NASA TECHNICAL NOTE

NASA TN D-3306

c.1

LOAN COPY: RETURN TO
AFWL (WLIL-2)
KIRTLAND AFB, N MEX

0130013

TECH LIBRARY KAFB, NM

NASA TN D-3306

A METHOD FOR COMPUTING NONEQUILIBRIUM CHANNEL FLOW OF A MULTICOMPONENT GASEOUS MIXTURE IN THE NEAR-EQUILIBRIUM REGION

by Walter E. Pearson and Barrett S. Baldwin, Jr.

Ames Research Center
Moffett Field, Calif.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1966

TECH LIBRARY KAFB, NM

0130013

A METHOD FOR COMPUTING NONEQUILIBRIUM CHANNEL FLOW OF A MULTICOMPONENT GASEOUS MIXTURE IN THE NEAR-EQUILIBRIUM REGION

By Walter E. Pearson and Barrett S. Baldwin, Jr.

Ames Research Center
Moffett Field, Calif.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – Price $2.00

A METHOD FOR COMPUTING NONEQUILIBRIUM CHANNEL FLOW OF A MULTICOMPONENT GASEOUS MIXTURE IN THE NEAR-EQUILIBRIUM REGION

By Walter E. Pearson and Barrett S. Baldwin, Jr.
Ames Research Center

SUMMARY

A method for computing one-dimensional, steady, nonequilibrium channel flow of an arbitrary mixture of diatomic and monatomic gases is presented. The method assumes the chemical and vibrational nonequilibrium rate processes are not coupled. The numerical formulation permits accurate evaluation of all variables appearing in the rate equations, and it precludes the necessity for computing expressions which become indeterminate in the near-equilibrium region.

INTRODUCTION

The flow of a multicomponent gaseous mixture which is influenced by thermochemical nonequilibrium has proven to be difficult to predict in the near-equilibrium region. In the analysis of a flow of this kind, the equations which describe the fluid dynamical processes must be solved simultaneously with equations which describe the nonequilibrium rate processes. These rate equations take the form of a coupled system of nonlinear differential equations, and in order to proceed toward a prediction of the flow, it is necessary to use numerical methods.

A numerical solution of the equations that govern the flow is possible in principle, but has not been demonstrated to be practical for all cases that may arise. Early investigators found excessive amounts of computation necessary in order to achieve numerical stability in the near-equilibrium regions (refs. 1, 2, 3). The instability arises in part from the necessity for evaluating expressions which, as equilibrium is approached, become indeterminate in the sense that their straightforward calculation leads to large numerical errors. Several methods (refs. 4, 5, 6) that have been of practical value were devised for the approximate numerical integration of such so-called "stiff equations," although they did not entirely remove the underlying cause of the difficulties. In these early studies, the interest was centered primarily on the physics of the problem, and the numerical difficulties were regarded as an inconvenience.

Recently, three new methods have appeared that greatly reduce the computing time in the near-equilibrium regions of the flow (refs. 7, 8, 9). These later papers indicate a growing interest in the mathematical problem which, evidently, has not been solved satisfactorily.

The nature of the problem may be defined by recalling that regions requiring special treatment are frequently encountered in numerical calculations. These are usually regions in which some physical quantity approaches an asymptotic value. A standard remedy is to find a closed-form solution of a simplified set of equations that apply in the asymptotic region. A difficulty at first appears to preclude the use of this device in the present problem. The trouble arises from the fact that the equations are nonlinear over extensive near-equilibrium regions so that a closed-form solution cannot be found. The method, however, can be applied if the equations are linearized independently in each small step of the numerical calculation, as was done by Moretti (ref. 8). At first, it appears unwieldy to incorporate such a procedure in a numerical integration program, but the resulting reduction in computing time gives good reason to do so (refs. 8, 9, 10). Also, such a linearization procedure provides the only method available at present for computing accurately the so-called reaction variables that appear in the rate equations.

The present method differs from that of Moretti (ref. 8) in that accurate evaluation of the reaction variables is included. To accomplish this, considerable manipulation of the original rate equations is necessary. However, upon completion of these steps, a system of equations is obtained that applies for equilibrium, near-equilibrium, or nonequilibrium flows. The method to be presented is based on the requirement that means be found for computing, as accurately as might be specified, all quantities appearing in the equations. This requirement was previously employed in conjunction with a simplified model for air (ref. 10) and has been discussed in connection with more general reacting systems (ref. 11).

Specifically, this report contains a method for computing one-dimensional, steady, nonequilibrium channel flow. The method pertains to an arbitrary multicomponent mixture of ideal diatomic and monatomic gases, free from transport effects and from interaction between the chemical and vibrational nonequilibrium rate processes. The numerical formulation makes unnecessary the computation of expressions which become numerically indeterminate in the near-equilibrium region, but it requires the solution of an eigenvalue problem at each field point of the one-dimensional flow.

The numerical difficulties inherent to calculating the eigenvalues of an arbitrary matrix are well known. However, with the numerical formulation of this report, the matrix in question is similar, at every field point, to a real symmetric matrix which is easily constructed. This fact is used to greatly simplify the computational problem.

SYMBOLS

A	matrix of coefficients (see eq. (A1))
A^{-1}	inverse of matrix A
A^T	transpose of matrix A

$A(x)$	cross-sectional area of the channel at point x
$D(t)$	diagonal matrix with diagonal elements $e^{-\lambda_i t}$ $(i = 1, 2, \ldots, r)$
$D_1(t)$	diagonal matrix with diagonal elements $\frac{1}{\lambda_i}$ $(i = 1, 2, \ldots, r)$
E	matrix whose column vectors are the eigenvectors of matrix A
e_{Dj}	energy of dissociation per mole of species j
e_j	internal energy per mole of species j
$\tilde{e}_j$	combined rotational, electronic, and translational energies per mole of species j
e_v	vibrational energy per mole of a given species
$\bar{e}_v(T)$	equilibrium vibrational energy per mole of a given species at temperature T
e_{vj}	vibrational energy per mole of species j
f	natural vibrational frequency for a given molecular species assuming it is a classical harmonic oscillator
H	matrix (see eq. (38c))
h	enthalpy per unit mass of the gas mixture
h_{ij}	element in the ith row and jth column of the matrix H (see eq. (38c))
h_o	Planck's constant
I	identity matrix
k	Boltzmann's constant
k_{bi}	backward rate coefficient of the ith reaction
k_{fi}	forward rate coefficient of the ith reaction
$K_i(T)$	equilibrium constant of the ith reaction
$k_{n,n+1}$	probability that a molecule vibrating in the nth energy level will make a transition to the $(n + 1)$th level in unit time
M	matrix (see eq. (38b))
M_j	chemical formula of species j
m_{ij}	element in the ith row and jth column of matrix M

N_o	Avogadro's number
n_{kj}	total number of atoms of element k in species j
p	pressure
Q_{ij}	rate of production of species M_j by the ith reaction per unit volume
$\mathcal{R}$	universal gas constant
r	number of chemical reactions
s	number of chemical species
T	temperature
t	time
U	see equation (27) and explanation thereafter
u	speed of flow
V	see equation (27) and explanation thereafter
x	distance along the axis of the channel
α_i	constant appearing in equation (40)
β_i	integer equal to $\nu_i' - \nu_i$
β_{ij}	integer equal to $\nu_{ij}' - \nu_{ij}$
γ_j	concentration of the jth species in moles per unit mass of the gas mixture
Δe_{vj}	increment in e_{vj} during the interval Δt
ΔT	increment in T during the interval Δt
Δt	incremental interval of time
$\Delta\gamma_j$	increment in γ_j during the interval Δt
$\Delta\rho$	increment in ρ during the interval Δt
ΔX_i	increment in X_i during the interval Δt
ϵ_n	energy of the nth vibrational level of a molecule
Λ	diagonal matrix whose elements are the eigenvalues of the matrix A

