations in nozzle flows of dissociated air. As discussed in Section 4.2, static pressure and translational temperature mainly reflect the energy balance, and therefore tend to be relatively insensitive to detailed features of the kinetics which do not involve much energy.

The foregoing discussion has been concerned only with the nonequilibrium behavior of the neutral species in nozzle flows of dissociated air. As already mentioned, for the conditions considered the energy in ionization is sufficiently small that ionization phenomena do not influence the thermo-gasdynamic behavior of the flow significantly. Thus ionization nonequilibrium phenomena can be considered separately on the basis of the thermo-gasdynamic history of the flow determined from the neutral species only. Estimates of nonequilibrium ionization phenomena occurring in shock-tunnel nozzle airflows for the regime of reservoir conditions previously mentioned (i.e. reservoir temperatures up to 8000°K and reservoir pressures in the range 100 to 1000 atm) were first reported by Eschenroeder and Daiber[65]. These authors considered the following two elementary reactions for electron (e^-) removal, or deionization, in the expanding flow:

(1) $NO^+ + e^- \rightarrow N + O$

(2) $NO^+ + e^- + M \rightarrow NO + M$ (M is any neutral particle).

In most of the range of air reservoir conditions considered, the dominant positive and negative species are NO^+ and e^- whose concentrations were assumed equal. The bimolecular reaction (1), termed dissociative recombination, involves dissociation of the NO molecule by the energy given up in electron recombination, whereas reaction (2) involves the classical Thomson-type three-body recombination with a third and neutral body M required to take up the energy of recombination. On the assumption of thermochemical equilibrium of the neutral species, the authors employed these ion kinetics to estimate the approximate freezing behavior of free electrons in shock-tunnel air expansions. These estimates indicated appreciable freezing of the electron mass concentration, and also that the dissociative-recombination reaction (1) was the dominant process in removing electrons, except possibly at quite high densities. Despite the appreciable freezing indicated for the electron fraction, the electron number densities for nozzle expansions to typical hypersonic test conditions were predicted to be sufficiently low to avoid significant attenuation of electromagnetic propagation for microwave frequencies above about 10^9 c/s. This consideration is important in connection with shock tunnel applications involving microwave transmission through the ionized shock layer formed about a test model.

Subsequent studies by the same authors included analysis of the effects of seeding air expansions with cesium, in order to increase the electron density[61]; machine solutions for nozzle airflow ionization considering chemical nonequilibrium as well as a variety of elementary ion kinetic mechanisms in addition to reactions (1) and (2)[61,63] and experimental determination of electron densities and collision frequencies in shock-tunnel nozzle airflows by means of microwave interferometry[63]. These further studies essentially confirmed the dominance of reaction (1) as regards the most important ion kinetic mechanism for electron removal in the regime of shock-tunnel airflows considered. The more exact solutions also indicated that the electron mass fraction does not typically freeze fully, but may continue to decrease with flow expansion. The typical nonequilibrium behavior of electron mass fraction and the neutral species as predicted by machine calculation is shown in Figure 4-13. The lack of complete freezing of the electron fraction is a consequence of the dominant bimolecular recombination reaction and the inverse 3/2 power dependence of the associated rate coefficient on temperature. As discussed by Eschenroeder[61], and more recently by Cheng and Lee[23,24], the asymptotic freezing behavior also depends on the frozen neutral-species chemistry and the nozzle geometry.

In the past few years, intensive effort has continued on the study of the complex ionization phenomena occurring in high-temperature airflows. Much of this effort has concerned ionization nonequilibrium in external flows about hypervelocity bodies, particularly the problem of electron density decay in wake flows. Considerable progress has been made in further identification of important elementary ion and electron reactions and determination of specific rate coefficients, as discussed in recent surveys of Dunn[128], and Carnicom[129], for example. As regards ionization phenomena in hypersonic nozzle flows of air, the more recent studies of ionization kinetics do not appear to offer any basis for serious conflict with the general picture indicated above for reservoir conditions in the range noted. In particular, the conclusion remains that the dissociative recombination of NO^+ dominates the removal of free electrons in nozzle airflows typical of current shock-tunnel techniques. However, it must be emphasized that there is still a serious lack of definitive experimental investigation of nozzle flows of ionized air; the need here is perhaps even greater than the need for data on the neutral species chemistry. One important basic question that remains to be clarified is that of the electron temperature behavior. Numerous experiments indicate that the electron temperature does not equilibrate with the translational temperature in nozzle expansions, but tends to remain relatively high[39,52]. Certain specific rate coefficients of elementary reactions involving free electrons depend strongly on this temperature. Of course, there is a continuing need for data on specific rate coefficients. Various elementary ionization reactions have been considered theoretically for which little or no rate data have been obtained in air. One example is that of electron recombination via a three-body collision process, with a free electron serving as a catalytic third body. On the basis of present estimates, which suggest a relatively large rate coefficient, this process could be of comparable importance to two-body dissociative recombination for electron removal at shock-tunnel reservoir conditions giving very high electron densities.

4.4.3 Nonequilibrium Effects in Hypersonic Testing

The occurrence of such nonequilibrium phenomena as discussed in the preceding section creates a serious problem as regards model testing in hypervelocity airflows obtained by nozzle expansion from high enthalpy conditions. The problem is now well recognized, if not solved. Current shock-tunnel and arc-jet test facilities already operate at sufficiently high reservoir temperatures to encounter significant nonequilibrium effects at lower pressures; the effects will become more severe with future facilities having higher enthalpy performance. While it has been suggested that nozzle flow nonequilibrium might be favorably exploited in hypersonic testing (e.g. Reference 112 as regards the increase in flow Mach number and Reynolds number due to freezing), the customary view is that such effects are undesirable and to be eliminated if possible. Of course, this view is in the vein of duplicating in the wind-tunnel model test the ambient air chemistry through which the corresponding flight vehicle flies.

In recent years, considerable effort has been devoted to studying possible means of alleviating, or at least minimizing, the nonequilibrium test-flow problem and also to assessing the consequences for typical hypersonic test bodies of interest. Although most of these studies have been theoretical, their predictions must be given general credence in view of the improved status of the knowledge of air kinetics today, and the nozzle flow experiments previously discussed.

In essence, the studies reported to data have not indicated any method by which nonequilibrium effects can be essentially eliminated in conventional nozzle expansion flows. Studies to determine optimum nozzle shapes giving sufficiently slow expansions to maintain near-equilibrium flow, and duct lengths required for equilibration of frozen flow, indicate these approaches to be of limited usefulness because the rather extreme lengths required would entail excessive boundary-layer growth[17, 18]. Likewise, within practical limitations the increase of nozzle scale, or size, for a given shape offers very limited benefits because of the relative insensitivity of chemical freezing to scale[17, 18, 100, 101]. The possibility of seeding dissociated air with small amounts of additive to introduce fast bimolecular paths for O-atom removal (similar to the seeding of H_2 expansions previously mentioned) has received limited study. The calculations of Reference 130 for such seeding of air expansions with 0.01 mole fraction of H_2 suggest that this technique probably offers quite limited benefits in a practical sense. Thus it seems that the most effective method for suppressing nozzle airflow nonequilibrium still remains that of using high reservoir pressures, as earlier calculations of nonequilibrium nozzle airflows have indicated[12, 99, 100]. Of course, this approach is compatible with the need for high reservoir pressures in order that the test flow duplicate ambient density conditions appropriate to hypervelocity flight at lower altitudes.

Before reviewing the general magnitude of nozzle test-flow nonequilibrium effects, it may be noted that even if such effects were completely eliminated, and ambient flight conditions duplicated, a problem would still remain as regards the proper tunnel simulation of nonequilibrium effects occurring in the flow about the flight vehicle. For similar geometries of the test model and flight vehicle, proper simulation requires, in general, that the model be full scale. As is well known, this is necessary in order that the various time scales governing nonequilibrium phenomena remain in the correct ratio with fluid particle transit times characterized by L/U_∞, where L is the body length, say, and U_∞ is ambient velocity in flight (and tunnel). Of course, the traditional usefulness of wind tunnels is in testing models of reduced scale. For ideal gas flows, this can be done without sacrificing correct similitude, at least in principle. However, for simulation of flight situations where nonequilibrium effects are important, the constraints are rather severe if correct similitude is to be attained. Of course, other than full-scale testing, success here depends on sufficient *a priori* understanding of the flight problem that limited similitudes or partial simulation techniques can be exploited.

