

A STUDY OF THE EFFECT OF CHEMICAL NON-EQUILIBRIUM IN THE
FLOW OF A HIGH TEMPERATURE REACTIVE GAS MIXTURE
THROUGH A CONVERGING-DIVERGING NOZZLE

By

Clarence Quentin Ford

AN ABSTRACT

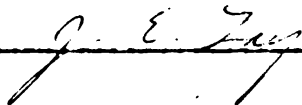
Submitted to the School for Advanced Graduates Studies of
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AN ABSTRACT

The object of this thesis was to investigate the recombination reactions of a dissociated high temperature gas mixture, as the mixture expands in a converging-diverging nozzle, and what effects these reactions might have on the expansion process.

As an approach to the problem, an analytical development was carried out, on the basis of collisional properties, to establish relationships which would describe the fluid dynamics and chemical kinetics. These relationships were combined to permit an analysis of the flow of a compressible mixture undergoing recombination reactions. The generalized analysis was then reduced to a simplified form, that would show only the effects of reactions occurring at a finite rate.

A particular nozzle shape was established, along with a set of initial conditions for a chemically reactive gas mixture, and a set of calculations were carried out to obtain physical properties along the nozzle axis. As a means of comparison, flow processes with recombination reaction rates of zero and infinity were calculated from the same initial conditions and for the same nozzle configuration. A zero reaction rate is equivalent to the "frozen" flow, while an infinite reaction rate is comparable to a process always in an equilibrium state.

Comparison of the finite reaction rate flow path calculations with those for the frozen and equilibrium paths shows that,

calculations with those for the frozen and equilibrium paths showed that, at the high temperatures resulting from a combustion process, the finite path remained close to the equilibrium path for the entire nozzle length. As the temperature decreased and velocity increased with expansion, the finite path diverged slowly from the equilibrium path. However, contrary to some published results on similar studies, performed on individual gases rather than a mixture, the flow path did not assume a frozen path in the diverging section of the nozzle.

Lack of experimental data on chemical reaction kinetics, especially in the high temperature regime, prevented a more thorough analysis of nozzle flow for a chemically reactive fluid. However, it was indicated in the results of this study that an equilibrium flow path, for which tabulated data are available, would approximate actual conditions more closely than the commonly employed frozen flow path.

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NOMENCLATURE

Symbols Used

A	frequency factor
$\mathbf{a}$	unit vector
B_i	net rate of formation of i^{th} species per unit volume per unit time
C_i	individual velocity of i^{th} species
$\bar{C}_i$	diffusion velocity of i^{th} species
c_p	heat capacity at constant pressure
c_v	heat capacity at constant volume
e	internal energy
E	activation energy
F	free energy function
f	distribution function
g	extensive variable
H	enthalpy
h	enthalpy per unit mass
K	equilibrium constant
k	reaction rate constant
M	chemical compound
N	number density
n	number of moles
P	pressure
R	molar gas constant
$\mathbf{r}$	position vector

NOMENCLATURE (cont.)

Symbols Used

S	surface
s	entropy
T	temperature
t	time
u_o	mass average velocity
u	linear velocity
$\bar{u}$	average velocity
V	volume
W	molecular weight
w	mass rate of flow
X	external force
x_i	mole fraction (i^{th} species)
x,y,z	rectangular coordinates
y	nozzle axis
$\mathcal{V}$	reaction velocity
$\mathbb{P}$	pressure tensor
γ	extensive variable flux vector
Γ	extensive variable rate of production
λ, Λ	transport function
ρ	mass density
ν'	stoichiometric coefficient of reactants
ν''	stoichiometric coefficient of products
ξ	reaction coordinate

NOMENCLATURE (cont.)

Symbols Used

ϕ	angle of convergence
θ	angle of divergence

Subscripts Used

b	backwork specific reaction rate
f	forward specific reaction rate
i,j	species index
t	throat conditions in nozzle
α	initial state for flow conditions
τ	reaction designator

Others

$\rightarrow$	vector quantity
$\frac{D}{Dt}$	Eulerian derivative, $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{u} \cdot \frac{\partial}{\partial r}$
[M]	concentration of chemical compound
*	non-equilibrium state

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INTRODUCTION AND ASSIGNMENT OF PROBLEM

The purpose of this study is to investigate the effects of chemical reaction as a high-temperature reactive gas mixture flows through a converging-diverging duct device. In practice, such a combination would exist in the nozzle arrangement located between a combustion chamber and the blading of a gas turbine, or it could be the exhaust nozzle for a jet powered aircraft or missile. The effects of chemical reaction in such cases is to cause the thermodynamics of the gas mixture to deviate from an equilibrium path during the expansion process, and as such, the true path would thus enter into the realm of non-equilibrium, irreversible, thermodynamics.

