NONEQUILIBRIUM NOZZLE FLOWS

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ABSTRACT

Nonequilibrium effects in supersonic nozzle flows are important in various technical applications such as propulsion, hypersonic wind tunnel testing, and simulation of streamtube flows occuring about a body in hypersonic flight. This report discusses such effects with emphases on analysing subsonic regions and on investigating roles of entropy in analyses of nonequilibrium nozzle flows.

The scope is limited to homogeneous gas-phase nozzle flows. Effort is mainly devoted to investigation of the effects of departure from thermochemical equilibrium arising from collisional relaxation of internal degrees of molecular excitation and from chemical reaction, including ionization.

Since the phenomena to be discussed in this report often involve considerable algebraic complexity, the description of the purely gasdynamic aspects of the flow is made as simple as possible. And the flow is treated as a continuum, and the equations of steady, quasi-one-dimensional adiabatic flow are used throughout.

In the gas-phase continuum regime, inviscid flows are considered, and nonequilibrium phenomena associated with classical viscous effects, condensation, rarefied gasdynamic effects, radiation are not investigated.

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INTRODUCTION

Expansion nozzles are used in many types of equipment to accelerate gases to high velocity or high Mach numbers. A very wide range of physical and chemical processes may be induced in a gas as a result of its rapid expansion through a nozzle, and departure from thermodynamic equilibrium can occur in any of these processes. Nonequilibrium effects in nozzle flows have long been investigated in the propulsion field because of the thrust loss resulting from chemical nonequilibrium occurring in the nozzle expansion process.

Nonequilibrium phenomena in a nozzle flow are also of importance in connection with hypersonic wind tunnel testing. Recently the conventional experimental tools such as supersonic and hypersonic wind tunnels have been used extensively for investigating many special problems arising in various fields such as chemistry, physics, fluid dynamics and astrophysics. These tools make use of nozzle expansions of gas from high-tempetature conditions where the gas is often highly dissociated or ionized. Usually some degree of freezing may occur in the nozzle expansion[1), which produces a test gas-flow which is not in an equilibrium state. In almost all cases, it is quite undesirable as it complicates interpretation of test data and may prevent proper simulation.

Furthermore the significance of nonequilibrium nozzle flows is emphasized by the fact that the thermo-gasdynamic environment occurring along the nozzle axis is representative of that occurring along stream tubes undergoing expansion about a body in hypersonic flight. However the available experimental data on the expansion of dissociated or ionized gases in a nozzle or over a body are still not enough.

Since the phenomena to be discussed in this article involve considerable algebraic complexity, the description of the purely gasdynamic aspects of the flow is made as simple as possible. Therefore the flow is treated as a continuum, and the equations of steady, quasi-one-dimensional adiabatic flow are used throughout.

Three types of solution to nonequilibrium flow problems will be discussed in this report, namely, analytical, numerical, and semiempirical solutions.[1] Each type has the merits for the study of some aspect of the problem, and each has its own limitations. Analytical solutions can be found only for the simplest possible nonequilibrium processes. The purpose of these laborious analytical solutions is usually not to solve practical engineering problems, which are generally much more readily solved numerically. The most important task is to obtain a physical picture of the nonequilibrium flows through a nozzle. Limiting solutions such as very fast nonequilibrium processes, or conditions very far downstream, which may not be easily accessible numerically, can also be obtained. Another useful contribution of the analytical methods is to investigate the accuracy and regime of validity of semi-empirical methods. The simplest and most successful of the semiempirical methods is the "sudden freezing" approximation,[1] which is probably the most widely used in practice. Because of its empiricism, however, it cannot be extrapolated to new situations without uncertainty.

In nonequilibrium nozzle flows, the nonequilibrium processes inevitably increase the entropy of gases in nozzles.

This increased entropy in turn affects flowfields and relaxation phenomena themselves. The analyses of nonequilibrium phenomena in nozzle flows are, in almost all cases, equivalent to those of flowfields themselves. It is regretful, however, that in spite of the large number of researchers, few good studies on this problem have been done because of the difficulties in analysing theoretically these flowfields. In light of such circumstances, our effort is partly devoted to investigation of the roles of entropy in the analyses of nonequilibrium nozzle flows.

The contents of this report are arranged as follows. Chapter I deals with the problem of predicting critical mass flows in nozzle flows of a vibrationally relaxing diatomic gas, an ideal dissociating diatomic gas and a singly ionizing monatomic gas. Analytical and numerical solutions of nonequilibrium flows of vibrationally relaxing diatomic gases are obtained under various reservoir conditions in Chapter II. Chapter III discusses the roles of entropy in the analyses of nonequilibrium nozzle flows. Especially, detailed discussions are made on the equilibrium-frozen (E-F) flow approximation which is one of the most important approximations to a nonequilibrium nozzle flow. Finally the problem of solving the nonequilibrium flows of an ideal dissociating diatomic gas is treated analytically by the method of strained coordinates in Chapter IV.

CHAPTER I CRITICAL MASS FLOWS

1. Introductory Remarks

There are two things which complicate the analyses of nozzle flows with physical-chemical rate processes. The one is the complexity of the rate equations which govern the relaxation phenomena of vibration and electronic excitation, chemical reactions of neutral species, and ionization, and the uncertainty and uncompleteness of mathematical description of various physical-chemical rate processes. The other is the difficulties in the determination of position of the critical (sonic) point near the throat in connection with the critical mass flow.

Though there is no simple definition of a speed of sound in a nonequilibrium, relaxing gas, so far as the relaxation time does not tend to zero, the frozen speed of sound is the reference one in fluid mechanics. In the flow which starts from the equilibrium reservoir conditions, in general, the sonic point is just downstream of the throat, and it is a saddle-type singular point of the flow equations.[1)2)]

In a usual convergent-divergent supersonic nozzle, the critical mass flow of a general nonequilibrium flow is permitted to take only such one value that the regularity condition at the sonic point of the flow equations is satisfied.

In the past, much research has been directed at solving problems associated with the determination of the sonic point. Various approaches to the problem have already been presented; for example, equilibrium-throat-assumption method,[1)3)4)] equilibrium-frozen-flow approximation method,[1)] direct try and error method,[1)5)] inverse try and error method,[6)] iterative method,[7)] transonic approximation method[8] and so on. In the actual analysis of the nozzle flow of a nonequilibrium, relaxing gas, the choice of method to be applied, mainly depends upon two conditions; the ratio of the energy stored in the lagging mode to the total enthalpy of the gas and that of the relaxation length to the reference nozzle length.

Two conditions must be satisfied if the relaxation of a particular degree of freedom is to affect the flow through a nozzle; the relaxation time must be comparable in magnitude with the time for the flow to pass through the nozzle, and the change in energy associated with the relaxation mode must form a significant part of the total change of the enthalpy of the gas. The latter depends entirely upon the given reservoir conditions, while the former depends in addition upon the rate equation and the nozzle geometry.

It must be noticed that the entropy rise due to the nonequilibrium processes will also affect the critical mass flow. Here the effects on the critical mass flow of the degree of departure from thermo-chemical equilibrium of the relaxation modes with the rotational-translational mode of the gas particles and of the entropy rise in the subsonic region from the reservoir to the sonic point will be investigated in detail.

2. Nozzle Flow Equations for a Single Nonequilibrium Process

For a steady, adiabatic, quasi-one-dimensional flow through a nozzle, the equations of continuity, momentum, energy, relaxation rate are respectively

$$\rho V(1+A)=\rho_* V_*(1+A_*)=\rho_t V_t=m=\text{const.}, \tag{1}$$

$$\rho V\frac{dV}{dx}=-\frac{dp}{dx}; \tag{2}$$

$$h+\frac{1}{2}V^2=h_0, \tag{3}$$

$$V\frac{dq}{dx}=\frac{U(\rho,p,q)}{L(\rho,p,q)}, \tag{4}$$

in the gas-phase continuum regime, where ρ, p, V, h and (1+A) are, respectively, the density, pressure, velocity, enthalpy of the gas and nozzle area ratio with respect to the cross section of the throat; and x is the distance measured from the nozzle throat along its axis. The quantity q is a progress variable which may denote, for example, the vibrational energy, dissociated mass fraction or ionized mass fraction, and m is the critical mass flow. $L(\rho, p, q)$, $U(\rho, p, q)$ and h are functions of state, e. g., of ρ, p and q. It is also assumed that the nozzle cross-sectional area distribution is given, so that

$$A = A(x) \,. \tag{5}$$

Subscripts 0, t and * represent, respectively, the stagnation point, throat and critical or sonic point.

In order to solve the above system of equations under the given reservoir conditions, the functions U, L (or U/L) and h, and the relation among ρ, p and q, namely the equation of state must be known. For the diatomic gas at a relatively low temperature where the dissociation phenomenon does not yet take place appreciably, the enthalpy per unit mass is

$$h=\frac{7}{2}\frac{R}{W_2}T+\frac{\frac{R}{W_2}\theta}{\left[\exp\left(\frac{\theta}{T_v}\right)-1\right]}, \tag{6}$$

where T, T_V, θ, R and W are, respectively, the rotational-translational temperature, vibrational temperature, characteristic temperature of vibration, universal gas constant and molecular weight of a molecule. The subscript 2 denotes the molecule.

For the diatomic gas in which the dissociation and recombination reactions are most predominant, the so called ideal dissociating gas model approximation[9)10)] can be made and the enthalpy is

$$h=(4+\alpha)\frac{R}{W_2}\cdot T+\frac{R}{W_2}D\alpha \quad , \tag{7}$$

where α and D are, respectively, the dissociated mass fraction and dissociation energy. It must be noticed that for the diatomic gases given above translational-rotational equilibrium is assumed.

For the singly ionizing monatomic gas such as N or O at high temperature, one has

$$h=\left[\left(\frac{5}{2}+a\right)+\left(\frac{5}{2}+b\right)\phi\right]\frac{R}{W_1}\cdot T+\frac{R}{W_1}I\phi \quad , \tag{8}$$

where ϕ and I are, respectively, the ionized mass fraction and ionization energy, and a and b are constants.[10)] The subscript 1 denotes an atom.

Though Eqs. (6) and (7) can be used in the general nonequilibrium state, Eq. (8) is valid only in the equilibrium state. For the singly ionizing monatomic gas, there has been no simple way in order to improve Eq. (8) so as to become valid even in the general nonequilibrium state.

According to Eqs. (6-8), the equations of state are, respectively,

$$p=\frac{R}{W_2}\rho T\,, \tag{9}$$

$$p=\frac{R}{W_2}\rho T(1+\alpha)\,, \tag{10}$$

$$p=\frac{R}{W_1}\rho T(1+\phi). \tag{11}$$

The rate equation for a diatomic gas which governs the relaxation of the vibrational mode takes the form[2) 11)]

$$V\frac{dE_V}{dx}=\frac{U}{L}=\Gamma\rho T^w\exp(lT^s)\left[1-\exp\left(\frac{-\theta}{T}\right)\right]\left\{\frac{\frac{R}{W_2}\theta}{\left[\exp\left(\frac{\theta}{T}\right)-1\right]}-E_V\right\}. \tag{12}$$

where E_V is the vibrational energy and given by

$$E_V=\frac{\frac{R}{W_2}\theta}{\left[\exp\left(\frac{\theta}{T_V}\right)-1\right]}, \tag{13}$$

and where Γ, w, ℓ and s are constants and depend upon the kind of a gas. For the ideal dissociating gas,[12)] we have

$$V\frac{d\alpha}{dx}=\frac{U}{L}=r_D-r_R\,, \tag{14}$$

where r_D and r_R are functions which represent the absolute dissociation rate and recombination one, and given by

$$\begin{aligned} r_D&=\left(\frac{\rho}{W_2}\right)(1-\alpha)[k_{f_1}(1-\alpha)+2k_{f_2}\alpha]\,,\\ r_R&=\left(\frac{2\rho}{W_2}\right)^2\alpha^2[k_{r_1}(1-\alpha)+2k_{r_2}\alpha]\,, \end{aligned} \tag{15}$$

where

$$k_{r_1}=\frac{k_{f_1}}{K(T)}\,,\qquad k_{r_2}=\frac{k_{f_2}}{K(T)}\,, \tag{16}$$

and where k_{f1}, k_{f2} and K(T) are the functions of temterature only. Unfortunately, for the ionization and neutralization phenomena, there has been no satisfactory rate equation for the analyses of nozzle flows under a wide range of stagnation conditions.[13) 14) 15)]

A limiting form of the rate equation implies the equilibrium relation. For the vibrating diatomic gas, it is

$$E_V=E=\frac{\frac{R}{W_2}\cdot\theta}{\left[\exp\left(\frac{\theta}{T}\right)-1\right]}, \quad \text{or} \quad T_V=T, \tag{17}$$

and for the ideal dissociating diatomic gas, it is

$$\frac{\alpha^2}{1-\alpha}=\frac{C_D}{\rho}\cdot T^{-d}\cdot\exp\left(-\frac{D}{T}\right), \tag{18}$$

where C_D is a constant and d can be taken to be almost constant. For the singly ionizing monatomic gas, in spite of the uncertainty of the rate equation it is known to be

$$\frac{\phi^2}{1-\phi}=\frac{C_I}{\rho}\cdot T^{i}\exp\left(-\frac{I}{T}\right), \tag{19}$$

where C_I is a constant and i is also taken to be almost constant. This has often been called as "Saha Equation".

3. Singular Points

Since the enthalpy of the gases considered here is generally represented as a function of the pressure p, density ρ and progress variable q, it can be written generally in the form,

$$h=h(\rho, p, q). \tag{20}$$

Substituting it into the momentum equation with the aid of the equations of energy and continuity yields

$$\frac{1}{V}\left\{\frac{\frac{1}{\rho}-\left(\frac{\partial h}{\partial p}\right)_{\rho,q}}{\left(\frac{\partial h}{\partial \rho}\right)_{p,q}}V^2-1\right\}\frac{dV}{dx}+\frac{\left(\frac{\partial h}{\partial q}\right)_{\rho,p}}{\rho\left(\frac{\partial h}{\partial \rho}\right)_{p,q}}\frac{dq}{dx}=\frac{\left(\frac{dA}{dx}\right)}{(1+A)}. \tag{21}$$

By the definition of speed of sound, the equilibrium speed of sound and the frozen one are given as follows[2)16)]

$$a_e^2=\frac{\left(\frac{\partial h}{\partial \rho_e}\right)_{p_e,q_e}+\left(\frac{\partial h}{\partial q_e}\right)_{\rho_e,p_e}\cdot\left(\frac{\partial q_e}{\partial \rho_e}\right)_{p_e}}{\frac{1}{\rho_e}-\left(\frac{\partial h}{\partial p_e}\right)_{\rho_e,q_e}-\left(\frac{\partial h}{\partial q_e}\right)_{\rho_e,p_e}\cdot\left(\frac{\partial q_e}{\partial p_e}\right)_{\rho_e}}, \tag{22}$$

$$a_f^2=\frac{\left(\frac{\partial h}{\partial \rho}\right)_{p,q}}{\frac{1}{\rho}-\left(\frac{\partial h}{\partial p}\right)_{\rho,q}}, \tag{23}$$

where subscripts e and f denote, respectively, the equilibrium flow and the frozen one. With these definitions of speeds of sound the equilibrium and frozen Mach numbers are defined by

$$M_e=\frac{V_e}{a_e}, \qquad M_f=\frac{V}{a_f}. \tag{24}$$

Substituting these Mach numbers into the corresponding momentum equations yields finally, for the general nonequilibrium flow,

$$\frac{1}{V}(M_f^2-1)\cdot\frac{dV}{dx}+\frac{\left(\frac{\partial h}{\partial q}\right)_{\rho,p}}{\rho\left(\frac{\partial h}{\partial \rho}\right)_{p,q}}\frac{dq}{dx}=\frac{\left(\frac{dA}{dx}\right)}{(1+A)}, \tag{25}$$

for the equilibrium flow

$$\frac{1}{V_e}(M_e^2-1)\frac{dV_e}{dx}=\frac{\left(\frac{dA}{dx}\right)}{(1+A)}, \tag{26}$$

and for the frozen flow

$$\frac{1}{V_f}(M_f^2-1)\frac{dV_f}{dx}=\frac{\left(\frac{dA}{dx}\right)}{(1+A)}. \tag{27}$$

From these equations the following can be concluded with respect to the critical point; for the general nonequilibrium flow, it is at $x = x_*$ where $M_f = 1$, and

$$\left(\frac{1}{1+A}\cdot\frac{dA}{dx}\right)_* = \left[\frac{\left(\frac{\partial h}{\partial q}\right)_{\rho,p}}{\rho\cdot\left(\frac{\partial h}{\partial \rho}\right)_{p,q}}\cdot\left(\frac{dq}{dx}\right)\right]_*, \tag{28}$$

for the equilibrium flow, it is at $x = x_{e*} = x_t = 0$ where $M_e = 1$, and for the frozen flow, it is at $x = x_{e*} = x_t = 0$ where $M_f = 1$. It must be noticed that the positions of the critical points of the equilibrium and frozen flows coincide.

Some attention must be paid about the sonic speeds in the nozzle flow problems. Though the equilibrium speed of sound is of significance only in the gas in the equilibrium state, the frozen one is significant not only in the completely frozen flow but also in the general nonequilibrium one.

There is some difference in meaning between in saying that a flow in a nozzle is in equilibrium and in saying that a common uniform flow is in equilibrium. Namely the equilibrium state for the uniform flow means that the internal mode of a molecule, dissociated mass fraction or ionized mass fraction is in the thermal or chemical equilibrium with the rotational-translational temperature. In such a uniform flow there can be both the equilibrium and frozen speeds of sound. In the nozzle flow analyses, however, the equilibrium means the infinitely large vibrational relaxation, dissociation-recombination or ionization-neutralization rate. Clearly in the equilibrium flow through a nozzle, the frozen speed of sound is of no more physical meaning and become the quantity defined only mathematically, though it is significant not only in the nonequilibrium flow but also in the completely frozen one. It must be emphasized that these two quantities by no means coincide even in the equilibrium limit. The frozen Mach number in the equilibrium limit is denoted by M_{fe} from now on in this paper.

4. Critical Mass Flows

In a supersonic convergent-divergent nozzle in which the gas flows from subsonic region to supersonic one through the sonic point, the only one value of the critical mass flow with which the regularity condition of the flow equations at the sonic point is satisfied, can be taken, and to which only the real flow can corresponds. The effect of the relaxation phenomena on the critical mass flow is considered in this section.

In the real flows, the relaxation phenomena of vibration, dissociation and recombination, and ionization and neutralization can not strictly be separated as has been done in our treatment.[2) 3) 10) 17)] (In the ideal dissociating gas, the effect of vibrational excitation is taken into account approximately.) Nevertheless, it is the case that there are rather clear distinctions among the conditions under which the each phenomenon takes place predominantly. Furthermore it must be emphasized that it is not necessarily required for us to treat these phenomena separately in order to develop our discussions, and of course these phenomena can be taken into consideration altogether. It is more preferable, however, to consider separately than to do altogether in order to investigate the effect of the each phenomenon on the critical mass flow.

4. 1 Critical Mass Flows of Vibrating Diatomic Gas

As the dependent variables, next quantities are considered,

$$\xi=\frac{\theta}{T}, \quad \xi_V=\frac{\theta}{T_V} \quad \text{and} \quad M_f, \tag{29}$$

and a parameter φ is introduced by

$$\varphi=\frac{1}{h_0}\cdot\frac{R}{W_2}\cdot\theta. \tag{30}$$

If the quantity q is taken to be ξ_V, required quantities can be obtained as follows:

$$\begin{aligned}
\rho &= m\sqrt{\frac{5}{7h_0\varphi}}\cdot\frac{\xi^{1/2}}{(1+A)M_f}, \\
a_f^2 &= \frac{7}{5}h_0\varphi\frac{1}{\xi}, \\
a_e^2 &= h_0\varphi\cdot\frac{\left[\frac{7}{2}+\frac{\xi^2\cdot\exp\xi}{(\exp\xi-1)^2}\right]}{\xi\left[\frac{5}{2}+\frac{\xi^2\cdot\exp\xi}{(\exp\xi-1)^2}\right]},
\end{aligned} \tag{31}$$

The equations of energy and momentum become, respectively,

$$\frac{7}{2}+\frac{\xi}{\exp\xi_V-1}+\frac{7}{10}M_f^2=\frac{\xi}{\varphi}. \tag{32}$$

$$\frac{1}{M_f}(M_f^2-1)\frac{dM_f}{dx}-\frac{1}{2}\cdot\frac{(M_f^2-1)}{\xi}\cdot\frac{d\xi}{dx}=-\frac{2}{7}\cdot\frac{\xi\exp\xi_V}{(\exp\xi_V-1)^2}\cdot\frac{d\xi_V}{dx}+\frac{\left(\frac{dA}{dx}\right)}{(1+A)}. \tag{33}$$

Combining these two equations, one has

$$\frac{(M_f^2+5)^3}{(1+A)\cdot M_f}=\text{const}\cdot\exp\left\{-\int_{\xi_0}^{\xi_V}\frac{\xi\exp\xi_V}{(\exp\xi_V-1)^2}\left[1-\frac{30}{7}\frac{1}{(5+M_f^2)}\right]d\xi_V\right\}. \tag{34}$$

From the density equation, we get

$$\lim_{\text{stagnation}}[(1+A)M_f]=\sqrt{\frac{5}{7h_0\varphi}}\cdot\frac{m\xi_0^{1/2}}{\rho_0},$$

This yields

$$\text{const.}=125\sqrt{\frac{7}{5}h_0\varphi}\cdot\frac{\rho_0}{m\xi_0^{1/2}},$$

with which Eq. (34) yields finally

$$F_V(M_f)\frac{(1+A)}{m}=F_{V_0}\exp G_V \quad , \tag{35}$$

where

$$F_V(M_f)=\frac{M_f}{(M_f^2+5)^3} \quad ,$$

$$F_{V_0}=\frac{1}{125}\cdot\sqrt{\frac{5}{7h_0\varphi}}\cdot\frac{\xi_0{}^{1/2}}{\rho_0} \quad , \tag{36}$$

$$G_V=\int_{\xi_0}^{\xi_V}\frac{\xi\exp\xi_V}{(\exp\xi_V-1)^2}\left[1-\frac{30}{7}\cdot\frac{1}{(M_f^2+5)}\right]d\xi_V .$$

Now, we have

$$\frac{d}{dM_f}F_V(M_f)=0\,,\quad \text{at}\quad M_f=1\,,$$

and then

$$F_V(M_f)_{\max}=F_V(1)=\frac{1}{216}, \tag{37}$$

which yields

$$\left[\frac{d}{dx}\left(F_V(M_f)\frac{1+A}{m}\right)\right]_*=F_V(1)\left[\frac{d}{dx}\left(\frac{1+A}{m}\right)\right]_*=\left[\frac{d}{dx}(F_{V_0}\exp G_V)\right]_*. \tag{38}$$

This relation implies that the curve for $y_1 = F_V(1)(1+A)/m$ with x as an independent variable must be tangential to that for $y_2 = F_{V0}\exp G_V$ at $M_f = 1$ in the xy plane (Fig. 1).

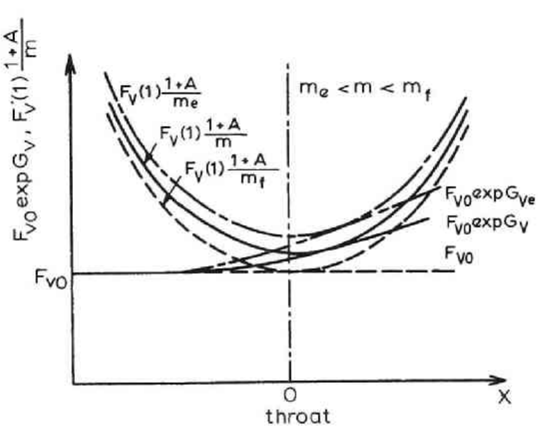

Fig. 1 Curves for $y_1 = F_V(1)(1+A)/m$ and $y_2 = F_{V0}\exp G_V$.

It is easy to understand that a difficulty must be expected when the nozzle throat is reached because the prescrived mass flow may not be able to pass through the throat, or in the case of a convergent-divergent nozzle, the flow decelerates instead of accelerates downstream of the throat(Fig. 2). Since the maximum

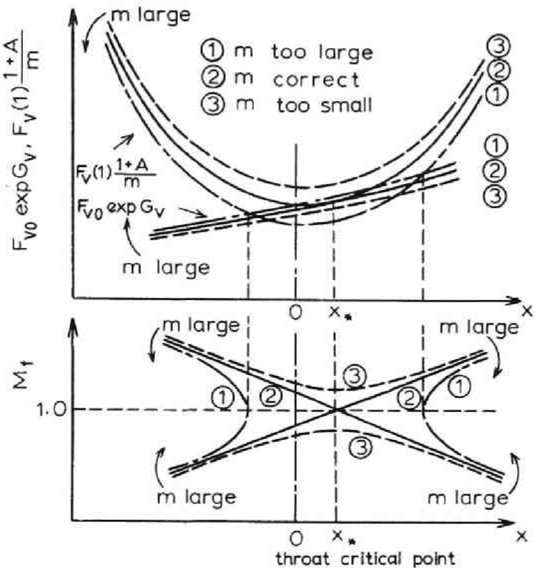

Fig. 2 Mass flows and their corresponding distributions of frozen Mach number.

flow rate that can just pass through a given throat satisfies the regularity condition Eq. (38) and then depends on the relaxation processes, the correct mass flow cannot be accurately prescribed beforehand. Mass flows and their corresponding distributions of the frozen Mach number are illustrated in Fig. 2.

It can be verified that an inequality

$$G_V > G_{V_f} = 0 \quad , \tag{39}$$

is satisfied in general for nonequilibrium nozzle flows, and this yields

$$m<m_f. \tag{40}$$

For almost all flows,

$$G_{V_e}>G_V \ , \tag{41}$$

is also satisfied. From these relations an important conclusion,

$$m_e<m<m_f, \tag{42}$$

can be drawn.

However the inequality Eq. (41) is not always satisfied for general nonequilibrium flows in nozzles with an arbitrary shape and size even under the equilibrium reservoir conditions. To account for this situation clearly, the entropy rise due to the nonequilibrium processes in the flow must be taken into account.

The equation of entropy for a diatomic gas with the vibrational energy mode is[2]

$$dS=\frac{R}{W_2}\frac{(\xi-\xi_V)\exp\xi_V}{(\exp\xi_V-1)^2}\cdot d\xi_V, \tag{43}$$

where S denotes the entropy of the gas. From this we can obtain

$$\xi_{V_e}=\xi_e, \quad dS_e=0 \ , \tag{44}$$

for the equilibrium flow, and

$$d\xi_{V_f}=0, \quad dS_f=0, \tag{45}$$

for the frozen flow.

Since the equilibrium-frozen flow, which was first proposed by Bray,[1] is composed of the upstream equilibrium branch and the downstream frozen one joined together at the freezing point, we have

$$dS_{ef}=0 \quad , \tag{46}$$

for this flow, where the subscript ef denotes the E-F (equilibrium-frozen) flow. Detailed discussion of this flow model will be given later in this paper.

For general nonequilibrium flows, Eq. (43) can be integrated formally to give

$$\frac{(S-S_0)}{\left(\frac{R}{W_2}\right)}=\ln\left(\frac{\exp\xi_V}{\exp\xi_V-1}\right)+\left(\frac{\xi_V}{\exp\xi_V-1}\right)-\ln\left(\frac{\exp\xi}{\exp\xi-1}\right)$$

$$-\left(\frac{\xi}{\exp\xi-1}\right)-\int_{\xi_0}^{\xi}\xi\cdot\frac{d}{d\xi}\left(\frac{1}{\exp\xi_V-1}-\frac{1}{\exp\xi-1}\right)d\xi\,. \tag{47}$$

Using this relation, G_V can be represented in the somewhat simple form,

$$G_V=3\ln\left(\frac{\frac{1}{\varphi}-\frac{1}{\exp\xi_0-1}}{\frac{1}{\varphi}-\frac{1}{\exp\xi_V-1}}\right)+\ln\left[\left(\frac{\exp\xi_0}{\exp\xi_0-1}\right)\left(\frac{\exp\xi_V-1}{\exp\xi_V}\right)\right]$$

$$+\left(\frac{\xi_0}{\exp\xi_0-1}-\frac{\xi_V}{\exp\xi_V-1}\right)+\frac{W_2}{R}(S-S_0)\,. \tag{48}$$

It must be noticed that the quantity G_V can be expressed completely in terms of the vibrational temperature and entropy of the gas.

As can easily be understood from the process through which Eq. (48) has been derived, it is generally valid without respect to the kind of a gas. At any point in the nozzle, only if the entropy rise is neglected, we can conclude that

$$G_{V\,\max}=G_{Ve}\;, \tag{49}$$

under the fixed reservoir conditions. In fact, at least theoretically there can be the case in which Eq. (49) is broken down, and then the inequality $m_e < m$ also can never be obtained. In almost all flows through nozzles with ordinary shapes studied in many laboratories, the increase in entropy due to nonequilibrium processes is in general so small that its effect on the flow field can reasonably be neglected. This gives one of the most powerful supports to the validity of the approximation by the equilibrium-frozen flow model.

The critical mass flows of the equilibrium, frozen and equilibrium-frozen flow are considered. For the equilibrium flow, the isentropic relation

$$dh - \frac{1}{\rho_e} \cdot dp_e = 0 \quad , \tag{50}$$

can be integrated to give

$$\xi_e^{5/2} \frac{\exp \xi_e - 1}{\exp \xi_e} \exp\left(-\frac{\xi_e}{\exp \xi_e - 1}\right) \cdot \rho_e = \xi_0^{5/2} \frac{\exp \xi_0 - 1}{\exp \xi_0} \cdot \exp\left(-\frac{\xi_0}{\exp \xi_0 - 1}\right) \rho_0$$
$$= C_e = \text{const.} \tag{51}$$

Using the condition $M_e = 1$ at the throat, the velocity there is given by

$$V_{e*} = V_{et} = \sqrt{h_0 \varphi} \cdot \left\{ \frac{1}{\xi_{et}} \cdot \frac{\left[\frac{7}{2} + \frac{\xi_{et}^2 \cdot \exp \xi_{et}}{(\exp \xi_{et} - 1)^2}\right]}{\left[\frac{5}{2} + \frac{\xi_{et}^2 \exp \xi_{et}}{(\exp \xi_{et} - 1)^2}\right]} \right\}^{1/2} . \tag{52}$$

Combining Eqs. (51) and (52), we get

$$m_e = \sqrt{h_0 \varphi} \cdot \frac{\rho_0}{\xi_0^{1/2}} \cdot \frac{\exp \xi_0 - 1}{\exp \xi_0} \cdot \exp\left(-\frac{\xi_0}{\exp \xi_0 - 1}\right) \cdot \left(\frac{\xi_0}{\xi_{et}}\right)^3$$
$$\cdot \frac{\exp \xi_{et}}{\exp \xi_{et} - 1} \exp\left(\frac{\xi_{et}}{\exp \xi_{et} - 1}\right) \cdot \left\{ \frac{\left[\frac{7}{2} + \frac{\xi_{et}^2 \exp \xi_{et}}{(\exp \xi_{et} - 1)^2}\right]}{\left[\frac{5}{2} + \frac{\xi_{et}^2 \exp \xi_{et}}{(\exp \xi_{et} - 1)^2}\right]} \right\}^{1/2} . \tag{53}$$

The value of ξ_{et} can be calculated from the energy equations at the reservoir and throat, which are, respectively,

$$\frac{7}{2}+\frac{\xi_0}{\exp\xi_0-1}=\frac{\xi_0}{\varphi}, \tag{54}$$

$$\frac{7}{2}+\frac{\xi_{et}}{\exp\xi_{et}-1}+\frac{1}{2}\cdot\frac{\left[\frac{7}{2}+\frac{\xi_{et}^2\exp\xi_{et}}{(\exp\xi_{et}-1)^2}\right]}{\left[\frac{5}{2}+\frac{\xi_{et}^2\exp\xi_{et}}{(\exp\xi_{et}-1)^2}\right]}=\frac{\xi_{et}}{\varphi}. \tag{55}$$

Similarly for the frozen flow, the isentropic relation

$$dh-\frac{1}{\rho_f}dp_f=0, \tag{56}$$

can be integrated to give

$$\xi_f^{5/2}\cdot\rho_f=\xi_0^{5/2}\rho_0=C_f=\text{const.}. \tag{57}$$

Using the condition $M_f = 1$ at the throat, we have the velocity there as follows,

$$V_{f*}=V_{ft}=\sqrt{\frac{7}{5}h_0\varphi}\cdot\frac{1}{\xi_{ft}^{1/2}}, \tag{58}$$

Eqs. (57) and (58) are combined to yield

$$m_f=\sqrt{\frac{7}{5}h_0\varphi}\cdot\frac{\rho_0}{\xi_0^{1/2}}\cdot\left(\frac{\xi_0}{\xi_{ft}}\right)^3, \tag{59}$$

where ξ_{ft} satisfies the energy equation at the critical point,

$$\frac{21}{5}+\frac{\xi_{ft}}{\exp\xi_0-1}=\frac{\xi_{ft}}{\varphi}, \tag{60}$$

or

$$\xi_{ft}=1.2\xi_0. \tag{61}$$

Considering the fact that the equilibrium-frozen flow is made of the equilibrium branch and the frozen one joined together at the freezing point which is determined by the freezing criterion first proposed by Bray, we can easily obtain

$$m_{ef}=\sqrt{2h_0\varphi}\cdot\rho_0\frac{\exp\xi_0-1}{\exp\xi_0}\cdot\exp\left(-\frac{\xi_0}{\exp\xi_0-1}\right)\cdot\frac{\exp\xi_{Veft}}{\exp\xi_{Veft}-1}\cdot\exp\left(\frac{\xi_{Veft}}{\exp\xi_{Veft}-1}\right)$$
$$\cdot\left(\frac{\xi_0}{\xi_{eft}}\right)^{5/2}\cdot\left(\frac{1}{\varphi}-\frac{7}{2\xi_{eft}}-\frac{1}{\exp\xi_{Veft}-1}\right)^{1/2}, \tag{62}$$

where

$$\xi_{Vef}=\begin{cases}\xi, & \xi\leq\xi_{Vf},\\ \xi_{Vf}=\text{const.}, & \xi>\xi_{Vf},\end{cases} \tag{63}$$

and where ξ_{Vf} denotes the frozen vibrational temperature, and ξ_{eft} is obtained also from the energy equation at the throat,

$$\frac{21}{5}+\frac{\xi_{eft}}{\exp\xi_{Veft}-1}=\frac{\xi_{eft}}{\varphi}, \qquad \text{if } \xi_{Veft}=\xi_{Vf}\leqq\xi_{et}. \tag{64}$$

The above discussions provide us with the relations among the three critical mass flows, m_e, m_f and m_{ef}:

$$\begin{aligned} &m_{ef}=m_f, && \xi_{Vf}=\xi_0 ,\\ &m_e\neq m_{ef}<m_f, && \xi_0<\xi_{Vf}\leqq\xi_{et} ,\\ &m_{ef};\ \text{unobtainable}, && \xi_{et}<\xi_{Vf}<\xi_{ft} ,\\ &m_{ef}=m_e, && \xi_{ft}\leqq\xi_{Vf}. \end{aligned} \tag{65}$$

The reason why m_{ef} is impossible to obtain in the case $\xi_{et}<\xi_{Vf}<\xi_{ft}$, is that there are two speeds of sound, the equilibrium speed of sound and the frozen one, in the real-gas flow.

The relation

$$\left(\frac{m_e}{m_f}\right)_{\min.}=\lim_{\xi_0\to 0}\left(\frac{m_e}{m_f}\right), \tag{66}$$

is easily found, and this yields, with the aid of the energy equation,

$$\left(\frac{m_e}{m_f}\right)_{\min.}\approx 0.9706.... \tag{67}$$

The ratio m_e/m_f is shown in Fig. 3.

Next, the investigation of the critical mass flow rate of the general nonequilibrium flow is made, and especially for the nearly equilibrium flow, the numerical calculations of it are carried out.