As a final remark in this digression, it may be mentioned that limited similitudes have been established which permit this requirement of a full-scale model to be relaxed for certain nonequilibrium flow situations. Obviously, the two limiting situations of either completely equilibrium or completely frozen flow about the flight vehicle permit model scale to be essentially arbitrary. This requires, of course, that the same limiting behavior obtains in the model flow field (which is generally difficult to accomplish for the equilibrium case) and that the appropriate fluid dynamic similitude is maintained (i.e. M_∞, Re_∞, etc.). An example here, which also offers flexibility as regards relaxing duplication of U_∞, is the equilibrium-flow inviscid similitude for blunt-nozed slender bodies due to Cheng (Reference 90, Appendix B). This similitude, which entails the assumptions of hypersonic small-disturbance theory, was also extended to include nonequilibrium flow. In the nonequilibrium case, U_∞ still need not be duplicated, but the scale L is no longer arbitrary but rather fixed according to the choice of U_∞ in order to preserve the flow transit time L/U_∞. Inger[15] has given the complete formalism for this type of similitude. A second special similitude which may be noted for nonequilibrium flows is that usually referred to as binary scaling. This entails an assumption about the nature of the nonequilibrium rate processes rather than about the fluid dynamics, namely, that all the rate processes involve only two-body or binary collisions. Thus three-body recombination is excluded. In this case, a simplifying similitude results in terms of the product ρL, where ρ is a characteristic density level in the flow field and L is the body scale. Detailed considerations and applications of binary scaling are given in References 111, 118, and References 37-40 and 53 or Appendix B.

Returning to the question of nozzle-flow nonequilibrium, it is instructive to review the magnitude of predicted effects in the expanded test gas for a range of reservoir conditions representative of the limits of current shock-tunnel testing techniques. Table I shows machine calculation results from Reference 111, for complete air kinetics, for the mass fractions of O, N, and NO frozen in nozzle air expansions from 6000 and 8000°K reservoir temperature and various reservoir pressures. The corresponding frozen enthalpy is also given. These results, which apply for the nozzle geometry $A/A_* = 1 + (Lx/a)^2$ with $L/a = 1$ cm, illustrate the need for high reservoir pressures to suppress nonequilibrium effects. This is particularly the case as regards oxygen-atom recombination which depends on three-body collisions. The effectiveness of the bimolecular reactions discussed for recombining nitrogen atoms is very evident in the results for 8000°K and 100 atm where essentially all N atoms are recombined. At the extreme of high reservoir temperatures and low reservoir pressures, the gasdynamic effects of freezing are very large; about 50% of the total enthalpy is frozen in the dissociated species at 8000°K and 10 atm. Whereas lower reservoir temperatures and higher reservoir pressures reduce the frozen mass fractions of O and N atoms, and also reduce the frozen enthalpy fraction, it will be noted in Table I that this trend is reversed for the frozen fraction of NO. Thus at low temperatures and high pressures, NO tends to become the dominant frozen "non-equilibrium" species, as illustrated in Table I for 6000°K and 1000 atm. At the extreme of low temperatures and high pressures in this respect, higher oxides of nitrogen not included in the present calculations might also be frozen at levels of some importance.

For expansions giving equilibrium airflow Mach numbers of 20, Table II shows results corresponding to Table I for the calculated ratios of actual (i.e. nonequilibrium) to equilibrium values of the test-flow gasdynamic quantities of interest. The Mach number in Table II is $u/[(dp/dx)/(d\rho/dx)]^{\frac{1}{2}}$, and the ratios of stream Reynolds numbers are based on a linear viscosity-temperature relation. The tabulated ratios are rather weakly dependent on the flow or nozzle expansion ratio in each case, so that the results are representative of an appreciable range of equilibrium Mach number. As expected from pure diatomic gas examples, the effects of freezing are largest on the translational temperature and pressure, and much smaller on the density and velocity. The reductions in temperature and pressure below corresponding equilibrium values become very large at 8000°K and 100 atm reservoir conditions. The reduction in temperature strongly increases the Mach number and more strongly the stream Reynolds number in this case*.

The generally large magnitude of predicted nonequilibrium effects in the test gas for expansions from high enthalpies emphasizes the need for much more complete measurement of test flow characteristics than has traditionally been necessary in wind-tunnel testing. Clearly the need here exceeds current state-of-the-art diagnostic techniques as regards routine measurement. This is most obvious for the determination of the frozen chemical composition of the test gas, but also applies to determination of the

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* Results similar to Tables I and II, but for reservoir temperatures to 15,000°K, are given by Lordi and Mates[100].

static temperature and pressure of a hypersonic test flow. The customary measurement of pitot pressure is of very limited usefulness as an indication of nonequilibrium effects since this quantity is essentially $\rho_\infty U_\infty^2$ and therefore is quite insensitive to nonequilibrium in hypersonic nozzle flows.

A number of studies have now been made, mostly theoretical, of the effects of test-flow nonequilibrium on the flow fields about typical hypersonic test bodies[109-118]. Typically a comparison is made of model flow-field quantities for equilibrium and nonequilibrium test streams expanded to the same area ratio from the same reservoir state. For equilibrium flow fields behind strong shock waves, the effects of test-flow nonequilibrium tend to be quite limited. An important example of this is the equilibrium stagnation-region flow on a blunt body. The reduction in pitot pressure p_0' due to nozzle freezing is roughly of the order

$$\frac{p_0' - p'_{0\ EQ}}{p'_{0\ EQ}} \simeq \frac{U_\infty - U_{\infty\ EQ}}{U_{\infty\ EQ}} \simeq -\frac{1}{2}\frac{h_F}{h_0}$$

for hypersonic frozen test flows, where subscript EQ denotes values for the corresponding equilibrium test stream. Thus p_0' cannot be very strongly reduced (see Table I for h_F/h_0), and since h_0 is unchanged, the entire equilibrium state determined by h_0 and p_0' must remain relatively insensitive. In particular, the gas temperature and composition tend to be quite insensitive, while the density is reduced roughly the same order as the pressure. Local equilibration behind a strong shock thus tends to erase the nonequilibrium history of the nozzle expansion process.

For nonequilibrium flow fields behind strong shocks, the local flow field chemistry can, of course, be strongly affected by test-flow nonequilibrium. Also, effects can be appreciable on local temperature and density. However, the pressure will tend to remain rather insensitive, particularly for blunt bodies where the flow is Newtonian in character. As an example, Figures 4-14 and 4-15 from Reference 111 show calculated local temperatures and species concentrations in the nonequilibrium flow field of an axisymmetric blunt nose for test-flow conditions attained by equilibrium and nonequilibrium expansions of air from a reservoir state of 6000°K and 100 atm. The air kinetic models for this example included the coupled reactions previously discussed. Figure 4-14 shows the temperature level of most of the nonequilibrium shock layer to be considerably reduced by the test stream nonequilibrium due to the energy initially frozen in dissociation. The shock layer density level is also reduced, as evidenced by the increase in shock standoff distance. Figure 4-15 shows the very large effect of nozzle freezing in greatly increasing the concentrations of atomic oxygen and nitric oxide along a ray at 7° to the body axis.

In the limiting situation where the chemistry is frozen throughout the model flow field, as tends typically to be the case with slender models of small scale, then the flow field is that of an ideal gas with a (frozen) specific heat ratio determined by the free-stream composition. For moderate degrees of nozzle freezing, the frozen specific heat ratio will be rather close to that of undissociated air. This is particularly true when diatomic NO dominates the frozen "nonequilibrium" species. Such frozen-flow model tests can provide useful data provided the free-stream properties are known. Of course, the key assumption involved, that of frozen flow about the test model, is usually difficult, if not impossible, to verify by direct measurement.

Usually theoretical estimates of the inviscid and boundary-layer flow behavior must be relied on in this respect. The possibility of surface catalytic effects arises in connection with surface heat transfer measurements in frozen boundary-layer flows (Refs. 35, 131, 132).