λ_i	ith eigenvalue of the matrix A
μ_n	number of molecules of a given species which are in the nth vibrational energy level
ν_i	integer equal to $\sum_{j=1}^{s} \nu_{ij}$
ν_i'	integer equal to $\sum_{j=1}^{s} \nu_{ij}'$
ν_{ij}	stoichiometric coefficient of species M_j on the left side of chemical equation i
ν_{ij}'	stoichiometric coefficient of species M_j on the right side of chemical equation i
ρ	density of gas mixture
σ	sum of all species concentration coefficients, γ_j $(j = 1, 2, . . ., s)$
τ_j	vibrational relaxation time for the jth species
χ_i	reaction variable (see eq. (5))
$\vec{\chi}$	column vector whose elements are χ_i $(i = 1, 2, . . ., r)$

Subscript

$(\ )_o$	used to indicate the numerical value of the quantity taken at the beginning of the interval Δt

ANALYSIS

Although they have been developed elsewhere, the basic equations for nonequilibrium channel flow will be derived here. This derivation will provide a background for the numerical method used in their solution.

Chemical Rate Equations

It is assumed that s chemical species, M_j $(j = 1, 2, . . ., s)$ are involved in r chemical equations. These equations are represented by

$$\sum_{j=1}^{s} \nu_{ij}M_j \underset{k_{bi}}{\overset{k_{fi}}{\rightleftarrows}} \sum_{j=1}^{s} \nu'_{ij}M_j \qquad (i = 1, 2, \ldots, r) \tag{1}$$

where ν_{ij} and ν'_{ij} are stoichiometric coefficients, the M_j are the chemical formulas of the species, and k_{fi} and k_{bi} are the forward and backward rate coefficients, respectively, of the ith reaction.

The ith reaction produces a quantity of species M_j at the rate Q_{ij} (moles/unit volume/unit time). For a fluid without gradients of concentration, pressure, or temperature, the law of mass action leads to the following expression for Q_{ij}

$$Q_{ij} = \beta_{ij}\left(k_{fi}\rho^{\nu_i} \prod_{j=1}^{s} \gamma_j^{\nu_{ij}} - k_{bi}\rho^{\nu'_i} \prod_{j=1}^{s} \gamma_j^{\nu'_{ij}}\right) \tag{2}$$

In this equation, γ_j (moles/unit mass) is the molar concentration of species M_j $(j = 1, 2, \ldots, s)$, ρ is the fluid density, and

$$\nu_i = \sum_{j=1}^{s} \nu_{ij} \ , \qquad \nu'_i = \sum_{j=1}^{s} \nu'_{ij} \ , \qquad \text{and} \quad \beta_{ij} = \nu'_{ij} - \nu_{ij}$$

It is assumed that equation (2) holds for a flowing gas.

The equilibrium constant for concentrations of the ith reaction, $K_i(T)$ is a known function of the temperature, T, and at equilibrium,

$$K_i(T) = \frac{k_{fi}(T)}{k_{bi}(T)} \qquad (i = 1, 2, \ldots, r)$$

It will be assumed that this relationship holds when the reaction is not in equilibrium as well.

The total rate of change of γ_j is given by

$$\rho \frac{d\gamma_j}{dt} = \sum_{i=1}^{r} Q_{ij} \qquad (j = 1, 2, \ldots, s)$$

Thus

$$\rho \frac{d\gamma_j}{dt} = \sum_{i=1}^{r} \beta_{ij}\left(k_{fi}\rho^{\nu_i} \prod_{l=1}^{s} \gamma_l^{\nu_{il}} - k_{bi}\rho^{\nu_i'} \prod_{l=1}^{s} \gamma_l^{\nu_{il}'}\right) \qquad (j = 1, 2, \ldots, s) \qquad (3)$$

These equations can be written

$$\frac{d\gamma_j}{dt} = \sum_{i=1}^{r} \beta_{ij}k_{fi}\rho^{\nu_i - 1}\left(\prod_{l=1}^{s} \gamma_l^{\nu_{il}}\right) X_i \qquad (j = 1, 2, \ldots, s) \qquad (4)$$

where the dimensionless variables X_i are defined by

$$X_i = 1 - \frac{1}{K_i(T)} \rho^{\beta_i} \prod_{l=1}^{s} \gamma_l^{\beta_{il}} \qquad (i = 1, 2, \ldots, r) \qquad (5)$$

and $\beta_i = \nu_i' - \nu_i$. (See ref. 3.) In near-equilibrium regions, the X_i approach zero, and they cannot be computed accurately from equations (5). Their accurate evaluation is essential if equations (4) are to be used, since the $d\gamma_j/dt$ cannot be set equal to zero in near-equilibrium regions. In the method to be developed here, equations (4) will not be evaluated numerically, but the method is capable of producing accurate values of the X_i if they are desired. When equations (5) are differentiated with respect to time, there is obtained a set of relations between the X_i $(i = 1, 2, \ldots, r)$, the γ_j $(j = 1, 2, \ldots, s)$, and the fluid dynamics variables ρ and T.

$$\frac{dX_i}{dt} = - \frac{1}{K_i(T)} \rho^{\beta_i} \sum_{l=1}^{s} \left(\frac{\beta_{il}}{\gamma_l}\right)\left(\frac{d\gamma_l}{dt}\right)\left(\prod_{l=1}^{s} \gamma_l^{\beta_{il}}\right)$$

$$- \frac{1}{K_i^2(T)}\left(- \frac{dK_i}{dT}\right)\left(\frac{dT}{dt}\right)\left(\rho^{\beta_i} \prod_{l=1}^{s} \gamma_l^{\beta_{il}}\right)$$

$$- \frac{1}{K_i(T)} \rho^{\beta_i} \prod_{l=1}^{s} \gamma_l^{\beta_{il}}\left(\frac{\beta_i}{\rho}\right)\left(\frac{d\rho}{dt}\right) \qquad (i = 1, 2, \ldots, r) \qquad (6)$$

Equations (6) are useful because they contain no forms which become indeterminate at some point in the flow field, including the near-equilibrium region.

Equations (4), (5), and (6) can be combined to obtain another set of equations which will also be used in the computation of the flow.

$$\frac{dX_i}{dt} = - \sum_{l=1}^{r} a_{il}X_l + F(T,X_i)\frac{dT}{dt} + G(\rho,X_i)\frac{d\rho}{dt} \qquad (i = 1, 2, \ldots, r) \qquad (7)$$

where

$$a_{il} = (1 - X_i)\left(\sum_{j=1}^{s} \frac{\beta_{ij}\beta_{lj}}{\gamma_j}\right)\left(k_{fl}\rho^{\nu_l - 1}\prod_{j=1}^{s}\gamma_j^{\nu_{lj}}\right) \qquad \begin{pmatrix} i = 1, 2, \ldots, r \\ l = 1, 2, \ldots, r \end{pmatrix}$$

and

$$F(T,X_i) = (1 - X_i)\left[\frac{1}{K_i(T)}\right]\left(\frac{dK_i}{dT}\right) \qquad (i = 1, 2, \ldots, r)$$

$$G(\rho,X_i) = (X_i - 1)\left(\frac{\beta_i}{\rho}\right) \qquad (i = 1, 2, \ldots, r)$$

Vibrational Rate Equations

It is assumed that the molecules of the gaseous mixture are free to vibrate only at a discrete set of energy levels

$$\epsilon_n = \left(n + \frac{1}{2}\right)h_0 f \qquad (n = 0, 1, 2, \ldots)$$

where h_0 is Planck's constant and f is the natural frequency for the species in question assuming it is a classical harmonic oscillator. It is further assumed that changes in energy can occur only between adjacent levels.