Here we consider the nozzle geometry given by

$$A=K\cdot x^2, \tag{68}$$

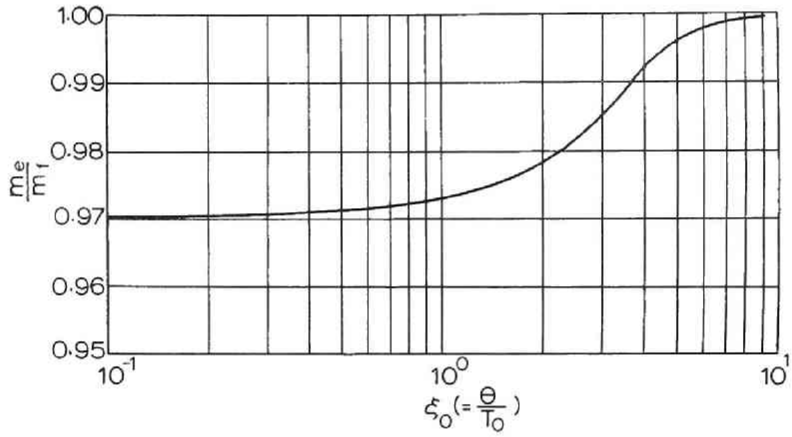

Fig. 3 Critical-mass-flow ratios of a vibrating diatomic gas.

where K is a positive constant. Then the regularity condition at the critical point can in general be written as

$$\left(\frac{1}{1+A}\cdot\frac{dA}{dx}\right)_*=2\sqrt{K}\cdot\frac{A_*^{1/2}}{1+A_*}\quad=-\frac{2}{7}\left[\xi\cdot\frac{d}{dx}\left(\frac{1}{\exp\xi_V-1}\right)\right]_*, \tag{69}$$

while the rate equation is

$$\frac{d}{dx}\left(\frac{1}{\exp\xi_V-1}\right)=-\frac{m}{(1+A)}\cdot\Psi(\xi)\left(\frac{1}{\exp\xi_V-1}-\frac{1}{\exp\xi-1}\right), \tag{70}$$

where

$$\Psi(\xi)=\left(\frac{5\Gamma\theta^w}{7h_0\varphi}\right)\frac{(\exp\xi-1)}{M_f{}^2\xi^{w+1}\cdot\exp\xi}\cdot\exp(l\theta^s\xi^{-s}). \tag{71}$$

Combining Eqs. (69) and (70), we get

$$A_*=\frac{m^2}{49K}\cdot\xi_*{}^2\Psi(\xi_*)^2\cdot\left(\frac{1}{\exp\xi_{V*}-1}-\frac{1}{\exp\xi_*-1}\right)^2. \tag{72}$$

Eq. (48) is substituted into Eq. (35) to give

$$(1+A_*)=\left(\frac{m_e{}^2}{2h_0\varphi C_e{}^2}\right)^{1/2}\cdot\left(\frac{m}{m_e}\right)\frac{\xi_*{}^{5/2}\dfrac{\exp\xi_{V*}-1}{\exp\xi_{V*}}\exp\left[-\dfrac{\xi_{V*}}{\exp\xi_{V*}-1}+\dfrac{W_2}{R}(S_*-S_0)\right]}{\left(\dfrac{1}{\varphi}-\dfrac{7}{2\xi_*}-\dfrac{1}{\exp\xi_{V*}-1}\right)^{1/2}}, \tag{73}$$

which yields, with the aid of Eq. (72),

$$\frac{m^2}{49K}\cdot\Psi(\xi_*)^2\cdot\xi_*^2\left(\frac{1}{\exp\xi_{V*}-1}-\frac{1}{\exp\xi_*-1}\right)^2$$

$$-\frac{m}{\sqrt{2h_0\varphi C_e^2}}\cdot\frac{\xi_*^{5/2}\dfrac{\exp\xi_{V*}-1}{\exp\xi_{V*}}\exp\left[-\dfrac{\xi_{V*}}{\exp\xi_{V*}-1}+\dfrac{W_2}{R}(S_*-S_0)\right]}{\left(\dfrac{1}{\varphi}-\dfrac{7}{2\xi_*}-\dfrac{1}{\exp\xi_{V*}-1}\right)^{1/2}}+1=0\quad, \tag{74}$$

where

$$\frac{21}{5}+\frac{\xi_*}{\exp\xi_{V*}-1}=\frac{\xi_*}{\varphi}\,,$$
$$\xi_0\leqq\xi_{V*}\leqq\xi_{e*}\quad. \tag{75}$$

Eq. (74) indicates that the critical mass flow depends not only on the departure of vibrational temperature from the equilibrium value or the rotational-translational temperature at the critical point but also on the increase in entropy in the subsonic region from the reservoir to the critical point. It is important that the critical mass flow is evaluated completely from the vibrational temperature and the entropy of the gas at the critical point, which is not always the case for the ideal dissociating gas or the singly ionizing gas.

Now, since Eq. (74) is a quadratic with respect to m, at least the next condition must be satisfied,

$$\frac{\xi_*^{5/2}}{\sqrt{2h_0\varphi C_e^2}}\,\frac{\exp\xi_{V*}-1}{\exp\xi_{V*}}\exp\left[-\frac{\xi_{V*}}{\exp\xi_{V*}-1}+\frac{W_2}{R}(S_*-S_0)\right]\left(\frac{1}{\varphi}-\frac{7}{2\xi_*}-\frac{1}{\exp\xi_{V*}-1}\right)^{-1/2}$$

$$\geq\frac{2}{7\sqrt{K}}\Psi(\xi_*)\cdot\xi_*\cdot\left(\frac{1}{\exp\xi_{V*}-1}-\frac{1}{\exp\xi_*-1}\right). \tag{76}$$

The value of the term about m^2 is usually much smaller than all others in Eq. (74), which yields the next approximate representation for m,

$$m\approx\left(\frac{2h_0\varphi C_e^2}{m_e^2}\right)^{1/2}\cdot\frac{m_e}{\xi_*^{5/2}}\cdot\left(\frac{1}{\varphi}-\frac{7}{2\xi_*}-\frac{1}{\exp\xi_{V*}-1}\right)^{1/2}\cdot\left(\frac{\exp\xi_{V*}}{\exp\xi_{V*}-1}\right)$$
$$\times\exp\left[\frac{\xi_{V*}}{\exp\xi_{V*}-1}-\frac{W_2}{R}(S_*-S_0)\right]\left\{1+\frac{2}{49K}h_0\varphi C_e^2\cdot\frac{\Psi(\xi^*)^2}{\xi_*^3}\cdot\left(\frac{1}{\exp\xi_{V*}-1}-\frac{1}{\exp\xi_*-1}\right)^2\right.$$
$$\left.\times\left(\frac{1}{\varphi}-\frac{7}{2\xi_*}-\frac{1}{\exp\xi_{V*}-1}\right)\left(\frac{\exp\xi_{V*}}{\exp\xi_{V*}-1}\right)^2\cdot\exp\left[\frac{2\xi_{V*}}{\exp\xi_{V*}-1}-2\frac{W_2}{R}(S_*-S_0)\right]+\cdots\right\}. \tag{77}$$

At a glance, it may easily be understood that the increase in entropy decreases the critical mass flow, and also the increase in radius of curvature of the nozzle wall at the critical point near the throat decreases it. The latter fact has already been verified numerically.[8)]

Especially, if a flow near the throat is almost frozen, all terms except the first in the curly bracket on the right hand side in Eq. (77) are negligibly small and can be omitted within an acceptable error. When the E-F flow model is employed for the approximation to this flow and the freezing point is determined so as to give

$$\xi_{Vf}=\xi_{V*} \quad , \tag{78}$$

we get

$$m_{ef}=\left(\frac{2h_0\varphi C_e^2}{m_e^2}\right)^{1/2}\cdot\frac{m_e}{\xi_*^{5/2}}\cdot\left(\frac{1}{\varphi}-\frac{7}{2\xi_*}-\frac{1}{\exp\xi_{V*}-1}\right)^{1/2}\cdot\frac{\exp\xi_{V*}}{\exp\xi_{V*}-1}\cdot\exp\left(\frac{\xi_{V*}}{\exp\xi_{V*}-1}\right). \tag{79}$$

From Eqs. (77) and (79), we can obtain

$$\frac{m}{m_{ef}}\approx\exp\left[-\frac{W_2}{R}(S_*-S_0)\right], \tag{80}$$

Finally it can be concluded that

$$m<m_{ef}\,. \tag{81}$$

for the flow in which the vibrational relaxation is almost frozen near the throat.

A numerical calculation of the critical mass flow is carried out for the nearly equilibrium flow. Determining the critical mass flow is equivalent to doing the corresponding flow field itself in the subsonic region, which may be understood from the aforementioned discussions. In general, the analytical treatment of this problem is almost impossible except in special cases. Furthermore even when an analytical treatment is possible to some degree, it is usually more or less numerical.

Here an iterative method applies to analysing the flow which remains nearly equilibrium at least to the critical point. Transforming the independent variable from x to ξ yields

$$\frac{d}{d\xi} h(\xi) = G\left(\frac{d\varepsilon_V}{d\xi}, \varepsilon_V, h(\xi); \xi\right), \tag{82}$$

$$\frac{7}{2} + \xi \cdot \varepsilon_V + \frac{7}{10} \cdot M_f^2 = \frac{\xi}{\varphi}, \tag{83}$$

$$\Pi\left(\frac{d\varepsilon_V}{d\xi}, \varepsilon_V, h(\xi); \xi\right) \frac{d\varepsilon_V}{d\xi} + \varepsilon_V = \varepsilon, \tag{84}$$

$$x = \frac{\delta}{\sqrt{K}} [h(\xi) - 1]^{1/2}, \qquad \delta = \begin{cases} -1 & \xi < \xi_t \\ 1 & \xi > \xi_t \end{cases} \tag{85}$$

where

$$\varepsilon_V = \frac{1}{\exp \xi_V - 1},$$

$$\varepsilon = \frac{1}{\exp \xi - 1},$$

$$\frac{G(\xi)}{h(\xi)} = \frac{\left\{\frac{2}{7} \cdot \left(\frac{1}{\varphi} - \varepsilon_V\right)\left[5\left(\frac{1}{\varphi} - \varepsilon_V\right)\xi - 21\right] - 2\left[\left(\frac{1}{\varphi} - \varepsilon_V\right)\xi - 8\right]\xi \cdot \frac{d\varepsilon_V}{d\xi}\right\}}{\left[2\left(\frac{1}{\varphi} - \varepsilon_V\right)\xi - 7\right]} - \frac{\left[5\left(\frac{1}{\varphi} - \varepsilon_V\right)\xi - 3\right]}{2\xi}. \tag{86}$$

$$\Pi(\xi) = \frac{864}{125} \cdot \sqrt{\frac{5}{7}} \cdot \frac{\sqrt{h_0 \varphi}}{\mu \Gamma \theta^w} \cdot \frac{\sqrt{K}}{\rho_0} \xi_0^{1/2} \cdot \frac{\xi^{w+1}\left(\frac{1}{\varphi} - \frac{7}{2\xi} - \varepsilon_V\right)^2 [h(\xi) - 1]^{1/2} \cdot \frac{\exp \xi}{\exp \xi - 1} \cdot \exp(-l\theta^s \xi^{-s})}{\left|\frac{5}{2}\left(\frac{1}{\varphi} - \frac{21}{5\xi} - \varepsilon_V\right) - \xi\left[\xi\left(\frac{1}{\varphi} - \frac{7}{2\xi} - \varepsilon_V\right) - \frac{1}{2}\right] \cdot \frac{d\varepsilon_V}{d\xi}\right|}.$$

$$\mu = \frac{m}{m_e}.$$

Again the nozzle which is given by Eq. (68) is considered.

When the flow is kept in nearly equilibrium, the first term on the left hand side in Eq. (84) is so small compared with the others that it can be neglected to the first approximation. Then the rate equation becomes the equilibrium relation. Substituting this into the remaining flow equations, we can determine the all flow variables to the first approximation. When the solution of the first approximation is used in π in the rate equation, the distribution of the vibrational temperature along the nozzle axis can be determined to the second approximation. Using this distribution of ξ_V or ε_V, the remaining flow equations of the second approximation can be solved quite easily. Repeating this process, we can obtain the solution of any higher approximate problem.

It must be emphasized that in this method the rate equation which govern the vibrational relaxation is completely uncoupled from the remaining flow equations, and then it can be integrated alone. Obviously this simplifies greatly the analysis, because the position of the critical point and the state of the gas there, and then the critical mass flow has already been determined strictly to each approximation before the flow equations are to be solved.

When ε_V of the i-th approximation is written as follows,

$$\varepsilon_{Vi}=\varepsilon+\varDelta\varepsilon_{Vi}\,, \qquad i=1 \text{ or } e, 2, 3, 4, \dots \quad , \tag{87}$$

the corresponding solution of the i-th approximation can be obtained in the forms,

$$\varDelta\varepsilon_{Vi}=\frac{14h_0\varphi\sqrt{K}}{5\Gamma m_{i-1}\theta^w}\cdot M_{fi-1}^2\frac{\exp\xi}{\exp\xi-1}\left[\frac{\exp\xi}{(\exp\xi-1)^2}-\frac{d}{d\xi}\varDelta\varepsilon_{Vi-1}\right]$$
$$\cdot\,\xi^{w+1}\frac{[h_{i-1}(\xi)-1]^{1/2}}{f_{i-1}(\xi)}\cdot\exp(-l\theta^s\xi^{-s})\,, \tag{88}$$

$$h_i(\xi)=\left(\frac{m_e^2}{2h_0\varphi C_e^2}\right)^{1/2}\cdot\frac{m_i}{m_e}\cdot\frac{\xi^{5/2}\,\dfrac{\exp\xi-1}{\exp\xi}\exp\left[-\dfrac{\xi}{\exp\xi-1}\right]\exp\left[-\int_{\xi_0}^{\xi}\xi\cdot\dfrac{d}{d\xi}(\varDelta\varepsilon_{Vi})\,d\xi\right]}{\left(\dfrac{1}{\varphi}-\dfrac{7}{2\xi}-\dfrac{1}{\exp\xi-1}-\varDelta\varepsilon_{Vi}\right)^{1/2}}, \tag{89}$$

$$\frac{7}{2}+\xi\cdot(\varepsilon+\varDelta\varepsilon_{Vi})+\frac{7}{10}M_{fi}^2=\frac{\xi}{\varphi}, \tag{90}$$

where

$$f_i(\xi)=\xi\cdot\frac{G_i(\xi)}{h_i(\xi)}=\frac{5}{7}\,\frac{M_{fi}^2-1}{M_{fi}^2}\left(\frac{1}{\varphi}-\varepsilon-\varDelta\varepsilon_{Vi}\right)-\frac{M_{fi}^2-1}{2\xi}$$

$$+\xi\,\frac{7M_{fi}^2-5}{7M_{fi}^2}\cdot\left[\frac{\exp\xi}{(\exp\xi-1)^2}-\frac{d}{d\xi}(\varDelta\varepsilon_{Vi})\right]. \tag{91}$$

In order to determine the critical mass flow to the i-th approximation, the regularity condition at the critical point of flow equations of the i-th approximation must be considered with the aid of the solutions of the (i-1)-th approximation. It must be noticed that the critical point of exact flow equations occurs in general downstream of the geometric throat, while that of the i-th approximation always occurs just at the geometric throat in the iterative method.

Using the conditions

$$h(\xi)=1 \qquad \text{and} \qquad dh(\xi)=0, \tag{92}$$

at the geometric throat, we get from the momentum equation

$$\frac{5}{2}\left\{\left(\frac{1}{\varphi}-\frac{1}{\exp\xi_{it}-1}-\varDelta\varepsilon_{Vit}\right)\xi_{it}-\frac{21}{5}\right\}$$

$$=\xi_{it}^2\left[\xi_{it}\left(\frac{1}{\varphi}-\frac{1}{\exp\xi_{it}-1}-\varDelta\varepsilon_{Vit}\right)-4\right]\cdot\left[\frac{d}{d\xi}\left(\frac{1}{\exp\xi_i-1}+\varDelta\varepsilon_{Vi}\right)\right]_t. \tag{93}$$

This is rearranged to yield

$$\frac{\xi_{it}}{\varphi}=\frac{7}{2}+\frac{\xi_{it}}{\exp\xi_{it}-1}+\frac{1}{2}\cdot\frac{\left[\dfrac{7}{2}+\dfrac{\xi_{it}^2\exp\xi_{it}}{(\exp\xi_{it}-1)^2}\right]}{\left[\dfrac{5}{2}+\dfrac{\xi_{it}^2\exp\xi_{it}}{(\exp\xi_{it}-1)^2}\right]}+\xi_{it}\cdot\varDelta\varepsilon_{Vit}$$

$$+\frac{\xi_{it}^2\cdot\left[\left(\frac{1}{\varphi}-\varepsilon_{Vit}\right)\xi_{it}-4\right]}{\left[\frac{5}{2}+\frac{\xi_{it}^2\exp\xi_{it}}{(\exp\xi_{it}-1)^2}\right]}\cdot\left[\frac{d}{d\xi}(\Delta\varepsilon_{Vi})\right]_t-\frac{\frac{1}{2}\cdot\xi_{it}^3\left[\frac{d}{d\xi}(\Delta\varepsilon_{Vi})^2\right]_t}{\left[\frac{5}{2}+\frac{\xi_{it}^2\exp\xi_{it}}{(\exp\xi_{it}-1)^2}\right]} \tag{94}$$

If $\Delta\mathcal{E}_{Vi}=0$, the above relation becomes that for the equilibrium flow, and if $\Delta\mathcal{E}_{Vi}=\mathcal{E}_0-\mathcal{E}$, that for the frozen flow. With the solution ξ_{it} of the above equation, the critical mass flow of the i-th approximation can be obtained finally as follows

$$\frac{m_i}{m_e}=\left(\frac{2h_0\varphi C_e^2}{m_e^2}\right)^{1/2}\cdot\xi_{it}^{-5/2}\cdot\left(\frac{\exp\xi_{it}}{\exp\xi_{it}-1}\right)\cdot\left(\frac{1}{\varphi}-\frac{7}{2\xi_{it}}-\frac{1}{\exp\xi_{it}-1}-\Delta\varepsilon_{Vit}\right)^{1/2}$$
$$\times\exp\left[\frac{\xi_{it}}{\exp\xi_{it}-1}+\int_{\xi_0}^{\xi_{it}}\xi\cdot\frac{d}{d\xi}(\Delta\varepsilon_{Vi})\,d\xi\right]. \tag{95}$$

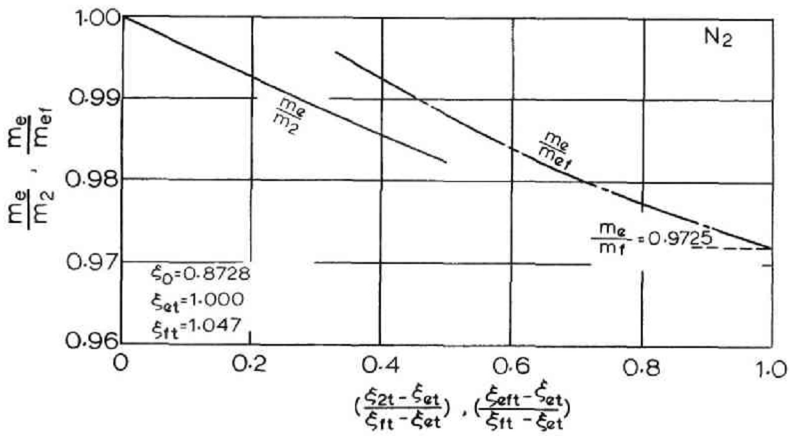

Fig. 4 Critical mass flows of nearly equilibrium and equilibrium-frozen flows of a vibrating diatomic gas.

As was already pointed out, the last term in the square bracket under the exponent in Eq. (95) can be integrated alone, because $\Delta\mathcal{E}_{Vi}$ has already been determined from the solution of the (i-1)-th approximation. Finally, an investigation must be made about the solution at the throat. The conditions at the geometric throat are written again as

$$h_i(\xi_{it})=1, \quad f_i(\xi_{it})=0 \quad , \tag{96}$$

which make it impossible to obtain the value of $\Delta\varepsilon_{V\,i+1t}$ at the throat numerically. Taylor's expansion of functions $h_i(\xi)$ and $f_i(\xi)$ about $\xi = \xi_{it}$ are given by

$$h_i(\xi)=1+\left[\frac{d}{d\xi}h_i(\xi_{it})\right](\xi-\xi_{it})+\frac{1}{2}\left[\frac{d^2}{d\xi^2}h_i(\xi_{it})\right]\cdot(\xi-\xi_{it})^2+\cdots, \tag{97}$$

$$f_i(\xi)=\left[\frac{d}{d\xi}f_i(\xi_{it})\right](\xi-\xi_{it})+\frac{1}{2}\left[\frac{d^2}{d\xi^2}f_i(\xi_{it})\right](\xi-\xi_{it})^2+\frac{1}{6}\left[\frac{d^3}{d\xi^3}f_i(\xi_{it})\right](\xi-\xi_{it})^3+\cdots. \tag{98}$$

Taking a relation

$$\frac{d}{d\xi}h_i(\xi)=\frac{1}{\xi}f_i(\xi)\cdot h_i(\xi) \quad ,$$

into consideration yields

$$\lim_{\xi\to\xi_{it}}\frac{[h_i(\xi)-1]^{1/2}}{f_i(\xi)}=\left[2\xi_{it}\cdot\frac{d}{d\xi}f_i(\xi_{it})\right]^{-1/2} \quad ,$$

$$\lim_{\xi\to\xi_{it}}\left\{\frac{d}{d\xi}\frac{[h_i(\xi)-1]^{1/2}}{f_i(\xi)}\right\}=-\frac{1}{3}\left[2\xi_{it}\cdot\frac{d}{d\xi}f_i(\xi_{it})\right]^{-1/2}\cdot\left[\frac{1}{\xi_{it}}+\frac{\frac{d^2}{d\xi_2}f_i(\xi_{it})}{\frac{d}{d\xi}f_i(\xi_{it})}\right] \quad , \tag{99}$$

etc..

Using these results, the solution of each approximation at the throat can be calculated numerically. The characteristic values of N_2 and O_2 gases are listed in Table 1.

	N_2	O_2
θ	3336°K	2228°K
Γ	8.878×10^8 m³/°K kg sec	8.300×10^9 m³/°K kg sec
w	1	1
s	$-1/3$	$1/3$
l	-181°K	0.6464°K$^{-1/3}$

Table 1 Characteristic values of N_2 and O_2 gases.[3) 11)]

Now it is convenient to introduce a "nonequilibrium parameter" P_e by

$$P_e = -\Pi_e \cdot \frac{1}{\varepsilon} \cdot \frac{d\varepsilon}{d\xi} \quad , \tag{100}$$

in order to calculate $\Delta\varepsilon_{V2} = P_e/(\exp\xi - 1)$ and to determine the freezing point in the E-F flow approximation, which is usually the point where the value of this parameter becomes about unity. Distributions of P_e along the nozzle axis are shown in Fig. 5 for N_2 gas.

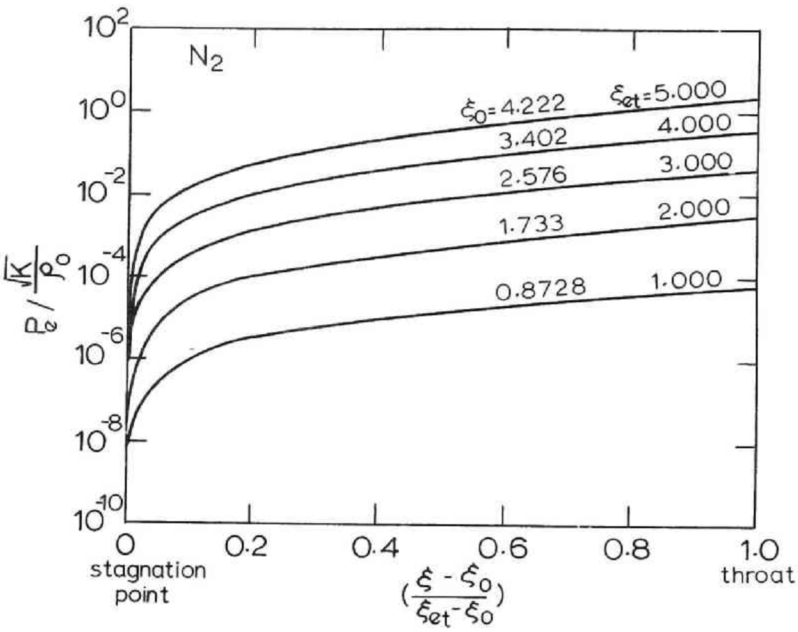

Fig. 5 Distributions of nonequilibrium parameter of a vibrating diatomic gas along the nozzle axis.

4. 2 Critical Mass Flows of Ideal Dissociating Diatomic Gas

The analysis can be carried out in almost the same manner as in the previous section. A parameter ψ is introduced by

$$\psi = \frac{1}{h_0} \cdot \frac{R}{W_2} \cdot D \, . \tag{101}$$

If the quantity q is taken to be α, the density and the speeds of sound are given by

$$\rho=\frac{m\left(\frac{6}{1+\alpha}+M_f^2\right)^{1/2}}{\sqrt{2h_0}\cdot(1+A)M_f(1-\psi\alpha)^{1/2}},$$

$$a_e^2=\frac{h_0}{3}\cdot\frac{(1-\psi\alpha_e)}{\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)}+\left[\frac{h_0(1-\psi\alpha_e)}{(4+\alpha_e)\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)}\right]\cdot\left[\frac{\psi(4+\alpha_e)\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)}{3(1-\psi\alpha_e)}-\frac{1}{1+\alpha_e}\right]$$

$$\cdot\frac{\left\{3(1-\psi\alpha_e)+(1+\alpha_e)\left[d(1-\psi\alpha_e)-\psi(4+\alpha_e)\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)\right]\right\}}{\left\{\psi\left(\frac{4+\alpha_e}{1-\psi\alpha_e}\right)\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)\left[\psi(4+\alpha_e)\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)-d(1-\psi\alpha_e)\right]+3\cdot\frac{(1-\psi\alpha_e)(2-\alpha_e)}{\alpha_e(1-\alpha_e)}\right\}},$$

$$a_f^2=2h_0\frac{(1-\psi\alpha)}{\left(\frac{6}{1+\alpha}+M_f^2\right)}. \tag{1o2}$$

The equations of energy and momentum become

$$T=\left(\frac{D}{\psi}\right)\frac{(1-\psi\alpha)}{(4+\alpha)\left(1+\frac{1+\alpha}{6}M_f^2\right)}, \tag{103}$$

$$\frac{2(1-M_f^2)}{\left(2+\frac{1+\alpha}{3}M_f^2\right)}\cdot\frac{1}{M_f}\cdot\frac{dM_f}{dx}+\frac{1}{1+A}\cdot\frac{dA}{dx}=\frac{[3+(4+\alpha)M_f^2]}{[6+(1+\alpha)M_f^2]}$$

$$\cdot\left\{\frac{3}{(4+\alpha)(1+\alpha)}-\frac{3(1-M_f^2)}{(4+\alpha)[3+(4+\alpha)M_f^2]}-\psi\frac{[6+(1+\alpha)M_f^2]}{6(1-\psi\alpha)}\right\}\left(\frac{d\alpha}{dx}\right). \tag{1o4}$$

In quite a similar way to the previous, integrating Eq. (104) yields after some manipulation,

$$F_D(M_f,\alpha)\cdot\frac{1+A}{m}=F_{D_0}\cdot\exp G_D, \tag{105}$$

where

$$F_D(M_f,\alpha)=\frac{M_f}{\left(M_f^2+\frac{6}{1+\alpha}\right)^{1/2\cdot(7+\alpha)/(1+\alpha)}},$$

$$F_{D0}=\frac{\left(\frac{1+\alpha_0}{6}\right)^{\cdot 3/(1+\alpha_0)}}{\sqrt{2h_0}\cdot\rho_0(1-\psi\alpha_0)^{1/2}}, \tag{106}$$

$$G_D=\int_{\alpha_0}^{\alpha}\left\{\frac{3}{(1+\alpha)^2}\left[\ln\left(M_f^2+\frac{6}{1+\alpha}\right)+\frac{\left(\frac{7+\alpha}{1+\alpha}\right)}{\left(M_f^2+\frac{6}{1+\alpha}\right)}\right]-\frac{[3+(4+\alpha)M_f^2]}{[6+(1+\alpha)M_f^2]}\right.$$

$$\cdot\left[\frac{\phi\left(1+\frac{1+\alpha}{6}M_f^2\right)}{(1-\phi\alpha)}+\frac{(1-M_f^2)}{(4+\alpha)\left(1+\frac{4+\alpha}{3}M_f^2\right)}-\frac{3}{(4+\alpha)(1+\alpha)}\right]\Bigg\}d\alpha .$$

It is easy to prove that

$$\frac{\partial}{\partial M_f}\cdot F_D(M_f,\alpha)=0\,,\quad \text{at}\quad M_f=1\,,$$

which yields

$$F_D(M_f,\alpha)\leqq F_D(1,\alpha)\quad . \tag{107}$$

The following is valid at $M_f=1$

$$\frac{1+A_*}{m}=\frac{F_{D0}}{F_D(1,\alpha_*)}\cdot\exp G_{D*}$$

$$=\frac{\left(\frac{1+\alpha_0}{6}\right)^{3/(1+\alpha_0)}\left(\frac{7+\alpha_0}{1+\alpha_0}\right)^{1/2\cdot(7+\alpha_0)/(1+\alpha_0)}}{\sqrt{2h_0}\quad\rho_0\cdot(1-\phi\alpha_0)^{1/2}}\exp\left\{-\int_{\alpha_0}^{\alpha_*}\frac{3}{(1+\alpha)^2}\right.$$

$$\times\left[\ln\left(\frac{\frac{7+\alpha}{1+\alpha}}{M_f^2+\frac{6}{1+\alpha}}\right)-\frac{(1+\alpha)(1-M_f^2)}{[6+(1+\alpha)M_f^2]}\right]\cdot d\alpha-\int_{\alpha_0}^{\alpha^*}\frac{[3+(4+\alpha)M_f^2]}{[6+(1+\alpha)M_f^2]}$$

$$\times\left.\left[\frac{\phi\left(1+\frac{1+\alpha}{6}M_f^2\right)}{(1-\phi\alpha)}+\frac{(1-M_f^2)}{(4+\alpha)\left(1+\frac{4+\alpha}{3}M_f^2\right)}-\frac{3}{(4+\alpha)(1+\alpha)}\right]d\alpha\right\}. \tag{108}$$

For the frozen flow, the conditions

$$A_*=0,\quad \alpha_*=\alpha_0\quad\text{at}\quad M_f=1, \tag{109}$$

give the critical mass flow by

$$m_f=\sqrt{2h_0}\cdot\rho_0(1-\phi\alpha_0)^{1/2}\cdot\left(\frac{6}{1+\alpha_0}\right)^{3/(1+\alpha_0)}\cdot\left(\frac{1+\alpha_0}{7+\alpha_0}\right)^{1/2\cdot(7+\alpha_0)/(1+\alpha_0)}, \tag{110}$$

with which Eq. (108) can be rewritten in the form,

$$\frac{1+A_*}{m}=\frac{1}{m_f}\cdot\exp G'_{D*}\quad , \tag{111}$$

where

$$G_D' = -\int_{\alpha_0}^{\alpha} \frac{3}{(1+\alpha)^2} \left[\ln \left(\frac{\frac{7+\alpha}{1+\alpha}}{M_f^2 + \frac{6}{1+\alpha}} \right) - \frac{(1+\alpha)\cdot(1-M_f^2)}{[6+(1+\alpha)M_f^2]} \right] \cdot d\alpha - \int_{\alpha_0}^{\alpha} \frac{[3+(4+\alpha)M_f^2]}{[6+(1+\alpha)M_f^2]}$$

$$\times \left[\frac{\phi\left(1+\frac{1+\alpha}{6}M_f^2\right)}{(1-\phi\alpha)} + \frac{(1-M_f^2)}{(4+\alpha)\left(1+\frac{4+\alpha}{3}M_f^2\right)} - \frac{3}{(4+\alpha)(1+\alpha)} \right] d\alpha . \qquad (112)$$

Except in cases where the temperature of the gas is extremely high, G_D' always satisfies an inequality

$$G_D' > 0 . \qquad (113)$$

It is quite reasonable to consider that the above inequality is valid in general for nozzle flows of an ideal dissociating gas, because the temperature of the gas, in which the dissociation phenomenon is taking place predominantly, is never so high as to make the relation Eq. (113) broken.

At any point in the nozzle, it is satisfied that

$$\frac{1+A}{m} = \frac{F_D(1,\alpha)}{F_D(M_f,\alpha)} \cdot \frac{1}{m_f} \exp G_D' , \qquad (114)$$

Eq. (107) implies

$$\frac{F_D(1,\alpha)}{F_D(M_f,\alpha)} \geq 1 . \qquad (115)$$

From these relations, we get

$$\frac{1+A}{m} > \frac{1}{m_f} \exp G_D' , \qquad (116)$$

at any point except the sonic one in the nozzle, which indicates that

$$\frac{m}{m_f} < \exp(-G_{Dt}') < 1 . \qquad (117)$$

at the throat.

Now the equation of the entropy for an ideal dissociating gas can be written as[2)]

$$dS=\frac{W_2}{R}\ln\left(\frac{c^2}{1-c}\cdot\frac{1-\alpha}{\alpha^2}\right)d\alpha\,, \tag{118}$$

where the quantity c satisfies

$$\frac{c^2}{1-c}=\frac{C_D}{\rho}\cdot T^{-d}\cdot\exp\left(-\frac{D}{T}\right). \tag{119}$$

It is easy to prove that both the equilibrium and frozen flows are isentropic。

For general nonequilibrium flows the entropy equation is formally integrated to give

$$\frac{W_2}{R}(S-S_0)=(\alpha-\alpha_0)(1+\ln C_D)+\ln\left[\frac{(1-\alpha_0)^{(1-\alpha_0)}}{(1-\alpha)^{(1-\alpha)}}\right]-2\ln\left(\frac{\alpha^\alpha}{\alpha_0{}^{\alpha_0}}\right)+\alpha\ln\left(\frac{T^{3/(1+\alpha)}}{\rho}\right)$$

$$-\alpha_0\ln\left(\frac{T_0{}^{3/(1+\alpha_0)}}{\rho_0}\right)-\int_{\alpha_0}^{\alpha}\frac{1}{(1+\alpha)}\left(\frac{D}{T}\right)d\alpha-\int_{\alpha_0}^{\alpha}\frac{3\ln T}{(1+\alpha)^2}\cdot d\alpha-d\cdot\int_{\alpha_0}^{\alpha}\ln T\cdot d\alpha\,, \tag{120}$$

while the right hand side of the third equation of Eqs. (106) is also integrated formally to give

$$G_D=\ln\left(\frac{1-\psi\alpha_0}{1-\psi\alpha}\right)^{1/2}+\ln\left\{\left[\frac{(1-\psi\alpha_0)}{(4+\alpha_0)(1+\alpha_0)}\right]^{3/(1+\alpha_0)}\cdot\left[\frac{(4+\alpha)(1+\alpha)}{(1-\psi\alpha)}\right]^{3/(1+\alpha)}\right\}$$

$$-3\ln\left(\frac{6}{\psi}D\right)\left(\frac{1}{1+\alpha}-\frac{1}{1+\alpha_0}\right)-\int_{\alpha_0}^{\alpha}\frac{3\ln T}{(1+\alpha)^2}\,d\alpha-\int_{\alpha_0}^{\alpha}\frac{1}{(1+\alpha)}\cdot\left(\frac{D}{T}\right)d\alpha\,. \tag{121}$$

Substituting the entropy equation into Eq. (121), we get

$$G_D=\frac{W_2}{R}(S-S_0)-\int_{\alpha_0}^{\alpha}\ln\left(\frac{C_D}{T^d}\right)d\alpha+\ln\left(\frac{\rho^\alpha}{\rho_0{}^{\alpha_0}}\right)-\ln\left(\frac{T^{3\alpha/(1+\alpha)}}{T_0{}^{3\alpha_0/(1+\alpha_0)}}\right)$$

$$-\ln\left[\frac{(1-\alpha_0)^{(1-\alpha_0)}}{(1-\alpha)^{(1-\alpha)}}\cdot\left(\frac{\alpha_0{}^{2\alpha_0}}{\alpha^{2\alpha}}\right)\right]-(\alpha-\alpha_0)-\left(\frac{3}{1+\alpha}-\frac{3}{1+\alpha_0}\right)\cdot\ln\left(6\frac{D}{\psi}\right)$$

$$+\ln\left(\frac{1-\psi\alpha_0}{1-\psi\alpha}\right)^{1/2}+\ln\left\{\left[\frac{(1-\psi\alpha_0)}{(1+\alpha_0)(4+\alpha_0)}\right]^{3/(1+\alpha_0)}\left[\frac{(1+\alpha)(4+\alpha)}{(1-\psi\alpha)}\right]^{3/(1+\alpha)}\right\} \tag{122}$$

Especially when d is equal to zero, the integr .tion of the second term on the right hand side in Eq. (122) can be carried out analytically.