As a final remark, it should perhaps be emphasized that current hypersonic test facilities are being used for research studies in a performance range where appreciable nozzle freezing does occur. For example, recent shock-tunnel applications at the Cornell Aeronautical Laboratory include studies of hypersonic airflows over blunt and slender bodies at conditions where nonequilibrium effects are significant[133-136]. These applications have included extension of shock-tunnel techniques to measurements of electromagnetic-microwave transmission through the ionized shock layer on the model, including determination of radiation patterns from antennae located in the model[133,134]. In conjunction with such studies, methods of accounting for the effects of nozzle freezing are being developed, and this trend will undoubtedly continue. A promising approach to more general simulation relationships appropriate to the problem has already been made by Gibson[116]. It is clear that the more sophisticated applications of wind-tunnel testing methods in this respect will require much more complete measurement of local flow properties, as previously noted.

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TABLE I

Percentage of O, N, NO, and Reservoir Enthalpy Frozen in Hypersonic Nozzle Airflow

$l = 1$ cm

T_o °K ⟶	6000		8000		
P_o ATM ⟶	100	1000	10	100	1000
FROZEN MASS % OF O	9.5%	1.12%	23.2 %	22.5 %	6.20%
FROZEN MASS % OF N	0	0	30.2	0.120	0
FROZEN MASS % OF NO	6.75	9.36	0.033	0.771	7.29
FROZEN ENTHALPY 100 h_F/h_o	15.5	4.80	50.8	19.4	8.13

TABLE II

Ratios of Actual to Equilibrium Airflow Variables for Coupled-Reaction Expansions Giving Equilibrium Mach Number 20

$l = 1$ cm

T_o	6000 °K		8000 °K	
P_o	100 atm	1000 atm	100 atm	1000 atm
P/P_{EQ}	0.425	0.875	0.159	0.544
T/T_{EQ}	0.359	0.855	0.121	0.497
ρ/ρ_{EQ}	1.095	1.014	1.110	1.045
u/u_{EQ}	0.913	0.987	0.901	0.957
M/M_{EQ}	1.455	1.06	2.30	1.305
$Re_x/Re_{x_{EQ}}$	2.79	1.17	8.25	2.01

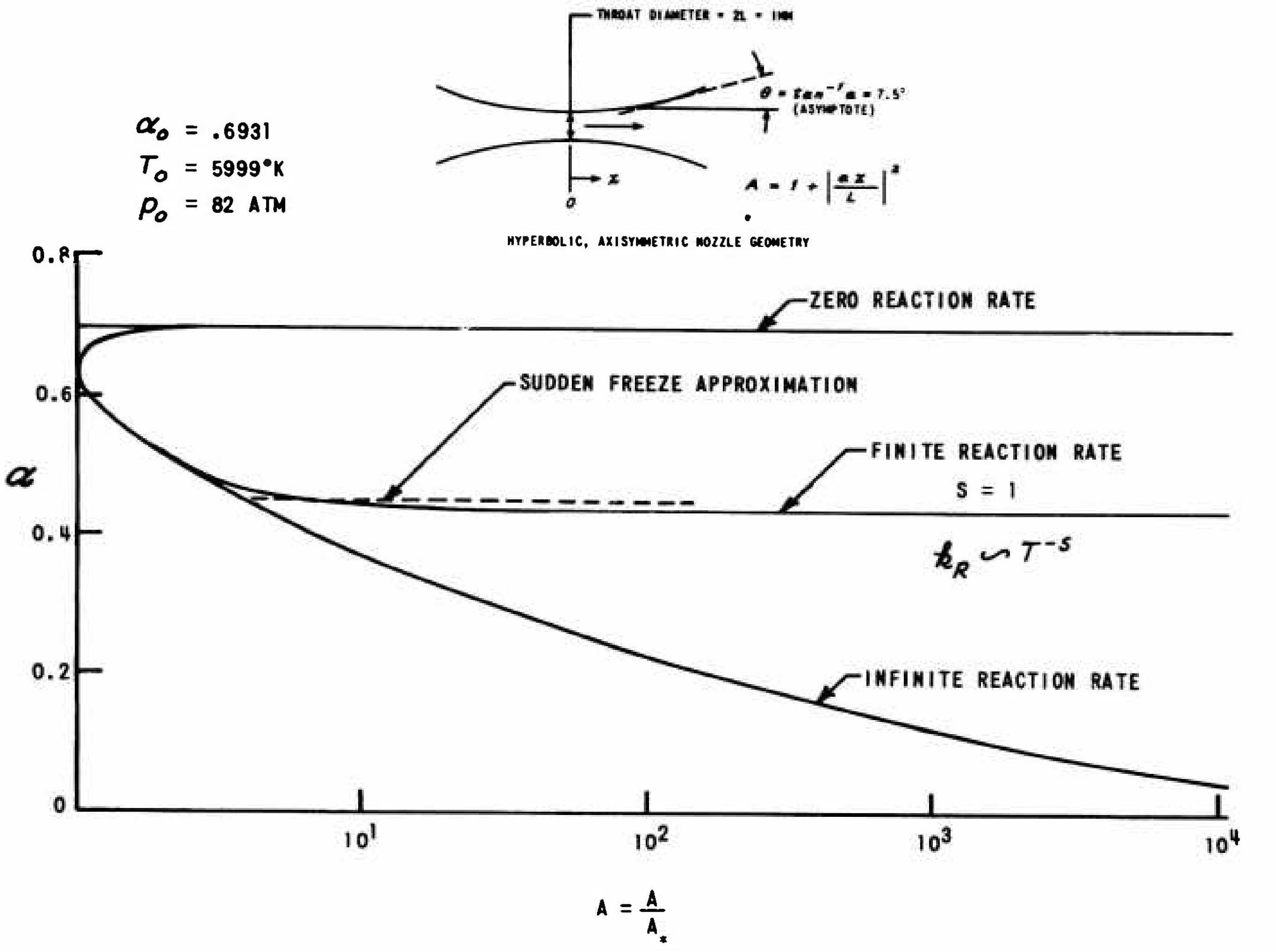

Fig. 4-1 Numerical solution for degree of dissociation in nozzle flow of oxygen (from Reference 18)