Classical thermodynamics is based on equilibrium phenomena, conditions which are not necessarily fulfilled in high speed, high temperature flow situations of reactive gas mixtures. Non-equilibrium is brought about primarily by the inability of the molecules in the mixture to react (combine) at a rate comparable to the changes in pressure and temperature, which is referred to as "chemical lag." Another effect comes about in a similar manner, where the molecules are unable to absorb the energy made available to them as fast as this energy is supplied, which is the "relaxation lag."

What is normally sought for in a thermodynamic analysis are the conditions of the system at any point along its flow path, when the initial state is known. Specifically, the quantities of main interest in nozzle flow are the temperature, pressure, composition and

enthalpy; from which other quantities such as velocity, thrust, density, etc. can be calculated.

Combustion in engines which rely upon a nozzle as a part of their driving mechanism may be assumed as an adiabatic process, and thus results in temperatures in the order of 4500°R to 5000°R . At temperatures of this magnitude, products resulting from the chemical combustion of a stoichiometric mixture, of a hydrocarbon fuel and air will not be carbon dioxide, water, and nitrogen; rather, a highly reactive mixture consisting of atomic states, free-radicals, complete molecular forms, free electrons, etc. Thus, the products are actually those of "incomplete" or "partial" combustion, and as such will continue the combustion phenomenon as expansion, with its attendant temperature decrease, takes place.

The analysis here is to examine the situation of flow with continuing combustion, in conjunction with changing physical conditions. Nozzle flow with a non-reactive system accounts for the increase in kinetic energy by removing just sufficient sensible energy from the gases through temperature change. With a reactive system, a reduction in temperature brings about a series of chemical recombination reactions, most of which are exothermic, and thus latent energy is released along with sensible energy. In comparison to non-reactive flow, it is seen that for a given change in kinetic energy, less temperature change is necessary with reactive mixtures by virtue of the additional energy of formation being released.

Current practices of thermodynamic analyses of the flow of reactive mixtures either neglects the reactive potential of a high tem-

perature, dissociated mixture or assumes that the system is always in a state of equilibrium. Some reactions occur very rapidly, and are thus always in a quasi-equilibrium condition, while other reactions proceed so slowly that for practical purposes, they constitute a non-reactive system, or are so-called "frozen" reactions (more properly a frozen reaction is a "pure mixture"). A reactive system in equilibrium then must have either an infinitely fast reaction rate or else an infinitely long period of time available for the reaction to take place. Real reactive systems are not infinitely fast, and only finite times are of interest in applied problems, so it is not correct to neglect the "chemical lag" phenomena, just as it is not correct to neglect the possibility of reaction. Reaction half-times are a function of temperature and are very short, in the order of 10^{-6} seconds for the higher temperatures, but are still long enough to cause chemical lag at high velocities. In fact, at the high velocities and relatively low temperatures existing at the exit of a nozzle, the reaction might take such a long period of time as to be essentially frozen. Deviation from equilibrium flow results and appears as a lower temperature and velocity; even so, this temperature and velocity would be higher than for an entirely frozen flow.

Just where the true intermediate physical properties lie, is the sought for answer. Only a few studies have been reported on reactive flow, and they were made on a highly restricted basis.^{1,2} The

¹Heims, S. P., Effect of Oxygen Recombination on One-Dimensional Flow at High Mach Numbers, N.A.C.A., TN 4114, 1958.

²Bray, K.N.C., Departure from Dissociation Equilibrium in a Hypersonic Nozzle, A.R.C. 19,983, March 1958.

major problem is that of being able to adequately describe the recombination reactions and postulating the proper reaction rates. There is only partial agreement on the proper theory to describe reaction rates, and even less agreement on what probable sequence of reactions actually occurs in a given recombination process. Experimental data of reaction rates are wholly lacking in the high temperature domain, reliable values being reported up to only about 2000°R. Extrapolation beyond these limits appears to be quite risky.