Using the isentropic relation for an equilibrium flow, we obtain

$$G_{De}=\ln\left(\frac{T_e}{T_0}\right)^d+\left(\frac{D}{T_e}-\frac{D}{T_0}\right)+\ln\left(\frac{1-\alpha_0}{\alpha_0{}^2}\right)+\ln\left(\frac{\alpha_e{}^2}{1-\alpha_e}\right)-(\ln 6)\cdot\left(\frac{3}{1+\alpha_e}-\frac{3}{1+\alpha_0}\right)$$

$$+\ln\left(\frac{1-\phi\alpha_0}{1-\phi\alpha_e}\right)^{1/2}-\frac{3}{(1+\alpha_0)}\ln(1+\alpha_0)+\frac{3}{(1+\alpha_e)}\cdot\ln\left[\frac{(1+\alpha_e)}{\left(1+\frac{1+\alpha_e}{6}M_{fe}^2\right)}\right]. \tag{123}$$

Finally for the equilibrium flow, Eq. (105) becomes

$$\frac{M_{fe}}{\left(M_{fe}^2+\frac{6}{1+\alpha_e}\right)^{1/2\cdot(7+\alpha_e)/(1+\alpha_e)}}\cdot\frac{1+A}{m}=F_{D_0}\cdot\left(\frac{T_e}{T_0}\right)^d\cdot\left(\frac{1-\alpha_0}{\alpha_0{}^2}\right)\left(\frac{\alpha_e{}^2}{1-\alpha_e}\right)\left(\frac{1-\phi\alpha_0}{1-\phi\alpha_e}\right)^{1/2}$$

$$\cdot(1+\alpha_0)^{-3/(1+\alpha_0)}\cdot(1+\alpha_e)^{3/(1+\alpha_e)}\cdot 6^{-3/(1+\alpha_e)+3/(1+\alpha_0)}$$

$$\cdot\left[\frac{6}{6+(1+\alpha_e)M_{fe}^2}\right]^{3/(1+\alpha_e)}\cdot\exp\left(\frac{D}{T_e}-\frac{D}{T_0}\right). \tag{124}$$

The fact that the critical point is located at the throat yields the critical mass flow by

$$m_e=\sqrt{2h_0C_D{}^2}\,\frac{1-\alpha_{e*}}{\alpha_{e*}^2}\,M_{fe*}\left(\frac{1-\phi\alpha_{e*}}{M_{fe*}^2+\frac{6}{1+\alpha_{e*}}}\right)^{1/2}T_{e*}^{-d}\cdot\exp\left(-\frac{D}{T_{e*}}\right) \tag{125}$$

where the quantities α_{e*} and M_{fe*} must be determined as follows. From the isentropic relation for the equilibrium flow, we can obtain, after the suitable manipulation, an ordinary differential equation with respect to α_e (or M_{fe}) with M_{fe} (or α_e) as an independent variable, which is usually integrated numerically and analytically only if d is equal to zero, with the boundary values $\alpha_{e0}=\alpha_0$ and $M_{fe0}=0$ at the reservoir. The regularity condition at the throat yields

$$1=\phi\alpha_{e*}+\frac{7}{6}\frac{(1-\phi\alpha_{e*})}{\left(1+\frac{1+\alpha_{e*}}{6}M_{fe*}^2\right)}+\frac{1}{2}\left[\frac{\phi}{3}-\frac{(1-\phi\alpha_{e*})}{(1+\alpha_{e*})\cdot(4+\alpha_{e*})\cdot\left(1+\frac{1+\alpha_{e*}}{6}M_{fe*}^2\right)}\right]$$

$$\cdot\frac{\left\{3(1-\phi\alpha_{e*})+(1+\alpha_{e*})\cdot\left[d(1-\phi\alpha_{e*})-\phi(4+\alpha_{e*})\left(1+\frac{1+\alpha_{e*}}{6}M_{fe*}^2\right)\right]\right\}}{\left\{\phi\left(\frac{4+\alpha_{e*}}{1-\phi\alpha_{e*}}\right)\left(1+\frac{1+\alpha_{e*}}{6}M_{fe*}^2\right)\left[\phi(4+\alpha_{e*})\left(1+\frac{1+\alpha_{e*}}{6}M_{fe*}^2\right)-d(1-\phi\alpha_{e*})\right]+3\frac{(1-\phi\alpha_{e*})(2-\alpha_{e*})}{\alpha_{e*}(1-\alpha_{e*})}\right\}}. \tag{126}$$

As a result, the solution α_{e*} and M_{fe*} of the equilibrium isentropic relation which satisfy the above regularity condition are substituted into the right hand side of Eq. (125) in order to obtain the value of m_e.

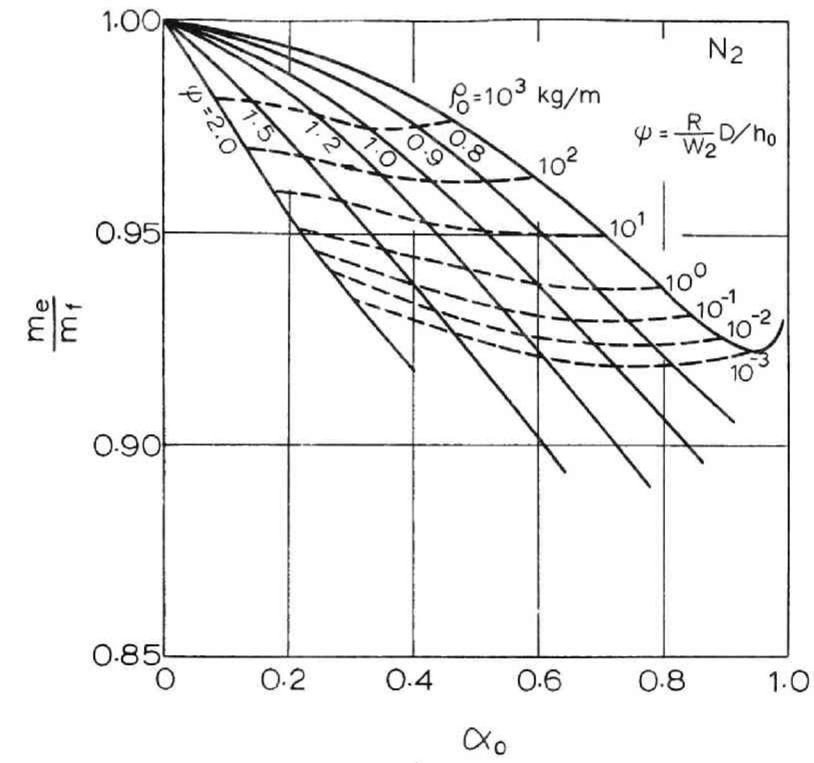

Fig. 6 Critical mass flows of an idéal dissociating diatomic gas.

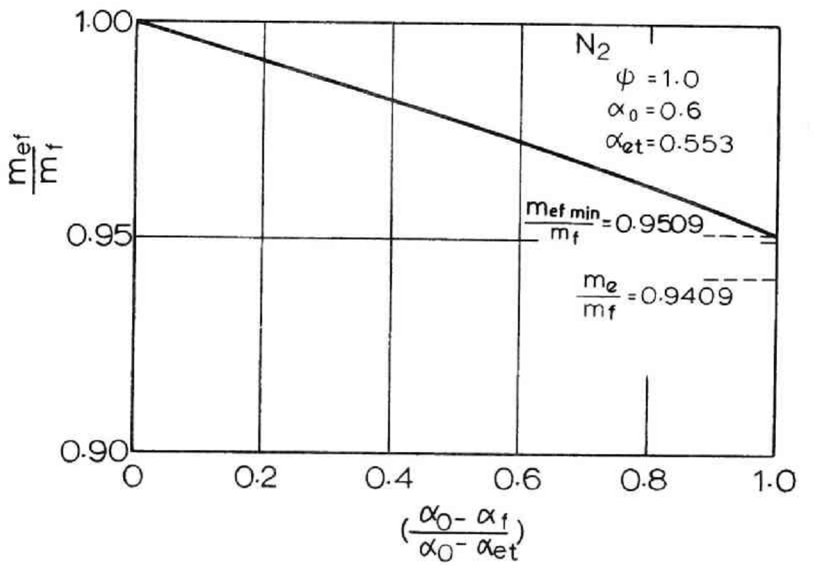

Fig. 7 Critical mass flow of equilibrium frozen flows of an ideal dissociating diatomic gas.

Next the critical mass flow of the E-F flow is considered. The values of α, M_f and T at a freezing point are denoted, respectively, by α_f, M_{feff} and T_{eff}. In the region from the reservoir to the freezing point, the equilibrium state is maintained and then the equilibrium isentropic relation holds. Downstream of the freezing point, the flow freezes suddenly and completely and then the value of G_D remains constant. The conditions at the throat

$$A=0, \quad \text{and} \quad M_{f\cdot ef\cdot t}=1 \quad , \tag{127}$$

yield

$$m_{ef}=\sqrt{2h_0C_D{}^2}\cdot\frac{1-\alpha_f}{\alpha_f{}^2}\cdot(1-\phi\alpha_f)^{1/2}\cdot\left(\frac{1+\alpha_f}{7+\alpha_f}\right)^{1/2\cdot(7+\alpha_f)/(1+\alpha_f)}$$

$$\times\left(\frac{6}{1+\alpha_f}+M_{fef\cdot f}^2\right)^{3/(1+\alpha_f)}\cdot T_{eff}^{-d}\cdot\exp\left(-\frac{D}{T_{eff}}\right), \tag{128}$$

where T_{eff} is related to M_{feff} and α_f by

$$T_{eff}=\left(\frac{D}{\phi}\right)\cdot\left(\frac{1-\phi\alpha_f}{4+\alpha_f}\right)\cdot\left(1+\frac{1+\alpha_f}{6}M_{feff}^2\right)^{-1}. \tag{129}$$

It can easily be proved that the minimum value of m_{ef} is given for $\alpha_f=\alpha_{e*}$ by

$$\frac{m_e}{m_{ef\cdot\min.}}=\left[\frac{(7+\alpha_{e*})}{(1+\alpha_{e*})M_{fe*}^2+6}\right]^{1/2\cdot(7+\alpha_{e*})/(1+\alpha_{e*})}\cdot M_{fe*}\,. \tag{130}$$

It indicates that the ratio $m_e/m_{ef\ \min}$ can never exceed unity, namely

$$m_e<m_{ef\cdot\min.} \tag{131}$$

However Eq. (128) indicates directly that

$$m_{ef\cdot\max.}=m_f \tag{132}$$

From these considerations, it can be concluded that

$$m_e < m_{ef} \leqq m_f \tag{133}$$

The critical mass flow of the general nonequilibrium flow is obtained. Considering the nozzle geometry given by Eq. (68), we get from the momentum equation and the regularity condition at the critical point

$$m^2\left[1-\kappa_*\cdot g_*\cdot \exp\left(\frac{G''_{D*}}{1+\alpha_*}\right)\right]^2 - m\kappa_*^2 g_*^3 \cdot D_*^3 \cdot \exp\left(\frac{3G''_{D*}}{1+\alpha_*}\right) + \kappa_*^2 g_*^2 D_*^2 \exp\left(2\frac{G''_{D*}}{1+\alpha_*}\right) = 0 , \tag{134}$$

where

$$\kappa_* = \frac{12\sqrt{2}}{W_2 h_0^{1/2}} \cdot \frac{1}{K(T_*)} \cdot \frac{\alpha_*^2}{(1-\alpha_*^2)(1-\phi\alpha_*)^{1/2}} \quad ,$$

$$G''_{D*} = G_{D*} - \alpha_* \cdot \ln \rho_* \quad , \tag{135}$$

$$D_* = \frac{2}{3} W_2 \cdot h_0 \sqrt{K} \cdot \frac{(1-\alpha_*)}{(1+\alpha_*)^{3/2}} \cdot \frac{(7+\alpha_*)}{(1-\phi\alpha_*)} \cdot \left[\frac{3}{(4+\alpha_*)(1+\alpha_*)} - \frac{(7+\alpha_*)}{6}\left(\frac{\phi}{1-\phi\alpha_*}\right)\right] \cdot$$

$$[k_{f1*}(1-\alpha_*) + 2k_{f2*}\alpha_*] ,$$

$$g_* = F_{D0}^{1/(1+\alpha_*)} \cdot \left(\frac{7+\alpha_*}{1+\alpha_*}\right)^{1/2\cdot(7+\alpha_*)/(1+\alpha_*)^2} \cdot \left[\frac{3}{h_0(1+\alpha_*)(1-\phi\alpha_*)}\right]^{\alpha_*/2(1+\alpha_*)} .$$

When d = 0, which is the case, for example, for the nitrogen gas approximately, G_{D*} becomes the function of α_* and S_* only. In such a case this quadratic relates the critical mass flow with the dissociated mass fraction and entropy at the critical point. Since the term about m^2 is in general much smaller than all others in Eq. (134), m can be given approximately by

$$m \approx \frac{1}{g_*} \exp\left(-\frac{G''_{D*}}{1+\alpha_*}\right)\left\{1 + \frac{\left[1-\kappa_* g_* \exp\left(\frac{G''_{D*}}{1+\alpha_*}\right)\right]^2}{\kappa_*^4 g_*^6 D_*^4} \exp\left(-\frac{3G''_{D*}}{1+\alpha_*}\right) + \cdots\right\} . \tag{136}$$

From this it can be concluded that the increase in entropy decreases the critical mass flow, and the minimum value of it under the fixed reservoir conditions is given by the equilibrium one only if the increase in entropy is neglected.

N_2
$D=113260°K$
$d=0$
$k_{f1}=3.0\times10^{18}\,T^{-3/2}\exp\left(\frac{D}{T}\right)\ m^3/k\cdot mol\cdot sec$
$k_{f2}=1.5\times10^{19}\,T^{-3/2}\exp\left(\frac{D}{T}\right)\ m^3/k\cdot mol\cdot sec$
$K(T)=C_D\exp\left(-\frac{D}{T}\right)\ k\cdot mol/m^3$
$C_D=1.26\times10^5\ k\cdot mol/m^3$

Table 2 Characteristic values of N_2 gas.[18]

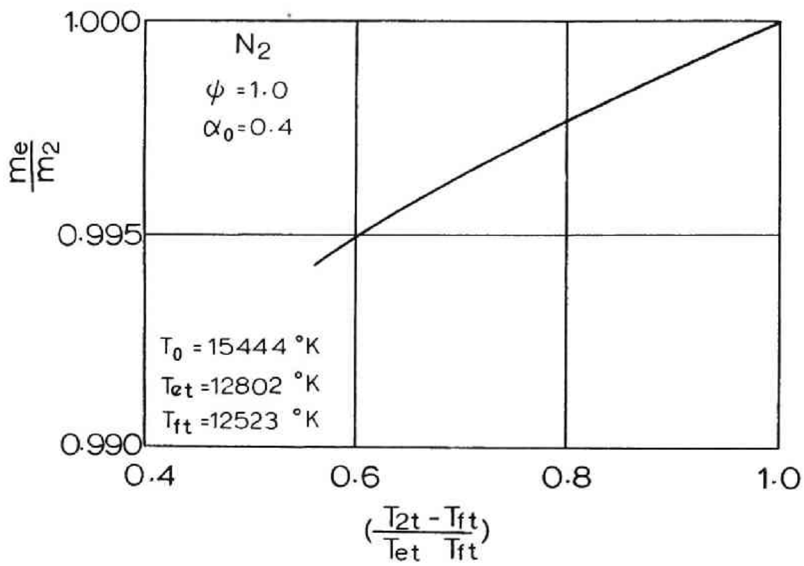

Fig. 8 Critical mass flow of nearly equilibrium flows of an ideal dissociating diatomic gas.

In all the same manner as in the analysis of the vibrationally relaxing gas, the problem of predicting the critical mass flow can be treated analytically to some degree, if the flow is kept in the near-equilibrium at least up to the critical point. Of course the solution of the first approximation is the equilibrium one. Here only the calculated result is presented in Fig. 8, where the subscript 2 denotes the second approximation.

Characteristic values of N_2 gas which was used in this numerical calculation are listed in Table 2.

4. 3 Critical Mass Flows of Singly Ionizing Monatomic Gas

If q is taken to be ϕ, next relations are yielded

$$\rho=\frac{m}{(1+A)M_f}\cdot\left[\frac{2h_0(1-\eta\phi)}{\left(M_f^2+3+2\cdot\frac{a+b\phi}{1+\phi}\right)}\right]^{-1/2},$$

$$a_f^2=\frac{2h_0\cdot(1-\eta\phi)}{\left(M_f^2+3+2\cdot\frac{a+b\phi}{1+\phi}\right)}, \tag{137}$$

$$a_e^2=\frac{h_0(1-\eta\phi_e)\cdot\left(3+2\frac{a+b\phi_e}{1+\phi_e}\right)}{\left(5+2\cdot\frac{a+b\phi_e}{1+\phi_e}\right)\left(M_{fe}^2+3+2\frac{a+b\phi_e}{1+\phi_e}\right)}\left\{1-\frac{\phi_e(1-\phi_e)}{(1+\phi_e)(2-\phi_e)}\right.$$

$$\left.+\frac{\left[1+\frac{\phi_e(1-\phi_e)}{(1+\phi_e)(2-\phi_e)}\left(i+\frac{I}{T_e}\right)\right]\left[(1+\phi_e)+\left(\frac{I}{T_e}+b+\frac{3}{2}\right)\frac{\phi_e(1-\phi_e)}{(2-\phi_e)}\right]}{\left[\frac{3}{2}(1+\phi_e)+(a+b\phi_e)+\left(i+\frac{I}{T_e}\right)\cdot\left(\frac{3}{2}+b+\frac{I}{T_e}\right)\cdot\frac{\phi_e(1-\phi_e)}{(2-\phi_e)}\right]}\right\}.$$

where the parameter η is defined by

$$\eta=\frac{1}{h_0}\cdot\frac{R}{W_1}\cdot I \quad , \tag{138}$$

and the equations of energy and momentum are expressed in the forms,

$$T=2\frac{I}{\eta}\cdot\frac{(1-\eta\phi)\left[3+2\left(\frac{a+b\phi}{1+\phi}\right)\right]}{(1+\phi)\left(5+2\frac{a+b\phi}{1+\phi}\right)\cdot\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)}, \tag{139}$$

$$\frac{M_f\cdot\left(3+2\frac{a+b\phi}{1+\phi}\right)}{\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)}\cdot\left(\frac{1}{M_f^2}-1\right)\frac{dM_f}{dx}+\frac{1}{1+A}\cdot\frac{dA}{dx}$$

$$=\left\{\left(\frac{3}{2}+\frac{a+b\phi}{1+\phi}\right)\cdot\left[\frac{(1+\eta)}{(1+\phi)(1-\eta\phi)}+\frac{2\cdot\frac{(b-a)}{(1+\phi)^2}}{\left(5+2\frac{a+b\phi}{1+\phi}\right)}-\frac{2\cdot M_f^2\cdot\frac{(b-a)}{(1+\phi)^2}}{\left(3+2\frac{a+b\phi}{1+\phi}\right)\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)}\right]\right.$$

$$+\frac{\left[\eta\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)+2\cdot\frac{(b-a)(1-\eta\phi)}{(1+\phi)^2}\right]}{2(1-\eta\phi)\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)}-\left(\frac{3}{2}+b+\frac{I}{T}\right)\frac{1}{(1+\phi)}\Bigg\}\cdot\frac{d\phi}{dx}\,. \tag{140}$$

The last equation is formally integrated to give

$$F_I(M_f,\phi)\cdot\frac{1+A}{m}=F_{IO}\cdot\exp G_I \quad , \tag{141}$$

where

$$F_I(M_f,\phi)=\frac{M_f}{\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)^{(2+(a+b\phi)/(1+\phi))}} \quad ,$$

$$F_{IO}=\left\{\sqrt{2h_0}\cdot\rho_0(1-\eta\phi_0)^{1/2}\cdot\left(3+2\frac{a+b\phi_0}{1+\phi_0}\right)^{(3/2+(a+b\phi_0)/(1+\phi_0))}\right\}^{-1},$$

$$G_I=\int_{\phi_0}^{\phi}\left\{-\frac{I}{T\cdot(1+\phi)}-\frac{\left(\frac{3}{2}+b\right)}{(1+\phi)}-\frac{(b-a)}{(1+\phi)^2}\ln\left(M_f^2+3+2\frac{a+b\phi}{1+\phi}\right)\right. \tag{142}$$

$$\left.+\left(\frac{3}{2}+\frac{a+b\phi}{1+\phi}\right)\left[\frac{(1+\eta)}{(1+\phi)(1-\eta\phi)}+\frac{2\frac{(b-a)}{(1+\phi)^2}}{\left(5+2\frac{a+b\phi}{1+\phi}\right)}\right]+\frac{1}{2}\frac{\eta}{1-\eta\phi}-\frac{(b-a)}{(1+\phi)^2}\right\}d\phi\,.$$

At the first glance of these equations, it is easily understood that the results obtained previously are also valid in this case. So the final results only are presented here. The critical mass flows of the three limiting flows are

$$m_f=\frac{F_I(1,\phi_0)}{F_{IO}}=\sqrt{2h_0}\cdot\rho_0\cdot(1-\eta\phi_0)^{1/2}\cdot\frac{\left(3+2\cdot\frac{a+b\phi_0}{1+\phi_0}\right)^{\cdot(3/2+(a+b\phi_0)/(1+\phi_0))}}{\left(4+2\frac{a+b\phi_0}{1+\phi_0}\right)^{\cdot(2+(a+b\phi_0)/(1+\phi_0))}}\,. \tag{143}$$

$$m_e=\sqrt{2h_0C_I^2}\cdot\frac{(1-\phi_{e*})}{\phi_{e*}^2}\cdot\left\{\frac{2\cdot\frac{I}{\eta}\cdot\left(\frac{1-\eta\phi_{e*}}{1+\phi_{e*}}\right)\cdot\left(3+2\frac{a+b\phi_{e*}}{1+\phi_{e*}}\right)}{\left(5+2\cdot\frac{a+b\phi_{e*}}{1+\phi_{e*}}\right)\cdot\left(M_{fe*}^2+3+2\frac{a+b\phi_{e*}}{1+\phi_{e*}}\right)}\right\}^{i}. \tag{144}$$

$$M_{f,*}\left(\frac{1-\eta\phi_{e*}}{M_{fe*}^2+3+2\frac{a+b\phi_{e*}}{1+\phi_{e*}}}\right)^{1/2}\exp\left\{-\frac{\eta}{2}\left(\frac{1+\phi_{e*}}{1-\eta\phi_{e*}}\right)\cdot\frac{\left(5+2\frac{a+b\phi_{e*}}{1+\phi_{e*}}\right)\left(M_{fe*}^2+3+2\frac{a+b\phi_{e*}}{1+\phi_{e*}}\right)}{\left(3+2\frac{a+b\phi_{e*}}{1+\phi_{e*}}\right)}\right\} \quad ,$$

$$m_f=\sqrt{2h_0}\cdot\rho_0(1-\eta\phi_0)^{1/2}\cdot\frac{\left(3+2\frac{a+b\phi_0}{1+\phi_0}\right)^{\cdot(3/2+(a+b\phi_0)/(1+\phi_0))}}{\left(4+2\frac{a+b\phi_f}{1+\phi_f}\right)^{(2+(a+b\phi_f)/(1+\phi_f))}}\cdot\exp\left(-G_{I\phi_f}\right) \quad , \tag{145}$$

where

$$G_{Ieff}=\int_{\phi_0}^{\phi_f(\leq\phi_{el})}\left\{-\frac{\left(\frac{I}{T_{ef}}+\frac{3}{2}+b\right)}{(1+\phi_{ef})}-\frac{(b-a)}{(1+\phi_{ef})^2}\ln\left(M_{fef}^2+3+2\frac{a+b\phi_{ef}}{1+\phi_{ef}}\right)\right.$$

$$\left.+\left(\frac{3}{2}+\frac{a+b_{ef}}{1+\phi_{ef}}\right)\left[\frac{(1+\eta)}{(1+\phi_{ef})(1-\eta\phi_{ef})}+\frac{2\cdot\frac{(b-a)}{(1+\phi_{ef})^2}}{5+2\frac{(a+b\phi_{ef})}{(1+\phi_{ef})}}\right]+\frac{1}{2}\frac{\eta}{1-\eta\phi_{ef}}-\frac{(b-a)}{(1+\phi_{ef})^2}\right\}d\phi_{ef}. \tag{146}$$

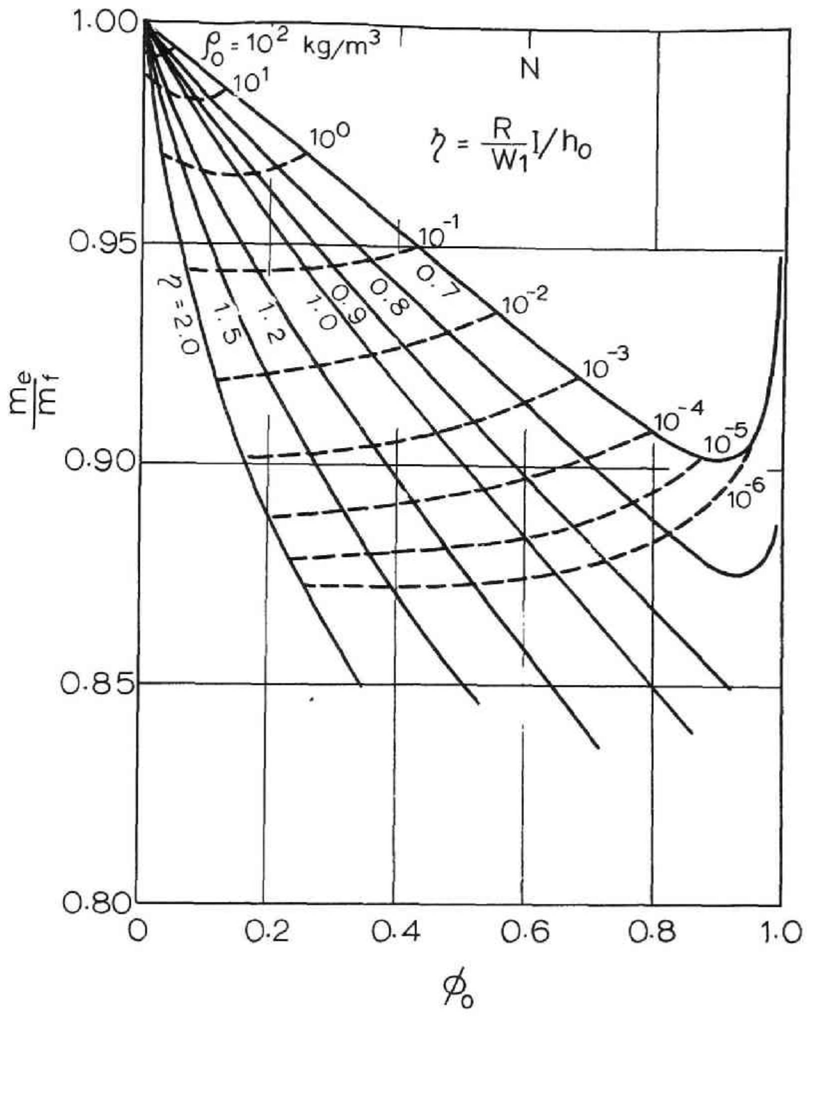

Fig. 9 Critical mass flows of a singly ionizing monatomic gas.

and it can be obtained

$$\frac{m_e}{m_{ef\cdot\min.}}=\frac{F_I(M_{fet},\phi_{et})}{F_I(1,\phi_{et})}=\left(\frac{4+2\dfrac{a+b\phi_{et}}{1+\phi_{et}}}{M_{fet}^2+3+2\dfrac{a+b\phi_{et}}{1+\phi_{et}}}\right)^{(2+(a+b\phi_{et})/(1+\phi_{et}))}\cdot M_{fet}<1\ . \qquad (147)$$

From these results it can finally be concluded that

$$m_e < m_{ef} \leqq m_f\ . \qquad (148)$$

Calculated values of ratios m_e/m_f and m_{ef}/m_f are shown in Figs. 9 and 10, respectively.

N	
$I=1.683\times10^{5}$°K	
$i=1.25$	
$a=0.35$	4000°K$<T<$40000°K
$b=-0.20$	4000°K$<T<$40000°K
$C_I=1.989\times10^{-6}$ k·mol/m³	

Table 3 Characteristic values of N gas.[10)]

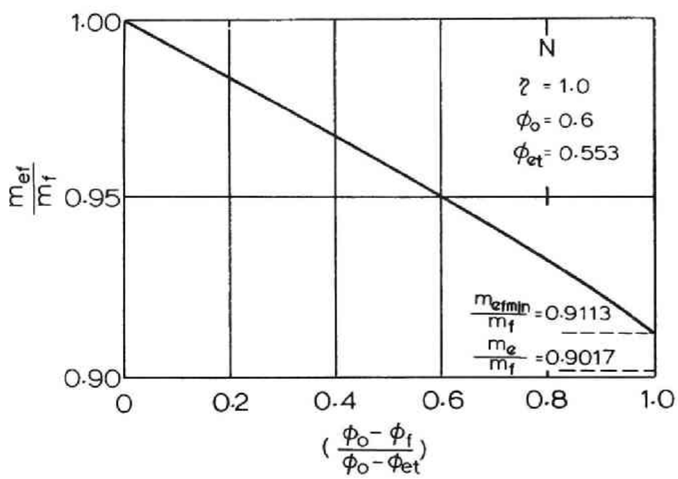

Fig. 10 Critical mass flow of an equilibrium-frozen flow of a singly ionizing monatomic gas.

Because of the uncertainty of the rate equations which govern the ionization and neutralization, the critical mass flow for the nearly equilibrium flow is not obtained.

5. Concluding Remarks

Critical mass flows have been obtained numerically and in part analytically for the flows of three kind of gases under a

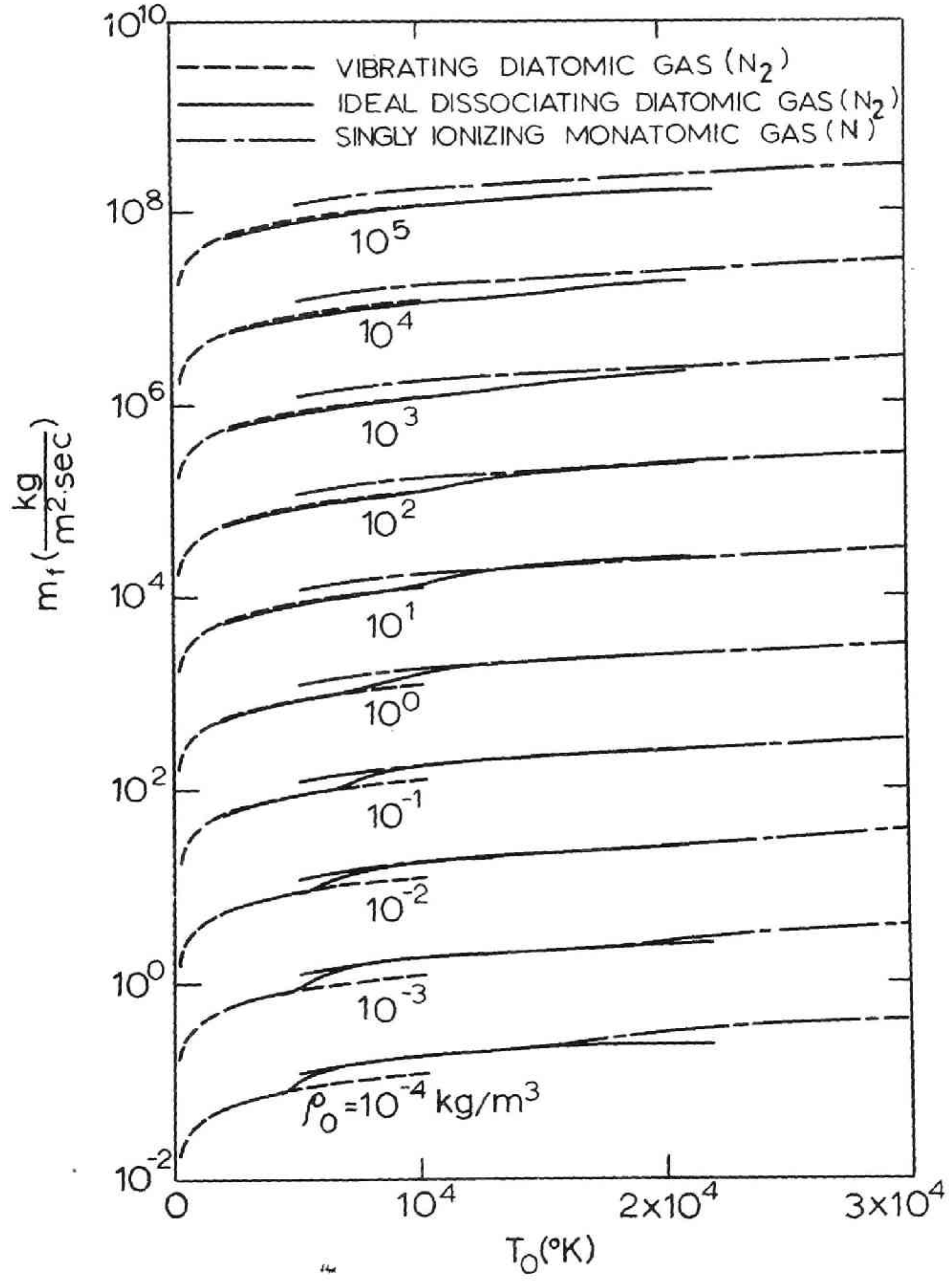

Fig. 11 Frozen critical mass flows of a vibrating diatomic gas, an ideal dissociating diatomic gas and a singly ionizing monatomic gas.

wide range of reservoir conditions. For frozen flows, the critical mass flows of these gases are shown in Fig. 11.

For the vibrating diatomic gas, the values of ratio m_e/m_f are in a range from 1.0 to 0.9706, for the ideal dissociating diatomic gas from 1.0 to about 0.97, and for the singly ionizing monatomic gas from 1.0 to about 0.90.

It must be emphasized that it is very difficult to treat numerically the nearly equilibrium flow, because the numerical integration of the rate equation together with the flow ones by the digital electric computer requires the more consuming time for the nearer equilibrium flow. Therefore the analytical treatment of nearly equilibrium flows is very important.

There is one thing which is definitely unfavourable for the approximate analysis of the nozzle flow problem by the E-F flow model, in connection with the definitions of the speed of sound in nonequilibrium relaxing gases. It has already been argued that for an equilibrium flow the reference velocity is the equilibrium speed of sound and the critical point of flow equations is located at the throat where $M_e = 1$, and that for a frozen flow the former is the frozen speed of sound and the latter is located at the throat where $M_f = 1$. The value M_{fe} of M_f in the equilibrium limit does not coincide with M_e, and furthermore the inequality $M_e > M_{fe}$ is generally satisfied in the relaxing gas. If the transition from an equilibrium flow to a frozen one occurs at some point in the region where $M_e > 1$ and $M_{fe} < 1$, then the flow which has already passed through the throa where $M_e = 1$ must again pass through it where $M_f = 1$, which is clearly a contradiction. Therefore it can reasonably be conclud that the E-F flow approximation cannot be applied very well to such a case in which the transition from the equilibrium to the frozen takes place at ξ in the range of $\xi_{et} < \xi < \xi_{ft}$ for a diatomic gas with the vibrational energy mode only, and at α_e in the range of $\alpha_{e*} < \alpha_e < \tilde{\alpha}_{e*}$ for an ideal dissociating diatomic gas, and at ϕ_e in the range of $\phi_{e*} < \phi_e < \tilde{\phi}_{e*}$ for a singly ionizing monatomic gas, where $\tilde{\alpha}_{e*}$ and $\tilde{\phi}_{e*}$ are, respectively, the value of α_e and ϕ_e at the point where $M_{fe} = 1$.

Furthermore it must be noticed that the curve for the solution in which the transition from the equilibrium to the frozen occurs at $\xi < \xi_{et}$ differs in its pattern from that in which the transition occurs at $\xi > \xi_{et}$. This is wholly due to the exictence of two reference speeds a_e and a_f defined quite differently. Fig. 12 shows qualitatively these situations for a vibrationally relaxing diatomic gas. The freezing point in a

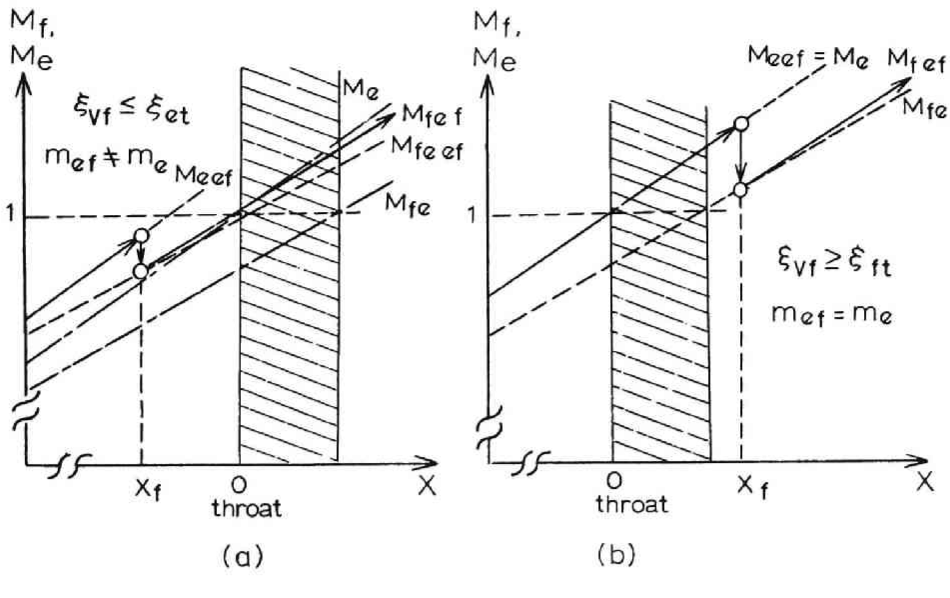

Fig. 12 Distributions of M_f and M_e along the nozzle axis in a equilibrium-frozen flow.

nozzle is denoted by x_f, and the shaded regions are the broken-down ones of validity of the E-F flow approximation. The quantities M_{eef}, M_{fef} and M_{feef} denote, respectively, the equilibrium Mach number in the equilibrium branch, the frozen Mach number in the frozen branch, and the frozen Mach number in the equilibrium branch of the E-F flow.

CHAPTER II NONEQUILIBRIUM FLOWS OF VIBRATIONALLY RELAXING DIATOMIC GASES

1. Introductory Remarks

One of the simplest cases of nonequilibrium phenomena in nozzle flows of real gases is the vibrational relaxation of a molecule. However even for this relaxation phenomenon, the analytical treatment of nozzle flow problems is almost impossible except in a few special cases.[4)] Though a few discussions about its reasons are already presented in the previous chapter, the closer investigation makes it clear that another one of the most important reasons exists in the great width of range of variation of the thermodynamic state of a gas in a nozzle.

In a flow through a nozzle, three flow regions, the nearly equilibrium region, nearly frozen one and transition one from the former to the latter, can in general be found. Furthermore the boundaries between these regions are found to be somewhat sharp and the width of the transition region is, in almost all cases considered previously, by far smaller than those of others. To such a flow, so called Bray's E-F flow approximation can often be made with sufficient reasonableness and accuracy.