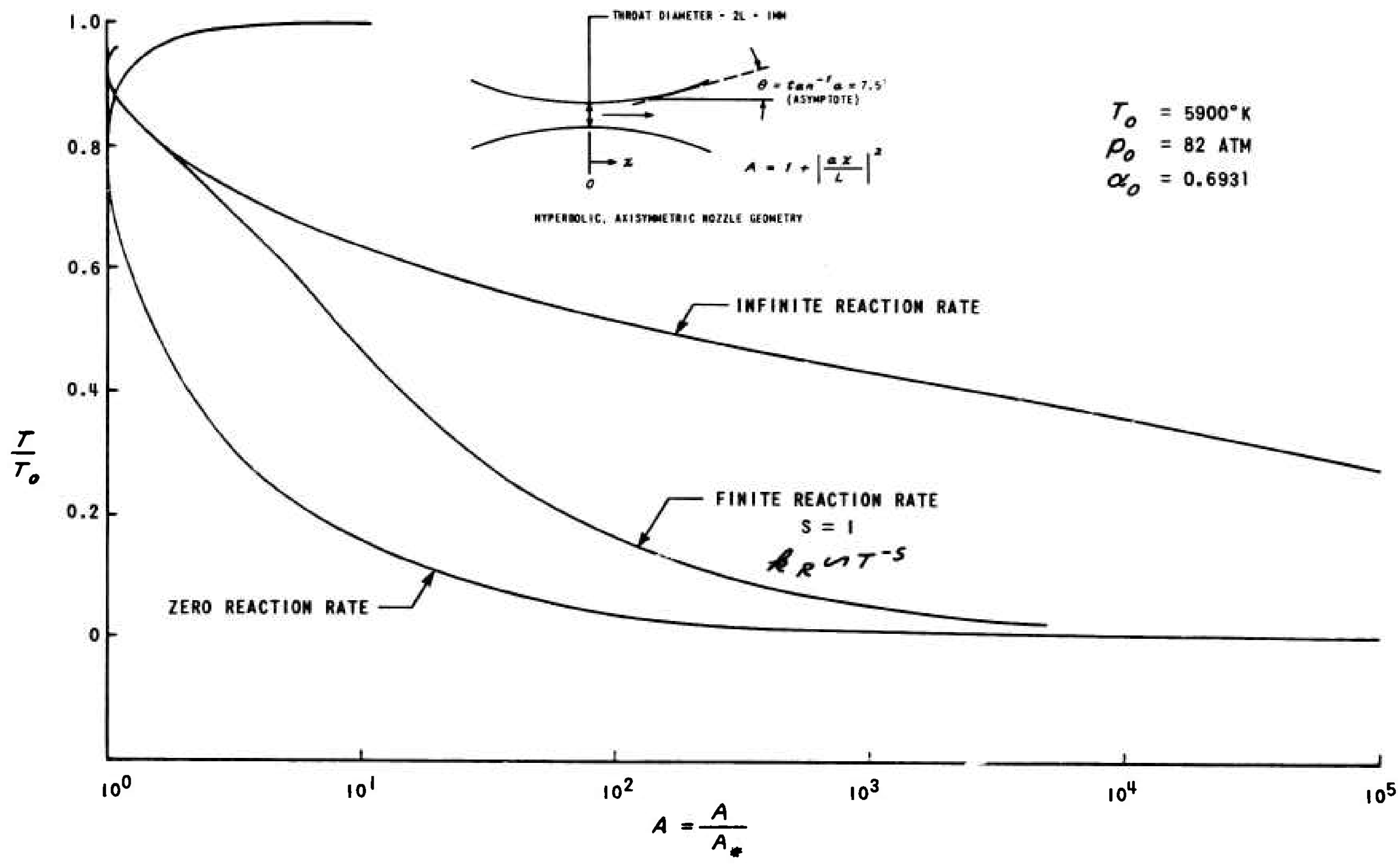

Fig. 4-2 Numerical solution for translational temperature in nozzle flow of dissociated oxygen (from Reference 18)

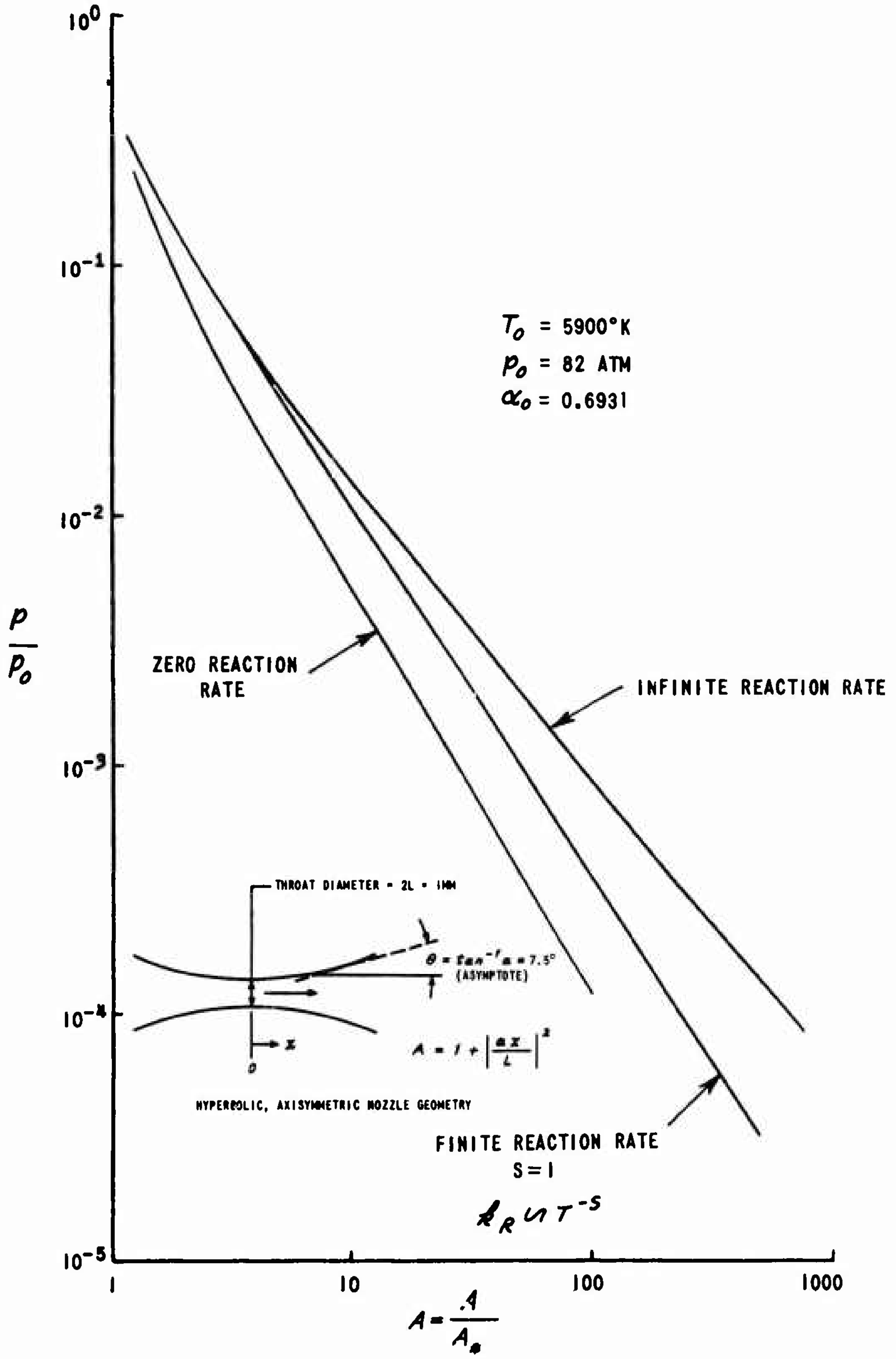

Fig. 4-3 Numerical solution for pressure in nozzle flow of dissociated oxygen (from Reference 18)