The probability that a molecule vibrating in the nth level will make a transition to the (n + 1)th level in a unit time is designated by $k_{n,n+1}$. With this notation, $k_{0,1}$ and $k_{1,0}$ are the probabilities of excitation and de-excitation per unit time, respectively, between the ground state and the first excited energy level. Let μ_n be the number of molecules in the nth vibrational energy level. Then

$$\frac{d\mu_n}{dt} = k_{n-1,n}\mu_{n-1} - k_{n,n-1}\mu_n + k_{n+1,n}\mu_{n+1} - k_{n,n+1}\mu_n \qquad (8)$$

In reference 12 it is developed that

$$k_{o,1} = k_{1,o} \exp\left(\frac{-h_o f}{kT}\right) \tag{9}$$

where k is the Boltzmann constant. For other energy levels

$$k_{n,n+1} = k_{n+1,n} \exp\left(\frac{-h_o f}{kT}\right)$$

and from the quantum-mechanical study of transition probabilities

$$k_{n,n-1} = nk_{1,o} \tag{10}$$

If equation (8) is combined with equations (9) and (10), it is possible to obtain

$$\frac{d\mu_n}{dt} = k_{1,o}\left\{(n + 1)\mu_{n+1} - n\mu_n + \left[\exp\left(\frac{-h_o f}{kT}\right)\right][n\mu_{n-1} - (n + 1)\mu_n]\right\} \tag{11}$$

Let N_o be Avogadro's number, and

$$N = \sum_{n=o}^{\infty} \mu_n$$

If e_v is used to denote the vibrational energy above the ground $(n = o)$ state of a given species, per mole of species

$$e_v = \frac{N_o}{N} \sum_{n=o}^{\infty} \epsilon_n \mu_n = \frac{N_o h_o f}{N} \sum_{n=o}^{\infty} n\mu_n$$

Therefore

$$\frac{de_v}{dt} = \frac{N_o h_o f}{N} \sum_{n=1}^{\infty} n \frac{d\mu_n}{dt}$$

When equation (11) is combined with this last equation, it is possible to manipulate the resulting expression into the form

$$\frac{de_V}{dt} = k_{1,0}\left[1 - \exp\left(\frac{-h_0 f}{kT}\right)\right]\left\{\frac{N_0 h_0 f}{\left[\exp\left(\frac{-h_0 f}{kT}\right)\right] - 1} - e_V\right\} \tag{12}$$

The expression

$$\bar{e}_V(T) = \frac{N_0 h_0 f}{\left[\exp\left(\frac{-h_0 f}{kT}\right)\right] - 1}$$

is defined to be the vibrational energy, per mole of species, corresponding to equilibrium conditions at temperature T. Also, the relaxation time, τ, is defined by the relation

$$\frac{1}{\tau} = k_{1,0}\left[1 - \exp\left(\frac{-h_0 f}{kT}\right)\right] \tag{13}$$

With these definitions, equation (12) can be written in a more compact form.

$$\frac{de_V}{dt} = \frac{[\bar{e}_V(T) - e_V]}{\tau} \tag{14}$$

Since $k_{1,0}$ is a function of density, temperature, and chemical species, τ is a function of these variables. It is customary to write, for the jth chemical species, the vibrational nonequilibrium equations in the form

$$\frac{de_{Vj}}{dt} = \frac{[\bar{e}_{Vj}(T) - e_{Vj}]}{\tau_j(\rho,T)} \qquad (j = 1, 2, \ldots, s) \tag{15}$$

The vibrational energy of species j is related to the total internal energy per mole, e_j, of species j by the equation

$$e_j = \tilde{e}_j + e_{Vj} + e_{Dj} \tag{16}$$

where $\tilde{e}_j(T)$ is a function of temperature which expresses the rotational, electronic, and translational energies per mole of species j. The term e_{Dj}, a constant, is the energy of dissociation per mole of species j.

Fluid Dynamical Equations

Since the flow under consideration is to be one-dimensional and steady, all quantities used in its description are functions of a single independent variable. The channel is presumed to be described by some function of x, the distance along the axis of the channel from some fixed point. However, the flow variables will be considered as functions of time, t. In the conservation equations which follow, the speed of the flow is represented by u, the pressure by p, the cross-sectional area of the channel by A, and the enthalpy per unit mass by h. The conservation equations are

Mass
$$\rho u A = c_1 \tag{17}$$

Energy
$$\frac{1}{2} u^2 + h = c_2 \tag{18}$$

Momentum
$$\frac{1}{2} u^2 + \int \frac{dp}{\rho} = c_3 \tag{19}$$

The numbers c_1, c_2, and c_3 are constants of integration.

It is assumed that either a function $A(x)$ or a function $p(x)$ is given. When $A(x)$ is given, the cross-sectional area of the channel is prescribed; when $p(x)$ is given, the pressure is a known function along the channel.

For a mixture of gases composed of s species, the thermal equation of state is

$$p = \left(\sum_{j=1}^{s} \gamma_j \right) \rho \mathfrak{R} T \tag{20}$$

In this equation, $\mathfrak{R}$ is the universal gas constant. In later equations, the notation

$$\sum_{j=1}^{s} \gamma_j = \sigma$$

will be used. Thus

$$p = \sigma \rho \mathfrak{R} T \tag{21}$$

By differentiating equation (21) with respect to time, and using

$$\frac{d}{dt} = \frac{dx}{dt} \frac{d}{dx} = u \frac{d}{dx}$$

it is found that

$$\frac{uT}{p}\frac{dp}{dx} = \frac{dT}{dt} + \frac{T}{\rho}\frac{d\rho}{dt} + \frac{T}{\sigma}\sum_{j=1}^{s}\frac{d\gamma_j}{dt} \tag{22}$$

Equation (22) is useful when $p(x)$ is specified. When $A(x)$ is given instead, equation (22) can be adapted by using the equations for conservation of mass and momentum. To this end, the conservation of mass equation can be written

$$(uA)\frac{d\rho}{dt} + (\rho A)\frac{du}{dt} + (\rho u)\frac{dA}{dt} = 0 \tag{23}$$

and from the conservation of momentum

$$u\frac{du}{dx} + \frac{1}{\rho}\frac{dp}{dx} = 0$$

or

$$\frac{du}{dt} = -\frac{1}{\rho}\frac{dp}{dx} \tag{24}$$

When equations (23) and (24) are combined, there is obtained

$$\frac{dp}{dx} = u\frac{d\rho}{dt} + \frac{\rho u^2}{A}\frac{dA}{dx} \tag{25}$$

Finally, by substituting the right side of equation (25) for dp/dx in equation (22), it is seen that

$$\frac{u^3}{A\mathcal{R}\sigma}\frac{dA}{dx} = \frac{dT}{dt} + \frac{T}{\rho}\left(1 - \frac{u^2\rho}{p}\right)\frac{d\rho}{dt} + \frac{T}{\sigma}\sum_{j=1}^{s}\frac{d\gamma_j}{dt} \tag{26}$$

This equation will be useful when $A(x)$ is specified.