Complete analytical solutions can be obtained only for the equilibrium, frozen and E-F limiting flows. Notwithstanding for such gases as the N_2 gas and the O_2 gas considered here, the fact that the energy stored in the vibrational mode is much smaller than the total enthalpy of the gas, yields us ways for approaches to the analytical treatment of nonequilibrium nozzle flows. Such an idea has already been applied to the problem, for example in Ref. 7 where an iterative method is used on the basis of the completely frozen flow. Conversely, our analysis is done by using an approximate rate equation on the basis of the completely equilibrium flow. It will be made clear that the latter treatment is far superior to the former in the theoretical reasonableness and accuracy. The greatest merit of our method investigated in this chapter exists in the possibility of solving the rate equation and the corresponding flow equations separately. Furthermore our method in combination with a mathematical technique of the steepest descent method can yield a very powerful way for the analysis of whole flow fields in nonequilibrium nozzle flows.

A problem of determining the entropy rise due to the nonequilibrium process in a nozzle, which has scarcely been studied in earlier papers, is also investigated.

Calculations of distributions of the vibrational temperature and entropy along the nozzle axis are carried out for the N_2 and O_2 gases by the electric digital computer HITAC 5020 at the computing center in Kyoto Univ..

Finally discussions on the validity and accuracy of the equilibrium-throat-approximation method, which has been widely used in analysing nonequilibrium nozzle flows, are given.

2. Analytical Solutions

Notations used in this chapter are the same ones that was used in CHAPTER I, unless otherwise defined. Considering the nozzle geometry given by $A = Kx^2$, we again get the basic equations Eqs. (82-86) in the previous chapter governing a nonequilibrium flow of a vibrationally relaxing diatomic gas through a nozzle.

It must be noticed that in this system of equations the independent variable is not x but ξ. The characteristic values used in this chapter are also given in Table 1 in Ch. I for the N_2 and O_2 gases.

2. 1 Solutions of Equilibrium, Frozen and Equilibrium-Frozen Flows

In the rate equation, letting

$$\Pi \equiv 0, \tag{1}$$

yields an equilibrium relation,

$$\varepsilon_V = \varepsilon_{V_e} = \varepsilon \quad \text{or} \quad \xi_V = \xi_{V_e} = \xi. \tag{2}$$

Using this equilibrium relation, the equation of momentum can easily be integrated to give

$$h_e(\xi) = \frac{125}{216}\sqrt{\frac{7}{10}}\frac{\mu_e}{\xi_0^3}\frac{\exp\xi_0}{\exp\xi_0 - 1}\exp\left(\frac{\xi_0}{\exp\xi_0 - 1}\right)\frac{\exp\xi - 1}{\exp\xi}$$

$$\exp\left(-\frac{\xi}{\exp\xi - 1}\right)\xi^{5/2}\cdot\left(\frac{1}{\varphi} - \frac{7}{2\xi} - \frac{1}{\exp\xi - 1}\right)^{-1/2}. \tag{3}$$

On the contrary, letting

$$\Pi \equiv \infty, \tag{4}$$

in the rate equation, yields

$$\frac{d\varepsilon_V}{d\xi} \equiv 0 \quad \text{or} \quad \varepsilon_V = \varepsilon_{V_f} = \varepsilon_0 \quad \text{or} \quad \xi_V = \xi_{V_f} = \xi_0, \tag{5}$$

Using this, the equation of momentum can also be integrated to give

$$h_f(\xi) = \frac{125}{216}\cdot\sqrt{\frac{7}{10}}\cdot\frac{1}{\xi_0^3}\cdot\xi^{5/2}\left(\frac{1}{\varphi} - \varepsilon_0 - \frac{7}{2\xi}\right)^{-1/2}. \tag{6}$$

An upstream equilibrium branch and a downstream frozen one are joined together at the freezing point to yield the E-F flow, and then the solution of this flow is given by

$$\left.\begin{aligned} &\varepsilon_{Vef}=\varepsilon\,, \\ &h_{ef}(\xi)=\left(\frac{\mu_{ef}}{\mu_e}\right)h_e(\xi)\,, \end{aligned}\right\} \quad \text{for} \quad \xi\leqq\xi_{Vf}\,, \tag{7}$$

and

$$\left.\begin{aligned} &\varepsilon_{Vef}=\varepsilon_{Vf}=\frac{1}{\exp\xi_{Vf}-1}\,, \\ &h_{ef}(\xi)=\frac{125}{216}\cdot\frac{\mu_{ef}}{\xi_0{}^3}\,\frac{\exp\xi_0}{\exp\xi_0-1}\exp\left(\frac{\xi_0}{\exp\xi_0-1}\right) \\ &\quad\cdot\frac{\exp\xi_{Vf}-1}{\exp\xi_{Vf}}\exp\left(-\frac{\xi_{Vf}}{\exp\xi_{Vf}-1}\right)\cdot\xi^{5/2}\left(\frac{1}{\varphi}-\frac{1}{\exp\xi_{Vf}-1}-\frac{7}{2\xi}\right)^{-1/2}, \end{aligned}\right\} \quad \text{for} \quad \xi>\xi_{Vf}\,, \tag{8}$$

where ξ_{Vf} denotes a frozen vibrational temperature.

The numerical results obtained by using the analytical solutions of these three limiting flows are shown in Figs. 1 and 2. These results well illustrate appreciable effects of the molecular vibration and the freezing of its relaxation on

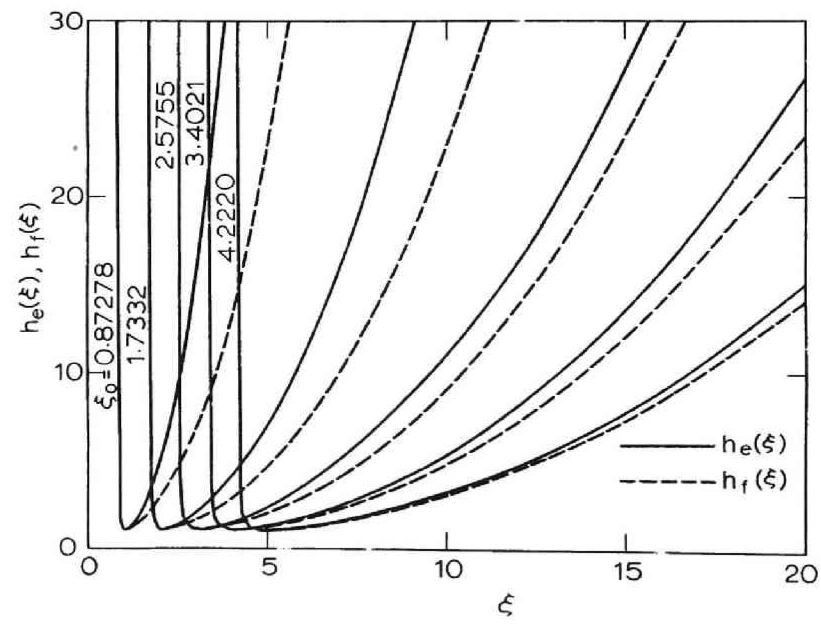

Fig. 1 Distributions of area ratios $h_e(\xi)$ and $h_f(\xi)$.

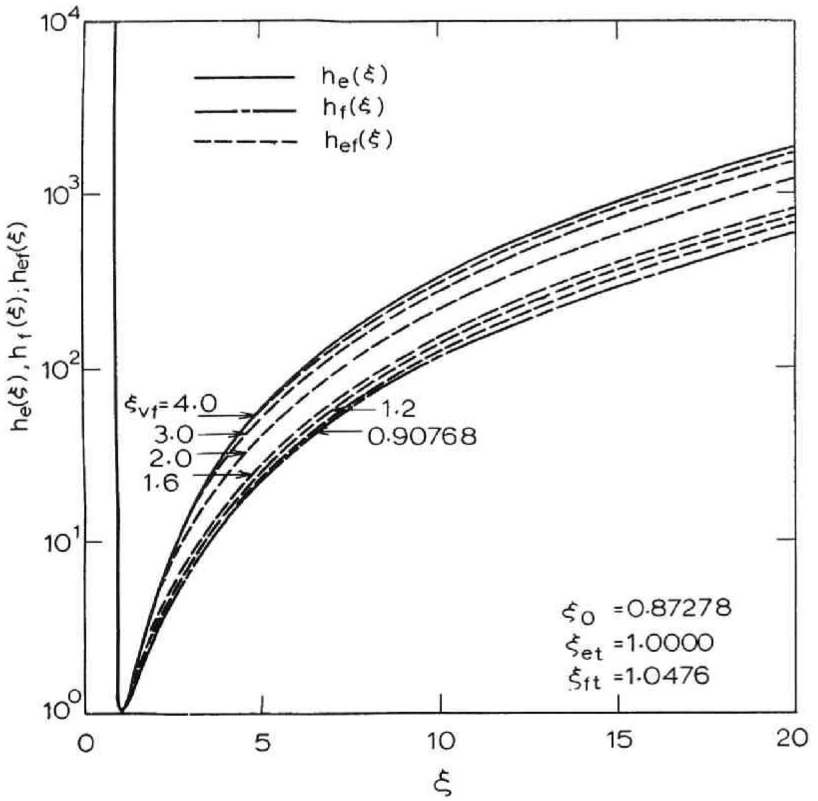

Fig. 2 Distributions of area ratios $h_e(\xi)$, $h_f(\xi)$ and $h_{ef}(\xi)$.

the flow fields. Obviously, however, for values of ξ_0 greater than or equal to about 4, the real gas effects on the flow fields are almost negligibly small. It is quite easy but very significant to notice that the effects on a flow field of the part of the vibrational energy which has been released into the flowfield and of the freezing of the vibrational relaxation become more and more significant, though quite slowly, as the flow proceeds more and more downstream through a nozzle.

Fig. 2 shows the result of a sample calculation of $h_{ef}(\xi)$ in which a condition $\xi_{Vf} < \xi_{et}$ is satisfied. It must be noticed that in this case even the equilibrium part of the E-F flow does never coincide with the corresponding part of the completely equilibrium flow under the same reservoir conditions. We can easily find that the reason exists in the discrepancy in the values of m_e and m_{ef}.

2. 2 Solutions of Nonequilibrium Flows: Approximate Rate Equation

For the convenience of the later analysis, it may be assumed without loss of generality that the flow starts from the equilibrium reservoir conditions, passes through a sonic point near the throat, and expands into vacuum infinitely downstream. Then Π in the rate equation Eq. (84) in Ch. 1 is zero at the reservoir and increase monotonically to infinity as the flow proceeds downstream, so that we can put

$$0 \leq \Pi \leq \infty .$$

The flow field splits into three regions corresponding to the magnitude of the quantity Π:

(i) near equilibrium region $\quad \varepsilon_V \approx \varepsilon,\ \Pi \approx \Pi_e, \quad$ for $\quad \Pi \ll 1, \qquad$ (9)

(ii) transition region $\quad \dfrac{\varepsilon_V - \varepsilon}{\varepsilon} = O(1), \quad$ for $\quad \Pi = O(1), \qquad$ (10)

(iii) near frozen region $\quad \dfrac{1}{\varepsilon_V} \cdot \dfrac{d\varepsilon_V}{d\xi} \ll 1, \quad$ for $\quad \Pi \gg 1. \qquad$ (11)

As was already pointed out, each boundary between the succesive regions can be found to be somewhat sharp.

It should be naturally expected that there can be some way for predicting beforehand, even though roughly, the position and width of each region in a nozzle. For this purpose, it is quite convenient to introduce Bray's nonequilibrium parameter Eq. (100) in Ch. 1. Using the fourth equation of Eqs. (86) in Ch. 1, this can be written down as

$$P_e = -\Pi_e \cdot \frac{1}{\varepsilon} \frac{d\varepsilon v_e}{d\xi} = \frac{\exp\xi}{\exp\xi - 1} \cdot \Pi_e = \frac{864}{125} \cdot \sqrt{\frac{5}{7}} \cdot \frac{\sqrt{h_0 \varphi}}{\mu \Gamma \theta^w} \cdot \frac{\sqrt{K}}{\rho_0} \xi_0{}^{1/2}$$

$$\cdot \frac{\xi^{w+1}\left(\dfrac{\exp\xi}{\exp\xi-1}\right)^2 \exp\left(-l\theta^S \xi^{-S}\right)\left(\dfrac{1}{\varphi} - \dfrac{7}{2\xi} - \dfrac{1}{\exp\xi - 1}\right)^2 [h_e(\xi) - 1]^{1/2}}{\left|\dfrac{5}{2}\left(\dfrac{1}{\varphi} - \dfrac{21}{5\xi} - \dfrac{1}{\exp\xi - 1}\right) + \dfrac{\xi \exp\xi}{(\exp\xi - 1)^2}\left[\xi\left(\dfrac{1}{\varphi} - \dfrac{7}{2\xi} - \dfrac{1}{\exp\xi - 1}\right) - \dfrac{1}{2}\right]\right|}. \tag{12}$$

It can be seen from the above relation that for values of ξ greater than or at least equal to about unity,

$$O(P_e) = O(\Pi_e)\ . \tag{13}$$

For flows in which the vibrational relaxation takes place most predominantly among all possible relaxation phenomena, the values of ξ are at least about unity even at the reservoir, and then the relation Eq. (13) is valid in almost all flows considered. The condition Eq. (9) specifying the nearly equilibrium region can therefore be rewritten in terms of P_e instead of Π. Similarly the transition region can be defined interms of P_e by

$$P_e = O(1)\ , \tag{14}$$

which is directly derived from Eq. (13) under an assumption

$$P_e \approx P \quad \text{or} \quad \Pi_e \approx \Pi. \qquad \text{in the transition region,} \tag{15}$$

This assumption can not only be seen quite plausible from Eqs. (9) and (10) but also actually be verified from the numerical results a posteriori. Moreover this is, in general, the case for almost all flows ever considered in many previous papers.

Now it is very useful and of importance for our purpose to know the behaviour of Π as precisely as possible. However it is known only after determining the flow field. Nevertheless we can estimate it to some degree by invesigating the behaviours of Π in the frozen, equilibrium and equilibrium-frozen flow limits. We can easily obtain

$$\frac{\Pi_f}{\Pi_e}=\mu_e\left[\frac{h_f(\xi)-1}{h_e(\xi)-1}\right]^{1/2}\left(\frac{\frac{1}{\varphi}-\frac{7}{2\xi}-\varepsilon_0}{\frac{1}{\varphi}-\frac{7}{2\xi}-\varepsilon}\right)^2\left|\frac{\frac{5}{2}\left(\frac{1}{\varphi}-\frac{21}{5\xi}-\varepsilon\right)+\frac{\xi\exp\xi}{(\exp\xi-1)^2}\left[\xi\left(\frac{1}{\varphi}-\frac{7}{2\xi}-\varepsilon\right)-\frac{1}{2}\right]}{\frac{5}{2}\left(\frac{1}{\varphi}-\frac{21}{5\xi}-\varepsilon_0\right)}\right|, \tag{16}$$

$$\frac{\Pi_{ef}}{\Pi_e}=\left(\frac{\mu_e}{\mu_{ef}}\right)\cdot\left[\frac{h_{ef}(\xi)-1}{h_e(\xi)-1}\right]^{1/2}, \qquad \text{for} \quad \xi\leq\xi_{Vf}\ ,$$

$$\frac{\Pi_{ef}}{\Pi_e}=\left(\frac{\mu_e}{\mu_{ef}}\right)\cdot\left[\frac{h_{ef}(\xi)-1}{h_e(\xi)-1}\right]^{1/2}\left(\frac{\frac{1}{\varphi}-\frac{7}{2\xi}-\varepsilon_{Vf}}{\frac{1}{\varphi}-\frac{7}{2\xi}-\varepsilon}\right)^2\cdot\left|\frac{\frac{5}{2}\left(\frac{1}{\varphi}-\frac{21}{5\xi}-\varepsilon\right)+\frac{\xi\exp\xi}{(\exp\xi-1)^2}\left[\xi\left(\frac{1}{\varphi}-\frac{7}{2\xi}-\varepsilon\right)-\frac{1}{2}\right]}{\frac{5}{2}\left(\frac{1}{\varphi}-\frac{21}{5\xi}-\varepsilon_{Vf}\right)}\right|, \tag{17}$$

$$\text{for} \quad \xi\geqq\xi_{Vf}\ .$$

It must be noticed that the distributions of Π_e, Π_f and Π_{ef} are already known before the system of equations of the real non-equilibrium flow is solved. From the above relations, it can be seen that

$$\Pi_f<\Pi_{ef}<\Pi_e\ .$$

Furthermore from the fact that the E-F flow can usually be a very good approximation to the corresponding real nonequilibrium flow, it may reasonably be guessed that

$$\Pi\approx\ \Pi_{ef}\ ,$$

so that

$$\Pi_f<\Pi<\Pi_e\ . \tag{18}$$

This will also be confirmed from the numerical results for flows considered here. The distributions of P_e and P_f are shown in Fig. 3, where the latter is defined by

$$P_f=-\Pi_f\cdot\frac{1}{\varepsilon}\frac{d\varepsilon}{d\xi}\ . \tag{19}$$

Perhaps the maximum effect of the internal energy released into the flow on the rate equation under the fixed reservoir conditions may be estimated from Fig. 3 by comparing the curves for

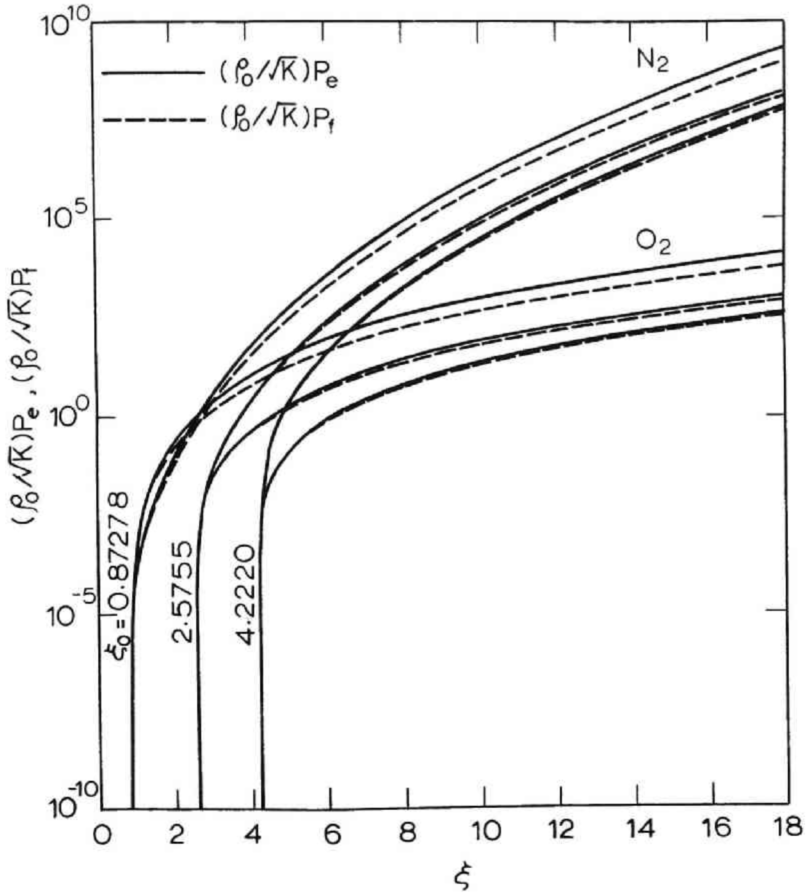

Fig. 3 Distributions of P_e and P_f.

the two limiting cases with each other. The most important informations which can be drawn from these results are described in terms of mathematical expressions:

$$\text{(i)} \quad \frac{d\Pi}{d\xi} \gg \Pi \quad \text{or at least} \quad \frac{d\Pi}{d\xi} = O(1) \, , \tag{20}$$

$$\text{(ii)} \quad \left| \frac{d}{d\xi}\left(1 - \frac{\Pi_e}{\Pi}\right) \right| \ll 1 \, , \tag{21}$$

throughout a nozzle. Since

$$\left| 1 - \frac{\Pi_e}{\Pi} \right| \ll 1, \qquad \text{for} \qquad \Pi \ll 1 \, ,$$

we can get, considering the above relations,

$$\left| 1 - \frac{\Pi_e}{\Pi} \right| \ll 1 \, , \qquad \text{for} \qquad \Pi \ll 1, \qquad \text{or at most} \quad \Pi = O(1). \tag{22}$$

Here the analyses will be carried out only for the flows which satisfies the conditions Eqs. (20 - 22). It must, however, be emphasized that for flows of such gases as N_2 and O_2, these are in almost all cases ever considered well satisfied.

The rate equation may be written in the form

$$\varepsilon_V=\exp\left(-\int_{\xi_r}\frac{d\xi}{\Pi}\right)\int_{\xi_0}\frac{\varepsilon}{\Pi}\exp\left(\int_{\xi_r}\frac{d\xi}{\Pi}\right)d\xi \tag{23}$$

where ξ_r is a reference value of ξ greater than ξ_0. Integrating it by parts yields

$$\varepsilon_V=\exp\left(-\int_{\xi_r}\frac{d\xi}{\Pi}\right)\left\{\left[\varepsilon\exp\left(\int_{\xi_r}\frac{d\xi}{\Pi}\right)\right]_{\xi_0}^{\xi}-\int_{\xi_0}\frac{d\varepsilon}{d\xi}\exp\left(\int_{\xi_r}\frac{d\xi}{\Pi}\right)d\xi\right\},$$

Using the boundary condition $\Pi = 0$ at $\xi = \xi_0$, we can rewrite it as follows

$$\varepsilon_V=\varepsilon+\Delta\varepsilon_V \tag{24}$$

where

$$\Delta\varepsilon_V=-\exp\left(-\int_{\xi_r}\frac{d\xi}{\Pi}\right)\cdot\int_{\xi_0}\frac{d\varepsilon}{d\xi}\exp\left(\int_{\xi_r}\frac{d\xi}{\Pi}\right)d\xi=\sum_{m=1}^{\infty}\Delta\varepsilon_{Vm} \tag{25}$$

and where

$$\Delta\varepsilon_{Vm}=\int_{\xi_0}^{\xi}m\exp\left[-\Phi_m(\eta,\ \xi)\right]d\eta, \tag{26}$$

$$\Phi_m(\eta,\ \xi)=m\eta+\int_{\eta}^{\xi}\frac{d\eta}{\Pi} \tag{27}$$

and η is a dummy variable. When ξ is fixed, the functions $\Phi_m(\eta, \xi)$ take their minimum values for the values of η which satisfy

$$\Pi(\eta)=\frac{1}{m},\ m=1,\ 2,\ 3\cdots\ . \tag{28}$$

It can easily be seen that the term $\Delta\varepsilon_{V1}$ is the largest one in the series Eq. (25). Moreover, seeing Eqs. (26) and (27), we can find that the region of η satisfying

$$\Pi(\eta)=O(1) \tag{29}$$

makes a principal contribution to the integral $\Delta\mathcal{E}_{V1}$. Thus, the contribution to $\Delta\mathcal{E}_{V1}$ from the other part of integral over η outside this small region may be small and insignificant. Similarly the contribution to $\Delta\mathcal{E}_{Vi}$ (i=2, 3, 4,...) from the part of integral over η outside the region satisfying $i\Pi(\xi) = O(1)$ is very small. If, therefore, we consider an integral defined by

$$\Delta\bar{\varepsilon}_V=-\exp\left(-\int_{\xi_r}\frac{d\xi}{\Pi_e}\right)\cdot\int_{\xi_0}\frac{d\varepsilon}{d\xi}\exp\left(\int_{\xi_r}\frac{d\xi}{\Pi_e}\right)d\xi\,, \tag{30}$$

this can be used as a good approximation to $\Delta\mathcal{E}_V$, that is

$$\Delta\varepsilon_V\approx\Delta\bar{\varepsilon}_V\,. \tag{31}$$

This is also justified by the condition Eq. (22). The greater becomes the value of ξ which satisfies $\Pi(\xi) = 1$ (or $\Pi_e(\xi) = 1$), the closer the integral $\bar{\mathcal{E}}_V$ approaches $\mathcal{E}_V$.

We can easily find that calculating $\bar{\mathcal{E}}_V$ is strictly equivalent to solving the ordinary differential equation

$$\Pi_e\cdot\frac{d\bar{\varepsilon}_V}{d\xi}+\bar{\varepsilon}_V=\varepsilon \tag{32}$$

with the boundary value $\bar{\mathcal{E}}_V=\mathcal{E}_0$ at a reservoir, which is clearly linear and decoupled from the remaining flow equations. The solution can be represented in the form

$$\bar{\varepsilon}_V=\varepsilon+\Delta\bar{\varepsilon}_V\,, \tag{33}$$

Then the approximate rate equation is transformed into the form

$$\frac{d}{d\xi}\bar{\varepsilon}_V=-\frac{\Delta\bar{\varepsilon}_V}{\Pi_e}. \tag{34}$$

Since Π_e is a known function of ξ, $\Delta\bar{\mathcal{E}}_V$ or $\bar{\mathcal{E}}_V$ can be calculated only by the integration procedure. By using the solution $\Delta\bar{\mathcal{E}}_V$ or $\bar{\mathcal{E}}_V$, the corresponding nozzle area ratio $\bar{h}(\xi)$ and frozen Mach number $\bar{M}_f(\xi)$ are given, respectively, by

$$\bar{h}(\xi)=\sqrt{\frac{5}{7h_0\varphi}}\cdot\frac{\bar{m}\xi_0^{1/2}}{\rho_0}\cdot\frac{\exp\xi_0}{\exp\xi_0-1}\exp\left(\frac{\xi_0}{\exp\xi_0-1}\right)$$

$$\cdot\frac{1}{\bar{M}_f}\left(\frac{\xi}{\xi_0}\right)^3\cdot\left(\frac{\exp\xi-1}{\exp\xi}\right)\cdot\exp\left(-\frac{\xi}{\exp\xi-1}\right)\exp\left[-\int_{\xi_0}^{\xi}\xi\frac{d}{d\xi}\Delta\bar{\varepsilon}_V d\xi\right], \qquad (35)$$

$$\bar{M}_f{}^2=\frac{10}{7}\cdot\left(\frac{1}{\varphi}-\varepsilon-\Delta\bar{\varepsilon}_V\right)\xi-5 \qquad (36)$$

where $\bar{m}$ is the critical mass flow corresponding to the approximate distribution of vibrational energy $\bar{\mathcal{E}}_V$. Since $\bar{h}(\xi_t)=1$ at the throat, the critical mass flow $\bar{m}$ is obtained from Eq. (35) as follows

$$\bar{m}=\sqrt{2h_0\varphi}\cdot\frac{\rho_0}{\xi_0^{1/2}}\cdot\frac{\exp\xi_0-1}{\exp\xi_0}\cdot\exp\left(-\frac{\xi_0}{\exp\xi_0-1}\right)\cdot\left[\left(\frac{1}{\varphi}-\varepsilon_t-\Delta\bar{\varepsilon}_{Vt}\right)\xi_t-\frac{7}{2}\right]^{1/2}$$

$$\left(\frac{\xi_0}{\xi_t}\right)^3\cdot\frac{\exp\xi_t}{\exp\xi_t-1}\cdot\exp\left(\frac{\xi_t}{\exp\xi_t-1}\right)\exp\left(\int_{\xi_0}^{\xi_t}\xi\frac{d}{d\xi}(\Delta\bar{\varepsilon}_V)d\xi\right) \qquad (37)$$

where ξ_t is determined from the regularity condition of the flow equations at the throat,

$$\frac{\xi_t}{\varphi}=\frac{7}{2}+\frac{\xi_t}{\exp\xi_t-1}+\frac{1}{2}\frac{\left[\frac{7}{2}+\frac{\xi_t^2\exp\xi_t}{(\exp\xi_t-1)^2}\right]}{\left[\frac{5}{2}+\frac{\xi_t^2\exp\xi_t}{(\exp\xi_t-1)^2}\right]}+\xi_t\cdot\Delta\bar{\varepsilon}_{Vt}$$

$$-\frac{\left\{\xi_t^2\left[\left(\frac{1}{\varphi}-\frac{1}{\exp\xi_t-1}\right)\xi_t-4\right]-\xi_t^3\Delta\bar{\varepsilon}_{Vt}\right\}\left[\frac{\Delta\bar{\varepsilon}_{Vt}}{\Pi_{ct}}-\frac{\exp\xi_t}{(\exp\xi_t-1)^2}\right]}{\left[\frac{5}{2}+\frac{\xi_t^2\exp\xi_t}{(\exp\xi_t-1)^2}\right]}. \qquad (38)$$

By using Eq. (37), $\bar{m}$ can be calculated for all possible nonequilibrium flows. Since the corresponding equation of entropy is written in the form,

$$\frac{W_2}{R}\cdot\Delta\bar{S}=\frac{W_2}{R}(\bar{S}-S_0)$$

$$=\left[\ln\left(\frac{\exp\bar{\xi}_V}{\exp\bar{\xi}_V-1}\right)+\frac{\bar{\xi}_V}{\exp\bar{\xi}_V-1}\right]-\left[\ln\left(\frac{\exp\xi}{\exp\xi-1}\right)+\frac{\xi}{\exp\xi-1}\right]-\int_{\xi_0}\xi\frac{d}{d\xi}\Delta\bar{\varepsilon}_V d\xi \qquad (39)$$

with which Eqs. (35) and (37) can be rewritten as follows, respectively,

$$\bar{h}(\xi)=\sqrt{\frac{5}{7h_0\varphi}}\cdot\frac{\bar{m}\xi_0^{1/2}}{\rho_0}\cdot\frac{\exp\xi_0}{\exp\xi_0-1}\cdot\exp\left(\frac{\xi_0}{\exp\xi_0-1}\right)$$

$$\times\frac{1}{\bar{M}_f}\left(\frac{\xi}{\xi_0}\right)^3\left(\frac{\exp\bar{\xi}_V-1}{\exp\bar{\xi}_V}\right)\exp\left(-\frac{\bar{\xi}_V}{\exp\bar{\xi}_V-1}\right)\exp\left[\frac{W_2}{R}\Delta\bar{S}\right], \tag{40}$$

$$\bar{m}=\sqrt{2h_0\varphi}\frac{\rho_0}{\xi_0^{1/2}}\frac{\exp\xi_0-1}{\exp\xi_0}\exp\left(-\frac{\xi_0}{\exp\xi_0-1}\right)\left(\frac{\xi_0}{\xi_t}\right)^3\left[\left(\frac{1}{\varphi}-\frac{1}{\exp\xi_t-1}-\Delta\bar{\varepsilon}_{Vt}\right)\xi_t-\frac{7}{2}\right]^{1/2}$$

$$\times\frac{\exp\bar{\xi}_{Vt}}{\exp\bar{\xi}_{Vt}-1}\exp\left(\frac{\bar{\xi}_{Vt}}{\exp\bar{\xi}_{Vt}-1}\right)\exp\left(-\frac{W_2}{R}\Delta\bar{S}_t\right). \tag{41}$$

The last equation indicates clearly that the increase in entropy decreases the critical mass flow, which has already been pointed out.

Especially for a nearly equilibrium flow, repeating the integration of $\Delta\bar{\varepsilon}_V$ by parts yields an asymptotic expansion

$$\Delta\bar{\varepsilon}_V=-\sum_{n=1}^{N}(-1)^{n-1}(\Pi_eD)^n\cdot\varepsilon$$

$$+(-1)^{n-1}\exp\left(-\int_{\xi_r}\frac{d\xi}{\Pi_e}\right)\int_{\xi_0}\left[\frac{1}{\Pi_e}(\Pi_eD)^N\cdot\varepsilon\right]\exp\left(\int_{\xi_r}\frac{d\xi}{\Pi_e}\right)d\xi \quad , \tag{42}$$

where

$$D=\frac{d}{d\xi} \quad ,$$

$$(\Pi_eD)^n=\Pi_eD\cdot(\Pi_eD)^{n-1} \quad , \tag{43}$$

and n is a positive integer. If there is an integer N greater than or equal to two satisfying the condition

$$(\Pi_eD)^N\cdot\varepsilon\ll(\Pi_eD)\cdot\varepsilon \quad , \tag{44}$$

then for such an integer N, $\Delta\bar{\varepsilon}_V$ can be approximated by

$$\Delta\bar{\varepsilon}_V\approx-\sum_{n=1}^{N}(-1)^{n-1}\cdot(\Pi_eD)^n\cdot\varepsilon \quad , \tag{45}$$

in the sense of the asymptotic approximation. Using this approximation, we can represent $\Delta\bar{S}(\xi)$ and $\bar{h}(\xi)$ in the forms, respectively,

$$\Delta S \sim \left[\ln\left(\frac{\exp \bar{\xi}_V}{\exp \bar{\xi}_V - 1}\right) + \frac{\bar{\xi}_V}{\exp \bar{\xi}_V - 1}\right] - \left[\ln\left(\frac{\exp \xi}{\exp \xi - 1}\right) + \frac{\xi}{\exp \xi - 1}\right] + \int_{\xi_0} \xi \frac{d}{d\xi}\left(\Pi_e \frac{d\varepsilon}{d\xi}\right) d\xi + \cdots \tag{46}$$

$$\bar{h}(\xi) \sim \sqrt{\frac{5}{7 h_0 \varphi}} \cdot \frac{\bar{m} \xi_0^{1/2}}{\rho_0} \frac{\exp \xi_0}{\exp \xi_0 - 1} \exp\left(\frac{\xi_0}{\exp \xi_0 - 1}\right)$$

$$\cdot \frac{1}{\bar{M}_f} \cdot \left(\frac{\xi}{\xi_0}\right)^3 \frac{\exp \xi - 1}{\exp \xi} \exp\left(-\frac{\xi}{\exp \xi - 1}\right) \exp\left[\int_{\xi_0} \xi \frac{d}{d\xi}\left(\Pi_e \frac{d\varepsilon}{d\xi}\right) d\xi + \cdots\right]. \tag{47}$$

In the nearly equilibrium region, the integral terms on the right hand side of Eq. (46) and in the square bracket in Eq. (47 are sufficiently small and negligible within an acceptable error In such a case, of course, $\Delta\bar{\varepsilon}_V$ can be approximated by

$$\Delta\bar{\varepsilon}_V \sim -\Pi_e D\varepsilon = \frac{\exp \xi}{(\exp \xi - 1)^2} \cdot \Pi_e = \frac{P_e}{\exp \xi - 1}. \tag{48}$$

2. 3 Solutions of Nonequilibrium Flows: The Saddle Point Method

When the value of ξ which satisfies $\Pi_e = 1$ is much greater than unity, $\Delta\bar{\varepsilon}_V$ can easily be evaluated by the saddle point method. Denoting the values of ξ which satisfy the conditions

$$\Pi_e(\xi) = \frac{1}{m}, \quad m = 1,\ 2,\ 3 \cdots \quad , \tag{49}$$

by ξ_{rm}, we can introduce three new quantities by

$$\eta_m' = \frac{\eta}{\xi_{rm}}, \qquad \xi_m' = \frac{\xi}{\xi_{rm}},$$

$$\Phi_m'(\eta_m',\ \xi_m') = \frac{\Phi_m(\eta,\ \xi)}{m\xi_{rm}} = \eta_m' + \int_{\eta_m'}^{\xi_m'} \frac{d\eta_m'}{m\Pi_e'(\eta_m')} \quad , \tag{50}$$

where

$$\Pi_e'(\eta_m') = \Pi_e(\eta). \tag{51}$$

It is easy to prove that

$$\Phi_m'(\eta_m',\ \xi_m')_{\min.} = \Phi_m'(1,\ \xi_m') = 1 + \int_1^{\xi_m'} \frac{d\eta_m'}{m\Pi_e'}, \tag{52}$$

with ξ_m' fixed, so that the asymptotic expansion of $\Delta\bar{\varepsilon}_{Vm}$ can be obtained by the saddle point method as

$$\Delta\bar{\varepsilon}_{Vm} \sim Z_m \exp\left[-Z_m \cdot \Phi_m'(1, \xi_m')\right] \sqrt{\frac{\pi a_{0m}^2}{Z_m}} \sum_{l=0}^{\infty} \left(\frac{a_{2lm}}{a_0}\right) \cdot \frac{\Gamma\left(l+\frac{1}{2}\right)}{\Gamma\left(\frac{1}{2}\right)} \cdot \left(\frac{1}{Z_m}\right)^l, \tag{53}$$

where

$$Z_m = m\xi_{rm},$$

$$a_{0m} = \frac{1}{A_{om}^{1/2}}, \qquad \frac{a_{2m}}{a_{0m}} = \frac{15}{8}\frac{A_{1m}^2}{A_{0m}^3} - \frac{3}{2}\cdot\frac{A_{2m}}{A_{0m}^2}, \tag{54}$$

$\cdots\cdots,$

and where

$$A_{0m} = \frac{1}{2} m\xi_{rm} \cdot \left(\frac{d\Pi_e}{d\xi}\right)_{\xi=\xi_{rm}},$$

$$A_{1m} = \frac{1}{6}\left\{m\xi_{rm}^2\left(\frac{d^2\Pi_e}{d\xi^2}\right)_{\xi=\xi_{rm}} - 2m^2\xi_{rm}^2\left[\left(\frac{d\Pi_e}{d\xi}\right)_{\xi=\xi_{rm}}\right]^2\right\} \tag{55}$$

$$A_{2m} = \frac{1}{24}\left\{m\xi_{rm}^3\left(\frac{d^3\Pi_e}{d\xi^3}\right)_{\xi=\xi_{rm}} - 6m^2\xi_{rm}^3\left(\frac{d\Pi_e}{d\xi}\right)_{\xi=\xi_{rm}} \cdot \left(\frac{d^2\Pi_e}{d\xi^2}\right)_{\xi=\xi_{rm}} + 6m^3\xi_{rm}^3\left[\left(\frac{d\Pi_e}{d\xi}\right)_{\xi=\xi_{rm}}\right]^3\right\},$$

$\cdots\cdots.$

Especially in the case of $\xi_{r1} \gg 1$, $\Delta\bar{\varepsilon}_V$ is satisfactorily approximated by

$$\Delta\bar{\varepsilon}_V \approx \Delta\bar{\varepsilon}_{V1} \sim \left[\frac{2\pi}{\left(\frac{d\Pi_e}{d\xi}\right)_{\xi=\xi_{r1}}}\right]^{1/2} \exp\left(-\xi_{r1} - \int_{\xi_{r1}}^{\xi}\frac{d\xi}{\Pi_e}\right), \tag{56}$$

and then infinitely downstream

$$\Delta\bar{\varepsilon}_V(\infty) \sim \left[\frac{2\pi}{\left(\frac{d\Pi_e}{d\xi}\right)_{\xi=\xi_{r1}}}\right]^{1/2} \exp\left(-\xi_{r1} - \int_{\xi_{r1}}^{\infty}\frac{d\xi}{\Pi_e}\right). \tag{57}$$

Obviously the accuracy of this solution will closely be concerned with the behaviour of Π_e near the point where $\Pi_e = 1$, and with the magnitude of $Z_1 = \xi_{r1}$.