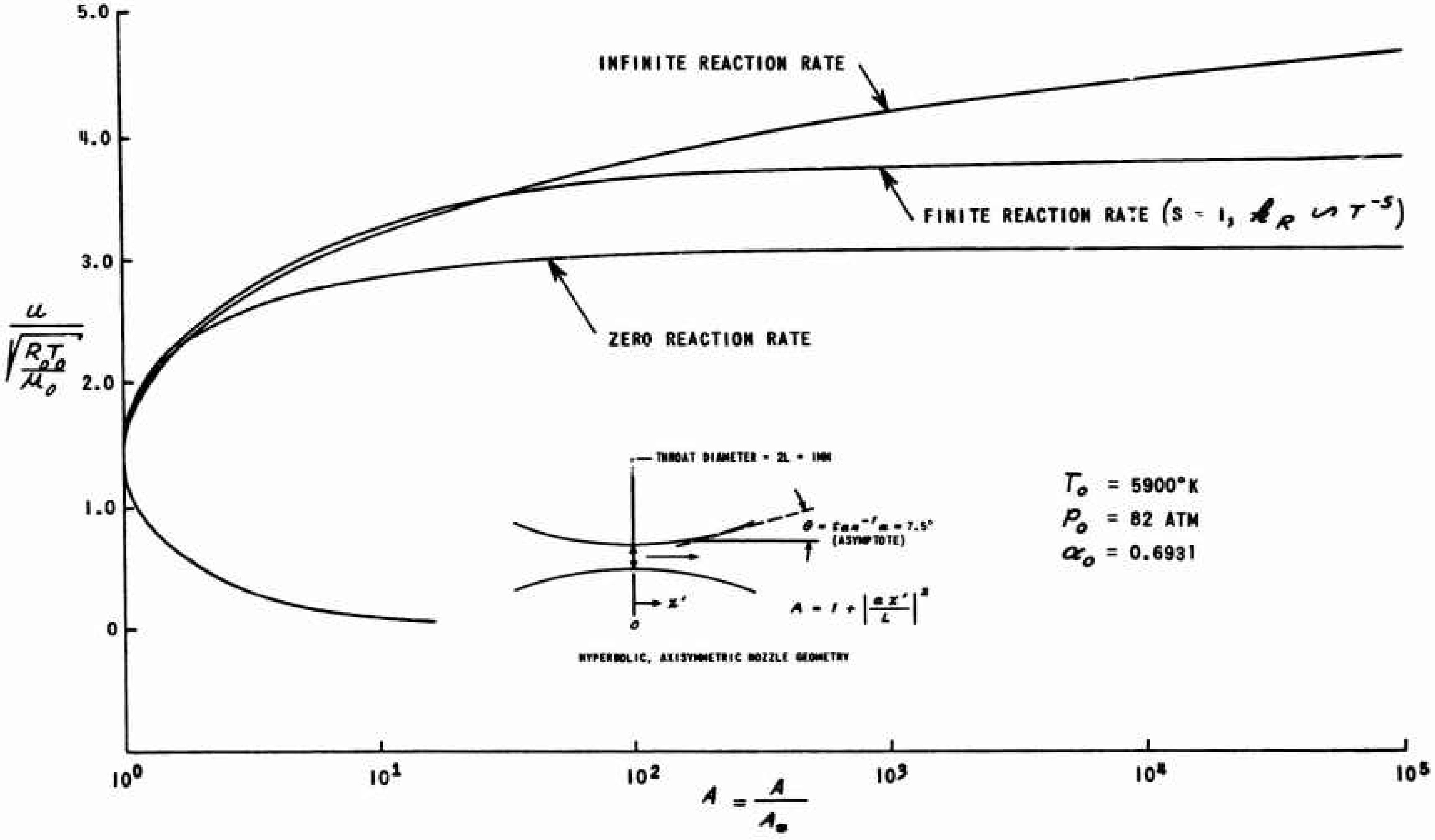

Fig. 4-4 Numerical solution for velocity in nozzle flow of dissociated oxygen (from Reference 18)

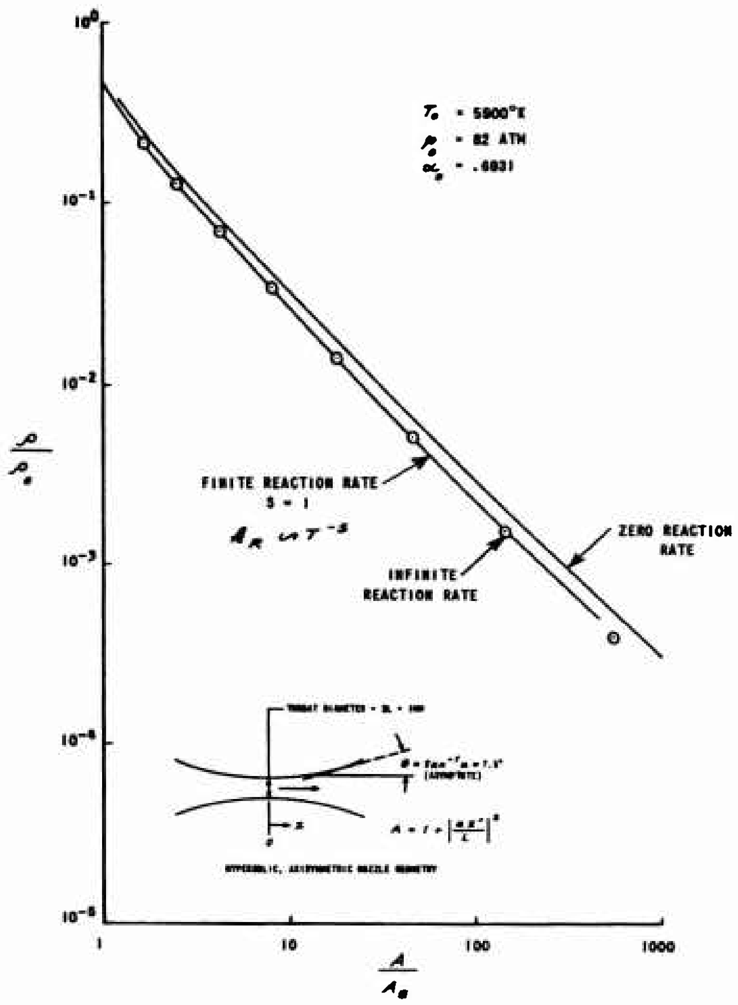

Fig. 4-5 Numerical solution for density in nozzle flow of dissociated oxygen (from Reference 18)

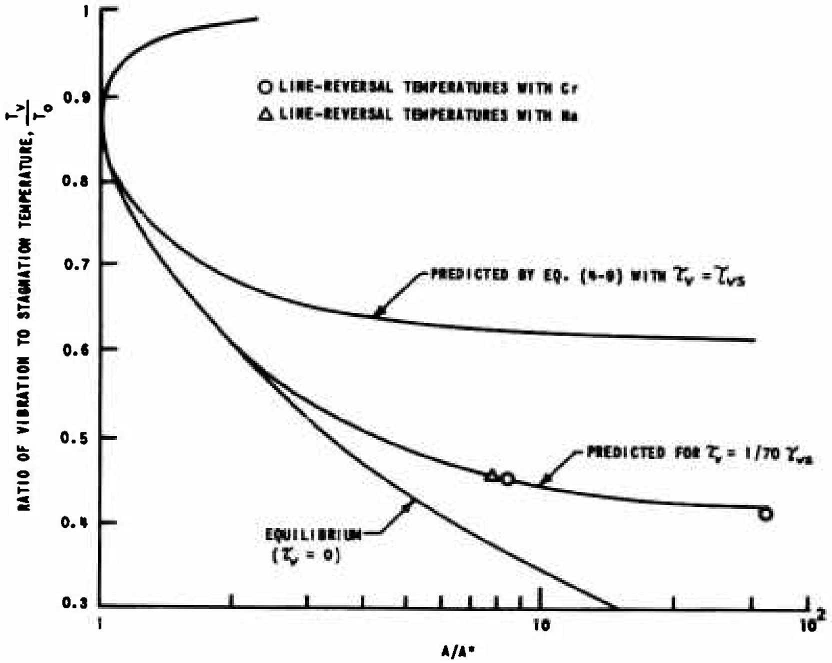

Fig. 4-6 Comparison of measured vibration temperatures with harmonic-oscillator theory for nozzle flow of undissociated nitrogen. $T_0 = 4500^\circ K$, $P_0 = 50$ atm (from Reference 48)