Mathematically, reactive flow processes can be described completely in a relatively compact notation, but to obtain a solution of the resulting differential equations is extremely difficult, the difficulty arising primarily from a lack of knowledge concerning the attendant physical phenomena. Thus, in order to effect a solution, it is necessary to apply the best available information and synthesize a solution around these conditions.

Such a procedure is followed herein, to determine as accurately as possible, the conditions existing in reactive-gas expansion. By this means, it is possible to obtain a more accurate solution than would be possible with either "equilibrium" or "frozen" analyses, but much more time consuming. This method also indicates the probable error involved in using either of the simpler methods.

In order to study the effects of non-equilibrium during flow, due to chemical reaction, it is necessary to initially describe the flow analytically and then solve the resulting expressions for the situation in question. The approach taken in this study is to first develop the fundamental equations for the fluid dynamics and chemical

kinetics in as general terms as possible, and then reduce these equations to a form suitable for nozzle flow. After this system of differential equations is available, a set of assumed data is used to obtain numerical results.

Underlying all of the study is the assumption that the fluid is a high temperature, low pressure, reactive mixture of gases, that has an equation of state like that of an ideal gas. This does not mean that the fluid has all the properties of a thermodynamically ideal gas, but only that

$$p = R \rho T \quad (1)$$

where p is pressure, ρ is density, T is absolute temperature, and R is the gas constant. The use of (1) as such is not important to the general theory, but its implication and dependence on the principles of kinetic theory does make it important. As chemical kinetics is primarily a collisional phenomenon, using kinetic theory as the basis for the fluid dynamics leads to an easier combination of the two phenomena.

Once the dynamics has been established, it is desirable to have a means of measuring the amount of chemical lag. This is done by means of a reaction coordinate, ξ , which establishes the extent of reaction as the fluid moves through the nozzle. Such a parameter is not a portion of the flow theory as such, but in a sense, gives the effect of finite reaction rates.

Combining the fluid, chemical, and reaction coordinate expressions gives the system of simultaneous equations describing reactive flow in general. However, to make this system usable, the final

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equations are expressed in terms of the following assumptions:

1. One-dimensional flow
2. Non-viscous fluid
3. Adiabatic system
4. No external forces
5. Steady flow
6. Thermodynamic equilibrium

The first four of these assumptions simply establish the flow as being that of a stream tube internal to the main body of fluid. Steady flow requires that there be no sinks or sources in the flow, that the system is "closed." Thermodynamic equilibrium requires that there be no gradients of pressure or temperature in any plane normal to the direction of flow.

The second part of this study is to examine a specific situation to obtain numerical data sufficient to demonstrate the effects of chemical reaction during flow. Selection of the fluid, operating conditions, and duct shape is entirely arbitrary; therefore, to make the situation reasonable and simple, the following set of boundary conditions are assumed, which apply in conjunction with the assumptions given above for general development.

Reactive products of combustion which are flowing are those which would result from the burning of a C_nH_{2n} fuel in air with a stoichiometric ratio. This mixture is presumed to be moving slowly and to be in a chemical and thermodynamic state of equilibrium at the time it enters the nozzle. The nozzle is a uniformly converging-diverging duct, with a configuration as given in Appendix A. Inlet

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conditions are a pressure of ten atmospheres and a temperature of 5000°R, expanding through the nozzle to an exit pressure of one atmosphere.

Sources of reaction data will be given in a later section where the calculations are described. Where specific data are not available, they will be approximated from what data are available or by recommended procedures as appears in the literature.

ANALYTICAL DEVELOPMENT

The first portion of this study is devoted to developing the analytical expressions for reactive flow. Rather than consider the flow and chemical phenomena at the same time, suitable expressions will be developed for each and then these will be brought together into a common analytical tool. The sequence to be followed is:

1. Governing Flow Equations
2. Reaction Kinetics
3. Reactive Flow

Chemical reaction is primarily a collisional phenomenon and for consistency in approach, flow analysis is developed on such a basis.