In general

$$\frac{dT}{dt} + \frac{T}{\rho}U\frac{d\rho}{dt} + \frac{T}{\sigma}\sum_{j=1}^{s}\frac{d\gamma_j}{dt} = V \tag{27}$$

When $A(x)$ is specified, $U = [1 - (u^2/\sigma\mathcal{R}T)]$ and $V = (u^3/A\mathcal{R}\sigma)(dA/dx)$. When $p(x)$ is specified, $U = 1$ and $V = (uT/p)(dp/dx)$.

Equation (27) is one of the two fluid dynamical equations which will be used in the numerical solution of the nonequilibrium flow. The other such relation is derived from the equations for conservation of energy and momentum.

The specific enthalpy, h, is given by

$$h = e + \frac{p}{\rho}$$

For a mixture of s chemical species, the internal energy, e, per unit mass is

$$e = \sum_{j=1}^{s} \gamma_j e_j$$

Therefore

$$h = \sum_{j=1}^{s} \gamma_j e_j + \frac{p}{\rho} \tag{28}$$

When this equation is differentiated with respect to time, there is obtained

$$\frac{dh}{dt} = \sum_{j=1}^{s} \gamma_j \frac{de_j}{dt} + \sum_{j=1}^{s} e_j \frac{d\gamma_j}{dt} + \frac{1}{\rho}\frac{dp}{dt} - \frac{\sigma \mathfrak{R} T}{\rho}\frac{d\rho}{dt} \tag{29}$$

When the equations for the conservation of energy and momentum are differentiated and then combined, it is possible to show that

$$\frac{dh}{dt} = \frac{1}{\rho}\frac{dp}{dt} \tag{30}$$

From equation (16),

$$\frac{de_j}{dt} = \frac{d\tilde{e}_j}{dt} + \frac{de_{vj}}{dt} \qquad (j = 1, 2, \ldots, s)$$

and since $d\tilde{e}_j/dT$ is a known function of T, it is convenient to write

$$\frac{de_j}{dt} = \frac{d\tilde{e}_j}{dT}\frac{dT}{dt} + \frac{de_{vj}}{dt} \qquad (j = 1, 2, \ldots, s) \tag{31}$$

When equations (29), (30), and (31) are combined, there results

$$\left(\sum_{j=1}^{s} \gamma_j \frac{d\tilde{e}_j}{dT}\right)\frac{dT}{dt} + \sum_{j=1}^{s} \gamma_j \frac{de_{vj}}{dt} + \sum_{j=1}^{s} e_j \frac{d\gamma_j}{dt} - \frac{\sigma \mathcal{R} T}{\rho}\frac{d\rho}{dt} = 0 \tag{32}$$

Equation (32) together with equation (27) will be used with the equations of the nonequilibrium rate processes in the numerical procedure which is to be described.

NUMERICAL PROCEDURE

For one-dimensional channel flow, the field points can be stationed along a line which extends the length of the channel. The variables ρ, T, γ_j, and e_{vj} $(j = 1, 2, \ldots, s)$ from which all other flow variables can be obtained must be computed at each of these stations.

As a fluid element moves downstream from one station to the next, an interval of time Δt elapses, and there are corresponding increments $\Delta\rho$, ΔT, $\Delta\gamma_j$, and Δe_{vj}. Let it be assumed that the fluid element is at a given station at time t_o and at the next downstream station at time $(t_o + \Delta t)$. Then

$$\begin{aligned}
\rho(t_o + \Delta t) &= \rho(t_o) + \Delta\rho \\
T(t_o + \Delta t) &= T(t_o) + \Delta T \\
\gamma_j(t_o + \Delta t) &= \gamma_j(t_o) + \Delta\gamma_j \qquad (j = 1, 2, \ldots, s) \\
e_{vj}(t_o + \Delta t) &= e_{vj}(t_o) + \Delta e_{vj} \qquad (j = 1, 2, \ldots, s)
\end{aligned}$$

The computational problem is to find numerical values for the increments $\Delta\rho$, ΔT, $\Delta\gamma_j$, and Δe_{vj} when numerical values of the flow variables are known at the upstream station. Since values for all quantities are assumed known at the beginning of the interval $(t_o, t_o + \Delta t)$, there is no loss in generality in taking $t_o = 0$ and denoting values at the beginning of the interval by the subscript o. Thus

$$\begin{aligned}
\rho(\Delta t) &= \rho_o + \Delta\rho \\
T(\Delta t) &= T_o + \Delta T \\
\gamma_j(\Delta t) &= (\gamma_j)_o + \Delta\gamma_j \qquad (j = 1, 2, \ldots, s) \\
e_{vj}(\Delta t) &= (e_{vj})_o + \Delta e_{vj} \qquad (j = 1, 2, \ldots, s)
\end{aligned}$$

Computation of the Increments Δe_{vj}

As a consequence of the assumption that vibrational and chemical relaxation rates are not coupled, an expression for the Δe_{vj} $(j = 1, 2, \ldots, s)$ can be found independently of the increments $\Delta\gamma_j$. Since ρ and T are functions of time, equations (15) can be written

$$\left(\frac{de_{vj}}{dt}\right)_o = \frac{(\bar{e}_{vj} - e_{vj})_o}{(\tau_j)_o} \qquad (j = 1, 2, \ldots, s)$$

It might be presumed, then, that the increment Δe_{vj} could be computed from

$$\Delta e_{vj} = \left[\frac{(\bar{e}_{vj} - e_{vj})_o}{(\tau_j)_o}\right]\Delta t \qquad (j = 1, 2, \ldots, s)$$

However, use of these equations are not practical because of the behavior of the right-hand side in the near-equilibrium region of the flow. In the near-equilibrium region, $1/\tau_j$ is very large while $(\bar{e}_{vj} - e_{vj})$ is very small. This makes an accurate evaluation of Δe_{vj} impossible even for small Δt. Apart from this, the use of $(\bar{e}_{vj} - e_{vj})_o$ over the entire interval, Δt, is of questionable validity. The quantities τ_j, $\bar{e}_{vj}$, and e_{vj} can be described as slowly varying in the near-equilibrium region, because their change during a short-time interval is small enough that their value during the interval can be approximated by a constant. On the other hand, $(\bar{e}_{vj} - e_{vj})$ can change by several times its own magnitude during a small interval of time when the upstream station is in the near-equilibrium region.

A means of avoiding these numerical difficulties is provided by the behavior of $\bar{e}_{vj}$. Since it is a slowly varying function, $d\bar{e}_{vj}/dt$ can be considered constant over an interval Δt. Likewise, τ_j can be considered constant over the interval.