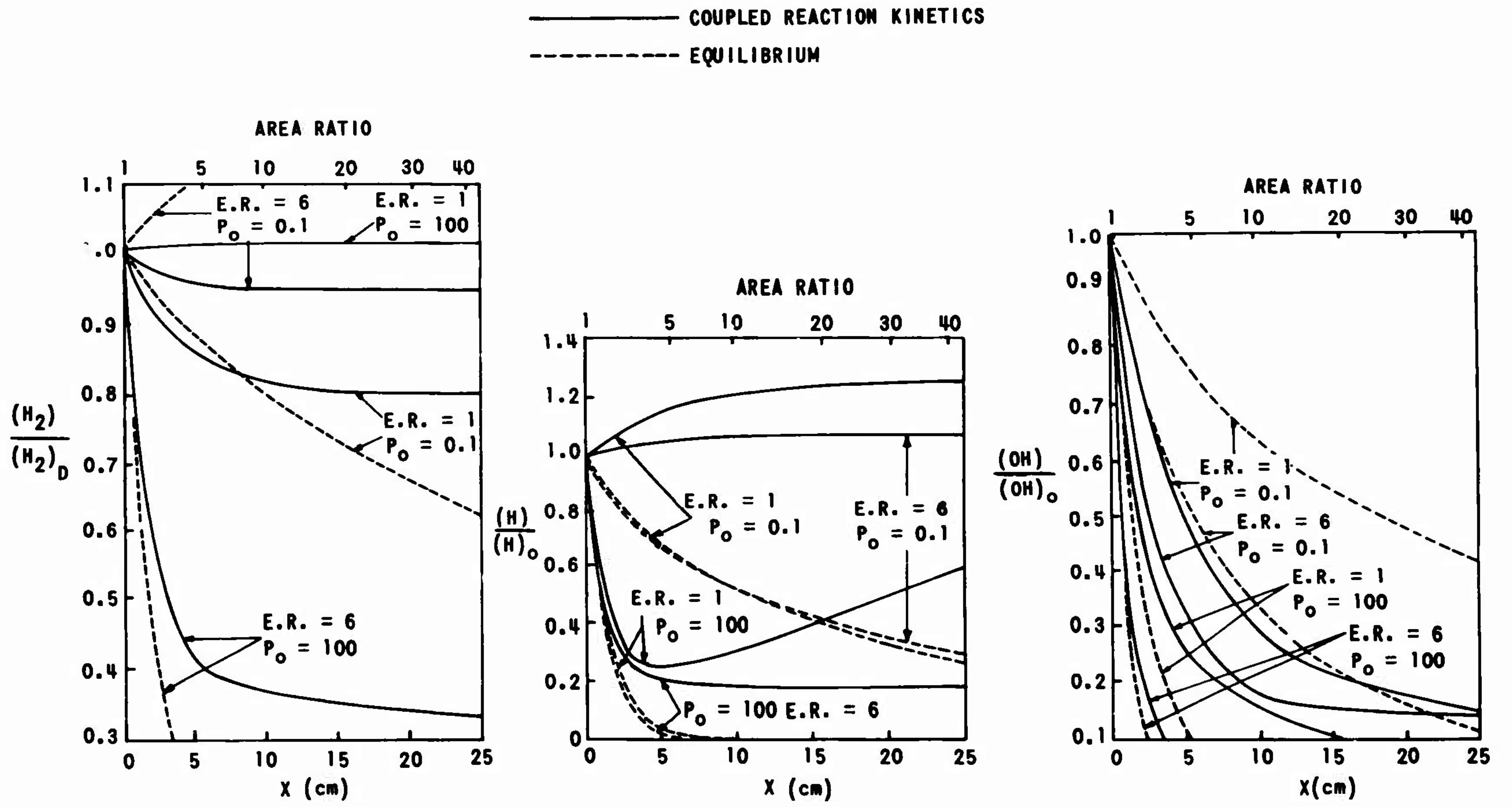

Fig. 4-7 Numerical solution for species concentrations in nozzle flow of H_2/air combustion products (from Reference 84)

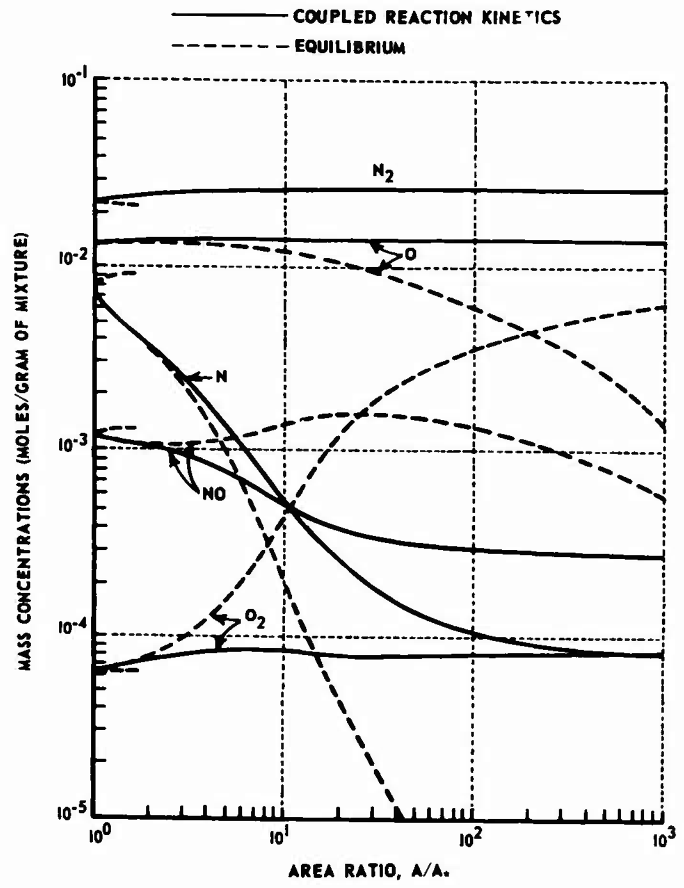

Fig. 4-8 Numerical solution for species concentrations in nozzle flow of air (from Reference 97)

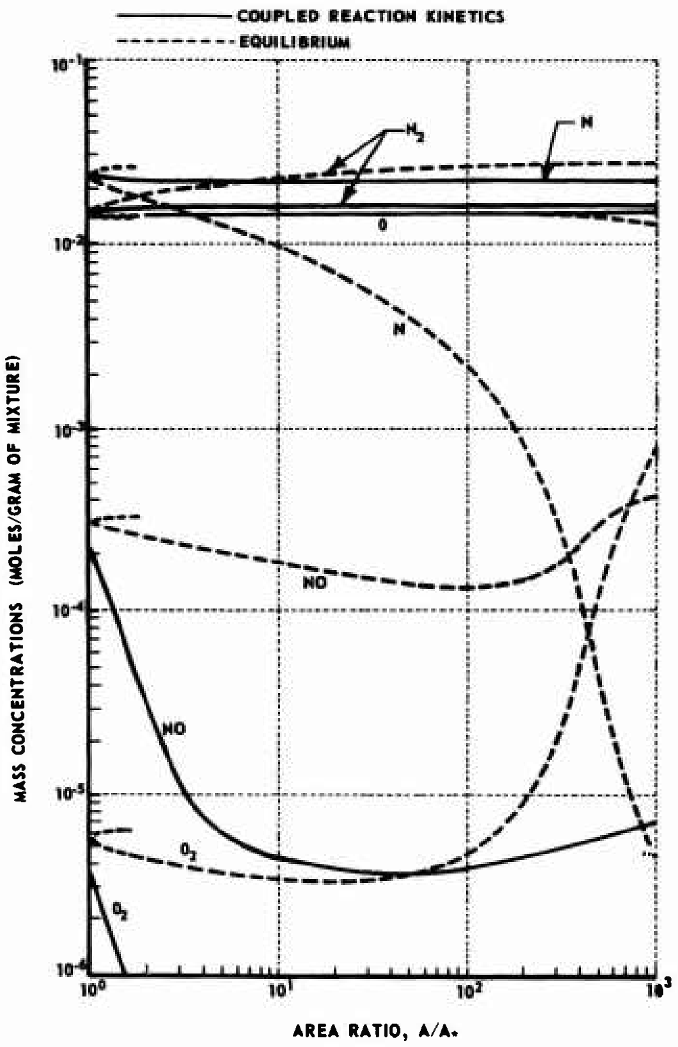

Fig. 4-9 Numerical solution for species concentrations in nozzle flow of air (from Reference 97)

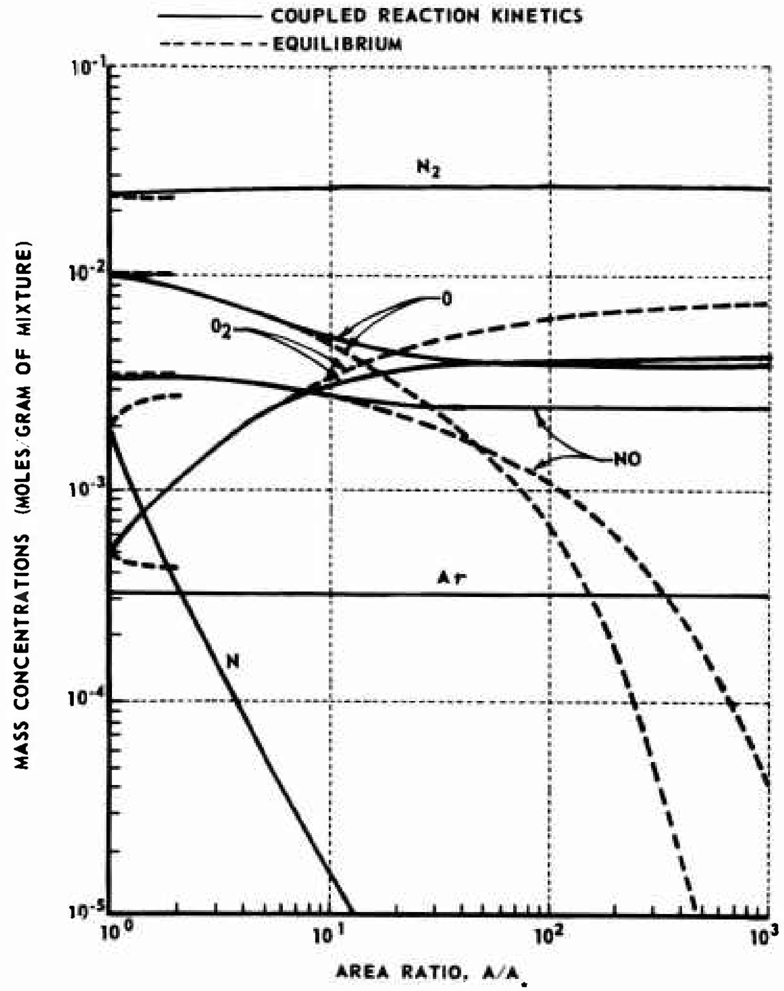

Fig. 4-10 Numerical solution for species concentrations in nozzle flow of air (from Reference 97)