Governing Flow Equations

A formal solution of any flow problem with chemical reaction requires not only knowledge of the manner of chemical changes, but also the appropriate forms of the usual conservation equations of equilibrium, non-reactive, flow corrected to account for the reacting gas mixture. Such corrections are required because reactive flow is a non-equilibrium situation, except for infinitely fast or infinitely slow chemical reaction rates, and there will be gradients in density, temperature, and velocity. In any case, the following fundamental equations are necessary to obtain a solution to a flow problem:

- (1) The continuity equation
- (2) The equation of motion
- (3) The conservation of energy equation
- (4) The thermal equation of state, $P = P(V, T)$
- (5) The caloric equation of state, $E = E(V, T)$

The first three of these equations are known as the "equations of change," and they can be compactly written so as to completely describe the dynamics of a fluid in many types of phenomena. In this section, these equations of change will be developed in most general terms, from the Boltzmann equation of kinetic theory, and will be expressed in vector notation, even though a one-dimensional application is to be made from them and the assumption of an adiabatic, non-viscous, flow will cause several of the terms to drop. It is felt that a development in general terms is more satisfactory, in that the effects of various assumptions will then be more explicit.

Even though the equations of change are general and will apply to any fluid, they are, however, only useful under conditions that make it physically meaningful to speak of point properties. Local density, temperature, and velocity can be defined formally, but any such definition would be reasonable only where the fluid behaves as continuum. Where the macroscopic properties have large differences over a distance in the order of a mean free path, the distribution of velocities of the molecules can no longer be considered as Maxwellian, and flux vectors can no longer be expressed in terms of the local density, temperature, and flow velocity and their first derivatives. These equations of change describe the change of the macroscopic properties of the fluid (the local density, stream velocity, and temperature) in terms of the flux of the mass (the diffusion velocity), the flux of the momentum (the pressure tensor), the flux of the energy, and the chemical reaction kinetics.

The properties of a gas at low densities can be completely described by a distribution function $f(\vec{r}, \vec{u}, t)$, defined in such a manner that $f(\vec{r}, \vec{u}, t) d\vec{r} d\vec{u}$ is the probable number of molecules which at the time t have position coordinates between $\vec{r}$ and $\vec{r} + d\vec{r}$ and have a velocity $\vec{u}$ between $\vec{u}$ and $d\vec{u}$. This distribution function is given as the Boltzmann integro-differential equation. Using a form given by Kirkwood,^{1,2} This equation can be expressed as

¹Kirkwood, J. G., Journal of Chem. Phys. 15, 72, 1947; Journ. of Chem. Phys. 18, 817, 1950.

²Hirschfelder, J. O., C. F. Curtiss, R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, 1954.

$$\begin{aligned}
& \frac{\partial f_i}{\partial t} + (\vec{u}_i \cdot \nabla f_i) + \frac{1}{m_i} (\vec{x}_i \cdot \nabla f_i) \\
& - \sum \iiint (f'_i f'_j - f_i f_j) g_{ij} db d\epsilon d u_j \quad (2)
\end{aligned}$$

An explanation of the terms of (2) is given in Appendix B.

When a gas is under non-equilibrium conditions, gradients occur in one or more of the macroscopic physical properties of the system: composition, mass average velocity, and temperature. Molecular transport of mass (m_j), momentum ($m_j \vec{C}_j$), and kinetic energy ($\frac{1}{2} m_j \vec{C}_j^2$), through the gas, will result from the effect of these gradients. The velocity $\vec{C}_j$ is the velocity of a molecule of species j with respect to an axis moving with the mass average velocity $\vec{u}_0$. Velocities pertinent to this study are defined as:

(a) Linear velocity of a molecule of species j is denoted as $\vec{u}_j$, with space coordinates of u_x, u_y, u_z . Its magnitude $|u_j|$ is the molecular speed u_j .