With this in mind, the following equations are derived from equations (15).

$$\frac{d\bar{e}_{vj}}{dt} - \frac{de_{vj}}{dt} = -\left(\frac{\bar{e}_{vj} - e_{vj}}{\tau_j}\right) + \frac{d\bar{e}_{vj}}{dt} \qquad (j = 1, 2, \ldots, s)$$

These can also be written

$$\frac{d}{dt}(\bar{e}_{vj} - e_{vj}) = -\frac{1}{\tau_j}(\bar{e}_{vj} - e_{vj}) + \frac{d\bar{e}_{vj}}{dt} \qquad (j = 1, 2, \ldots, s) \qquad (33)$$

Over the interval Δt, $\tau_j = (\tau_j)_o$ and

$$\frac{d\bar{e}_{vj}}{dt} = \frac{\Delta\bar{e}_{vj}}{\Delta t}$$

Hence, over this interval, equations (33) become linear differential equations with constant coefficients. Their solution is found to be

$$[\bar{e}_{vj}(t) - e_{vj}(t)] = \frac{\Delta\bar{e}_{vj}}{\Delta t}(\tau_j)_o + \left[(\bar{e}_{vj} - e_{vj})_o - (\tau_j)_o \frac{\Delta\bar{e}_{vj}}{\Delta t}\right]\left\{\exp\left[-\frac{t}{(\tau_j)_o}\right]\right\}$$

$$(j = 1, 2, \ldots, s)$$

where $0 \leq t \leq \Delta t$. From this solution, the increment in $(\bar{e}_{vj} - e_{vj})$ corresponding to Δt can be found

$$\Delta(\bar{e}_{vj} - e_{vj}) = \left\{\exp\left[-\frac{\Delta t}{(\tau_j)_o}\right] - 1\right\}\left[(\bar{e}_{vj} - e_{vj})_o - (\tau_j)_o \frac{\Delta\bar{e}_{vj}}{\Delta t}\right] \qquad (j = 1, 2, \ldots, s) \tag{34a}$$

Equations (34a) show that as $(\tau_j)_o \to 0$ (equilibrium is approached), the increments $\Delta(\bar{e}_{vj} - e_{vj}) \to -(\bar{e}_{vj} - e_{vj})_o$. There is no difficulty in computing these increments in the near-equilibrium region by means of equations (34a). The increments Δe_{vj} can now be determined accurately.

$$\Delta e_{vj} = \Delta\bar{e}_{vj} - \Delta(\bar{e}_{vj} - e_{vj}) \qquad (j = 1, 2, \ldots, s)$$

and

$$\Delta\bar{e}_{vj} = \left(\frac{d\bar{e}_{vj}}{dT}\right)_o\left(\frac{\Delta T}{\Delta t}\right)\Delta t = \left(\frac{d\bar{e}_{vj}}{dT}\right)_o \Delta T \qquad (j = 1, 2, \ldots, s)$$

These last two sets of equations are combined with equations (34a) to give

$$\Delta e_{vj} = \left(\frac{d\bar{e}_{vj}}{dT}\right)_o \Delta T - \left\{\exp\left[\frac{-\Delta t}{(\tau_j)_o}\right] - 1\right\}\left[(\bar{e}_{vj} - e_{vj})_o - \frac{(\tau_j)_o}{\Delta t}\left(\frac{d\bar{e}_{vj}}{dT}\right)_o \Delta T\right]$$

$$(j = 1, 2, \ldots, s) \tag{34b}$$

Computation of the Increments ΔX_i

When the increments Δe_{vj} $(j = 1, 2, \ldots, s)$ have been found by the method just outlined, there remain the $(s + 2)$ increments $\Delta\rho$, ΔT, and $\Delta\gamma_j$ $(j = 1, 2, \ldots, s)$ yet to be computed. These will be found by solving a system of $(s + 2)$ linear equations in which the variables are the $(s + 2)$ increments in question. However, these equations contain the increments ΔX_i $(i = 1, 2, \ldots, r)$ taken by the variables X_i during the interval Δt. It will be shown that upon solution of an eigenvalue problem, each ΔX_i becomes a linear function of $\Delta\rho$ and ΔT.

The variables X_i $(i = 1, 2, \ldots, r)$ satisfy the coupled system of rate equations (7)

$$\frac{dX_i}{dt} = - \sum_{l=1}^{r} a_{il} X_l + F(T,X_i)\,\frac{dT}{dt} + G(\rho,X_i)\,\frac{d\rho}{dt}$$

where

$$a_{il} = (1 - X_i)\left(\sum_{j=1}^{s} \frac{\beta_{ij}\beta_{lj}}{\gamma_j}\right)\left(k_{fl}\,\rho^{\nu_l - 1} \prod_{j=1}^{s} \gamma_j^{\nu_{lj}}\right) \qquad \begin{pmatrix} i = 1, 2, \ldots, r \\ l = 1, 2, \ldots, r \end{pmatrix}$$

$$F(T,X_i) = (1 - X_i)\left[\frac{1}{K_i(T)}\right]\left(\frac{dK_i}{dT}\right)$$

$$G(\rho,X_i) = -(1 - X_i)\left(\frac{\beta_i}{\rho}\right)$$

With the exception of X_i itself, all the variables which appear in the coefficients a_{il}, $F(T,X_i)$, and $G(\rho,X_i)$ are assumed to be slowly varying in the sense that they change by only a small percentage of their magnitude during an interval Δt. Hence, they will be approximated by a constant value over this interval. In the near-equilibrium region, however, the variables X_i $(i = 1, 2, \ldots, r)$ can change by several times their own magnitude during the interval. This magnitude must be small because $X_i \to 0$ as equilibrium is approached. However, in any region of channel flow, including the near-equilibrium region, $(1 - X_i)$ can change by only a small percentage of its value during a small interval of time. This fact allows the coupled, first-order system, equations (7), to be "linearized" by taking the coefficients to be constant over the interval Δt. Equations (7) are then written

$$\frac{dX_i}{dt} = - \sum_{l=1}^{r} (a_{il})_0 X_l + [F(T,X_i)]_0\left(\frac{\Delta T}{\Delta t}\right) + [G(\rho,X_i)]_0\,\frac{\Delta\rho}{\Delta t}$$

$$(i = 1, 2, \ldots, r) \qquad (0 \leq t \leq \Delta t) \qquad (35)$$

When the constants N_i are defined through the equation

$$N_i = \frac{[F(T,X_i)]_0}{\Delta t}\,\Delta T + \frac{[G(\rho,X_i)]_0}{\Delta t}\,\Delta\rho \qquad (i = 1, 2, \ldots, r)$$

the differential equations (35) can be written in vector form

$$\frac{d\vec{X}}{dt} = -A\vec{X} + \vec{N} \qquad (36)$$

where

$$\vec{X} = \begin{pmatrix} X_1 \\ X_2 \\ \cdot \\ \cdot \\ \cdot \\ X_r \end{pmatrix}, \quad \vec{N} = \begin{pmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ \cdot \\ N_r \end{pmatrix}, \quad \text{and} \quad A = \begin{pmatrix} (a_{11})_o & (a_{12})_o & \cdot\cdot\cdot & (a_{1r})_o \\ (a_{21})_o & (a_{22})_o & \cdot\cdot\cdot & (a_{2r})_o \\ \cdot & \cdot & \cdot\cdot\cdot & \cdot \\ \cdot & \cdot & \cdot\cdot\cdot & \cdot \\ \cdot & \cdot & \cdot\cdot\cdot & \cdot \\ (a_{r1})_o & (a_{r2})_o & \cdot\cdot\cdot & (a_{rr})_o \end{pmatrix}$$

Although numerical values cannot be assigned to N_i $(i = 1, 2, \ldots, r)$ until ΔT and $\Delta\rho$ have been found, this must not obscure the fact that each N_i can be considered to be a constant over the interval Δt.

If $\vec{X}(t)$ is a vector function which satisfies the differential equation (36) such that $\vec{X}_o = \vec{X}(0)$, then each ΔX_i $(i = 1, 2, \ldots, r)$ is determined by the equation

$$\Delta\vec{X} = \vec{X}(\Delta t) - \vec{X}(0)$$

Consequently, a general solution must be found for equation (36).

Toward this end, a transformation will be used to replace equation (36) with an uncoupled system. Theorem 3 in the appendix shows that such a transformation exists. This theorem states that there are eigenvectors, η_i $(i = 1, 2, \ldots, r)$, of the matrix A which are linearly independent at every point in the flow. A simplified method for finding the eigenvalues and eigenvectors of A is provided by theorems 1 and 2 in the appendix.