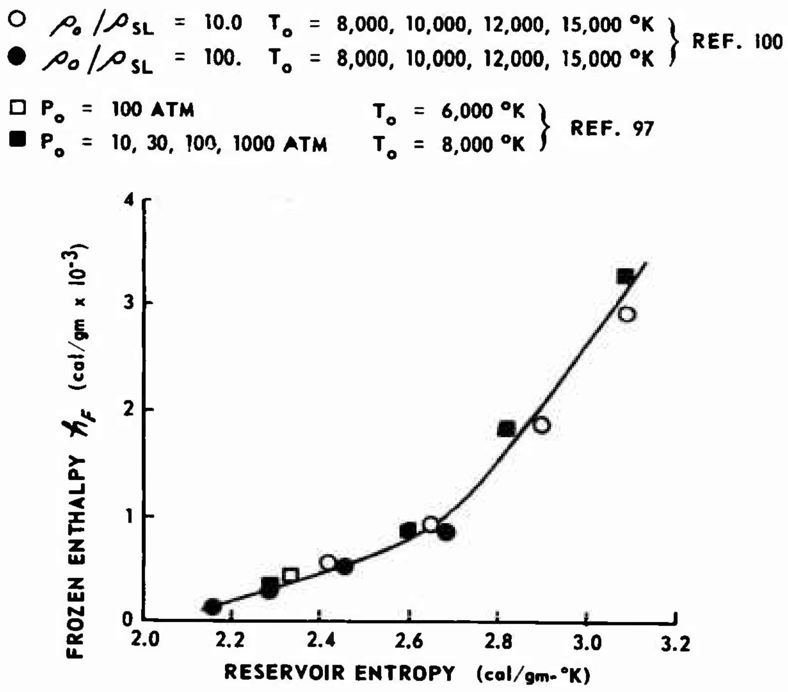

Fig. 4-11 Correlation of calculated frozen enthalpy for nozzle flows of air (from Reference 101)

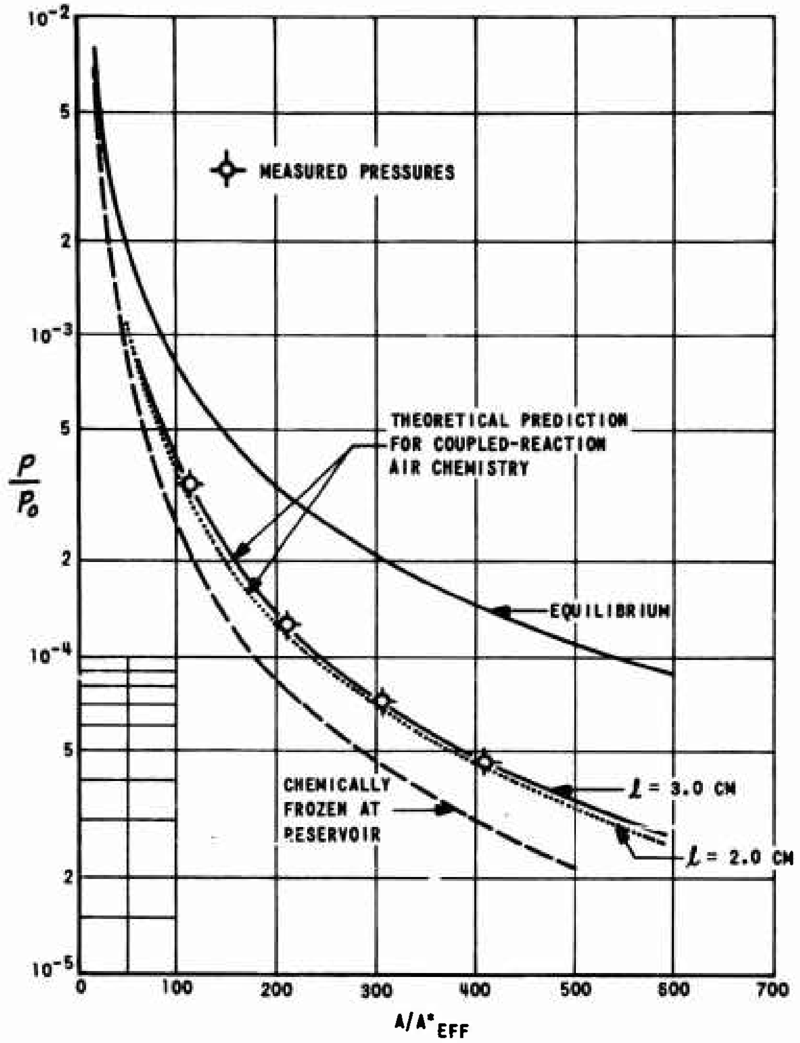

Fig. 4-12 Comparison of measured and predicted pressure distributions for nozzle flow of air. $T_0 = 7000^\circ K$, $P_0 = 250\ lb/in^2$ absolute, $l = 2.75$ cm (from Reference 106)

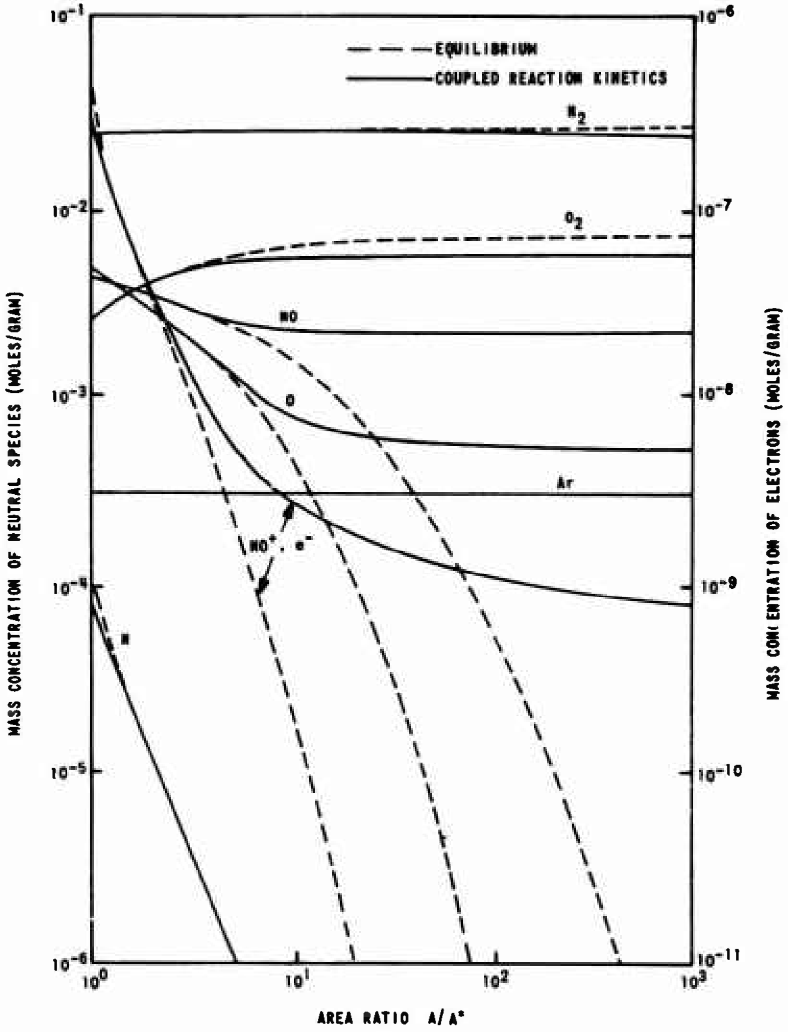

Fig. 4-13 Numerical solution for ionized and neutral species concentrations in nozzle flow of air. $T_0 = 5800^\circ K$, $P_0 = 657$ atm (from Reference 134)