3. Numerical Solutions

With the intension of estimating the accuracy and reasonableness of our results obtained in the previous section, exact reference solutions are needed, and so the equilibrium-throat-approximation method is applied.

3. 1 Solutions by the Equilibrium-Throat-Approximation Method

This method can be used only for flows which are kept nearly equilibrium at least up to the critical point near the geometric throat. In this method, the flows are assumed to be completely equilibrium up to points somewhat downstream of the critical points, from which the flows are analysed numerically as nonequilibrium flows.

Though this method is in many cases very convenient and powerful for the numerical analysis of nozzle flow problems of real gases, there is only one disadvantage in it. It is the fact that there is no strict criterion for determining the starting points of the downstream nonequilibrium branches. Namely there is only one condition that must be satisfied by these starting points, which is

$$\Pi_e \ll 1 , \qquad \text{or} \qquad P_e \ll 1 . \tag{58}$$

So far it has inevitably led to the result that there can always be some ambiguity and unreliability about the accuracy of the numerical results obtained by this method.

From the foregoing, it will be natural to consider that some estimation of accuracy and validity of this method is urgently needed. At first, for this purpose, our calculations are carried out for several starting points of the nonequilibrium branches satisfying Eq. (58) under fixed reservoir conditions and for a fixed nozzle shape and size, and the results are compared with each other.

Three numerical solutions are illustrated in Fig. 4. In these calculations, the nonequilibrium branchese start from the points where Π_e are, respectively, 0.00620, 0.02918 and 0.09696.

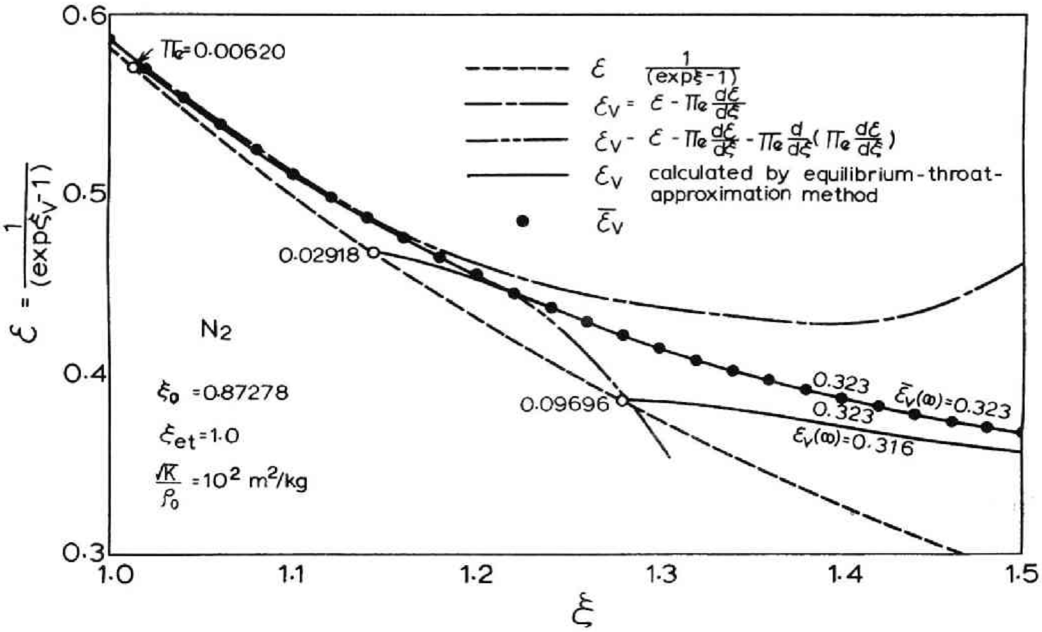

Fig. 4 Distributions of vibrational energy calculated by several methods.

The first two curves rapidly approach with each other as soon as they start from their corresponding starting points, and furtheremore their final values of $\varepsilon_V(\infty)$ almost coincide. The last curve, however, does not converge to the others. These clearly indicate that in order to assert that the results calculated by the equilibrium-throat-approximation method is sufficiently accurate and can be taken as the exact reference solutions, some additional condition must be imposed on the condition Eq. (58). From the numerical results, we can draw an empirical criterion for the validity of this method, which can be said as follows: The magnitude of Π_e at the starting point of a nonequilibrium branch must be at most $O(10^{-2})$ for N_2 and O_2 gases. By using the solutions satisfying this criterion as the reference ones, we can estimate the validity and the accuracy of the analytical solutions obtained in the previous section. The possible regions of the equilibrium-throat-approximation method are shown in Fig. 5 for reservoir conditions.

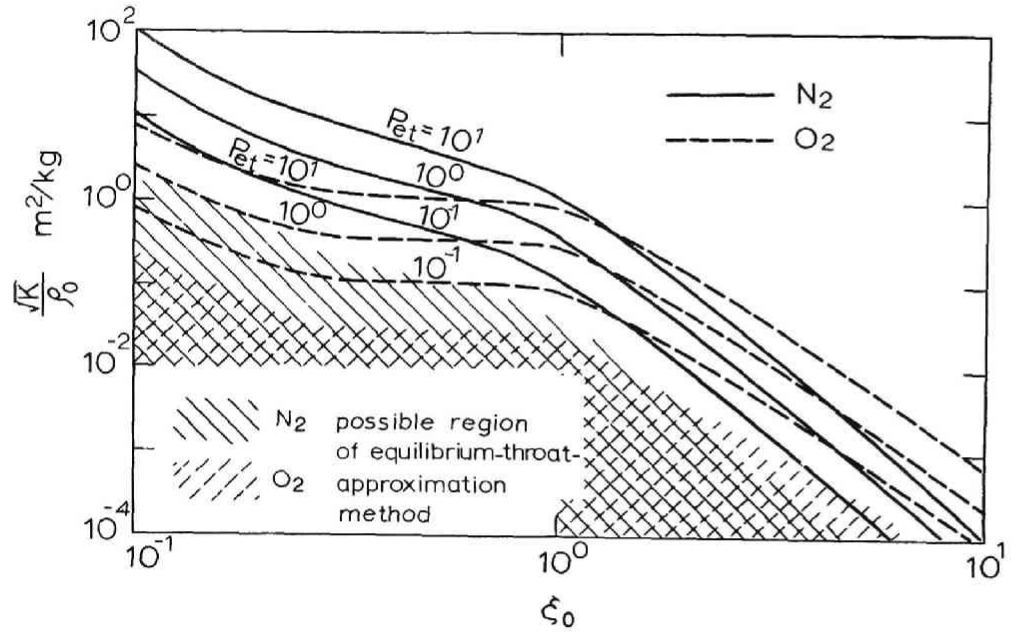

Fig. 5 Possible regions of the equilibrium-throat-approximation method for N_2 and O_2 gases.

Distributions of ε_V are shown in Figs. 6 and 7 under a wide variety of boundary conditions. Only those for $\sqrt{K}/\rho_0 = 10^3$ and 10^2 are the solutions of approximate rate equation, and the others are those calculated by the equilibrium-throat-approximation method. On each curve, the location of the point where

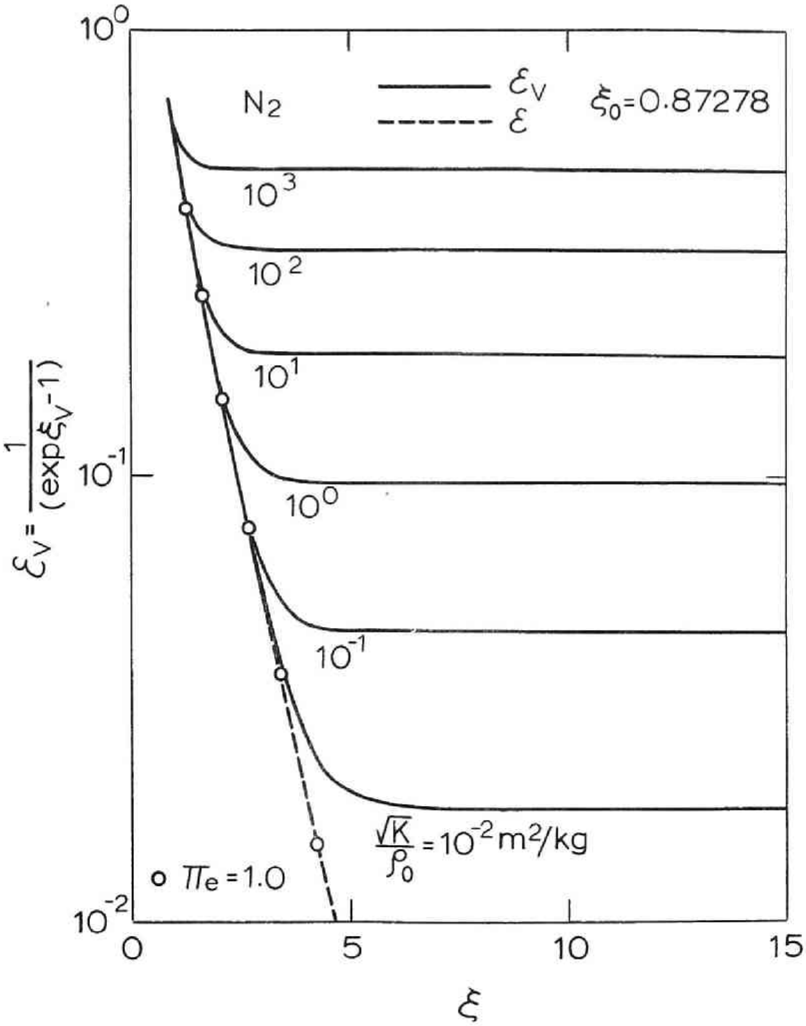

Fig. 6 Distributions of $\mathcal{E}_V$ for various values of ratio $\sqrt{K}/\rho_0$ and a fixed reservoir temperature.

$\Pi_e = 1$ is indicated, which is found to be located about at the center of the transition region.

Also distributions of $h(\xi)$ and $\Pi(\xi)$ calculated by the equilibrium-throat-approximation method are shown in Fig. 8 being compared with, respectively, $h_e(\xi)$ and $h_f(\xi)$, and $\Pi_e(\xi)$ and $\Pi_f(\xi)$. These show well that our approach is quite reasonable and accurate. Because of the artificially imposed boundary values of ξ and $\mathcal{E}_V$ at the starting point of the nonequilibrium branch, our results indicate a contradictory tendency to our theoretical estimations only near the starting point of the nonequilibrium branch.

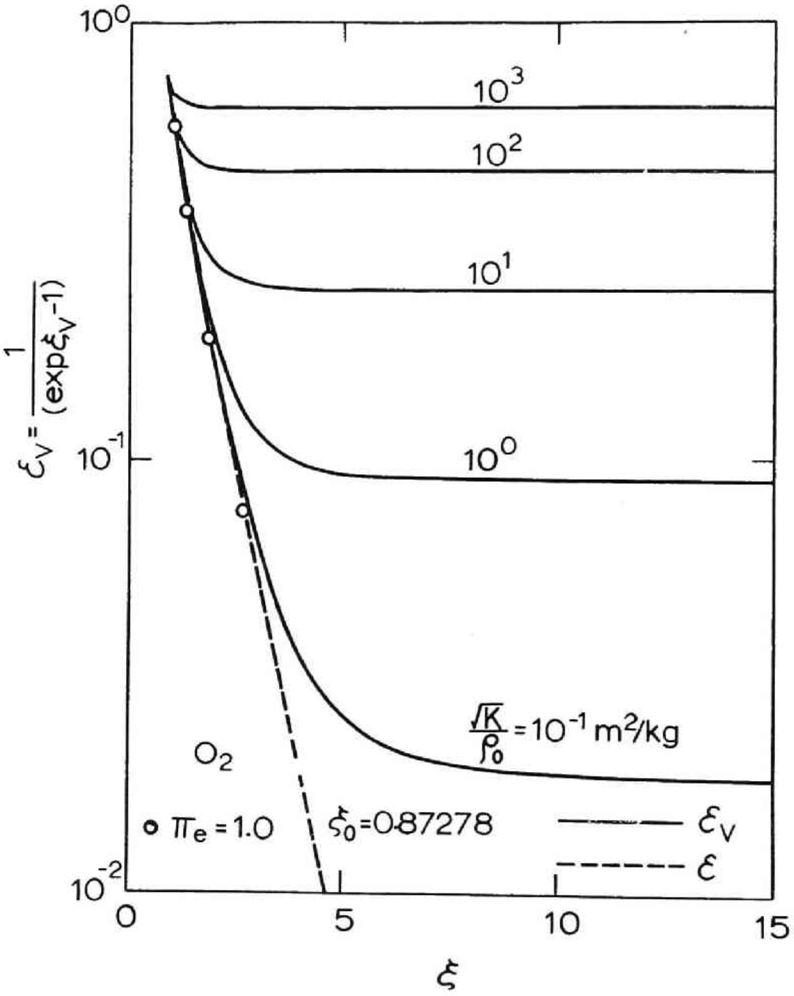

Fig. 7 Distributions of $\mathcal{E}_V$ for various values of ratio $\sqrt{K}/\rho_0$ and a fixed reservoir temperature.

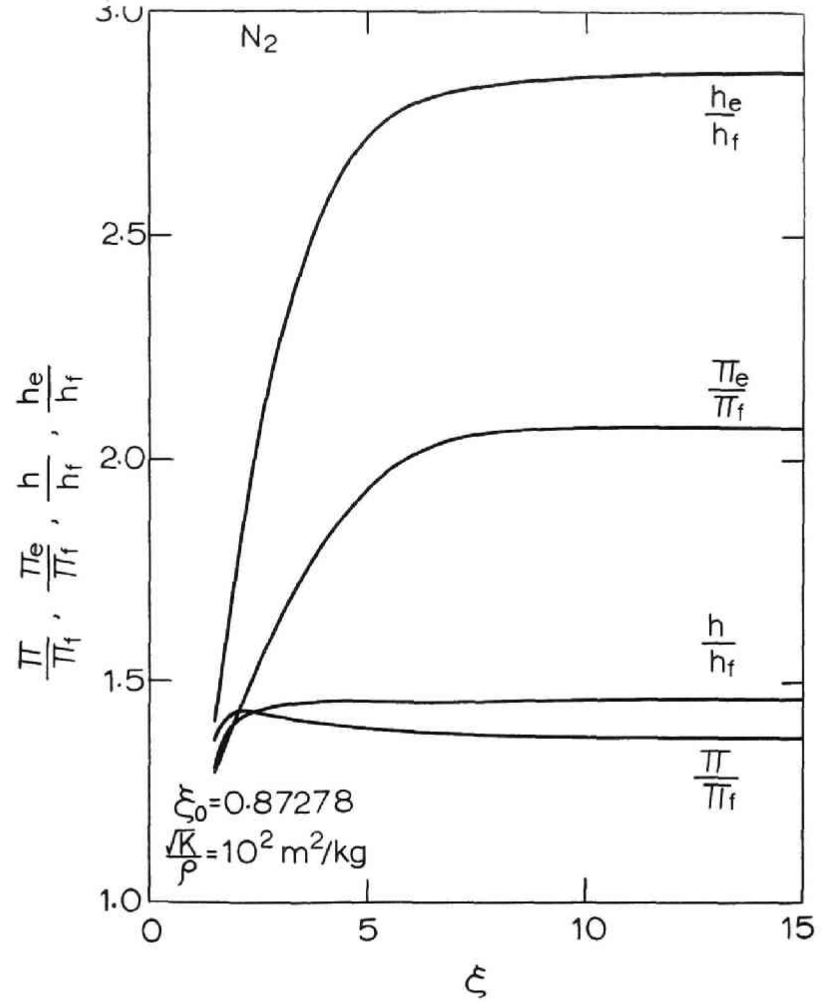

Fig. 8 Distributions of ratios Π/Π_f, Π_e/Π_f, h/h_f and h_e/h_f.

3. 2 Solutions Far Downstream of the Throat

Asymptotic Behaviours of nonequilibrium flows far downstream of the throat are investigated. Letting

$$\xi \gg 1, \quad M_f \gg 1, \tag{59}$$

in Eqs. (82) and (86) in Ch. I and Eqs. (3), (6), (8), (12), (16), and (17), yields

$$h_e(\xi) \approx \frac{125}{216}\sqrt{\frac{7}{10}} \cdot \frac{\mu_e}{\xi_0{}^3} \cdot \frac{\exp \xi_0}{\exp \xi_0 - 1} \exp\left(\frac{\xi_0}{\exp \xi_0 - 1}\right) \varphi^{1/2} \cdot \xi^{5/2}, \tag{60}$$

$$\frac{h_f(\xi)}{h_e(\xi)} \approx \frac{1}{\mu_e} \cdot \frac{\frac{\exp\xi_0 - 1}{\exp\xi_0} \cdot \exp\left[-\frac{\xi_0}{\exp\xi_0 - 1}\right]}{\left(1 - \frac{\varphi}{\exp\xi_0 - 1}\right)^{1/2}} = \text{const.}, \tag{61}$$

$$\frac{h_{ef}(\xi)}{h_e(\xi)} \approx \left(\frac{\mu_{ef}}{\mu_e}\right) \frac{\frac{\exp\xi_{Vf} - 1}{\exp\xi_{Vf}} \cdot \exp\left(-\frac{\xi_{Vf}}{\exp\xi_{Vf} - 1}\right)}{\left(1 - \frac{\varphi}{\exp\xi_{Vf} - 1}\right)^{1/2}} = \text{const.}, \tag{62}$$

$$\frac{h(\xi)}{h_e(\xi)} \approx \left(\frac{\mu}{\mu_e}\right) \frac{\frac{\exp\xi_V - 1}{\exp\xi_V} \exp\left(-\frac{\xi_V}{\exp\xi_V - 1} + \frac{W_2}{R}\Delta S\right)}{\left(1 - \frac{\varphi}{\exp\xi_V - 1}\right)^{1/2}}, \tag{63}$$

$$\Pi_e \approx \frac{288}{125\sqrt[4]{2520}} \cdot \frac{\sqrt{\frac{h_0\varphi}{\mu_e}}}{\Gamma\theta^w\varphi^{3/4}} \cdot \frac{1}{\xi_0} \cdot \xi^{(w+9/4)} \cdot \exp\left(-l\theta^S\xi^{-S}\right), \tag{64}$$

$$\frac{\Pi_f}{\Pi_e} \approx \sqrt{\mu_e} \cdot \left(1 - \frac{\varphi}{\exp\xi_0 - 1}\right)^{3/4} \cdot \left(\frac{\exp\xi_0 - 1}{\exp\xi_0}\right)^{1/2} \cdot \exp\left(-\frac{1}{2}\frac{\xi_0}{\exp\xi_0 - 1}\right) = \text{const.}, \tag{65}$$

$$\frac{\Pi_{ef}}{\Pi_e} \approx \sqrt{\frac{\mu_e}{\mu_{ef}}} \cdot \left(1 - \frac{\varphi}{\exp\xi_{Vf} - 1}\right)^{3/4} \cdot \left(\frac{\exp\xi_{Vf} - 1}{\exp\xi_{Vf}}\right)^{1/2} \cdot \exp\left(-\frac{1}{2}\frac{\xi_{Vf}}{\exp\xi_{Vf} - 1}\right) = \text{const.}, \tag{66}$$

$$\frac{\Pi}{\Pi_e} \approx \sqrt{\frac{\mu_e}{\mu}} \left(1 - \frac{\varphi}{\exp\xi_V - 1}\right)^{3/4} \left(\frac{\exp\xi_V - 1}{\exp\xi_V}\right)^{1/2} \exp\left(-\frac{1}{2}\frac{\xi_V}{\exp\xi_V - 1} + \frac{W_2}{2R}\Delta S\right). \tag{67}$$

Especially the values of ratios

$$\frac{h_f(\infty)}{h_e(\infty)} \quad \text{and} \quad \frac{\Pi_f(\infty)}{\Pi_e(\infty)},$$

are of importance in estimating the effects of molecular vibration on the limiting behaviours of a flow and the relaxation phenomenon itself. From Eqs. (63) and (67), it can well be seen that the increase in entropy due to the nonequilibrium process plays important roles in analyses of nonequilibrium nozzle flows. The increase in entropy due to the vibrational relaxation is not large in our sample calculations. It is significant, however, to notice that wheather an real nonequilibrium flow can well be approximated by the E-F flow or not depends strongly upon the behaviour of entropy as $\xi \to \infty$.

Now for a nonequilibrium flow, the rate equation may be rewritten in a form

$$\frac{d}{d\xi}\Delta\varepsilon_V=\frac{\exp\xi}{(\exp\xi-1)^2}-\frac{\Delta\varepsilon_V}{\Pi}, \tag{68}$$

For sufficiently large value of ξ, it can be approximated by

$$\frac{d}{d\xi}\Delta\varepsilon_V\approx-\frac{\Delta\varepsilon_V}{\Pi}<0. \tag{69}$$

Furthermore the followngs hold

$$\Delta\varepsilon_V=0 \qquad \text{and} \qquad \frac{d}{d\xi}\Delta\varepsilon_V=0, \tag{70}$$

at $\xi = \xi_0$. By virtue of Eq. (69), these mean that $\Delta\varepsilon_V$ has the maximum value for the value of ξ satisfying

$$\frac{\Delta\varepsilon_V}{\Pi}=\frac{\exp\xi}{(\exp\xi-1)^2}. \tag{71}$$

From these considerations, it can be concluded that in general

$$\Delta\varepsilon_{V\max}\leq\left[\Pi\frac{\exp\xi}{(\exp\xi-1)^2}\right]_{\max}. \tag{72}$$

for every flow, and similarly

$$\Delta\bar{\varepsilon}_{V\max}\leq\left[\Pi_e\frac{\exp\xi}{(\exp\xi-1)^2}\right]_{\max}=\left[\frac{P_e}{\exp\xi-1}\right]_{\max}. \tag{73}$$

Since the second term or the last in Eq. (73) is easily calculated in advance, we can obtain some significant informations on the features of distribution of $\Delta\bar{\varepsilon}_V$ and then $\Delta\varepsilon_V$ from these in advance.

Again for extremely large value of ξ, we have

$$\Delta\varepsilon_V\propto\exp\left(-\int\frac{d\xi}{\Pi}\right), \tag{74}$$

$$\Delta S\propto\int\xi\cdot\frac{\Delta\varepsilon_V}{\Pi}d\xi. \tag{75}$$

According to the limiting values of $\Delta\mathcal{E}_V$ and ΔS which are represented by, respectively, $\Delta\mathcal{E}_V(\infty)$ and $\Delta S(\infty)$, four types of flow patterns can be identified at least theoretically:

(i) $\Delta\varepsilon_V(\infty)=$finite, $\Delta S(\infty)=$finite,	frozen-isentropic flow
(ii) $\Delta\varepsilon_V(\infty)=$finite, $\Delta S(\infty)=\infty$,	frozen-nonisentropic
(iii) $\Delta\varepsilon_V(\infty)=0$, $\Delta S(\infty)=$finite,	self-limiting-isentropic flow
(iv) $\Delta\varepsilon_V(\infty)=0$, $\Delta S(\infty)=\infty$,	self-limiting-nonisentropic flow .

Which flow can occur in a nozzle entirely depends upon the values of integrals Eqs. (74) and (75). In our sample calculations, only the frozen-isentropic flow is possible at infinitely downstream, which can also be verified analytically from the from of Π.

3. 3 The Maximum Entropy Flows

Some discussions on the entropy rise in nonequilibrium flows are given. As has already been mentioned, the entropy rise vanishes both in the equilibrium limit and the frozen one. Since in the limit $\sqrt{K}/\rho_0 \to \infty$ the frozen flow is given while in the limit $\sqrt{K}/\rho_0 \to 0$ the equilibrium flow is given, the flow of the maximum entropy rise can occur for some finite value of $\sqrt{K}/\rho_0$ when the value of ζ_0 is fixed. To know the magnitude of the entropy rise is very significant for the theoretical analysis of nonequilibrium nozzle flows. For instance, it gives an estimation of the validity of the E-F flow approximation to a nonequilibrium flow.

4. Concluding Remarks

A distribution of $\mathcal{E}_V$, which is calculated from the approximate rate equation Eq. (32), is also shown in Fig. 4. The most important conclusion that can be drawn from it is that the solution of the approximate rate equation Eq. (32) is quite accurate and can be taken almost as an exact solution. It indicates that our approximation to the rate equation based upon the theoretical inspections may be judged to be quite reasonable and accurate. Furthermore it must be emphasized that the greatest merit expected by using this approximate rate equation is to be able to exclude out the difficulties in connection with the singularity of the flow equations at the sonic point, which is usually unavoidable in nonequilibrium nozzle flow problems.

The distributions of entropy along the nozzle axis are shown in Fig. 9. Detailed discussions of the entropy rise are also given in Chs. III and IV.

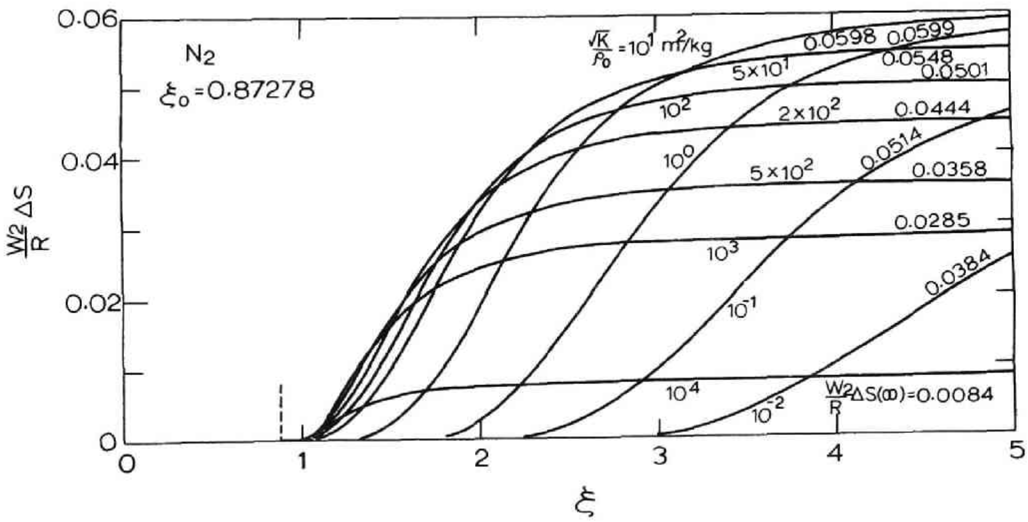

Fig. 9 Distributions of entropy.

The solutions of the first, second and third approximations to $\bar{\varepsilon}_V$ are illustrated in Fig. 4. These are good approximations at least in the nearly equilibrium region. An extremely nearly equilibrium region is very difficult and laborious to analyse, because the closer the flow is to equilibrium, the more time it takes to compute the flow field. The approximate solutions obtained here are therefore of much value.

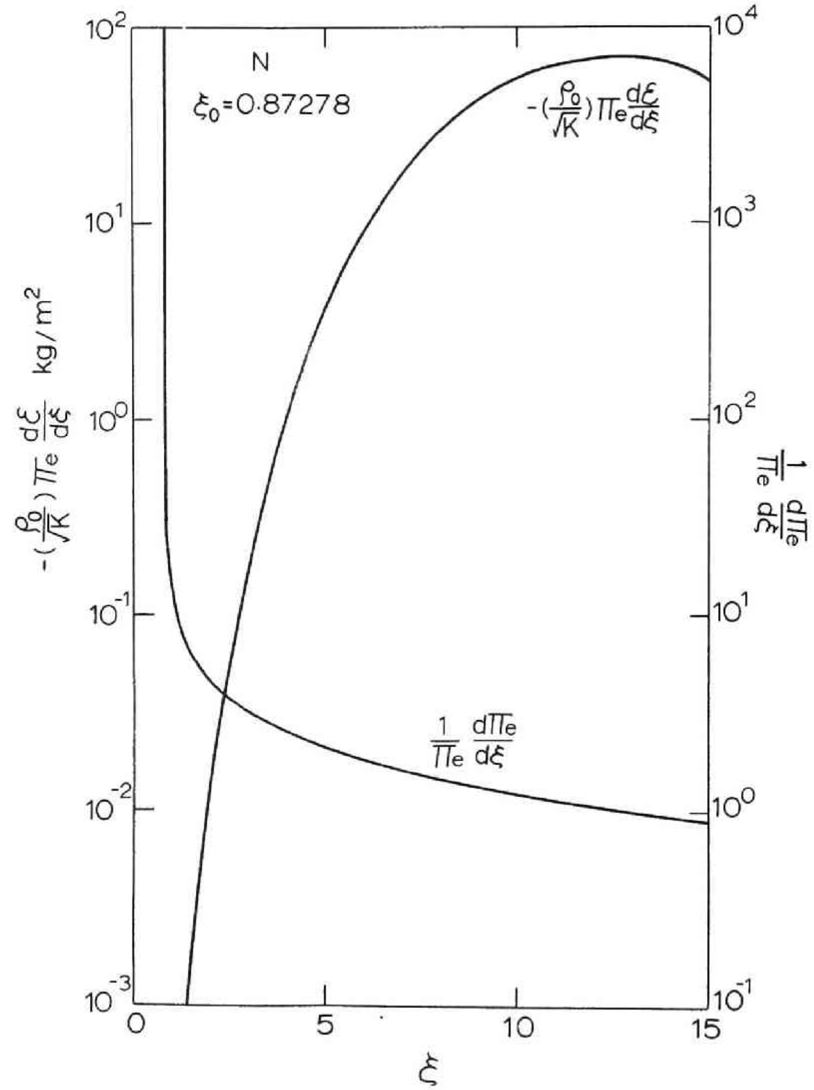

Fig. 10 Distributions of $\Pi_e(d\varepsilon/d\xi)$ and $(1/\Pi_e)(d\Pi_e/d\xi)$.

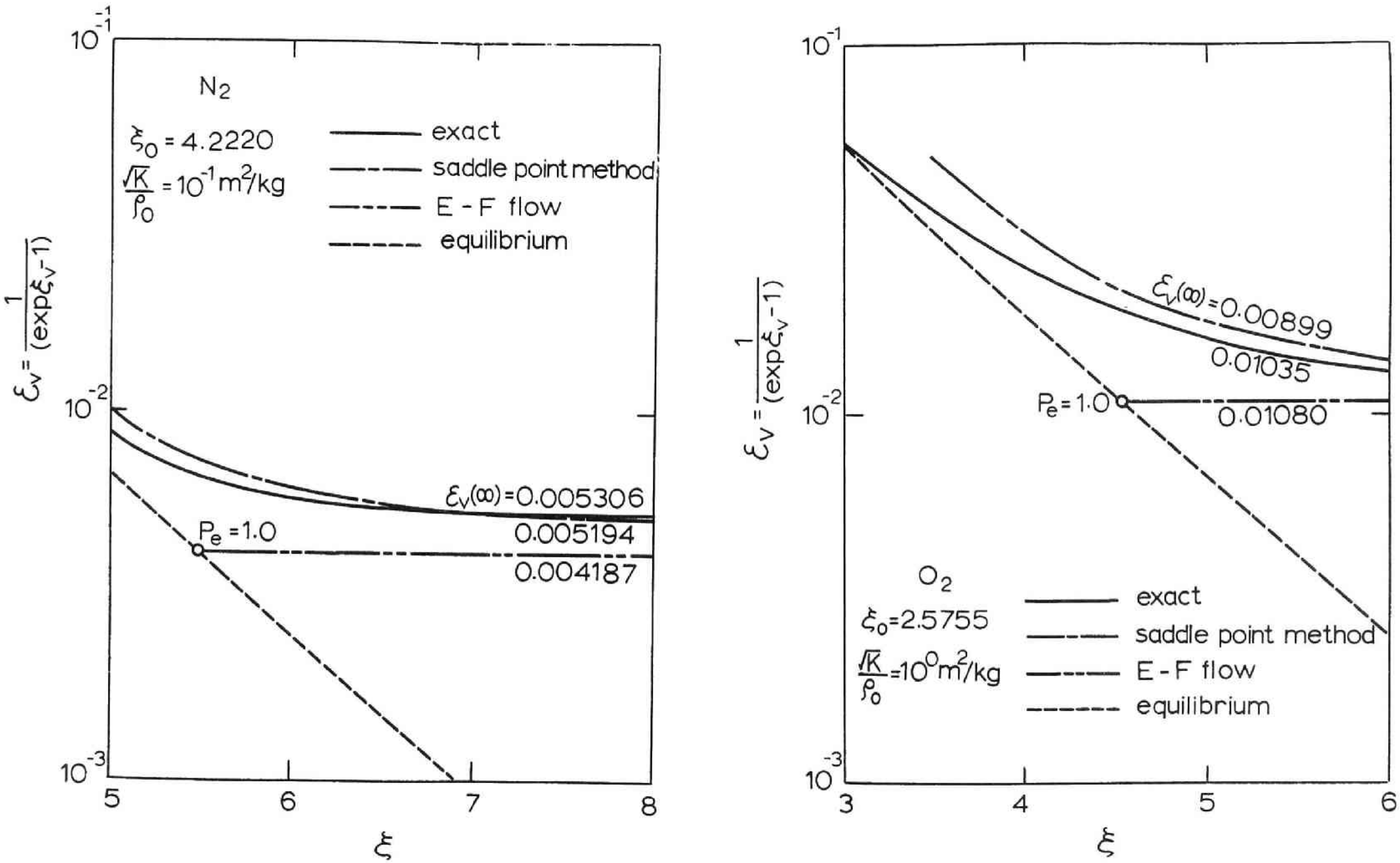

Fig. 11 Distributions of vibrational energy.

In order to confirm the validity of our assumptions made in deriving the approximate rate equation, distributions of $d(\ln\Pi_e)/d\xi$ and $\Pi_e(d\mathcal{E}/d\xi)$ are presented in Fig. 10. the latter can also be used for calculating Bray's nonequilibrium parameter and the first approximate solution to $\bar{\mathcal{E}}_V$.

Solutions by the saddle-point method illustrated in Fig. 11 show the satisfactory accuracy, which has been expected theoretically at least for large value of ξ_0.

CHAPTER III ROLES OF ENTROPY

1. Introductory Remarks

In nonequilibrium nozzle flows of vibrationally relaxing or chemically reacting gases, the nonequilibrium processes inevitably increase the entropy of gases in nozzles. This increased entropy affects not only flowfields but also relaxation phenomena themselves. It is regretful that in spite of the large number of researchers, few good studies on this problem have been done because of the difficulties in analysing theoretically these flowfields.[19)20)21)] For example in Ref. 19, Conner, L. N. and Erickson, W. D. studied the entropy production in the vibrational-nonequilibrium nozzle flows. They calculated it for convenient evaluation of the total pressure of nonequilibrium flows. However, their approach is completely numerical and then it cannot sufficiently clarify and appreciate the effect of entropy production on the flow fields and the relaxation phenomenon itself. There are obviously two kinds of nonequilibrium effect on the flow parameters in a nozzle, one of which is due to the entropy production and another of which is due to the departure from the thermo-chemical equilibrium. Though Conner and Erickson do not distinguish these two effects, it is quite necessary and significant to consider seperately these two effects. In this chapter, our efforts are mainly devoted to investigation of the roles of entropy in the analyses of nonequilibrium nozzle flows. First the maximum and minimum critical mass flows for vibrationally relaxing diatomic gases under the fixed reservoir conditions are obtained. Next a new criterion for the validity of the equilibrium-frozen flow approximation is proposed. Finally the effects due to increasing in entropy on the asymptotic behaviours of flows far downstream of the throat are examined. All these analyses are based upon the new system of basic equations which has been derived by the author.

2. Entropy and Critical Mass Flows

It has already been pointed out that the difficulty in determining critical mass flows is one of the most significant reasons which complicate greatly the analyses of nonequilibrium nozzle flows. Nevertheless, there are only a few theoretical works of this problem.[6] In practice, this difficulty has usually been overcomed purely numerically by using the high speed electric digital computer. In almost all cases, obtained results have indicated that the critical mass flows of general nonequilibrium flows are smaller than the frozen one and greater than the equilibrium. This tendency, however, is rather empirical and has never been proved theoretically.