If E is the matrix whose ith column is the eigenvector $\vec{\eta}_i$ which corresponds to the eigenvalue λ_i of A, then E is nonsingular since its column vectors are linearly independent (see ref. 13). Moreover,

$$A = E \Lambda E^{-1}$$

where Λ is the diagonal matrix whose diagonal elements are the eigenvalues of A.

$$\Lambda = \operatorname{diag}(\lambda_1, \lambda_2, \ldots, \lambda_r) = \begin{pmatrix} \lambda_1 & & & & & \\ & \lambda_2 & & & & \\ & & \cdot & & & \\ & & & \cdot & & \\ & & & & \cdot & \\ & & & & & \lambda_r \end{pmatrix}$$

Equation (36) can be written

$$\frac{d\vec{X}}{dt} = -(E\,\Lambda\,E^{-1})\vec{X} + \vec{N}$$

or

$$E^{-1}\frac{d\vec{X}}{dt} = -\Lambda E^{-1}\vec{X} + E^{-1}\vec{N}$$

Setting $\vec{\psi} = E^{-1}\vec{X}$ yields

$$\frac{d\vec{\psi}}{dt} = -\Lambda\vec{\psi} + E^{-1}\vec{N} \qquad (37)$$

Equation (37) is an uncoupled system because Λ is a diagonal matrix of constants.

If $\vec{\psi}(t)$ is a general solution of equation (37) then

$$\vec{X}(t) = E\vec{\psi}(t)$$

is a general solution of equation (36).

The general solution, $\vec{\psi}(t)$, is found by obtaining a general solution $\vec{\psi}_h(t)$ of the homogeneous equation

$$\frac{d\vec{\psi}}{dt} = -\Lambda\vec{\psi}$$

then adding to it any particular solution, $\vec{\psi}_p(t)$ of the equation (37).

$$\vec{\psi}(t) = \vec{\psi}_h(t) + \vec{\psi}_p(t)$$

The solution, $\vec{\psi}_h(t)$, of the homogeneous equation is easily verified to be

$$\vec{\psi}_h(t) = D(t)\vec{C}$$

where

$$\vec{C} = \begin{pmatrix} C_1 \\ C_2 \\ \cdot \\ \cdot \\ \cdot \\ C_r \end{pmatrix} \quad \text{and} \quad D(t) = \begin{pmatrix} e^{-\lambda_1 t} & & & & \\ & e^{-\lambda_2 t} & & & \\ & & \cdot & & \\ & & & \cdot & \\ & & & & \cdot \\ & & & & & e^{-\lambda_r t} \end{pmatrix}$$

A particular solution, $\vec{\psi}_p(t)$ of equation (37), can be obtained by solving

$$\vec{0} = -\Lambda\vec{\psi}_p + E^{-1}\vec{N}$$

This gives

$$\vec{\psi}_p = D_1(t)E^{-1}\vec{N}$$

where the diagonal matrix D_1 can take two possible forms. If all the eigenvalues of A are nonzero

$$D_1(t) = \Lambda^{-1} = \text{diag}\left(\frac{1}{\lambda_1}, \frac{1}{\lambda_2}, \ldots, \frac{1}{\lambda_r}\right)$$

The possibility that some of the eigenvalues may vanish, however, cannot be excluded. This will happen, for example, when there are more chemical equations than distinct chemical species. Each eigenvalue of A which vanishes must have its reciprocal in $D_1(t)$ replaced by t. For example, if the second and rth eigenvalues vanish, $D_1(t)$ takes the form

$$D_1(t) = \text{diag}\left(\frac{1}{\lambda_1}, t, \frac{1}{\lambda_3}, \ldots, \frac{1}{\lambda_{r-1}}, t\right)$$

Finally,

$$\vec{\psi}(t) = \vec{\psi}_h(t) + \psi_p(t)$$

$$= D(t)\vec{C} + D_1(t)E^{-1}\vec{N}$$

Therefore

$$\vec{X}(t) = [ED(t)]\vec{C} + [ED_1(t)E^{-1}]\vec{N}$$

It is possible to determine the constants $C_1, C_2, \ldots, C_r$ from the equation

$$\vec{X}_o = \vec{X}(0) = [ED(0)]\vec{C} + [ED_1(0)E^{-1}]\vec{N}$$

From the definition of $D(t)$, it is seen that $D(0) = I$, the identity matrix. Consequently,

$$\vec{C} = E^{-1}\vec{X}_o - [D_1(0)E^{-1}]\vec{N}$$

and this yields

$$\vec{X}(t) = ED(t)\left\{E^{-1}\vec{X}_o - [D_1(0)E^{-1}]\vec{N}\right\} + [ED_1(t)E^{-1}]\vec{N} \qquad (38a)$$

The increments, ΔX_i $(i = 1, 2, \ldots, r)$, for the interval Δt are found from

$$\Delta\vec{X} = \vec{X}(\Delta t) - \vec{X}_o$$

Therefore

$$\Delta\vec{X} = [ED(\Delta t)E^{-1} - I]\vec{X}_0 + [ED_1(\Delta t)E^{-1} - ED(\Delta t)D_1(0)E^{-1}]\vec{N}$$

For a fixed value of Δt, the diagonal matrices $D(\Delta t)$ and $D_1(\Delta t)$ become matrices with constant elements. For purposes of notation, let

$$[ED(\Delta t)E^{-1} - I] = M = m_{ij} \qquad (i, j = 1, 2, \ldots, r) \tag{38b}$$

and

$$[ED_1(\Delta t)E^{-1} - ED(\Delta t)D_1(0)E^{-1}] = H = h_{ij} \qquad (i, j = 1, 2, \ldots, r) \tag{38c}$$

Then

$$\Delta\vec{X} = M\vec{X}_0 + H\vec{N}$$

In terms of the increments $\Delta\rho$ and ΔT, this is written

$$\Delta X_i = \sum_{j=1}^{r} m_{ij}(X_j)_0 + \left[\sum_{j=1}^{r} h_{ij} \frac{F(T,X_j)_0}{\Delta t}\right]\Delta T + \left[\sum_{j=1}^{r} h_{ij} \frac{G(\rho,X_j)_0}{\Delta t}\right]\Delta\rho$$

$$(i = 1, 2, \ldots, r) \tag{39}$$

Computation of the Increments $\Delta\rho$, ΔT, and $\Delta\gamma_j$

With equations (6) and (39) combined there is obtained

$$\left\{\left[\frac{1}{K_i(T)}\frac{dK_i}{dT}\right]_0 - \alpha_i\left[\sum_{l=1}^{r} h_{il}\frac{F(T,X_l)_0}{\Delta t}\right]\right\}\Delta T - \left\{\left(\frac{\beta_i}{\rho}\right)_0 + \alpha_i\left[\sum_{l=1}^{r} h_{il}\frac{G(\rho,X_l)_0}{\Delta t}\right]\right\}\Delta\rho$$

$$- \sum_{j=1}^{s}\left(\frac{\beta_{ij}}{\gamma_j}\right)_0 \Delta\gamma_j = \alpha_i \sum_{l=1}^{r} m_{il}(X_l)_0 \qquad (i = 1, 2, \ldots, r) \tag{40}$$

where

$$\alpha_i = \left[\frac{K_i(T)}{\rho^{\beta_i}\prod_{j=1}^{s}\gamma_j^{\beta_{ij}}}\right]_0$$