(b) Average velocity $\vec{\bar{u}}_j$, for a chemical species j present with a number density N_j , is defined as:

$$\vec{\bar{u}}_j (\vec{r}, t) = \frac{1}{N_j} \int \vec{u}_j f_j (\vec{r}, \vec{u}_j, t) d \vec{u}_j \quad (3)$$

(c) Mass average velocity, $\vec{u}_0$, is the stream or flow velocity and,

$$\vec{u}_0 (\vec{r}, t) = \frac{1}{\rho} \sum N_j m_j \vec{\bar{u}}_j \quad (4)$$

in which $\rho (r, t)$ is the over all density at a particular point.

$$\rho (\vec{r}, t) = \sum N_j m_j \quad (5)$$

- (d) Individual velocity, $\vec{c}_j$, is the velocity of a molecule with respect to an axis moving with the mass average velocity $\vec{u}_0$

$$\vec{c}_j (\vec{r}, \vec{u}_j, t) = \vec{u}_j - \vec{u}_0 \quad (6)$$

- (e) Diffusion velocity, $\vec{\bar{c}}_j$, is the rate of flow of molecules of j with respect to the mass average velocity,

$$\vec{\bar{c}}_j (\vec{r}, t) = \vec{\bar{u}}_j - \vec{u}_0 \quad (7)$$

As the mechanism of transport for each of the above molecular properties can be handled similarly, they will be denoted by λ_j . To investigate these transport phenomena on a microscopic level, visualize a cylinder as in Figure 1, which represents a cylinder formed by a surface dS moving through the gas with a velocity $\vec{u}_0$. A unit vector $\vec{a}$ normal to the surface specifies the orientation of the surface.

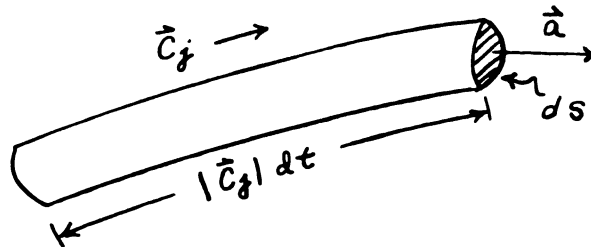


Fig. 1. Flow Cylinder

According to the definition of $\vec{c}_j$, it is the velocity of molecules of species j with respect to the surface element dS . Thus the cylinder with base dS and generators parallel to $\vec{c}_j$ and of length $|\vec{c}_j| dt$, must contain all of the molecules of species j which have a velocity in a small range $d\vec{c}_j$ about $\vec{c}_j$, which pass through dS in a time interval dt . The cylinder, so specified, would have a volume

$$\text{Volume} = \vec{a} \cdot d\vec{S} \cdot \vec{c}_j dt \quad (8)$$

As there are $f_j d\vec{c}_j$ molecules per unit volume which have a velocity $\vec{c}_j$, the number of molecules crossing dS in a time interval dt , is

$$(\vec{a} \cdot \vec{c}_j) f_j d\vec{c}_j dS dt \quad (9)$$

Associated with each of the molecules is some property, denoted above as λ_j , whose magnitude depends on $\vec{c}_j$; then the amount of this property transported across dS in the time dt , by those molecules in the velocity range $d\vec{c}_j$ about $\vec{c}_j$, is

$$(\vec{a} \cdot \vec{c}_j) \lambda_j f_j d\vec{c}_j dS dt \quad (10)$$

The amount which crosses per unit area per unit time, the flux, is

$$\lambda_j f_j (\vec{a} \cdot \vec{c}_j) d\vec{c}_j \quad (11)$$

When the contribution of all molecules in all velocity ranges is summed, the total flux is then

$$\int \lambda_j f_j (\vec{a}_j \cdot \vec{c}_j) d\vec{c}_j = \vec{a}_j \cdot \int \lambda_j f_j \vec{c}_j d\vec{c}_j \equiv \vec{a}_j \cdot \vec{\Lambda}_j \quad (12)$$

where,

$$\vec{\Lambda}_j = \int \lambda_j f_j \vec{c}_j d\vec{c}_j \quad (13)$$

is the "flux vector" associated with the property λ_j . The physical interpretation of this vector is that the component of the vector, in any direction $\vec{a}$, is the flux of the associated physical properties across a surface normal to $\vec{a}$.