For vibrationally relaxing diatomic gases, it is fairly favourable to use the independent variable ξ instead of x. Here again rearranging the basic equations, Eqs. (1) to (6), (9), (13), (23), (24), (29), (30) and (43) in Ch. I, we have

$$F_V(M_f)\frac{(1+A)}{m}=F_{V_0}\exp G_V(\xi_V;\xi)\,, \tag{1}$$

$$\frac{7}{10}M_f^2=\left(\frac{1}{\varphi}-\varepsilon_V\right)\xi-\frac{7}{2}\,, \tag{2}$$

$$\Pi(A,\xi_V;\xi)\frac{d\varepsilon_V}{d\xi}=-(\varepsilon_V-\varepsilon)\,. \tag{3}$$

$$\rho=\frac{m}{\left(\frac{7}{5}h_0\varphi\right)^{1/2}}\frac{\xi^{1/2}}{(1+A)M_f}\,, \tag{4}$$

$$p = \frac{m\left(\frac{7}{5}h_0\varphi\right)^{1/2}}{(1+A)M_f\xi^{1/2}}, \tag{5}$$

$$\frac{W_2}{R}(S-S_0) = \int_{\xi_0}^{\xi} (\xi_V - \xi)\left(\frac{d\varepsilon_V}{d\xi}\right)d\xi . \tag{6}$$

where

$$\xi = \frac{\theta}{T}, \qquad \xi_V = \frac{\theta}{T_V}, \tag{7}$$

$$\varepsilon = \frac{1}{(\exp\xi - 1)}, \qquad \varepsilon_V = \frac{1}{(\exp\xi_V - 1)} : \tag{8}$$

$$F_V(M_f) = \frac{M_f}{(M_f^2+5)^3} : \tag{9}$$

$$G_V(\xi_V;\xi) = -\int_{\xi_0}^{\xi}\left[\xi - \frac{3\varphi}{(1-\varphi\varepsilon_V)}\right]\left(\frac{d\varepsilon_V}{d\xi}\right)d\xi , \tag{10}$$

$$\Pi(A,\xi_V;\xi) = -(\varepsilon_V-\varepsilon)V\left(\frac{L}{U}\right)\Big/\left[\left(\frac{dA}{d\xi}\right)\left(\frac{dx}{dA}\right)\left(\frac{d\varepsilon_V}{d\xi_V}\right)\right], \tag{11}$$

and

$$\varphi = \frac{1}{h_0}\frac{R}{W_2}\theta , \qquad F_{V_0} = \frac{m}{125\left(\frac{7}{5}h_0\varphi\right)^{1/2}}\frac{\xi_0^{1/2}}{\rho_0} . \tag{12}$$

Eq. (1) in conjunction with Eqs. (2), (6), (9) and (10) can also be rewritten in the form

$$(1+A) = \frac{125}{216}\left(\frac{7}{10}\right)^{1/2}\left(\frac{m}{m_f}\right)\frac{\exp\xi_0}{\xi_0^3(\exp\xi_0-1)}\exp\left(\frac{\xi_0}{\exp\xi_0-1}\right)$$

$$\times\left\{\frac{\xi^{5/2}\left[\frac{(\exp\xi_V-1)}{\exp\xi_V}\right]\exp\left[-\frac{\xi_V}{(\exp\xi_V-1)}\right]}{\left[\frac{1}{\varphi}-\frac{1}{(\exp\xi_V-1)}-\frac{7}{2\xi}\right]^{1/2}}\right\}\exp\left[\frac{W_2}{R}(S-S_0)\right]. \tag{13}$$

Eq. (13) shows that the degree to which the flow parameters in nozzles are affected by the existence of nonequilibrium is completely determined by the entropy and the vibrational temperature. Thus, an algebraic equation is obtained, relating $A(x)$, ξ, ξ_V, and S, which in conjunction with the remainders of basic equations yields very simple analytical solutions not only for the frozen ($\xi_V = \xi_0$ and $S - S_0 = 0$) flow but also for the equilibrium ($\xi_V = \xi$ and $S - S_0 = 0$) one. With it, we can calculate all the flow quantities for these limiting flows without carrying out the tedious numerical calculations on the electronic digital computer. It must be emphasized that using Eq. (1) or Eq. (13) as one of the basic equations describing a nonequilibrium nozzle flow, we can expect considerable merits in investigating analytically non-equilibrium effects on the flowfields, especially in determining the critical mass flow, in estimating the validity or accuracy of the equilibrium-frozen flow approximation, and in analyzing the asymptotic behaviours of nonequilibrium flows far downstream of the throat.

Now imposing a condition

$$x(dA/dx) \geqq 0 \quad , \tag{14}$$

on the nozzle geometry, we can reasonably assume

$$d\xi_V/d\xi \geqq 0 \quad , \tag{15}$$

$$\xi_0 \leqq \xi_V \leqq \xi \quad , \tag{16}$$

for the flows considered here. Assuming (15) and (16) under the condition (14), from the discussions given in Ch. I we can obtain the next relation under the fixed reservoir conditions

$$m_{\min} \leqq m \leqq m_{\max} = m_f \quad , \tag{17}$$

where

$$\frac{m_e}{m_f} = \frac{F_V(M_{el})}{F_V(1)} \exp(-G_{Vel}) \quad , \tag{18}$$

$$\frac{m_{\min}}{m_e} = \frac{1}{(1+A_{e*})}\exp\left\{-\xi_{e*}(\mathcal{E}_0-\mathcal{E}_{e*})-\left[\ln\left(\frac{\exp\xi_{e*}}{\exp\xi_{e*}-1}\right)+\frac{\xi_{e*}}{(\exp\xi_{e*}-1)}\right]+\left[\ln\left(\frac{\exp\xi_0}{\exp\xi_0-1}\right)+\frac{\xi_0}{(\exp\xi_0-1)}\right]\right\} \quad , \tag{19}$$

where ξ_{et} and ξ_{e*} are determined from energy equations, respectively, at the throat and the critical point ($M_f = 1$). The result (17) is very significant not only physically but also practically in numerical analysis of the subsonic region, in which it often happens that the value of critical mass flow must be guessed beforehand for the given reservoir conditions and nozzle shape and size. Figure 1 shows the critical-mass-flow ratios m_e/m_f and m_{min}/m_e and the maximum entropy at the critical point. The explicit solution which gives the critical mass flow of a general nonequilibrium flow can also be easily obtained. It shows that the critical mass flow is completely determined by the entropy increase in the subsonic region and the vibrational temperature at the critical point.

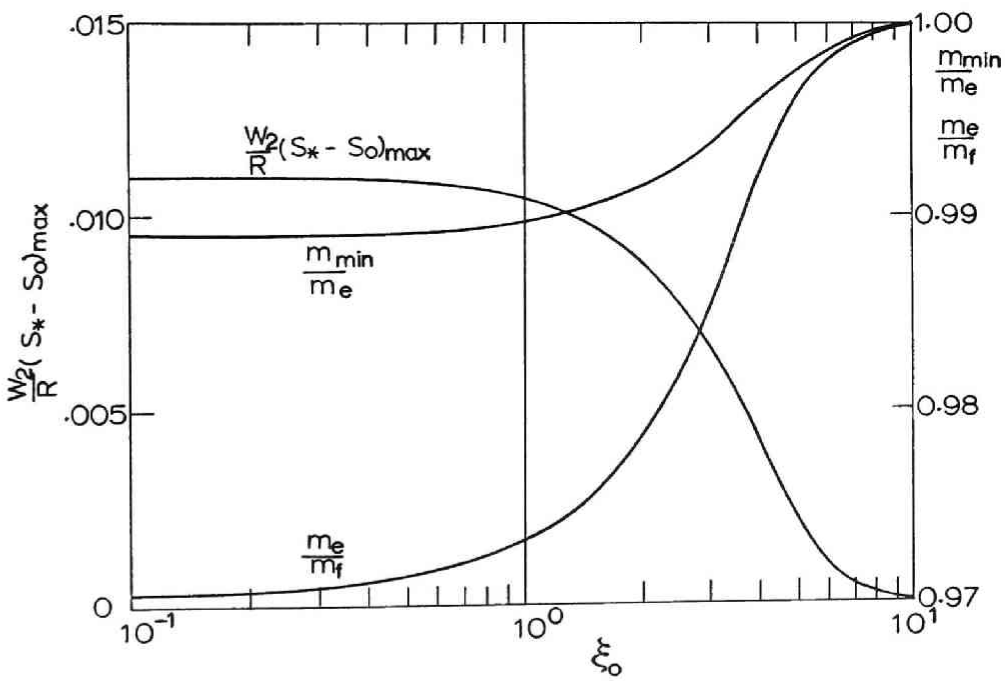

Fig. 1 Critical mass flow and the maximum entropy at the critical point.

3. Entropy and Equilibrium-Frozen Flow Approximation

The simplest and most significant approximation to a real flow is the equilibrium-frozen flow model, in which an upstream equilibrium branch and a downstream frozen branch are joined together at the freezing point. Many works on this problem have already been made by many authors, some of whome have supported the validity of this approximation for vibrationally relaxing gases as well as chemically reacting gases and others have not.[4) 22) 23)] Some proofs that this flow model cannot always well match the correct solution have been given numerically,[3)] but these are not sufficient in physical meaning. The freezing criteria for the approximate measure of the vibrational energy and the dissociated mass fraction being proposed by Bray et al., are rather empirical and moreover there is certain arbitrariness in their applications.

The equilibrium-frozen (E-F) flow approximation is completely based upon the freezing phenomenon of the relaxing energy at infinity and the flow concerned must be obviously isentropic. In practice, however, whether the real flow finally freezes or not entirely depends upon the form of rate equation and upon the nozzle shape and size. Furthermore, there can be two cases: In one, the entropy of the gas converges to a finite value and in another it diverges to infinity. In the latter case, the equilibrium-frozen flow approximation breakes down far downstream even when the flow does finally freeze. Hence we need a general and precise criterion for the validity of this approximation. Our efforts are in part devoted to proposing this new criterion. However the principal purpose of this section exists in investigating the physical meanings of this approximation as generally and precisely as possible. Our new type of a system of basic equations can provide us with a completely analytical solution for the equilibrium-frozen flow.

At first the problem of obtaining the approximate measure of state at a point $P(\xi, \xi_V)$ (Fig. 2) in a real nonequilibrium flow (corresponding to the path OCP) by using the equilibrium-frozen flow (corresponding to the path OFP) approximation is investigated. However, it must be noted that this equilibrium-frozen flow is not the so called "equilibrium-frozen flow" first proposed by Bray. The former here gives the approximate measure of the state at the only one point $P(\xi, \xi_V)$ and is denoted by the subscript OFP in this paper. The conventional equilibrium-frozen flow proposed by Bray is denoted by the subscript ef.

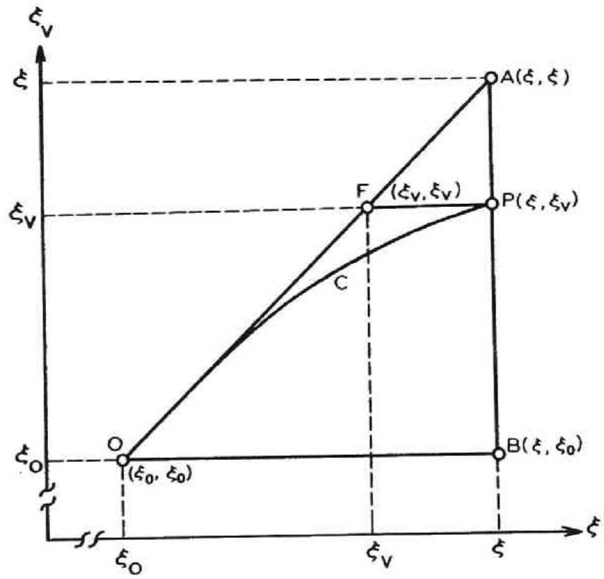

Fig. 2 Flow path in the $\xi - \xi_V$ plane.

Without much effort, the followings can be found from the system of basic equations, Eqs. (1) to (6)

$$\frac{(1+A_{OFP})}{(1+A)} = \frac{m_{OFP}}{m} \exp\left[-\frac{W_2}{R}(S-S_0)\right], \tag{20}$$

$$\frac{M_{fOFP}}{M_f}=1\,, \tag{21}$$

$$\frac{\rho_{OFP}}{\rho}=\exp\left[\frac{W_2}{R}(S-S_0)\right], \tag{22}$$

$$\frac{p_{OFP}}{p}=\exp\left[\frac{W_2}{R}(S_\infty-S_0)\right] \tag{23}$$

It is significant to point out that the difference between the flow histories of the real flow and its corresponding equilibrium-frozen one is completely represented in terms of the entropy and the critical mass flow appearing on the right hand side of Eqs. (20), (22) and (23). These indicate well the importance of roles of entropy in the analyses of nonequilibrium nozzle flows.

For the equilibrium-frozen flow in the conventional sense, corresponding to these equations one has

$$\frac{(1+A_{ef})}{(1+A)}=\frac{m_{ef}}{m}\frac{(\exp\xi_{Vef}-1)}{\exp\ \ \xi_{Vef}}\exp\left(\frac{\xi_{Vef}}{-\exp\xi_{Vef}-1}\right)\frac{\exp\xi_V}{(\exp\xi_V-1)}$$

$$\times\exp\left(\frac{\xi_V}{\exp\xi_V-1}\right)\frac{\left[\frac{1}{\varphi}-\frac{1}{(\exp\xi_V-1)}-\frac{7}{2\xi}\right]^{1/2}}{\left[\frac{1}{\varphi}-\frac{1}{(\exp\xi_{Vef}-1)}-\frac{7}{2\xi}\right]^{1/2}}\exp\left[-\frac{W_2}{R}(S-S_0)\right], \tag{24}$$

$$\frac{M_{fef}}{M_f}=\frac{\left[\frac{1}{\varphi}-\frac{1}{(\exp\xi_{Vef}-1)}-\frac{7}{2\xi}\right]^{1/2}}{\left[\frac{1}{\varphi}-\frac{1}{(\exp\xi_V-1)}-\frac{7}{2\xi}\right]^{1/2}}, \tag{25}$$

$$\xi_{Vef}=\begin{cases}\xi\,, & \text{for}\quad \xi\le\xi_{Vf}\,,\\ \xi_{Vf}\,, & \text{for}\quad \xi\ge\xi_{Vf}\,,\end{cases} \tag{26}$$

$$\frac{\rho_{ef}}{\rho}=\frac{\exp\xi_{Vef}}{(\exp\xi_{Vef}-1)}\exp\left(\frac{\xi_{Vef}}{\exp\xi_{Vef}-1}\right)\frac{(\exp\xi_V-1)}{\exp\xi_V}\exp\left(-\frac{\xi_V}{\exp\xi_V-1}\right)$$

$$\exp\left[\frac{W_2}{R}(S-S_0)\right], \tag{27}$$

$$\frac{p_{ef}}{p}=\frac{\rho_{ef}}{\rho}\,. \tag{28}$$

Based upon our discussions, a criterion for the validity of the

E-F flow approximation may be given and, at the same time, the pysical meaning of this approximation can be made clear. In order that the E-F flow matches well the exact solution in the whole of the flow region with an acceptable error, the following three conditions must be satisfied:

$$Q_1=\left|\frac{\varepsilon v_{ef}-\varepsilon v}{\varepsilon v}\right|_{max} \ll 1 \,, \tag{29}$$

$$Q_2=\left|\frac{m_{ef}-m}{m}\right| \ll 1 \,, \tag{30}$$

$$Q_3=\left\{ \exp\left[\frac{W_2}{R}(S_\infty - S_0)\right]-1\right\} \ll 1 \,, \tag{31}$$

where the subscript ∞ denotes the downstream limit. We can reasonably expect that the set of these three quantities Ω_1, Ω_2 and Ω_3 serves as a new type of a criterion for the validity of the E-F flow approximation. Of course it is obvious that the less values of Ω_1, Ω_2 and Ω_3 indicate the better approximation. Therefore it is easily seen that there are at least two necessary conditions for the validity of this approximation:

$$\varepsilon v_\infty=\text{const.}>0 \,, \tag{32}$$

$$S_\infty=\text{const.}<\infty \,, \tag{33}$$

which means that the real flow concerened must be a frozen-isentropic flow in the downstream limit for this approximation. We have already proved that for all flows of vibrationally relaxing diatomic gases the following is always satisfied:

$$Q_2 \ll 1 \,. \tag{34}$$

Then the remaining two quantities are important actually.

The distributions of vibrational temperature, vibrational energy and entropy along the nozzle axis are illustrated, respectively, in Figs. 3, 4 and 5. Fig. 3 shows a flow path in the

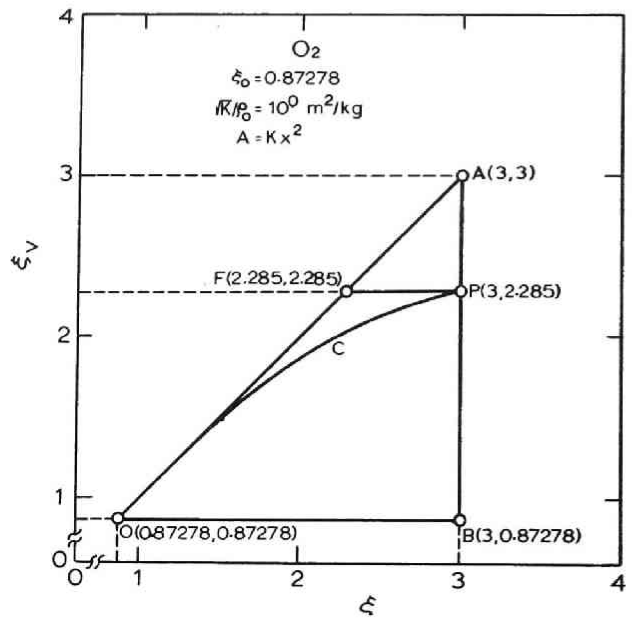

Fig. 3 Sample calculation of flow path.

$\xi - \xi_V$ plane corresponding to Fig. 2. The nozzle geometry used in these sample calculations are given by Eq. (68) in Ch. I. The final flow pattern of all these flows in the limit $\xi \to \infty$ is frozen-isentropic for both the N_2 and O_2 gases. The entropy rise in a flow of the N_2 gas is much smaller than that of the O_2 gas under the same reservoir conditions, which means that the width of transition region from the upstream near-equilibrium region to the downstream near-frozen one in the flow of the former is smaller than that of the latter. From this point of view to the entropy only, it can be concluded that the real flow of the N_2 gas may be matched much better by the E-F flow than that of the O_2 gas. The limiting values of S and $\mathcal{E}_V$ are shown in Figs. 6 and 7. These yield one of the powerful supports to the validity of the E-F flow approximation to the flows of these gases.

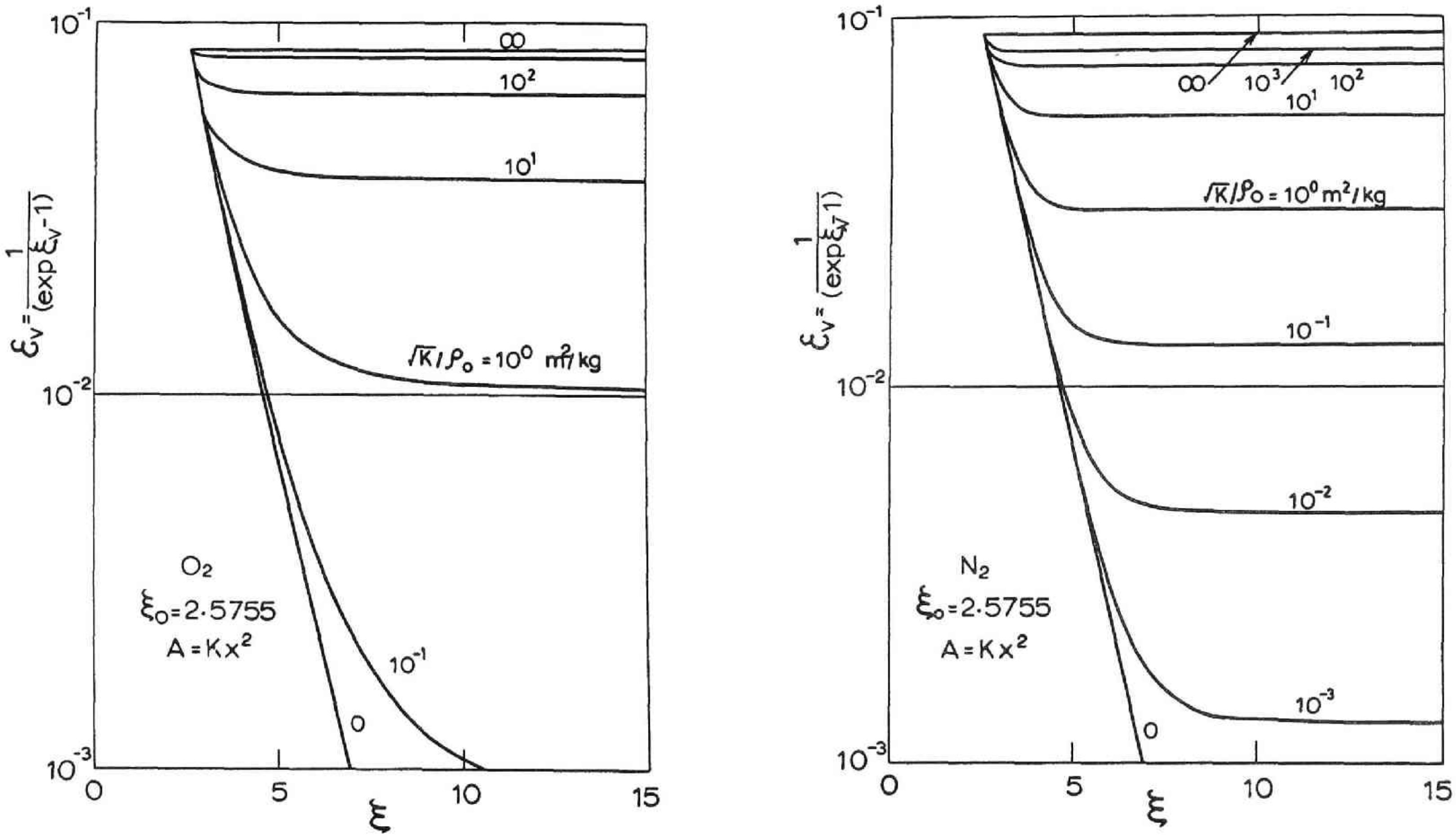

Fig. 4 Distribution of vibrational energy.

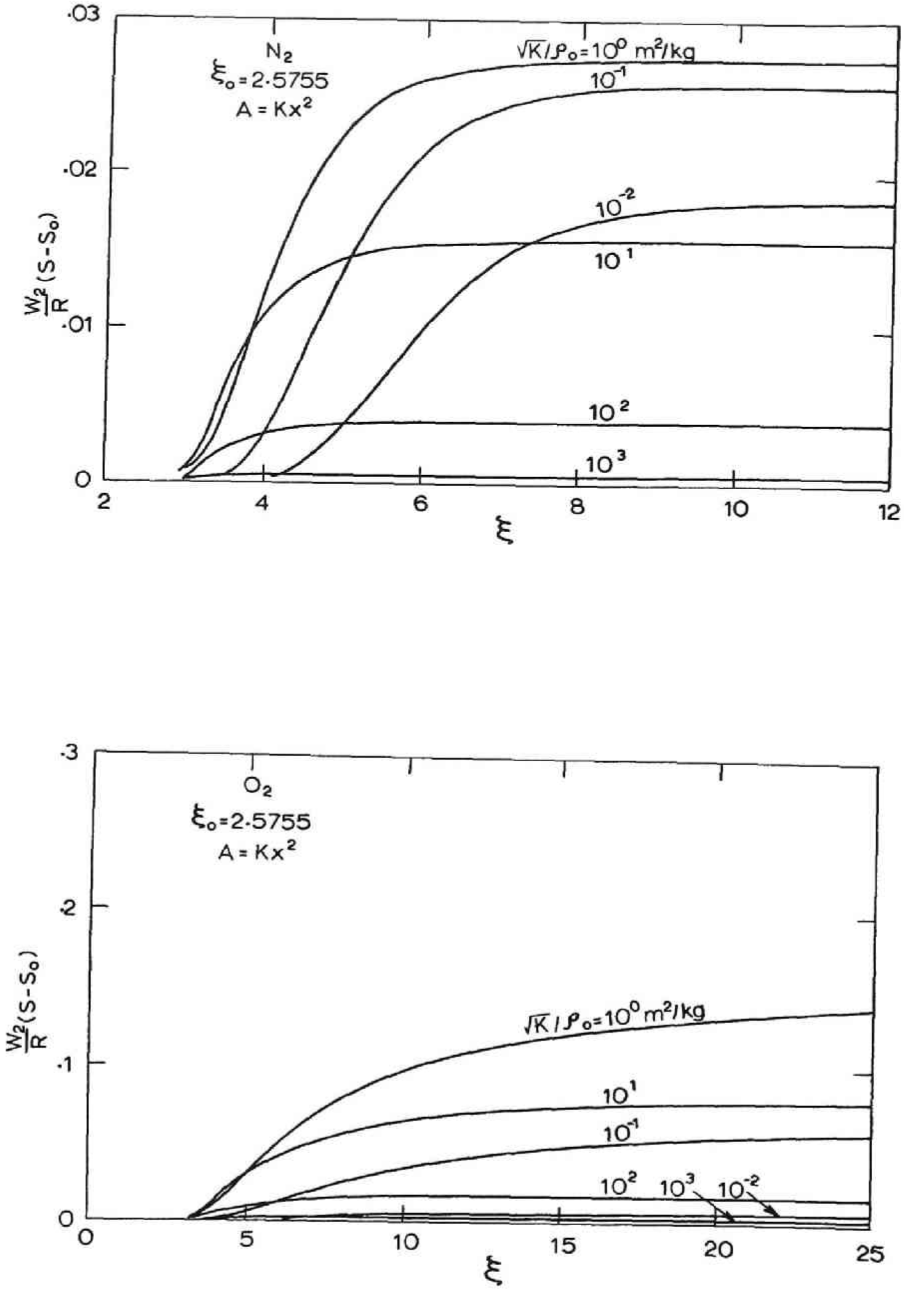

Fig. 5 Distribution of entropy.

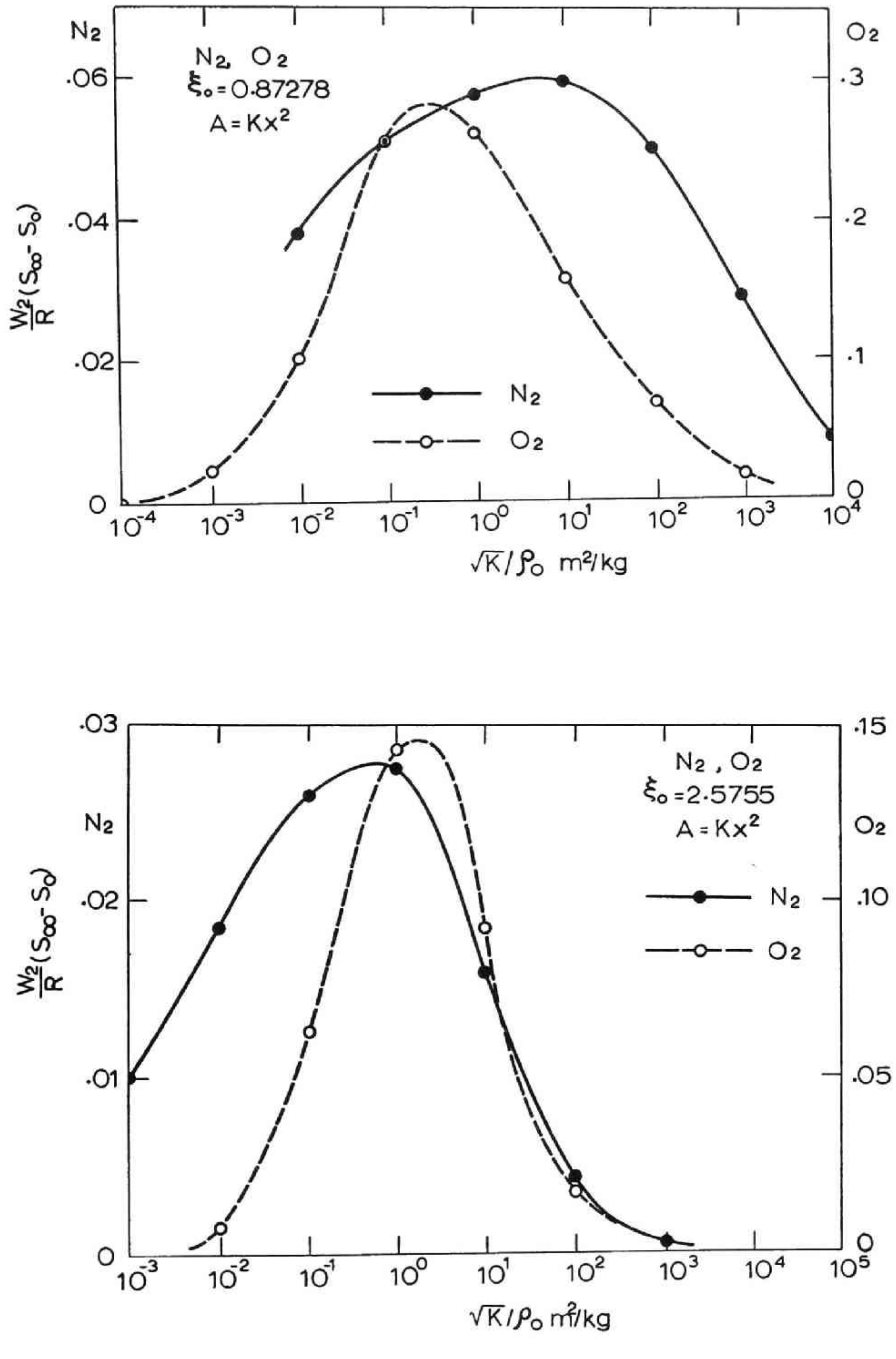

Fig. 6 Limiting value of emtropy.

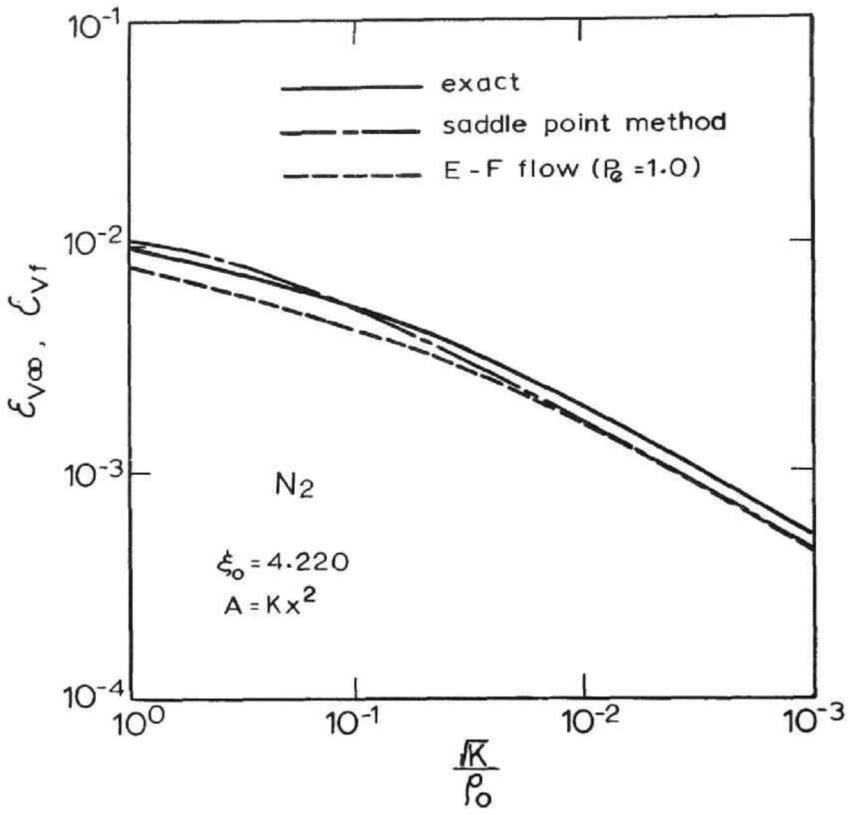

Fig. 7 Limiting value of vibrational energy.

4. Entropy and Asymptotic Behaviors of Flows Far Downstream

Our discussions given in the last section suggest the importance of investigation of the final flow patterns. Furthermore it is very interesting purely theoretically as well as practically to know how the increasing entropy affects the relaxation phenomenon.

Consider the region far downstream of a throat in a nozzle and consider the nozzle geometry described by

$$A = Kx^n \quad , \tag{35}$$

where K and n are positive constants and the latter is less than or equal to 2. Then the rate equation can be reduced finally to the form

$$[\lambda \xi^{\kappa} \exp(-l\theta^{s}\xi^{-s})\Theta - \tfrac{2}{5}\xi^{2}(\delta_V - \delta)] \frac{d\delta_V}{d\xi} \approx -(\delta_V - \delta) \,, \tag{36}$$

for N_2 and O_2 gases, where

$$\Theta = \exp[(1 - \frac{1}{n})\frac{W_2}{R}(S - S_0)] \,. \tag{37}$$

Parameters ℓ, s, and κ are constants characteristic to each gas, and λ is nearly constant depending upon the reservoir conditions, nozzle shape and size, vibrational temperature, and kind of a gas. It is surely worth noting that when $n > 1$, an increase in entropy has negative effect on the vibrational relaxation phenomenon, when $n < 1$ positive effect and when $n = 1$ no effect.

5. Concluding Remarks

The effects of increasing entropy on the flowfields in non-equilibrium nozzle flows of vibrationally relaxing diatomic gases have been studied in detail.

A conclusion can be drawn that, in general at least theoretically under the fixed reservoir conditions, the maximum critical mass flow is the frozen one, while the minimum is the one which is somewhat smaller than the equilibrium.

A new criterion for the validity of the equilibrium-frozen flow approximation have been suggested mainly in terms of the entropy. The quantities Ω_1, Ω_2, and Ω_3 defined here are not always independent with each other and usually the second is so small that it is less important than the others. Up to the present, almost all attempts to estimate the accuracy of this approximation have been done by using the values of Ω_1 only.

It may be worth noting once again that the most important result in the last section is the fact that when $n>1$, increasing entropy has negative effect on the vibrational relaxation phenomenon, when $n<1$ positive effect and when $n = 1$ no effect. The increase in entropy often affects seriously distributions of translational-rotational temperature and then the vibrational temperature. It is the case above all for the flows far downstream of a throat. When $n \neq 1$, the interaction between the entropy and the relaxation phenomenon is essential in the analyses of nonequilibrium flows at least far downstream of the throat..

It must be noticed that it is quite possible to repeat the above analyses for nonequilibrium flows of a dissociating gas or an ionizing gas.

CHAPTER IV ANALYTICAL TREATMENT BY THE METHOD OF STRAINED COORDINATES

1. Introductory Remarks

There have been many studies of nonequilibrium nozzle flows of vibrationally relaxing or chemically reacting gases, almost all of which have been numerical and only a few analytical.[4)22)] From the practical point of view, the numerical solutions themselves are valuable, but they are not always sufficient for developing general and theoretical discussions. The main reason lies in the "ambiguity" in the accuracy of the numerical results. This is particularly the case for the determination of critical mass flows in nonequilibrium nozzle flows. Therefore it is desirable and useful to obtain, if possible, an analytical solution for the subsonic region in nonequilibrium nozzle flows.

The author has already made some discussions of the problem of determining critical mass flows. Here the discussions will be taken further, and for an ideal dissociating diatomic gas, a new attempt at solving analytically the subsonic region of nonequilibrium nozzle flows will be made.

Up to the present, many devices for simplification of the analysis have been introduced for this problem. Among them, we will use Lighthill's gas model,[9)] the Freeman-type rate equation[24)] and the assumption $\epsilon \ll 1$,[22)23)] where the parameter ϵ is the ratio of the temperature at the critical point to the dissociation energy. All physical quantities are assumed to be capable of being expressed in the form of perturbation expansions in powers of ϵ. These expansions are, however, not always permitted without any restriction on the boundary conditions and nozzle shapes and sizes. Qualitative study on regimes of the subsonic region for the two limiting cases of equilibrium and frozen flows will make it clear that, at least when $K = O(1)$ Or $(1 - \epsilon K)/K = O(1)$, where the parameter K is the ratio of the dissociated mass fraction to the parameter ϵ, it is natural and reasonable to assume tentatively that perturbation expansions in powers of ϵ are possible for all flow variables. This also suggests that it may be possible to expand the flow variables in such perturbation expansions even for general nonequilibrium flows which are not markedly deviated from equilibrium at least in the subsonic region considered.

When the perturbation method is applied to the first approximation, a singularity appears near the throat. The method of strained coordinates, or the P. L. K. method, must therefore be applied in order to obtain a uniformly valid solution in the whole subsonic region.[25] The solution constructed by this method finally contains only the two parameters ϵ and K, the values of which are estimated beforehand as precisely as possible. This is applied to the stagnation point to determine the exact values of ϵ and K. Once these are determined, the solution is valid not only in the subsonic region but also in the supersonic region up to some point downstream of the throat. However, the solution cannot always be applied to an arbitrary region downstream of the throat. In order to improve the solution so that it is valid in any supersonic region, a few more difficulties must be overcomed, and in this point, the studies by Cheng and Lee[22][23] are significant and instructive. However, considerations on the supersonic region will not be made here.