The two linear equations below are easily obtained from equation (27) and a combination of equations (32) and (34b)

$$\Delta T + \left(\frac{T}{\sigma}\right)_o \sum_{j=1}^{s} \Delta\gamma_j + \left(U \frac{T}{\rho}\right)_o \Delta\rho = (V)_o \Delta t \tag{41}$$

$$\left\{ \sum_{j=1}^{s} (\gamma_j)_o \left[\left(\frac{d\tilde{e}_j}{dT}\right)_o + \left(\frac{d\bar{e}_{vj}}{dT}\right)_o \left(1 + \frac{(\tau_j)_o}{\Delta t}\left\{\exp\left[\frac{-\Delta t}{(\tau_j)_o}\right] - 1\right\}\right)\right]\right\} \Delta T - \left(\frac{\sigma \Re T}{\rho}\right)_o \Delta\rho$$

$$+ \sum_{j=1}^{s} (e_j)_o \Delta\gamma_j = \sum_{j=1}^{s}\left((\gamma_j)_o \left\{\exp\left[\frac{-\Delta t}{(\tau_j)_o}\right] - 1\right\} (\bar{e}_{vj} - e_{vj})_o\right) \tag{42}$$

Equations (40), (41), and (42) comprise a system of $(r + 2)$ linear equations in the $(s + 2)$ unknowns ΔT, $\Delta\rho$, and $\Delta\gamma_j$ $(j = 1, 2, \ldots, s)$. If it were possible that $r = s$ and that equations (40) form a linearly independent set, these $(s + 2)$ equations can be solved for the increments in question. However, both conditions cannot be satisfied simultaneously, and supplementary linear equations in the variables ΔT, $\Delta\rho$, and $\Delta\gamma_j$ $(j = 1, 2, \ldots, s)$ are needed. These supplementary equations can be obtained, just as in equilibrium from atom conservation equations.

The system of equations (40) always contains a linearly independent subset which can be determined by reference to the original chemical equations (1). The chemical equations (1) can be ordered so that each succeeding equation, after the first, contains a chemical species not appearing in any of the previous equations. If this ordering exhausts all of equations (1), there will be some number, say r_1 (where $r_1 < r$), of equations (40) which is linearly independent. This linearly independent subset of equations can be determined before any computation is begun, and the required atom conservation equations can be adjoined.

In the s species, there are a fixed number, m, of different elements. Let n_{kj} be the total number of atoms of element k $(k = 1, 2, \ldots, m)$ in species j. The total number of atoms of element k must be constant so that

$$\sum_{j=1}^{s} n_{kj} \frac{d\gamma_j}{dt} = 0 \qquad (k = 1, 2, \ldots, m)$$

When $d\gamma_j/dt$ is replaced by $\Delta\gamma_j/\Delta t$ and both sides of this equation are multiplied by Δt, there is obtained

$$\sum_{j=1}^{s} n_{kj} \Delta\gamma_j = 0 \qquad (k = 1, 2, \ldots, m)$$

From these m linear equations, the required supplementary equations can be obtained.

It should be noted that equations (40) were derived independently from the fluid dynamical equations (17), (18), and (19). They can be used, therefore, in conjunction with other sets of fluid equations which arise in, for example, three-dimensional flow, or unsteady flow.

CONCLUDING REMARKS

In order to compute accurately the nonequilibrium channel flow of a multicomponent gaseous mixture, a numerical formulation is needed which applies to the equilibrium and near-equilibrium regions of the flow as well as the nonequilibrium region. The needed formulation is obtainable when a proper choice has been made for the dependent variables, and the rate equations in these variables are linearized over small intervals of time. By a properly chosen transformation, these rate equations can also be uncoupled, and the problem of obtaining expressions for the reaction variables reduces to solving a system of linear, uncoupled, first-order differential equations. The solution is, of course, easily obtained. However, in order to determine the needed transformation, it is necessary to solve an eigenvalue problem. It has been found that the needed transformation exists for all regions of the channel, and a method has been developed which reduces the eigenvalue problem to finding the eigenvalues of a symmetric matrix. This greatly simplifies the computational problem because numerical methods for finding eigenvalues of a general matrix are unreliable in their accuracy.

The integration procedure used in reference 10 can be regarded as a special application of the present method. In that work matrix methods were not required because of the low rank of the system. The method is presently being applied to a more general case. It appears that the necessary matrix manipulations can be performed accurately, and without adding greatly to the computing time per case experienced in reference 10.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., Oct. 28, 1965

APPENDIX A

PROPERTIES OF THE MATRIX A

The $r \times r$ matrix $A = [a_{il}]$ of equation (36) has its elements defined in equations (7).

$$a_{il} = (1 - \chi_i)_0 \left(\sum_{j=1}^{s} \frac{\beta_{ij}\beta_{lj}}{\gamma_j} \right)_0 \left(k_{fl}\rho^{\nu_l - 1} \prod_{j=1}^{s} \gamma_j^{\nu_{lj}} \right)_0 \tag{A1}$$

This can be written

$$a_{il} = p_i b_{il} q_l$$

where

$$p_i = (1 - \chi_i)_0, \qquad q_l = \left(k_{fl}\rho^{\nu_l - 1} \prod_{j=1}^{s} \gamma_j^{\nu_{lj}} \right)_0$$

and

$$b_{il} = \left(\sum_{j=1}^{s} \frac{\beta_{ij}\beta_{lj}}{\gamma_j} \right)_0$$

It is seen that $b_{il} = b_{li}$ and hence the matrix $B = [b_{il}]$ is an $r \times r$ real symmetric matrix. Since $\chi_i < 1$, it follows that $p_i > 0$ $(i = 1, 2, \ldots, r)$. Likewise, from its definition, $q_l > 0$ $(l = 1, 2, \ldots, r)$.

Let $P = \mathrm{diag}\,(p_1, p_2, \ldots, p_r)$ and $Q = \mathrm{diag}\,(q_1, q_2, \ldots, q_r)$. Then, from the construction of P, B, and Q, it follows that

$$A = PBQ$$

Both P and Q are diagonal positive definite real matrices and B is real symmetric.

Theorem 1.

Let $A = PBQ$ where B is real symmetric and where P and Q are real, diagonal, and positive definite.

$$P = \mathrm{diag}\,(p_1, p_2, \ldots, p_r) \;; \quad p_i > 0 \,, \quad i = 1, 2, \ldots, r$$

$$Q = \mathrm{diag}\,(q_1, q_2, \ldots, q_r) \;; \quad q_1 > 0 \,, \quad i = 1, 2, \ldots, r$$

Then, the eigenvalues of A are the same as the eigenvalues of a real symmetric matrix

$$F = DBD$$

where

$$D = \mathrm{diag}\,(\sqrt{p_1q_1}, \sqrt{p_2q_2}, \; . \; . \; . \; , \sqrt{p_rq_r})$$

Proof:

Since P and Q are diagonal with rank r, each has an inverse. It is possible, then, to define a matrix

$$S^{-1} = PQ^{-1} = \mathrm{diag}\,(p_1/q_1, \; p_2/q_2, \; . \; . \; ., \; p_r/q_r)$$

Also, let

$$T = QBQ$$

Then

$$A = PBQ = PQ^{-1}QBQ = S^{-1}T$$

Now

$$[\lambda I - A] = [\lambda I - S^{-1}T] = [S^{-1}][\lambda S - T]$$

where

$$S = \mathrm{diag}\,(q_1/p_1, \; q_2/p_2, \; . \; . \; ., \; q_n/p_n)$$

Consequently

$$|\lambda I - A| = |S^{-1}| \cdot |\lambda S - T|$$

From the definition of S^{-1}, it is seen that $|S^{-1}| \neq 0$. Thus $|\lambda I - A| = 0$ if and only if $|\lambda S - T| = 0$. This shows that the eigenvalues of A are precisely the roots of $|\lambda S - T| = 0$.