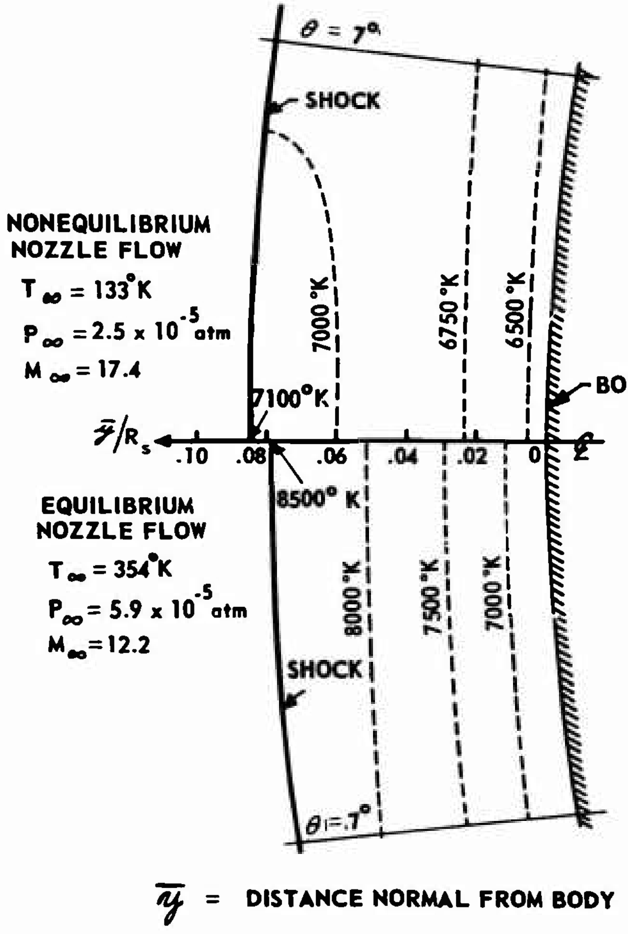

Fig. 4-14 Shock location and temperature distribution in nonequilibrium blunt-nosed flowfields for nonequilibrium and equilibrium nozzle airflows. $T_0 = 6000^\circ K$, $P_0 = 100$ atm, $A/A_* = 18,190$, $R_s = 0.493$ ft (from Reference 111)

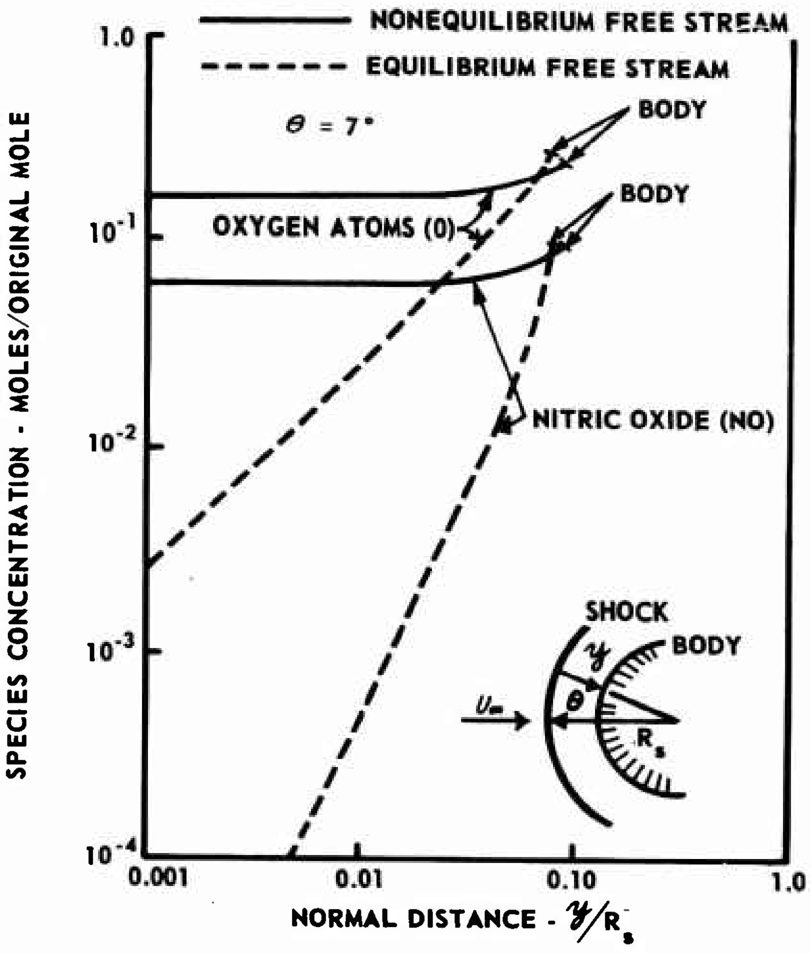

Fig. 4-15 Concentrations of O and NO in nonequilibrium blunt-nose flowfields for nonequilibrium and equilibrium nozzle airflows. $T_0 = 6000^\circ K$, $P_0 = 100$ atm, $A/A_* = 18,190$, $R_s = 0.493$ ft (from Reference 111)

SECTION 5

CONCLUSION

The experimental and theoretical research in the field of nonequilibrium expanding flows has been reviewed. Recent work concerning the basic physical-chemical processes involved are also summarized and separate bibliographies for various aspects of shock-heated flows are included. There is a strong emphasis throughout on air flows, although some discussion of other gas mixtures is included.

The basic equilibrium equations are summarized in Section 2 and several tables of thermodynamics properties of gases are described. The capabilities of available computer programs for the solution of the equilibrium equations are discussed. It is pointed out that the computer calculations are now so rapid as to provide efficient sub-routines for other aerodynamic-flow calculations.

Current problems associated with the description of nonequilibrium gases are reviewed in Section 3. The methods of treatment of vibrational relaxation is emphasized, and the work associated with translational and rotational equilibration is omitted entirely. The several methods available for the calculation of vibrational transition probabilities are compared, and the limitations of these calculations are discussed. Methods of treatment of the master equations for vibrational relaxation are then described, both for cases where exchange effects are unimportant and for cases of pure molecular gases and mixtures of gases where exchange effects are dominant. It is pointed out that the non-Boltzmann effects that can be obtained when vibrational energy exchange is important can greatly increase the vibrational relaxation rates. For electronic excitation, the limited information available for rates and mechanisms in the high-temperature range is summarized. The basic problems in understanding simple chemical dissociation processes are delineated, and the models that have been proposed for treatment of vibration-dissociation coupling are reviewed. Available experimental data are discussed for dissociation reactions and for the nitric oxide shuffle reactions. Recent reviews of chemical problems associated with reentry are referenced, as are reviews of relevant ionization and deionization rates.

Supersonic-nozzle flows are reviewed in Section 4. First, the pseudo-one-dimensional formulation is described briefly, and the particular difficulties associated with numerical nonequilibrium calculations of such flows are reviewed. The various methods that have been used to solve for the steady-state flow of a reacting, diatomic gas in a nozzle are then described. The relevant parameters for the separation of the non-equilibrium phenomena in the flow field are defined, and exact and approximate solutions are compared. The problem of vibrational relaxation in expanding flows, without dissociation, is treated separately. Recent data demonstrating the rapid relaxation of diatomic gases in such flows are reviewed and compared with theory.

The use of machine programs to treat more complicated chemical flows is next discussed in terms of gas mixtures of interest in propulsion. Graphical results of these calculations for different test conditions are compared and experiments are discussed. Similar calculations and experiments are then described for air, including the effects of seeding to increase the electron concentration. There is clearly a lack of definitive chemical experiments for expanding flows in air, and the need for measurements of chemical composition in such flows is demonstrated. Finally, the results of the calculations are reviewed in relation to the effect of nonequilibrium on hypersonic testing, and the complications that this introduces in aerodynamic scaling are discussed.

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APPENDIX A

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