2. Basic Equations

The governing equations for an ideal dissociating diatomic gas may be written as

$$\rho u A = \rho_t u_t = \rho_* u_* A_* = m \text{, const.} \tag{1}$$

$$\frac{1}{2}u^2 + h = h_0 \tag{2}$$

$$dh - \frac{1}{\rho}dp = 0 \tag{3}$$

$$u\frac{d\alpha}{dx} = CT^{-s}\rho\left[(1-\alpha)T^d e^{-D/T} - \frac{\rho}{\rho_D}\alpha^2\right] \tag{4}$$

$$h = (4+\alpha)\frac{R}{W_2}T + \frac{R}{W_2}D\alpha \tag{5}$$

$$p = \frac{R}{W_2}\rho T(1+\alpha), \tag{6}$$

where A is the cross-sectional area ratio (equal to (1+A) in the previous chapters) and the parameters ρ_D, C, d and s in the rate equation (4) are constants characteristic to each gas. The other notations in this chapter are the same as those in Ch. I, unless otherwise defined. For an equilibrium flow, Eq. (3) can be replaced by an equation expressing the constancy of entropy,[2) 26)] which becomes algebraic when d = 0, namely

$$3\ln\left(\frac{T}{D}\right) + (1+\alpha)\frac{D}{T} + \alpha + 2\ln\left(\frac{\alpha}{1-\alpha}\right) = \text{const.}, \tag{7}$$

and Eq. (4) can be replaced by the law of mass action

$$\frac{\alpha^2}{1-\alpha} = \frac{\rho_D}{\rho}\exp\left(-\frac{D}{T}\right). \tag{8}$$

In this chapter, we consider only the case of d = 0 for brevity. Here we introduce nondimensionalized quantities

$$\sigma = \frac{A}{A_*}, \quad \bar{\alpha} = \frac{\alpha}{\alpha_*}, \quad \bar{\rho} = \frac{\rho}{\rho_*},$$

$$\bar{u} = \frac{u}{u_*}, \quad \theta = \frac{T_*}{T}, \quad g(\sigma) = \left(\frac{dA}{dx}\right) \Big/ \left(\frac{dA}{dx}\right)_*, \tag{9}$$

and parameters

$$\left.\begin{aligned} &\epsilon = \frac{T_*}{D}, \quad K = \frac{D}{T_*}\alpha_* = \frac{\alpha_*}{\epsilon}, \quad \Gamma = \frac{2K}{M_*^2} \\ &\varphi = \frac{c_*}{\alpha_*}, \quad Q = -P\alpha_* \Big/ \left[K\left(\frac{d\alpha}{d\sigma}\right)_*\right], \end{aligned}\right\} \tag{10}$$

where

$$M_* = u_* \Big/ \sqrt{\frac{R}{W_2} T_*}, \tag{11}$$

$$P = -\left[\frac{u_*}{A_*}\left(\frac{d\alpha}{d\sigma}\right)_*\left(\frac{dA}{dx}\right)_*\right] \Big/ \left[\frac{C}{\rho_D} T_*^{-s} \rho_*^2 \alpha_*^2\right], \tag{12}$$

$$\frac{c_*^2}{1-c_*} = \frac{\rho_D}{\rho_*} \exp\left(-\frac{D}{T_*}\right). \tag{13}$$

Substituting these into the basic equations, we have

$$\bar{\rho}\bar{u}\sigma = 1, \tag{14}$$

$$\theta d\bar{\alpha} = \left(\frac{1}{K} + \epsilon\bar{\alpha}\right)\frac{d\bar{\rho}}{\bar{\rho}} + \frac{3}{K}\frac{d\theta}{\theta}, \tag{15}$$

$$\bar{u}^2 = 1 + \Gamma\left\{(1-\bar{\alpha}) + \frac{4}{K}\left(1-\frac{1}{\theta}\right) + \epsilon\left(1-\frac{\bar{\alpha}}{\theta}\right)\right\}, \tag{16}$$

$$\bar{u}\frac{d\bar{\alpha}}{d\sigma} = \frac{\theta^s\bar{\rho}}{KQg}\left\{\varphi^2\left(\frac{1-\epsilon K\bar{\alpha}}{1-\epsilon K\varphi}\right)\exp\left(-\frac{1}{\epsilon}(\theta-1)\right) - \bar{\rho}\bar{\alpha}^2\right\}, \tag{17}$$

Especially, for equilibrium flows, Eqs. (15) and (17) are replaced, respectively, by

$$(\theta-1) + \epsilon K(\bar{\alpha}\theta - 1) - 3\epsilon \ln\theta + \epsilon^2 K(\bar{\alpha}-1) + 2\epsilon\ln\bar{\alpha} + 2\epsilon\ln\left(\frac{1-\epsilon K}{1-\epsilon K\bar{\alpha}}\right) = 0, \tag{18}$$

$$\bar{\alpha}^2\left(\frac{1-\epsilon K}{1-\epsilon K\bar{\alpha}}\right) = \frac{1}{\bar{\rho}}\exp\left[\frac{1}{\epsilon}(1-\theta)\right]. \tag{19}$$

Now, for general nonequilibrium flows, combining Eqs. (14), (15) and (16) yields

$$\theta\left\{1-\frac{3}{4}\left(\frac{1+\epsilon\frac{1}{\theta}}{1+\frac{1}{4}\epsilon K\tilde{\alpha}}\right)\right\}d\tilde{\alpha}+\left(\frac{1}{K}+\epsilon\tilde{\alpha}\right)\frac{d\sigma}{\sigma}=\left\{\frac{6}{K\Gamma}\frac{\theta\tilde{u}^2}{\left(\frac{4}{K}+\epsilon\tilde{\alpha}\right)}-\left(\frac{1}{K}+\epsilon\tilde{\alpha}\right)\right\}\frac{d\tilde{u}}{\tilde{u}}. \tag{20}$$

The regularity condition of Eq. (20) at the sonic point yields

$$\Gamma=\frac{6K}{(4+\epsilon K)(1+\epsilon K)}, \tag{21}$$

$$\left(\frac{d\tilde{\alpha}}{d\sigma}\right)_*=-\frac{1}{K}\frac{(1+\epsilon K)(4+\epsilon K)}{[1+\epsilon(K-3)]}. \tag{22}$$

The equation defining Γ yields, with Eq. (21),

$$M_*^2=\frac{1}{3}(1+\epsilon K)(4+\epsilon K). \tag{23}$$

3. General Discussions

In our analysis in this chapter, the parameter ϵ plays a very important and indispensable role, since every discussion is made under the assumption

$$\epsilon\ll 1. \tag{24}$$

The Arrhenius factor with small ϵ makes the composition $\bar{\alpha}$ very sensitive to perturbation in the temperature or in θ. The next most important parameter is K, which is the ratio of the energy stored in dissociation to the energy associated with the translational motion.

Now Eq. (16) at the critical point can be written in the form

$$\alpha_*^2+\left(11+\frac{6}{\epsilon}\right)\alpha_*+\left(28-6\frac{\beta}{\epsilon}\right)=0, \tag{25}$$

where

$$\beta=h_0/\left(\frac{R}{W_2}\right)D. \tag{26}$$

Equation (25) can be taken as a quadratic with respect to α_*

and can be solved as follows

$$\alpha_* = \frac{1}{2\epsilon}\{-(6+11\epsilon)+\sqrt{36+(132+24\beta)\epsilon+9\epsilon^2}\},$$

or

$$K = \frac{1}{2\epsilon^2}\{-(6+11\epsilon)+\sqrt{36+(132+24\beta)\epsilon+9\epsilon^2}\}. \tag{27}$$

In Fig. 1, the parameter K is shown as a function of the parameter ϵ and the gas density at the critical point for equilibrium flows. In Figs. 2 and 3, the parameters ϵ and K for equilibrium flows, determined purely numerically, and those for frozen flows, which are determined from the following equations,

$$\epsilon_f = \frac{6(\beta-\alpha_0)}{(7+\alpha_0)(4+\alpha_0)}, \tag{28}$$

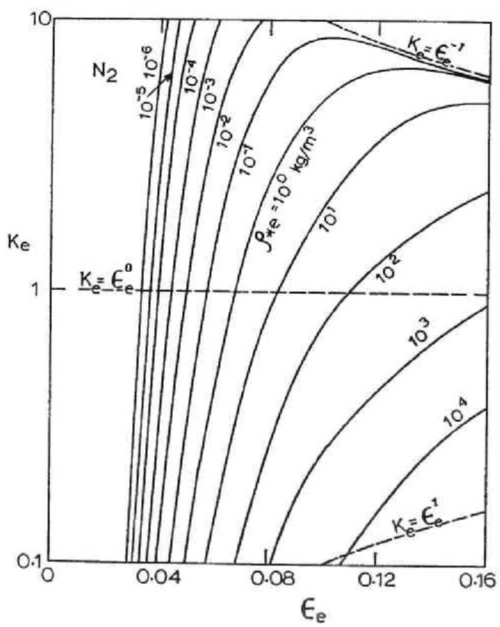

Fig. 1 Parameter K as a function of the parameter ϵ and density ρ_* for equilibrium flows.

$$K_f = \frac{\alpha_0(7+\alpha_0)(4+\alpha_0)}{6(\beta-\alpha_0)}. \tag{29}$$

are presented as functions of α_0 and β, the values of which are specified at the reservoir. It is quite easy to see that

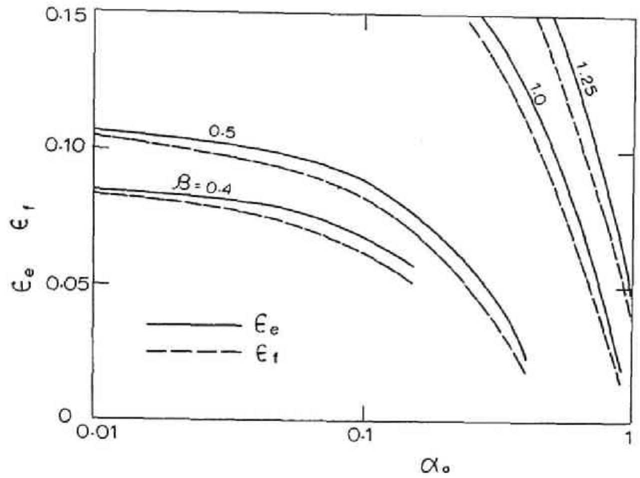

Fig. 2 Parameter ϵ for equilibrium flows and frozen flows as a function of the degree of dissociation α_0 and the parameter β.

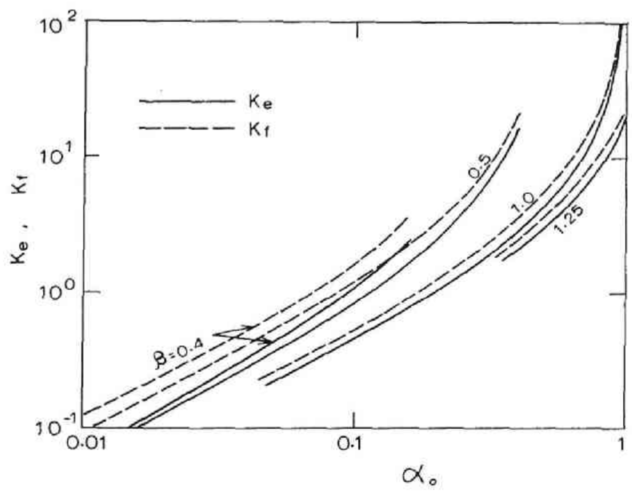

Fig. 3 Parameter K for equilibrium flows and frozen flows as a function of the degree of dissociation α_0 and the parameter β.

$$\epsilon_f < \epsilon < \epsilon_e \tag{30}$$

$$K_e < K < K_f . \tag{31}$$

These help considerably in roughly determining the values of ϵ and K beforehand in our analysis, as discussed below.

It may easily be seen that both the parameters P and φ indicate the degree of departure of the flow from equilibrium, and they are related to each other by the relation

$$P = \left\{1 - \left(\frac{1-\epsilon K}{1-\epsilon K\varphi}\right)\varphi^2\right\}. \tag{32}$$

For equilibrium flows, the equations of energy and entropy becomes as follows at the stagnation point

$$\left[\left(\frac{14}{3} - \frac{4}{\theta_0}\right) + K(1-\alpha_0)\right] + \epsilon K\left(\frac{11}{6} - \frac{\bar{\alpha}_0}{\theta_0}\right) + \frac{1}{6}\epsilon^2 K^2 = 0, \tag{33}$$

$$(\theta_0 - 1) + \epsilon K(\bar{\alpha}_0\theta_0 - 1) - 3\epsilon \ln \theta_0 + \epsilon^2 K(\bar{\alpha}_0 - 1) + 2\epsilon \ln \bar{\alpha}_0 + 2\epsilon \ln\left(\frac{1-\epsilon K}{1-\epsilon K\alpha_0}\right) = 0. \tag{34}$$

We can easily understand that the most significant flow regimes practically and theoretically are those in the cases of $K \gtrsim O(1)$ and $(1 - \epsilon K) = O(1)$. With Eqs. (33) and (34), under the condition of Eq. (24), we obtain the results in these cases as follows:

(i) the case of $\epsilon K = 0(1)$ and $(1-\epsilon K) = 0(1)$

$$\left.\begin{aligned} \bar{\alpha}_0 &= 1 + 0(\epsilon), \\ \theta_0 &= 1 + 0(\epsilon), \end{aligned}\right\} \tag{35}$$

(ii) the case of $\epsilon K = 0(\epsilon)$ or $K = 0(1)$

$$\left.\begin{aligned} \bar{\alpha}_0 &= \left(1 + \frac{2}{3K}\right) + 0(\epsilon), \\ \theta_0 &= 1 + 0(\epsilon). \end{aligned}\right\} \tag{36}$$

In Figs. 4 and 5, the nondimensionalized degree of dissociation and inverse temperature at the reservoir (obtained purely numerically) are presented as functions of α_0 and β, and it can be seen that these illustrate well the features which have been discussed. The characteristic values of N_2 gas used in these

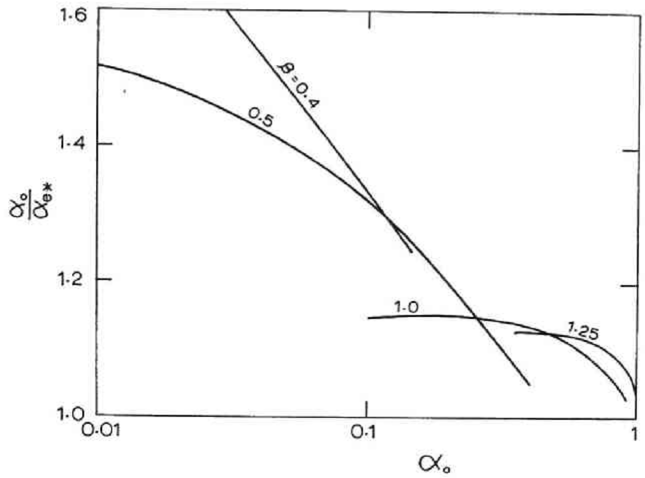

Fig. Ratio of the degree of dissociation at the reservoir to that at the throat, α_0/α_*, as a function of α_0 and β.

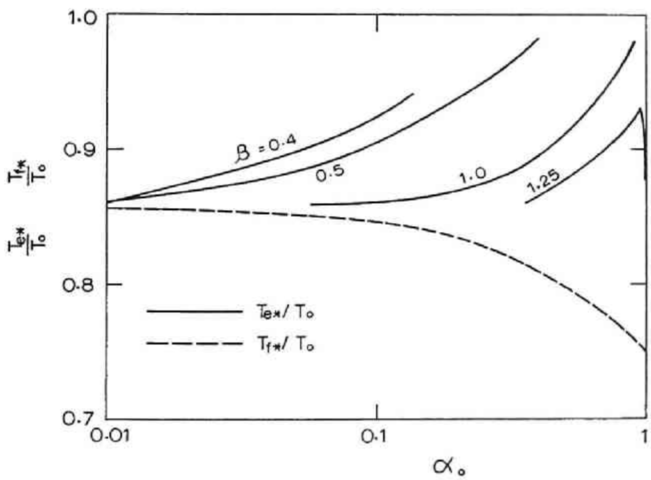

Fig. 5 Ratio of the temperature at the throat to that at the reservoir, T_*/T_0, as a function of α_0 and β.

calculations are shown in Table 1.

Table 1 Characteristic values of N_2 gas.

$W_2 = 28.0$	(kg/kmol)	$C = 3.0\times10^8/W_2$	(m^3/kg·sec)
$D = 113260.0$	(°K)	$\rho_D = 1.26\times10^5$	(kg/m^3)
$s = 1.5$			

4. Solution by the P. L. K. Method

4. 1 Nonequilibrium Solution

We consider the case where the nozzle geometry is given, for example, by

$$\frac{A}{A_t} = (1+kx^2), \tag{37}$$

where k is a positive constant. Then the function $g(\sigma)$ which was introduced in the process of nondimensionalization is determined in the form

$$g(\sigma) = \delta\left(\frac{\sigma-\sigma_t}{1-\sigma_t}\right)^{1/2}, \qquad \delta = \begin{cases} 1 & x<0, \\ -1 & x>0. \end{cases} \tag{38}$$

The following analysis is carried out under the conditions

$$\varphi = 0(1) \tag{39}$$

$$K = 0(1) \tag{40}$$

in addition to that of Eq. (24). The condition of Eq. (39) means that the flow at the critical point does not deviate markedly from equilibrium. Then it is natural and reasonable to assume that the flow variables can be expressed in the form of perturbation expansions in powers of ϵ as follows

$$\left.\begin{aligned}\bar{\alpha} &= a+\epsilon\alpha_1+\epsilon^2\alpha_2+0(\epsilon^3)\,,\\ \theta &= t+\epsilon\theta_1+\epsilon^2\theta_2+0(\epsilon^3)\,,\\ \bar{u} &= \eta+\epsilon u_1+\epsilon^2 u_2+0(\epsilon^3)\,,\\ \sigma &= \xi+\epsilon\sigma_1+\epsilon^2\sigma_2+0(\epsilon^3)\,,\end{aligned}\right\}\qquad(41)$$

where a, α_1, α_2 ..., t, θ_1, θ_2 ..., η, u_1, u_2 ..., and σ_1, σ_2 ... are all functions of a new independent variable ξ, and satisfy the boundary conditions

$$\left.\begin{aligned}&a_* = t_* = \eta_* = \xi_* = 1\,,\\ &\alpha_{i*} = \theta_{i*} = u_{i*} = \sigma_{i*} = 0\,, \quad (i=1,2,\dots)\,.\end{aligned}\right\}\qquad(42)$$

Furthermore the parameters K, Γ, φ and Ω can also be expanded in power series of ϵ as

$$\left.\begin{aligned}K &= \kappa+\epsilon K_1+\epsilon^2 K_2+0(\epsilon^3)\,,\\ \Gamma &= \gamma+\epsilon\Gamma_1+\epsilon^2\Gamma_2+0(\epsilon^3)\,,\\ \varphi &= f+\epsilon\varphi_1+\epsilon^2\varphi_2+0(\epsilon^3)\,,\\ Q &= q+\epsilon Q_1+\epsilon^2 Q_2+0(\epsilon^3)\,.\end{aligned}\right\}\qquad(43)$$

The justification for expanding the parameters in such forms as Eq. (43) comes from the assumption of Eq. (41), since the values of these parameters can be finally determined after solving the whole flowfield in the subsonic region, as carried out with Eq. (41).

Substituting Eq. (43) into Eq. (21), and considering the condition of Eq. (40), we have

$$\left.\begin{aligned}&\gamma = \frac{3}{2}\kappa\,, \qquad \Gamma_1 = -\frac{15}{8}\kappa^2+\frac{3}{2}K_1\,,\\ &\Gamma_2 = \frac{63}{32}\kappa^3-\frac{15}{4}\kappa K_1+\frac{3}{2}K_2,\,\dots\,.\end{aligned}\right\}\qquad(44)$$

Similarly substituting Eq. (43) into Eqs. (22), (32) and the last equation of Eq. (10), and considering the condition of Eq. (39) as well as that of Eq. (40), we have

$$\left.\begin{aligned} q &= \frac{1}{4}(1-f^2), \\ Q_1 &= -\frac{1}{2}f\varphi_1+\frac{1}{4}\kappa(1-f)f^2-\frac{1}{4}\left(3+\frac{1}{4}\kappa\right)(1-f^2), \\ Q_2 &= -\frac{1}{2}f\varphi_2-\frac{1}{4}\varphi_1^2+\frac{1}{4}\kappa(2-3f)f\varphi_1+\frac{1}{2}\left(3+\frac{1}{4}\kappa\right)f\varphi_1 \\ &\quad -\frac{1}{4}\left(3+\frac{1}{4}\kappa\right)\left[(1-f)f^2\kappa-\left(3+\frac{1}{4}\kappa\right)(1-f^2)\right] \\ &\quad -\frac{9}{4}\left(1-\frac{1}{4}\kappa\right)(1-f^2)+\frac{1}{4}(1-f)f^3\kappa^2,\ \cdots\cdots \end{aligned}\right\} \tag{45}$$

where it is assumed that

$$(1-\varphi^2) = 0(1), \tag{46}$$

in addition to the condition of Eq. (39). Systematic analysis requires that the function $g(\sigma)$ can also be expanded in power series, for example, as

$$g = G+\epsilon g_1+\epsilon^2 g_2+0(\epsilon^3), \tag{47}$$

where

$$\left.\begin{aligned} G &= \delta\left(\frac{\xi-\xi_t}{1-\xi_t}\right)^{1/2}, \\ \frac{g_1}{G} &= \frac{1}{2}\left(\frac{\sigma_1-\sigma_{1t}}{\xi-\xi_t}+\frac{\sigma_{1t}}{1-\xi_t}\right), \\ \frac{g_2}{G} &= \frac{1}{2}\left[\frac{\sigma_2-\sigma_{2t}}{\xi-\xi_t}+\frac{\sigma_{2t}}{1-\xi_t}+\frac{\sigma_{1t}(\sigma_1-\sigma_{1t})}{(1-\xi_t)(\xi-\xi_t)}+\left(\frac{\sigma_{1t}}{1-\xi_t}\right)^2\right] \\ &\quad -\frac{1}{8}\left[\frac{\sigma_1-\sigma_{1t}}{\xi-\xi_t}+\frac{\sigma_{1t}}{1-\xi_t}\right]^2,\ \cdots\cdots \end{aligned}\right\} \tag{48}$$

It is clear that these expansions are possible only when the two conditions

$$\xi \geqq \xi_t, \tag{49}$$

$$\frac{d\sigma_i}{d\xi} = \text{finite} = 0(1), \tag{50}$$

are satisfied. Combining Eq.(12) and the last equation of Eq. (10) with Eqs. (49) and (50), we have

$$
\left.
\begin{aligned}
&2\sqrt{k}\,\xi_t\left(\frac{1}{\xi_t}-1\right)^{1/2}=\left[Cq\rho_D\exp\left(-\frac{2}{\epsilon}\right)\right]\Big/\left[\frac{2}{\sqrt{3}}\sqrt{\frac{R}{W_2}}D^{1/2+s}\epsilon^{7/2+s}(f^2\kappa)^2\right],\\
&\frac{\sigma_{1t}}{\xi_t}-\frac{1}{2}\frac{\sigma_{1t}}{\xi_t(1-\xi_t)}=\frac{Q_1}{q}-2f\kappa-4\frac{\varphi_1}{f}-2\frac{K_1}{\kappa}-\frac{5}{8}\kappa,\\
&\frac{\sigma_{2t}}{\xi_t}-\frac{1}{2}\frac{\sigma_{2t}}{\xi_t(1-\xi_t)}-\frac{1}{8}\frac{\sigma_{1t}{}^2}{\xi_t{}^2(1-\xi_t)^2}=\frac{Q_2}{q}+\frac{Q_1K_1}{q\kappa}-2\frac{K_2}{\kappa}+f^2\kappa^2\\
&\quad+6f\kappa\left(\frac{\varphi_1}{f}+\frac{K_1}{\kappa}\right)+10\left(\frac{\varphi_1}{f}+\frac{K_1}{\kappa}\right)^2-4\left(\frac{\varphi_2}{f}+\frac{\varphi_1K_1}{f\kappa}\right)+\kappa\left(\frac{41}{128}\kappa-\frac{55}{48}\right)\\
&\quad+\frac{5}{8}\kappa\left(2f\kappa+4\frac{\varphi_1}{f}+3\frac{K_1}{\kappa}\right)-2\frac{K_1}{\kappa}\left(f\kappa+2\frac{\varphi_1}{f}+2\frac{K_1}{\kappa}\right)\\
&\quad-\left(\frac{K_1}{\kappa}+\frac{Q_1}{q}\right)\left(2f\kappa+4\frac{\varphi_1}{f}+3\frac{K_1}{\kappa}+\frac{5}{8}\kappa\right),\ \dots.
\end{aligned}
\right\}
\quad (51)
$$

These are used in order to determine the values of f, φ_1, φ_2, ...

Substituting Eqs. (41), (43) and (47) into Eqs. (14) to (17), we obtain

$$
\left.
\begin{aligned}
&t=1,\\
&\eta^2=1+\gamma\left[(1-a)+\frac{4}{\kappa}\left(1-\frac{1}{t}\right)\right],\\
&tda=-\frac{1}{\kappa}\left(\frac{d\xi}{\xi}+\frac{d\eta}{\eta}\right)+\frac{3}{\kappa}\frac{dt}{t},
\end{aligned}
\right\}
\quad (52)
$$

$$
\left.
\begin{aligned}
&\theta_1=2\ln f-\ln\left[\frac{a^2}{\xi\eta}+\frac{\kappa q\xi\eta^2}{t^s}G\left(\frac{da}{d\xi}\right)\right],\\
&2\eta u_1=\Gamma_1\left[(1-a)+\frac{4}{\kappa}\left(1-\frac{1}{t}\right)\right]+\gamma\left[\left(1-\frac{a}{t}\right)-\alpha_1+\frac{4}{\kappa}\frac{\theta_1}{t^2}-\left(1-\frac{1}{t}\right)\frac{4K_1}{\kappa^2}\right],\\
&\theta_1 da+td\alpha_1=-\frac{1}{\kappa}\left[\left(\frac{du_1}{\eta}-\frac{u_1d\eta}{\eta^2}\right)+\left(\frac{d\sigma_1}{\xi}-\frac{\sigma_1d\xi}{\xi^2}\right)\right]-\left(a-\frac{K_1}{\kappa^2}\right)\left(\frac{d\eta}{\eta}+\frac{d\xi}{\xi}\right)\\
&\quad+\frac{3}{\kappa}\left(\frac{d\theta_1}{t}-\frac{\theta_1dt}{t^2}\right)-3\frac{K_1}{\kappa^2}\frac{dt}{t},
\end{aligned}
\right\}
\quad (53)
$$

$$
\begin{aligned}
&\theta_2=2\frac{\varphi_1}{f}+\kappa(f-a)-2\frac{\alpha_1}{a}+\frac{u_1}{\eta}+\frac{\sigma_1}{\xi}\\
&\quad-\frac{\left(\dfrac{\kappa q\xi^2\eta^3}{a^2t^s}G\right)\left[\left(\dfrac{d\alpha_1}{d\xi}\right)+\left(\dfrac{da}{d\xi}\right)\left(\dfrac{Q_1}{q}+\dfrac{K_1}{\kappa}+\dfrac{g_1}{G}+2\dfrac{\sigma_1}{\xi}+3\dfrac{u_1}{\eta}-2\dfrac{\alpha_1}{a}-s\dfrac{\theta_1}{t}-\dfrac{d\sigma_1}{d\xi}\right)\right]}{\left[1+\dfrac{\kappa q\xi^2\eta^3}{a^2}G\left(\dfrac{da}{d\xi}\right)\right]},
\end{aligned}
$$

$$
\left.\begin{aligned}
u_1^2+2\eta u_2 &= \gamma\left\{\frac{4}{\kappa}\left(\frac{\theta_2}{t^2}-\frac{\theta_1^2}{t^3}\right)-\alpha_2-\left(\frac{\alpha_1}{t}-\frac{a\theta_1}{t^2}\right)-\frac{\theta_1}{t^2}\frac{4K_1}{\kappa^2}+\frac{4}{\kappa}\left(\frac{K_1^2}{\kappa^2}-\frac{K_2}{\kappa}\right)\right.\\
&\quad\left.\times\left(1-\frac{1}{t}\right)\right\}+\Gamma_1\left[\left(1-\frac{a}{t}\right)-\alpha_1+\frac{4}{\kappa}\frac{\theta_1}{t^2}-\left(1-\frac{1}{t}\right)\frac{4K_1}{\kappa^2}\right]\\
&\quad+\Gamma_2\left[(1-a)+\frac{4}{\kappa}\left(1-\frac{1}{t}\right)\right],\\
\theta_2 da+\theta_1 d\alpha_1+t d\alpha_2 &= -\frac{1}{\kappa}\left\{\left[\left(\frac{du_2}{\eta}-\frac{u_1 du_1}{\eta^2}\right)-\left(\frac{u_2}{\eta}-\frac{u_1^2}{\eta^2}\right)\frac{d\eta}{\eta}\right]+\left[\left(\frac{d\sigma_2}{\xi}-\frac{\sigma_1 d\sigma_1}{\xi^2}\right)\right.\right.\\
&\quad\left.\left.-\left(\frac{\sigma_2}{\xi}-\frac{\sigma_1^2}{\xi^2}\right)\frac{d\xi}{\xi}\right]\right\}-\left(a-\frac{K_1}{\kappa^2}\right)\left[\left(\frac{du_1}{\eta}-\frac{u_1 d\eta}{\eta^2}\right)+\left(\frac{d\sigma_1}{\xi}-\frac{\sigma_1 d\xi}{\xi^2}\right)\right]\\
&\quad-\left(\alpha_1+\frac{K_1^2}{\kappa^3}-\frac{K_2}{\kappa^2}\right)\left(\frac{d\eta}{\eta}+\frac{d\xi}{\xi}\right)+\frac{3}{\kappa}\left[\left(\frac{d\theta_2}{t}-\frac{\theta_1 d\theta_1}{t^2}\right)-\left(\frac{\theta_2}{t}-\frac{\theta_1^2}{t^2}\right)\frac{dt}{t}\right]\\
&\quad+\frac{3}{\kappa}\left[\left(\frac{K_1^2}{\kappa^2}-\frac{K_2}{\kappa}\right)\frac{dt}{t}-\frac{K_1}{\kappa}\left(\frac{d\theta_1}{t}-\frac{\theta_1 dt}{t^2}\right)\right].
\end{aligned}\right\} \quad (54)
$$

With the boundary conditions of Eq. (42), Eq. (52) yields

$$
\left.\begin{aligned}
&t=1,\\
&\eta^2=1+\gamma(1-a),\\
&a=1-\frac{1}{\kappa}\ln(\xi\eta).
\end{aligned}\right\} \quad (55)
$$

It can be found that

$$
\left(\frac{d\xi}{da}\right)=0, \quad \text{at} \quad \xi=\frac{2}{\sqrt{3}}e^{-1/6}, \quad (56)
$$

and so the condition of Eq. (49) is satisfied by setting

$$
\xi_t=\frac{2}{\sqrt{3}}e^{-1/6}, \quad \eta_t=\frac{\sqrt{3}}{2}, \quad a_t=\left(1+\frac{1}{4\gamma}\right). \quad (57)
$$

With Eq. (55) and the boundary conditions of Eq. (42), Eq. (63) yields

$$
\left.\begin{aligned}
&\theta_1=2\ln f-\ln\left[\frac{a^2}{\xi\eta}+\kappa q\xi\eta^2 G\left(\frac{da}{d\xi}\right)\right],\\
&\begin{bmatrix}1 & \frac{1}{\kappa}\\ 1 & \frac{2}{\gamma}\eta^2\end{bmatrix}\begin{bmatrix}\alpha_1\\ \frac{u_1}{\eta}\end{bmatrix}=\begin{bmatrix}-\frac{1}{\kappa}\left(\frac{\sigma_1}{\xi}\right)-\int_1\theta_1 da-\int_1\left(a-\frac{K_1}{\kappa^2}\right)\frac{d}{da}(\ln\xi\eta)da+\frac{3}{\kappa}\theta_1\\ \left(\frac{\Gamma_1}{\gamma}+1\right)(1-a)+\frac{4}{\kappa}\theta_1\end{bmatrix}.
\end{aligned}\right\} \quad (58)
$$

Letting

$$\Delta = \begin{vmatrix} 1 & \dfrac{1}{\kappa} \\ 1 & \dfrac{2}{\gamma}\eta^2 \end{vmatrix} = \left(\frac{2}{\gamma}\eta^2 - \frac{1}{\kappa}\right), \tag{59}$$

we have

$$\Delta = 0 \quad \text{at} \quad \eta = \eta_t \quad \text{or} \quad \xi = \xi_t . \tag{60}$$

Then it follows that

$$\begin{vmatrix} -\dfrac{1}{\kappa}\left(\dfrac{\sigma_1}{\xi}\right)_t - \displaystyle\int_1^{a_t} \theta_1 da - \int_1^{a_t}\left(a - \frac{K_1}{\kappa^2}\right)\frac{d}{da}(\ln \xi\eta)da + \frac{3}{\kappa}\theta_{1t} & \dfrac{1}{\kappa} \\ \left(\dfrac{\Gamma_1}{\gamma}+1\right)(1-a_t) + \dfrac{4}{\kappa}\theta_{1t} & \dfrac{2}{\gamma}\eta_t^2 \end{vmatrix} = 0, \tag{61}$$

which gives one of the conditions that must be satisfied by the straining function σ_1. Hence we consider the function σ_1 in the form

$$\frac{\sigma_1}{\xi} = \frac{1}{2}\kappa^2(a^2-1) + \kappa\left(1+\frac{\Gamma_1}{\gamma}\right)(a-1) - \theta_1 - \kappa\int_1 \theta_1 da - K_1(a-1)$$

$$-\eta^2(1-\eta^2)\left(1-\frac{2\kappa}{\gamma}\eta^2\right)\Theta_1(a), \tag{62}$$

where $\Theta_1(a)$ is an arbitrary regular function of a. It is easy to confirm that Eq. (62) satisfies the boundary conditions of Eq. (42). Since, moreover, the function σ_1 must satisfy the condition of Eq. (50), the regular function $\Theta_1(a)$ must satisfy

$$\left[\frac{d}{da}\left(\frac{\sigma_1}{\xi}\right)\right]_t = \kappa^2 a_t + \kappa\left(1+\frac{\Gamma_1}{\gamma}\right) - \left(\frac{d\theta_1}{da}\right)_t - \kappa\theta_{1t} - K_1 - \frac{3}{8}\kappa\Theta_1(a_t) = 0, \tag{63}$$

which is not the sufficient condition but the necessary one for Eq. (50). By choosing such σ_1, we obtain

$$\left.\begin{aligned} \frac{u_1}{\eta} &= \eta^2(1-\eta^2)\Theta_1(a), \\ \alpha_1 &= -\frac{2}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right) + \left(1+\frac{\Gamma_1}{\gamma}\right)(1-a) + \frac{4}{\kappa}\theta_1 . \end{aligned}\right\} \tag{64}$$

Similarly Eq. (52) in conjunction with the boundary conditions of Eq. (42) yields

$$
\left.\begin{aligned}
\theta_2 &= 2\frac{\varphi_1}{f}+\kappa(f-a)-2\frac{\alpha_1}{a}+\frac{u_1}{\eta}+\frac{\sigma_1}{\xi} \\
&\quad -\frac{\left(\frac{\kappa q\xi^2\eta^3}{a^2}G\right)\left[\left(\frac{d\alpha_1}{d\xi}\right)+\left(\frac{da}{d\xi}\right)\left(\frac{Q_1}{q}+\frac{K_1}{\kappa}+\frac{g_1}{G}+2\frac{\sigma_1}{\xi}+3\frac{u_1}{\eta}-2\frac{\alpha_1}{a}-s\theta_1-\frac{d\sigma_1}{d\xi}\right)\right]}{\left[1+\frac{\kappa q\xi^2\eta^3}{a^2}G\left(\frac{da}{d\xi}\right)\right]}, \\
\frac{u_2}{\eta} &= \eta^2(1-\eta^2)\Theta_2(a), \\
\alpha_2 &= -\frac{2}{\gamma}\eta^2\left(\frac{u_2}{\eta}\right)+2\frac{\Gamma_1}{\gamma^2}\eta^2\left(\frac{u_1}{\eta}\right)-\frac{1}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right)^2+\frac{4}{\kappa}(\theta_2-\theta_1{}^2)-\alpha_1+a\theta_1-\frac{4K_1}{\kappa^2}\theta_1 \\
&\quad +\frac{\Gamma_2}{\gamma}(1-a)-\left(\frac{\Gamma_1}{\gamma}\right)^2(1-a) \\
\frac{\sigma_2}{\xi} &= \frac{1}{2}\left(\frac{\sigma_1}{\xi}\right)^2-\kappa\int_1\theta_2 da-\kappa\int_1\theta_1\left(\frac{d\alpha_1}{da}\right)da-\kappa\int_1 a\frac{d}{da}\left(\frac{\sigma_1}{\xi}\right)da+\kappa^2\int_1\alpha_1 da \\
&\quad +\frac{K_1}{\kappa}\left(\frac{\sigma_1}{\xi}\right)+\kappa\left(\frac{K_1{}^2}{\kappa^2}-\frac{K_2}{\kappa}\right)(a-1)-\theta_2+\frac{5}{2}\theta_1{}^2+\frac{K_1}{\kappa}\theta_1+\kappa(\alpha_1-a\theta_1) \\
&\quad +\kappa\left(\frac{\Gamma_2}{\gamma}-\frac{\Gamma_1{}^2}{\gamma^2}\right)(a-1)+\frac{1}{2}\left(\frac{u_1}{\eta}\right)^2+\frac{\kappa}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right)^2-2\frac{\kappa\Gamma_1}{\gamma^2}\eta^2\left(\frac{u_1}{\eta}\right)+\frac{K_1}{\kappa}\left(\frac{u_1}{\eta}\right) \\
&\quad -\kappa\int_1 a\frac{d}{da}\left(\frac{u_1}{\eta}\right)da-\eta^2(1-\eta^2)\left(1-\frac{2\kappa}{\gamma}\eta^2\right)\Theta_2(a),
\end{aligned}\right\} \tag{65}
$$

where the function $\Theta_2(a)$ is also an arbitrary function of a, which satisfies

$$
\begin{aligned}
\left[\frac{d}{da}\left(\frac{\sigma_2}{\xi}\right)\right]_t &= -\kappa\theta_{2t}-\kappa\theta_{1t}+\kappa^2\alpha_{1t}+\kappa(1-\theta_{1t})\left(\frac{d\alpha_1}{da}\right)_t-\left(\frac{d\theta_2}{da}\right)_t+\left(5\theta_{1t}+\frac{K_1}{\kappa}-\kappa a_t\right) \\
&\quad \times\left(\frac{d\theta_1}{da}\right)_t+\kappa\left(\frac{K_1{}^2}{\kappa^2}-\frac{K_2}{\kappa}\right)+\kappa\left(\frac{\Gamma_2}{\gamma}-\frac{\Gamma_1{}^2}{\gamma^2}\right)+\kappa\left[\frac{27}{256}+\frac{3}{32}\left(\frac{\gamma}{\kappa}\right)\right](\Theta_1(a_t))^2 \\
&\quad +\kappa\left[\frac{1}{2}\frac{\gamma K_1}{\kappa^2}-\frac{3}{8}\frac{\Gamma_1}{\gamma}-\frac{1}{2}\gamma a_t\right]\Theta_1(a_t)-\frac{3}{8}\kappa\Theta_2(a_t)=0.
\end{aligned} \tag{66}
$$

We can obtain the solutions of the i-th approximation (i = 1, 2, 3, ...) by repeating the same procedure, but these are not presented here.