Now define the matrix R by

$$R = \mathrm{diag}\,(\sqrt{p_1/q_1}, \sqrt{p_2/q_2}, \; . \; . \; ., \sqrt{p_n/q_n})$$

This definition is made so that $RSR = I$. Consequently

$$|R| \cdot |\lambda S - T| \cdot |R| = |\lambda I - RTR|$$

Again, $|R| \neq 0$ so that the roots of $|\lambda S - T| = 0$ are the eigenvalues of the matrix

$$F = RTR$$

This shows that the eigenvalues of F are the same as the eigenvalues of A.

It will be shown that F is symmetric. Since R, Q, and B are all symmetric,

$$R^T = R, \quad Q^T = Q, \quad \text{and} \quad B^T = B$$

Then

$$F^T = R^T(QBQ)^T R^T = R^T Q^T B^T Q^T R^T = RQBQR = F$$

Since R and Q are diagonal, they commute. Let

$$D = RQ = QR = (\sqrt{p_1 q_1}, \sqrt{p_2 q_2}, \ldots, \sqrt{p_n q_n})$$

Then

$$F = DBD$$ Q.E.D.

Theorem 2.

Let A and F be the matrices of theorem 1, and let $R = \text{diag}\,(\sqrt{p_1/q_1}, \sqrt{p_2/q_2}, \ldots, \sqrt{p_r/q_r})$. If λ is an eigenvalue of F and $\vec{\xi}$ its corresponding eigenvector, then $\vec{\eta} = R\vec{\xi}$ is the eigenvector of A corresponding to λ.

Proof:

Theorem 1 shows that λ is an eigenvalue of both F and A. Since $\vec{\xi}$ is the corresponding eigenvector of F

$$F\vec{\xi} = (RQBRQ)\vec{\xi} = \lambda\vec{\xi}$$

Thus

$$PQ^{-1}R^{-1}(RQBRQ)\vec{\xi} = \lambda PQ^{-1}R^{-1}\vec{\xi}$$

The matrices R and Q commute since they are both diagonal. Hence

$$(PBQ)R\vec{\xi} = \lambda PQ^{-1}R^{-1}\vec{\xi}$$

Now $PQ^{-1}R^{-1} = R$, since $PQ^{-1} = \text{diag}\,(p_1/q_1, p_2/q_2, \ldots, p_r/q_r)$. Also $A = PBQ$, so that the above equation is

$$AR\vec{\xi} = \lambda R\vec{\xi}$$

Define $\vec{\eta}$ by

$$\vec{\eta} = R\vec{\xi}$$

Then

$$A\vec{\eta} = \lambda\vec{\eta}$$

so that $\vec{\eta}$ is the eigenvector of A corresponding to λ. Q.E.D.

Theorem 3.

The eigenvectors $\vec{\eta}_i$ $(i = 1, 2, \ldots, r)$ of the matrix $A = PBQ$ of theorem 1 are linearly independent.

Proof: Let $F = DBD$ be the matrix used in theorem 1. Since F is real symmetric, there is a nonsingular matrix H such that

$$H^{-1}FH = \text{diag}\,(\lambda_1, \lambda_2, \ldots, \lambda_r)$$

where $\lambda_1, \lambda_2, \ldots, \lambda_r$ are the eigenvalues of the matrix F. The possibility that some eigenvalues may have multiplicity greater than unity is not excluded. Let $L = \text{diag}\,(\lambda_1, \lambda_2, \ldots, \lambda_r)$. Then

$$FH = HL$$

Denote the column vectors of H by $\vec{\xi}_1, \vec{\xi}_2, \ldots, \vec{\xi}_r$. These column vectors of H are the eigenvectors of F, for

$$F\vec{\xi}_i = \lambda_i\vec{\xi}_i \qquad (i = 1, 2, \ldots, r)$$

It is to be noted that the $\vec{\xi}_i$ are linearly independent since H is nonsingular.

Now consider the matrix

$$G = RH$$

where

$$R = \text{diag}\,(\sqrt{p_1/q_1}, \sqrt{p_2/q_2}, \ldots, \sqrt{p_r/q_r})$$

The matrix G is nonsingular since it is the product of two nonsingular matrices, R and H. Thus, its column vectors form a linearly independent set. But the column vectors of G are

$$\vec{\eta}_i = R\vec{\xi}_i$$

The result of theorem 2 shows that these are the eigenvectors of $A = PBQ$.

Q.E.D.

REFERENCES

1. Vincenti, Walter G.: Calculations of the One-Dimensional Nonequilibrium Flow of Air Through a Hypersonic Nozzle. Interim Report AEDC TN-61-65, May 1961.

2. Emanuel, George; and Vincenti, Walter G.: Method for Calculation of the One-Dimensional Nonequilibrium Flow of a General Gas Mixture Through a Hypersonic Nozzle. Tech. Rep. AEDC-TDR-62-131, June 1962.

3. Marrone, Paul V.: Inviscid, Nonequilibrium Flow Behind Bow and Normal Shock Waves. Part I: General Analysis and Numerical Examples. Cornell Aero. Lab. Rep. Q.M.-1626-A-12(I), May 1963.

4. Curtiss, C. F.; and Hirschfelder, J. O.: Integration of Stiff Equations. Proc. Nat. Acad. Sci., vol. 38, no. 3, March 1952, pp. 235-243.

5. Emanuel, George: Problems Underlying the Numerical Integration of the Chemical and Vibrational Rate Equations in a Near-Equilibrium Flow. Tech. Rep. AEDC-TDR-63-82, March 1963.

6. Treanor, Charles E.: A Method for the Numerical Integration of Coupled First-Order Differential Equations With Greatly Different Time Constants. Cornell Aero. Lab. Rep. AG-1729-A-4, Jan. 1964.

7. Tyson, T. J.: An Implicit Integration Method for Chemical Kinetics. TRW Space Tech. Lab. Rep. 9840-6002-RU000, Sept. 1964.

8. Moretti, Gino: A New Technique for the Numerical Analysis of Nonequilibrium Flows. AIAA J., vol. 3, no. 2, Feb. 1965, pp. 223-229.

9. De Groat, James J.; and Abbett, Michael J.: A Computation of One-Dimensional Combustion of Methane. AIAA J., vol. 3, no. 2, Feb. 1965, pp. 381- 383.

10. Reinhardt, Walter A.; and Baldwin, Barrett S.: A Model for Chemically Reacting Nitrogen-Oxygen Mixtures With Application to Nonequilibrium Air Flow. NASA TN D-2971, 1965.

11. Baldwin, Barrett S.; and Reinhardt, Walter A.: Singular-Perturbation Effect in Nearequilibrium Chemically Reacting Flow. Bull Am. Phys. Soc., Series II, vol. 10, no. 2, Feb. 25, 1965, p. 279.

12. Landau, L.; and Teller, E.: Zur Theorie der Schalldispersion, Phys. Z. Sowjetunion, vol. 10, no. 1, 1936, pp. 34-43.

13. Perlis, Sam: Theory of Matrices. Addison-Wesley Pub. Co., Reading, Mass., 1952.

NASA-Langley, 1966 A-2243

> *"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*
>
> —NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546