4. 2 Equilibrium Solution

For equilibrium flows, the solution obtained above can be considerably simplified, since the rate equation, Eq. (17), is replaced by the law of mass action, Eq. (19), and then the function $g(\sigma)$ does not appear in the basic equations. In this case, we may put $\varphi = 1$ and the expansion of the function $g(\sigma)$ in powers of ϵ becomes unnecessary. Hence the conditions of Eqs. (49) and (50) can be omitted, and the position of the nozzle throat may be determined as the point where the function $\sigma(\xi)$ takes its minimum value. The retention of the conditions of Eqs. (49) and (50), however, even for the equilibrium flows would be convenient and useful in order to compare the equilibrium solution with the nonequilibrium one having the same reservoir conditions. The equilibrium solution are given below.

$$\left.\begin{aligned} & t = 1 , \\ & \eta^2 = 1+\gamma(1-a) , \\ & a = 1-\frac{1}{\kappa}\ln(\xi\eta) , \end{aligned}\right\} \tag{67}$$

$$\left.\begin{aligned} & \theta_1 = \kappa(1-a)-2\ln a , \\ & \frac{u_1}{\eta} = \gamma^2(a-1)\left[\left(1+\frac{1}{\gamma}\right)-a\right]\Theta_1(a) , \\ & \alpha_1 = \left(5+\frac{\Gamma_1}{\gamma}\right)(1-a)-\frac{8}{\kappa}\ln a-\frac{2}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right) , \\ & \frac{\sigma_1}{\xi} = \kappa^2(a^2-1)+\kappa\left(\frac{\Gamma_1}{\gamma}-\kappa-\frac{K_1}{\kappa}\right)(a-1)+2\kappa a\ln a+2\ln a \\ & \qquad +2\frac{\kappa}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right)-\left(\frac{u_1}{\eta}\right) , \\ & \Theta_1(a_t) = \frac{8}{3\kappa}\left\{\kappa^2(2a_t-1)+\kappa\left(2+\frac{\Gamma_1}{\gamma}\right)+\frac{2}{a_t}+2\kappa\ln a_t-K_1\right\} , \end{aligned}\right\} \tag{68}$$

$$\begin{aligned} & \theta_2 = \kappa(1-a)-2\frac{\alpha_1}{a}+\frac{\sigma_1}{\xi}+\frac{u_1}{\eta} , \\ & \frac{u_2}{\eta} = \gamma^2(a-1)\left[\left(1+\frac{1}{\gamma}\right)-a\right]\Theta_2(a) , \\ & \alpha_2 = -\frac{2}{\gamma}\eta^2\left(\frac{u_2}{\eta}\right)+2\frac{\Gamma_1}{\gamma^2}\eta^2\left(\frac{u_1}{\eta}\right)-\frac{1}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right)^2+\frac{4}{\kappa}(\theta_2-\theta_1{}^2)-\alpha_1+a\theta_1 \end{aligned}$$

$$\left.\begin{aligned}
&-\frac{4K_1}{\kappa^2}\theta_1+\frac{\Gamma_2}{\gamma}(1-a)-\frac{\Gamma_1^2}{\gamma^2}(1-a)\,,\\
&\frac{\sigma_2}{\xi}=\frac{1}{2}\left(\frac{\sigma_1}{\xi}\right)^2-\kappa\int_1^{\cdot}\theta_2da-\kappa\int_1\theta_1\left(\frac{d\alpha_1}{da}\right)da-\kappa\int_1 a\frac{d}{da}\left(\frac{\sigma_1}{\xi}\right)da\\
&\quad+\kappa^2\int_1\alpha_1da+\frac{K_1}{\kappa}\left(\frac{\sigma_1}{\xi}\right)+\kappa\left(\frac{K_1^2}{\kappa^2}-\frac{K_2}{\kappa}\right)(a-1)-\theta_2+\frac{5}{2}\theta_1^2\\
&\quad+\frac{K_1}{\kappa}\theta_1+\kappa(\alpha_1-a\theta_1)+\kappa\left(\frac{\Gamma_2}{\gamma}-\frac{\Gamma_1^2}{\gamma^2}\right)(a-1)+\frac{1}{2}\left(\frac{u_1}{\eta}\right)^2\\
&\quad+\frac{\kappa}{\gamma}\eta^2\left(\frac{u_1}{\eta}\right)^2-2\frac{\kappa\Gamma_1}{\gamma^2}\eta^2\left(\frac{u_1}{\eta}\right)+\frac{K_1}{\kappa}\left(\frac{u_1}{\eta}\right)-\kappa\int_1 a\frac{d}{da}\left(\frac{u_1}{\eta}\right)da\\
&\quad-\eta^2(1-\eta^2)\left(1-\frac{2\kappa}{\gamma}\eta^2\right)\Theta_2(a)\,,\\
&\Theta_2(a_t)=\frac{8}{3\kappa}\left\{-\kappa\theta_{2t}-\kappa\theta_{1t}+\kappa^2\alpha_{1t}+\kappa(1-\theta_{1t})\left(\frac{d\alpha_1}{da}\right)_t-\left(\frac{d\theta_2}{da}\right)_t+\left(5\theta_{1t}\right.\right.\\
&\quad\left.+\frac{K_1}{\kappa}-\kappa a_t\right)\left(\frac{d\theta_1}{da}\right)_t+\kappa\left(\frac{K_1^2}{\kappa^2}-\frac{K_2}{\kappa}\right)+\kappa\left(\frac{\Gamma_2}{\gamma}-\frac{\Gamma_1^2}{\gamma^2}\right)+\left[\frac{27}{256}\right.\\
&\quad\left.\left.+\frac{3}{32}\left(\frac{\gamma}{\kappa}\right)\right]\kappa[\Theta_1(a_t)]^2+\kappa\left[\frac{1}{2}\frac{\gamma K_1}{\kappa^2}-\frac{3}{8}\frac{\Gamma_1}{\gamma}-\frac{1}{2}\gamma a_t\right]\Theta_1(a_t)\right\}
\end{aligned}\right\}\qquad(69)$$

where the subscript e is omitted for brevity.

4. 3 Determination of Parameters ϵ and K.

Though our analysis has been carried out as if the values of the two parameters ϵ and K were known in advance, these are actually determined only after solving the whole subsonic region. Finally, these parameters must be determined from the reservoir conditions, which can be described in terms of the two parameters α_0 and β. The condition of Eq. (40) implies

$$\beta=\epsilon\beta_0\,, \qquad (70)$$

where β_0 is a constant of order unity. Then Eq. (27) yields for small ϵ

$$K=\left(\beta_0-\frac{14}{3}\right)-\frac{11}{6}\left(\beta_0-\frac{14}{3}\right)\epsilon+\left\{\left(\frac{11}{6}\right)^2\left(\beta_0-\frac{14}{3}\right)-\frac{1}{6}\left(\beta_0-\frac{14}{3}\right)^2\right\}\epsilon^2+0(\epsilon^3)\,, \qquad (71)$$

from which the parameters κ, K_1, K_2 ... can be determined as follows

$$\left.\begin{aligned}
\kappa &= \left(\beta_0 - \frac{14}{3}\right), \\
K_1 &= -\frac{11}{6}\left(\beta_0 - \frac{14}{3}\right), \\
K_2 &= \left(\frac{11}{6}\right)^2\left(\beta_0 - \frac{14}{3}\right) - \frac{1}{6}\left(\beta_0 - \frac{14}{3}\right)^2, \\
&\cdots\cdots
\end{aligned}\right\} \tag{72}$$

The solution of the degree of dissociation yields at the reservoir

$$\alpha_0 = \epsilon K \tilde{a}_0 . \tag{73}$$

Hence for the zeroth approximation, we have

$$\alpha_0 = \epsilon \kappa a_0 , \tag{74}$$

$$K = \kappa , \tag{75}$$

where

$$a_0 = 1 + \frac{1}{\gamma} = 1 + \frac{2}{3\kappa} , \tag{76}$$

which yields

$$\epsilon = \frac{1}{4}(\beta - \alpha_0) , \tag{77}$$

$$\kappa = \left(\frac{4\beta}{\beta - \alpha_0} - \frac{14}{3}\right) . \tag{78}$$

For the first approximation, we have

$$\alpha_0 = \epsilon(\kappa + \epsilon K_1)(a_0 + \epsilon \alpha_1) \approx \epsilon[\kappa a_0 + \epsilon(\kappa \alpha_{10} + K_1 a_0)] , \tag{79}$$

$$K = \kappa + \epsilon K_1 , \tag{80}$$

where

$$\alpha_{10} = \frac{8}{\kappa} \ln\left(\frac{f}{a_0}\right) - \frac{1}{\gamma}\left(5 + \frac{\Gamma_1}{\gamma}\right) , \tag{81}$$

and the values of ϵ and K must be determined numerically in this case. Similarly, for the second approximation, we have

$$\alpha_0 = \epsilon(\kappa + \epsilon K_1 + \epsilon^2 K_2)(a_0 + \epsilon \alpha_{10} + \epsilon^2 \alpha_{20})$$

$$\approx \epsilon[\kappa a_0+\epsilon(\kappa\alpha_{10}+K_1a_0)+\epsilon^2(K_2a_0+K_1\alpha_{10}+\kappa\alpha_{20})], \tag{82}$$

$$K=\kappa+\epsilon K_1+\epsilon^2K_2, \tag{83}$$

where

$$\left.\begin{aligned}
\theta_{10}&=2\ln\left(\frac{f}{a_0}\right)-\frac{\kappa}{\gamma},\\
\theta_{20}&=2\frac{\varphi_1}{f}+\kappa(f-a_0)-2\frac{\alpha_{10}}{a_0}+\frac{1}{2}\kappa^2(a_0^2-1)+\kappa\left(1+\frac{\Gamma_1}{\gamma}\right)(a_0-1)\\
&\quad+(\kappa-K_1)(a_0-1)-2\ln\left(\frac{f}{a_0}\right)-\kappa\int_1^{a_0}\theta_1da,\\
\alpha_{20}&=\frac{4}{\kappa}(\theta_{20}-\theta_{10}^2)-\alpha_{10}+a_0\theta_{10}-\frac{4K_1}{\kappa^2}\theta_{10}+\frac{\Gamma_2}{\gamma}(1-a_0)-\left(\frac{\Gamma_1}{\gamma}\right)^2(1-a_0).
\end{aligned}\right\} \tag{84}$$

As in the first approximation, the values of ϵ and K must be determined numerically.

5. Sample Calculations and Comparison with Numerical Results

In the basic equations, Eqs. (1) to (6), the independent variable is x, while in Eqs. (14) to (17), σ is chosen as an independent variable instead of x. However, in the analysis by the P. L. K. method, the new independent variable ξ is introduced. In the actual calculations, it is more convenient to consider $a = a(\xi)$ as an independent variable instead of ξ, because ξ decreases upstream from the sonic point to the throat, where $\xi = \xi_t$, and then increases upstream from there to the reservoir, which leads to complications in the numerical procedure. On the contrary, the variable a increases monotonically from the critical point to the reservoir, and moreover the relations

$$a_*=1 \text{ at } \xi=\xi_*, \quad a_t=1+\frac{1}{4\gamma} \text{ at } \xi=\xi_t \text{ and } a_0=1+\frac{1}{\gamma} \text{ at } \xi=\infty,$$

remain valid in the any higher approximation.

The actual numerical procedure is described below. For the given reservoir conditions, the values of the two parameters

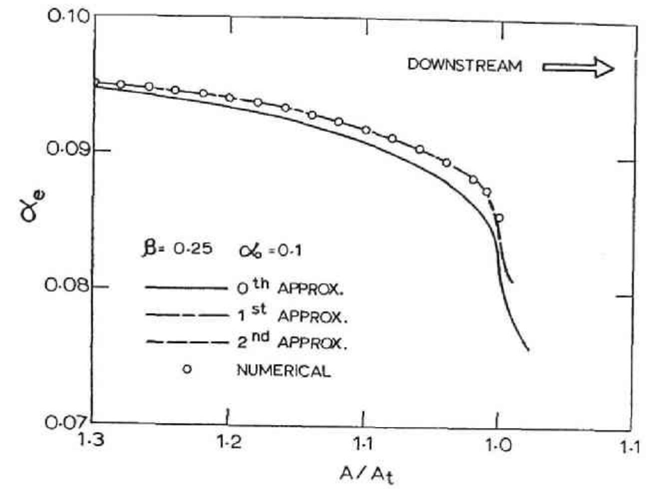

Fig. 6 Distribution of degree of dissociation α for an equilibrium flow along the nozzle axis.

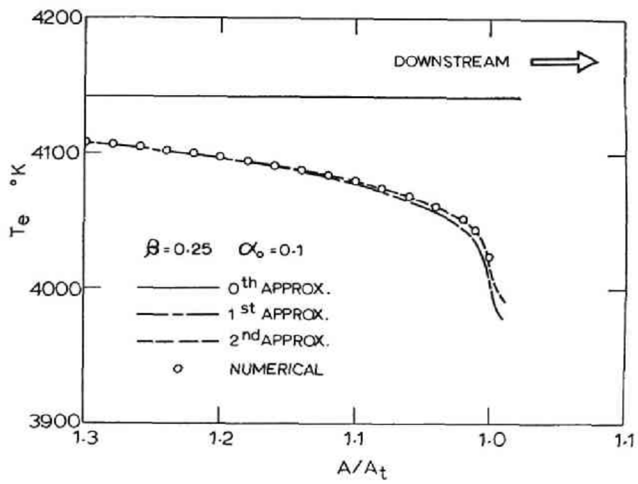

Fig. 7 Distribution of temperature T for an equilibrium flow along the nozzle axis.

ϵ and K are obtained from Eqs. (77) and (78), and it is confirmed that the conditions

$$\epsilon \ll 1, \quad \text{and} \quad K = 0(1),$$

are really satisfied by these parameters. These are substituted

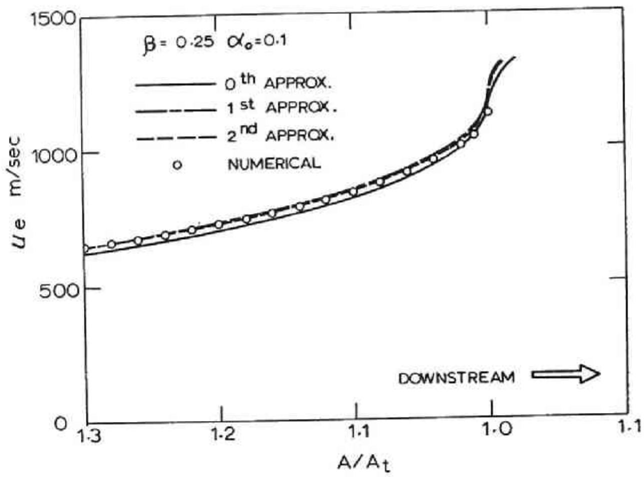

Fig. 8 Distribution of velocity u for an equilibrium flow along the nozzle axis.

into the first equation of Eq. (51) and the value of f is calculated, which will give the approximate measure of f for the first approximation. Next it is confirmed that the condition $(1-f^2)/f^2 = O(1)$ is really satisfied. From Eqs. (79) and (80) and the first equation of Eq. (51), the new values of f, ϵ and K for the first approximation are determined, and with these values of the parameters, the solution of the first approximation is completely determined. In a similar way, we can get the solution of any higher-order approximation. For the comparison with these solutions, the exact numerical solutions have been obtained by the R. K. G. method on a digital computer and are shown in Figs. 6, 7, and 8. In these sample calculations, the constants ν_1 and ν_2 are chosen as the regular functions $\Theta_1(a)$ and $\Theta_2(a)$, respectively.

6. Concluding Remarks

The analytical solutions of the subsonic region for equilibrium and nonequilibrium flows have been obtained by the P. L. K. method. Though the solutions are constructed under the conditions $\epsilon \ll 1$, $K = O(1)$ and $(1 - \varphi^2)/\varphi^2 = O(1)$, it can be modified so as to be valid even under the conditions

$$\text{(i)} \quad \epsilon \ll 1 , \quad K = 0(1) , \quad (1-\varphi^2) = 0(\epsilon^m) , \quad m = 1, 2, 3, \dots ,$$

$$\text{(ii)} \quad \epsilon \ll 1 , \quad \frac{1-\epsilon K}{\epsilon K} = 0(1) , \quad \varphi = 0(1) .$$

The conditions (i), (ii) and those considered in our analysis cover reasonably well almost all the important conditions under which the dissociation and recombination phenomena take place predominantly, and the ionization and neutralization phenomena does not appreciably in the expanding flows. The sample calculations are carried out only for an equilibrium flow of N_2 gas, but of course the same calculations may be done for equilibrium flows of O_2 gas and other diatomic gases. The main purpose of this work, however, lies in obtaining the analytical solution for nonequilibrium flows. The sample calculations for nonequilibrium flows are thus very important in order to evaluate the results obtained here, and will be carried out in the near future by the author. One of the most important merits of our method is that it yields exact distributions of flow parameters even near and at the critical point within the accuracy of the order of the approximation cosidered.

As mentioned in the introduction, once the values of φ, ϵ and K are determined, our solution is valid as far as some point downstream of the critical point. It is quite desirable for the solution to be valid at any point even downstream of the throat. Unfortunately, this is not possible, because on the downstream side, the quantity $\ln[a^2/\xi\eta + \kappa q \xi \eta^2 G(da/d\xi)]$ becomes negatively infinite at the location defined by

$$\left[1 + \frac{\kappa q \xi^2 \eta^3}{a^2} G\left(\frac{da}{d\xi}\right)\right] = 0 .$$

In the vicinity of this location and downstream of it, other forms of perturbation expansions, if possible, must be devised. The studies by Cheng and Lee[22) 23)] would be very instructive. This remains to be treated as well as the problem in the cases $\varphi^2 = O(\epsilon^m)$, where m = 1, 2, 3... .

SUMMARY

The nonequilibrium effects arising from the rate processes in nozzle flow expansions of real gases have been discussed in detail. Emphasis is placed upon the analyses of subsonic region and effects of entropy on the flowfields and relaxation phenomena themselves.

The problem of predicting critical mass flows in nozzle flows of the vibrationally relaxing gas, ideal dissociating gas and singly ionizing gas is treated in Ch. I. A conclusion is drawn that, in general, at least theoretically under the fixed reservoir conditions, the maximum critical mass flow is the frozen one, while the minimum is the one which is somewhat smaller than the equilibrium.

Analytical and numerical solutions of nonequilibrium flows of vibrationally relaxing diatomic gases through nozzles are obtained under the various reservoir conditions in Ch. II. Some appropriate approximations are made for the rate equation, which enables us to treat the rate equation and the corresponding flow equations seperately. It can exclude the difficulties in connection with the singularity of the flow equations at a sonic point. The proof of validity and reliability of the equilibrium-throat-approximation method is also given.

In Ch. III, the investigation of roles of entropy in the analyses of nonequilibrium nozzle flows is made. In the flows of vibrationally relaxing and chemically reacting gases, the nonequilibrium processes inevitably increase the entropy of gases. The effects of the increase in entropy on the critical mass flow, flow variables and relaxation phenomena themselves

are discussed.

The problem of solving the flows of an ideal dissociating diatomic gas is treated analytically by the method of strained coordinates (the P. L. K. method) in Ch. IV. The solution is constructed in the form of perturbation expansions in powers of ϵ, the ratio of the temperature at the critical point and the dissociation energy. The sample calculations are carried out and compared with the exact numerical results for the equilibrium flow.

The numerical technique which has been used to integrate the system of ordinary differential equations in this work is the R. K. G. method, and the numerical calculations are carried out on a digital computer HITAC 5020 at the computing center at Kyoto University.

Symbols for Ch. I

a	Constant in Eq. (8)
a_e	Equilibrium sound speed
a_f	Frozen sound speed
$1+A$	Nozzle cross-sectional-area ratio
b	Constant in Eq. (8)
c	Local equilibrium value of α corresponding to local values of T and ρ
C_e	Constant in Eq. (51)
C_f	Constant in Eq. (57)
C_D	Constant in Eq. (18)
C_I	Constant in Eq. (19)
d	Constant in Eq. (18)
D	Molecular dissociation energy of diatomic gas
D_*	Quantity defined in Eq. (135)
E	Local equilibrium value of E_V corresponding to local value of T
E_V	Vibrational energy
$f_i(\zeta)$	Function of ζ defined in Eq. (91)
$F_D(M_f,\alpha)$	Function of M_f and α defined in Eq. (106)
F_{DO}	Quantity defined in Eq. (106)
$F_I(M_f,\phi)$	Function of M_f and ϕ defined in Eq. (142)
F_{IO}	Quantity defined in Eq. (142)
$F_v(M_f)$	Function of M_f defined in Eq. (36)
F_{VO}	Quantity defined in Eq. (36)
$\mathcal{E}_*$	Quantity defined in Eq. (135)
G_D	Quantity defined in Eq. (106)

G_D'	Quantity defined in Eq. (112)
G_{D*}''	Quantity defined in Eq. (135)
G_I	Quantity defined in Eq. (142)
G_V	Quantity defined in Eq. (36)
$G(\xi)$	Function of ξ defined in Eq. (82)
h	Enthalpy per unit mole
$h(\xi)$	Function of ξ defined in Eq. (86), equal to 1+A
i	Constant in Eq. (19)
I	Ionization energy
k_{f1}, k_{f2}	Forward rate coefficients
k_{r1}, k_{r2}	Reverse rate coefficients
K	Nozzle constant
$K(T)$	Equilibrium constant
ℓ	Constant in Eq. (12)
$L(p,\rho,q)$	Function of p, ρ and q defined in Eq. (4)
m	Critical mass flow
M_e	Equilibrium Mach number
M_f	Frozen Mach number
p	Pressure
P_e	Bray's nonequilibrium parameter
q	Progress variable
r_D	Dissociation rate
r_R	Recombination rate
R	Universal gas constant
s	Constant in Eq. (12)
S	Entropy per unit mole
T	Temperature
T_V	Vibrational temperature
$U(p,\rho,q)$	Function of p, ρ, and q defined in Eq. (4)

V	Flow velocity
w	Constant in Eq. (12)
W_1	Molecular weight of monatomic gas
W_2	Molecular weight of diatomic gas
x	Distance along nozzle axis
α	Dissociated mass fraction
$\tilde{\alpha}_{e*}$	Dissociated mass fraction at $M_f = 1$ in equilibrium flow
Γ	Constant in Eq. (12)
δ	-1 for $\xi < \xi_t$ and 1 for $\xi > \xi_t$
$\mathcal{E}$	$E / \frac{R}{W_2}\theta$
$\mathcal{E}_V$	$E_V / \frac{R}{W_2}\theta$
$\mathcal{E}_{Vf}$	Frozen value of $\mathcal{E}_V$ in equilibrium-frozen flow
$\Delta\mathcal{E}_V$	$\mathcal{E}_V - \mathcal{E}$
η	$\frac{R}{W_1} I / h_0$
θ	Characteristic vibrational temperature
$\varkappa_*$	Quantity defined in Eq. (135)
μ	m / m_e
ξ	θ / T
ξ_V	θ / T_V
$\Pi(\xi)$	Function of ξ defined in Eq. (84)
ρ	Density
φ	$\frac{R}{W_2}\theta / h_0$
ϕ	Ionized mass fraction
$\tilde{\phi}_{e*}$	Ionized mass fraction at $M_f = 1$ in equilibrium flow
ψ	$\frac{R}{W_2} D / h_0$
$\Psi(\xi)$	Function of ξ defined in Eq. (71)

Subscripts

e	equilibrium

f	Frozen flow
ef	Equilibrium-frozen flow
i	i - th approximation
t	Nozzle throat
O	Reservoir or stagnation conditions
*	Sonic or critical point

Symbols for Ch. II

a_{1m}	Quantity defined in Eq. (54)
A_{1m}	Quantity defined in Eq. (54)
m	Positive integer in Eq. (49), also critical mass flow
N	Positive integer satisfying Eq. (44)
ΔS	$S - S_O$
Z_m	Quantity defined in Eq. (54)
ζ	Dummy variable
ζ'_m	ζ / ξ_{rm}
ξ'_m	ξ / ξ_{rm}
ξ_{rm}	Value of ξ satisfying Eq. (49)
$\Phi_m(\zeta, \xi)$	Function of ξ and ζ defined in Eq. (27)
$\Phi'_m(\zeta', \xi')$	$\Phi_m(\zeta, \xi)/m\xi_{rm}$
$(\bar{\ })$	Quantity ( ) corresponding to approximate rate equation

Subscripts

r	Reference value
∞	Far downstream, $(1 + A) \to \infty$

Symbols for Ch. III

K	Nozzle constant defined in Eq. (35)
n	Constant in Eq. (35)

Ω_1	Quantity defined in Eq. (29)
Ω_2	Quantity defined in Eq. (30)
Ω_3	Quantity defined in Eq. (31)
Θ	$\exp\left[(1 - \frac{1}{n}) \frac{W_2}{R}(S - S_0)\right]$
λ	Constant in Eq. (36)

Subscripts

OFP	Flow path in Fig. 2

Symbols for Ch. IV

a	The zeroth approximation of $\bar{\alpha}$
A	Nozzle cross-sectional-area ratio, equal to (1 + A) in Chs. I, II and III
c_*	Equilibrium value of α corresponding to local value of T and ρ at critical point
C	Constant in Eq. (4)
$g(\xi)$	Function of ξ defined in Eq. (9)
g_1, g_2	Quantities defined in Eq. (48)
G	The zeroth approximation of $g(\xi)$
f	The zeroth approximation of φ
k	Nozzle constant
K	α_*/ϵ
K_1, K_2	Quantities defined in Eq. (43)
M_*	$u_*/\sqrt{\frac{R}{W_2} T_*}$
P	Quantity defined in Eq. (12)
q	The zeroth approximation of Ω
Ω	Quantity defined in Eq. (10)
Ω_1, Ω_2	Quantities defined in Eq. (43)
u	Flow velocity
$\bar{u}$	u / u_*

u_1, u_2 Quantities defined in Eq. (41)

t The zeroth approximation of θ

$\bar{\alpha}$ α / α_*

α_1, α_2 Quantities defined in Eq. (41)

β $h_0 / \frac{R}{W_2} D$, $1/\psi$

β_0 Constant defined in Eq. (70)

γ The zeroth approximation of Γ

Γ $2K / M_*^2$

Γ_1, Γ_2 Quantities defined in Eq. (43)

ϵ T_* / D

ζ The zeroth approximation of $\bar{u}$

θ T_* / T

θ_1, θ_2 Quantities defined in Eq. (41)

$\Theta_1(a), \Theta_2(a)$

Arbitrary regular functions of a

κ The zeroth approximation of K

ν_1, ν_2 Constants chosen as regular functions

ξ Independent variable defined in Eq. (41)

ρ ρ / ρ_*

ρ_D Characteristic density for dissociation, equal to C_D in Ch. I

σ A / A_*

σ_1, σ_2 Quantities defined in Eq. (41)

φ c_* / α_*

φ_1, φ_2 Quantities defined in Eq. (43)

REFERENCES

1) Bray, K. N. C., Atomic Recombination in a Hypersonic Wind Tunnel Nozzle, J. Fluid Mech. 6, 1 (1959).

2) Clarke, J. F. and McChesney, M., The Dynamics of Real Gases, Butterworth & Co., London (1964).

3) Tirumalesa, D., Nozzle Flows with Coupled Vibrational and Dissociational Nonequilibrium, AIAA J. 5, 254 (1967).

4) Blythe, P. A., Non-Equilibrium Flow Through a Nozzle, J. Fluid Mech. 17, 126 (1963).

5) Stollery, J. L. and Park, C., Computer Solutions to the Problems of Vibrational Relaxation in Hypersonic Nozzle Flows, Imperial College Rept. No. 115 (1963).

6) Kinslow, M. and Miller, J. T., Nonequilibrium Expansion of a Diatomic Gas through a Convergent-Divergent Nozzle, Phys. Fluids, 9, 1703 (1966).

7) Stollery, J. L. and Smith, J. E., A Note on the Variation of Vibrational Temperature Along a Nozzle, J. Fluid Mech. 13, 225 (1962).

8) Takano, A., Higashino, F. and Yoshie, T., Character of Hypersonic Shock Tunnels with Real Gas Effects, 2. Dissociational Nonequilibrium Flow through a Convergent-Divergent Nozzle (in Japanese), J. Japan Soc. for Aeronautical and Space Sciences, Vol. 16, No. 174 (1968).

9) Lighthill, M. J., Dynamics of a Dissociating Gas, Part 1, Equilibrium Flow, J. Fluid Mech. 2, 1 (1957).

10) Cambel, A. B., Duclos, D. P., and Anderson, T. P., Real Gases, Academic Press, New York (1963).

11) Blackman, V., Vibrational Relaxation in Oxygen and Nitrogen,

J. Fluid Mech. 1, Part 1, 61 (1965).

12) Freeman, N. C., Nonequilibrium Flow of an Ideal Dissociating Gas, J. Fluid Mech. 4, 407 (1958).

13) Bray, K. N. C., Electron-Ion Recombination in Argon Flowing Through a Supersonic Nozzle, AGARDO graph 68: High Temperature Aspects of Hypersonic Flow (Wilbur C. Nelson ed.), Pergamon Press, 67 (1964).

14) McDaniel, E. W., Collision Phenomenon in Ionized Gases, John Wiley and Sons, Inc., N. Y. (1964).

15) Petschek, H. and Byron, S., Approach to Equilibrium Ionization Behind Strong Shock Waves in Argon, Ann. of Phys., 1, 270 (1957).

16) Vincenti, W. G., Nonequilibrium Flow Over a Wavy Wall, J. Fluid Mech. 17, 126 (1963).

17) Treanor, C. E. and Marrone, P. V., Effect of Dissociation on the Rate of Vibrational Relaxation, Phys. Fluid, 5, 1022 (1962).

18) Gordon J. H., Eschenroeder, A. Ω., and Marrone, P. V., Imviscid Hypersonic Airflows with Coupled Nonequilibrium Processes, IAS Paper 62-57 (1962).

19) Conner, L. N. and Erickson, W. D., Entropy Production in Vibrational-Nonequilibrium Nozzle Flow, AIAA J., 2, 397 (1964).

20) Harris, C. J. and Warren, W. D., Correlation of Nonequilibrium Chemical Properties of Expanding Air Flows, R64SD92, General Electric Co., Valley Forge, Pa. (1964).

21) Harris, C. J., Comment on Nonequilibrium Effects on High-Enthalpy Expansion of Air, AIAA J., 4, 1148(1966).

22) Cheng, H. K. and Lee, R. S., Freezing of Dissociation and

Recombination in Supersonic Nozzle Flows: Part 1. General Discussion and Special Analysis, AIAA J., 5, 823(1968).

23) Cheng, H. K. and Lee, R. S., Freezing of Dissociation and Recombination in Supersonic Nozzle Flows; Part 2. More General Analysis and Numerical Example, AIAA J., 6, 831 (1968).

24) Freeman, N. C., Non-equilibrium flow of an ideal dissociating gas, J. Fluid Mech., 4, 407(1958).

25) Van Dyke, M. D., Perturbation Methods in Fluid Mechanics, Academic Press, New York and London(1968).

26) Capiaux, R. and Washington , M., Nonequilibrium Flow Past a Wedge, AIAA J., 1, 650(1963).

27) Lick, W., Inviscid Flow of a Reacting Mixture of Gases around a Blunt Body, J. Fluid Mech., 6, 128(1959).

APPENDIX - SELECTED SUPPLEMENTARY BIBLIOGRAPHY

1) Bray, K. N. C., Coupling between atomic recombination and vibrational relaxation in expanding gas flows, Univ. of Southampton, England, Aeronautics Southampton Univ. Rept. 260 (1964).

2) Lordi, J. A. and Mates, R. A., Nonequilibrium expansions of high enthalpy air flows, Cornell Aeronautical Laboratory Rept. AD1716-A-3 (1964).

3) Eschenroeder, A. Ω., Boyer, D. W., and Hall, J. G., Exact solutions for nonequilibrium expansions of air with coupled chemical reactions, Cornell Aeronautical Laboratory Rept. AF-1413-A-1 (1961).

4) Bray, K. N. C., Electron-ion Recombination in Argon Flowing Through a Hypersonic Nozzle, in The High Temperature Aspect of Hypersonic Flow (Nelson, W. C., ed.), Pergamon Press, (1964).

5) Eschenroeder, A. Ω., Ionization Nonequilibrium in Expanding Flows, ARS Journal, 31, 196 (1961).

6) Harney, D. J., Similarity of Nonequilibrium Expansions in Hypersonic Nozzles, FDM-TM-67-1, Wright-Patterson Air Force Base, Ohio, (1967).

7) Vincenti, W. G., Calculations of the one-dimensional non-equilibrium flow of air through a hypersonic nozzle, Interim report, Stanford Univ. Dept. Aero. Eng. Rep. 101, (1961).

8) Ring, L. E., and Warren, W. R., Correlation and Prediction of Air Nonequilibrium in Nozzles, AIAA Paper 68-378, San Francisco, Calif., (1968).

9) Penner, S. S., Chemical Reactions in Flow Systems, Butterworths Sci. Pub., London (1955).

10) Penner, S. S., Chemistry Problems in Jet Propulsion, Pergamon Press (1957).

11) Vincenti, W. G., and Kruger, C. H. Jr., Introduction to Physical Gas Dynamics, John Wiley and Sons (1965).

12) Penner, S. S., Porter, J., and Kushida, R., Rate and Radiative Transfer Processes During Flow in De Laval Nozzles, Proc. 9th International Symposium on Combustion, Academic Press, New York (1963).

13) Olsen, W. T., Recombination and Condensation Processes in High Area Ratio Nozzles, ARS J. 32, 672 (1962).

14) Bloom, M. H. and Ting, L., On Near-Equilibrium and Near-Frozen Behavior of One-Dimensional Flow, Arnold Eng. Develop. Center TN-60-156 (1960).

15) Krieger, F. J., Chemical Kinetics and Rocket Nozzle Desigh, Jour. Amer. Rocket Soc. 21, 179 (1960).

16) Smith, F. T., On the Analysis of Recombination Reactions in an Expanding Gas Stream, Proc. 7th International Symposium on Combustion, Butterworths Sci. Pub. (1959).

17) Eschenroeder, A. Q., Entropy Changes in Nonequilibrium Flows, Phys. Fluids 6, 1408 (1963).

18) Bray, K. N. C., Simplified Sudden-Freezing Analysis for Nonequilibrium Nozzle Flows, ARS J. 31, 831 (1961).

19) Lordi, J. A., Comparison of Exact and Approximate Solutions for Nonequilibrium Nozzle Flows, ARS J. 32, 1285 (1962).

20) Wegener, P. P., Marte, J. E., and Thiele, C. Experiments on Chemical Kinetics in a Supersonic Nozzle, J. Aero. Sci. 25, 205 (1958).

21) Nagamatsu, H. T. and Sheer, R. E. Jr., Vibrational relaxation and Recombination of Nitrogen and Air in Hypersonic Nozzle Flows, AIAA J. 3, 1386 (1965).

22) Russo, A. L., Hall, J. G., and Lordi, J. A., Measurement of Nonequilibrium Static Pressures in Nozzle Flows of Dissociated Hydrogen, AIAA J, 4, 741 (1966).

23) Kuby, W. C., Experiments on Hydrogen Recombination in Nozzle Flows for the H_2/F_2 System, AIAA J, 4, 160 (1966).

24) Nagamatsu, H. T., Workman, J. B., and Sheer, R. E. Jr., Hypersonic Nozzle Expansion of Air With Atom Recombination Present, J. Aero/Space Sciences, 28, 833 (1961).

25) Whalen, R. J., Viscous and Inviscid Nonequilibrium Gas Flows. J. Aero/Space Sciences, 29, 1222 (1962).

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