Expressing the transport phenomena of mass, momentum, and kinetic energy in terms of flux vectors, there results:

(i) Transport of mass

$$\begin{aligned} \text{If } \lambda_j &= m_j \text{ then} \\ \vec{\Lambda}_j &= m_j \int f_j \vec{c}_j d\vec{c}_j = N_j m_j \vec{\bar{c}}_j \end{aligned} \quad (14)$$

the flux vector related to the transport of mass. It is to be noted that

$$\vec{\bar{c}}_j = \frac{1}{N_j} \int (\vec{u}_j - \vec{u}_0) f_j d\vec{u}_j \quad (15)$$

(ii) Transport of momentum

$$\begin{aligned} \text{If } \lambda_j &= m_j (\vec{u}_j - \vec{u}_0), \text{ then} \\ \vec{\Lambda}_j &= m_j \int \vec{c}_{jy} f_j \vec{c}_j d\vec{c}_j = N_j m_j \overline{\vec{c}_{jy} \vec{c}_j} \end{aligned} \quad (16)$$

is the flux vector associated with the transport of the y component of momentum, relative to $\vec{u}_0$. This vector has components proportional to $\overline{\vec{c}_{jy} \vec{c}_{jx}}$, $\overline{\vec{c}_{jy} \vec{c}_{jy}}$ and $\overline{\vec{c}_{jy} \vec{c}_{jz}}$. The x and z components of momentum have similar flux vectors, giving a total of three flux vectors for momentum transport. This gives a symmetric second order tensor $\mathbb{P}$, whose nine components are

$$\begin{aligned} (P_j)_{xx} &= m_j \int f_j c_{jx} c_{jx} d\vec{c}_j = N_j m_j \overline{c_{jx} c_{jx}} \\ (P_j)_{xy} &= m_j \int f_j c_{jx} c_{jy} d\vec{c}_j = N_j m_j \overline{c_{jx} c_{jy}} \end{aligned} \quad (17)$$

Which may be written in closed form as

$$\mathbb{P}_j = N_j M_j \overline{\vec{c}_j \vec{c}_j} \quad (18)$$

and is the tensor related to the partial pressure of the j^{th} species in the gas. The pressure tensor for the mixture is obtained by summing over all the partial pressure tensors, i.e.,

$$\mathbb{P} = \sum_j \mathbb{P}_j = \sum_j N_j M_j \overline{\vec{c}_j \vec{c}_j} \quad (19)$$

Such a pressure tensor has the physical significance that it represents the flux of momentum through a gas. Individual components are interpreted by noting that the diagonal elements P_{xx} , P_{yy} , P_{zz} are normal stresses; or P_{yy} is the force per unit area in the y direction exerted on a plane surface normal to the y direction. The non-diagonal elements are shear stresses; or P_{yx} is the force per unit area in the x direction exerted on a plane surface normal to y . Stresses or pressures represented by such a tensor are those relative to an axis moving with the flow velocity $\vec{u}_0$. At equilibrium the shear stresses are zero and the normal stresses are equal and thus

$$P_{xx} = P_{yy} = P_{zz} = P \quad (20)$$

(iii) Transport of kinetic energy.

$$\text{If } \lambda_j = \frac{1}{2} m_j (\vec{u}_j - \vec{u}_0)^2 = \frac{1}{2} m_j \vec{c}_j^2$$

$$\text{Then } \vec{\Lambda}_j = \frac{1}{2} m_j \int \vec{c}_j^2 \vec{c}_j f_j d\vec{c}_j = \frac{1}{2} m_j N_j \overline{\vec{c}_j^2 \vec{c}_j} \quad (21)$$

is the flux vector for the transport of kinetic energy for molecules.

Summed over all components of the gas mixture such vectors give the

"heat flux vector,"

$$\vec{q} = \sum_j \frac{1}{2} m_j N_j \overline{c_j^2 \vec{c}_j} \quad (22)$$

Returning now to the Boltzmann equation, (2), it is possible to transform it into a general equation of change known as the Enskog equation. This relationship is for a physical property λ_i associated with the i^{th} molecule, in which summation over all i gives the equation of change for the property λ . When (2) is multiplied by λ_i and integrated over $\vec{u}_i$, there results

$$\begin{aligned} & \int \lambda_i \left[\frac{\partial f_i}{\partial t} + (\vec{u}_i \cdot \nabla f_i) + \frac{1}{m_i} (\vec{x}_i \cdot \nabla f_i) \right] d\vec{u}_i \\ &= \sum_j \iiint \lambda_i (f'_i f'_j - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_j d\vec{u}_i \quad (23) \end{aligned}$$

Taking $\vec{r}$, $\vec{u}_i$, and t , as independent variables, and noting that λ_i may depend on $\vec{r}$ and t through $u_0(\vec{r}, t)$, the three left-hand terms may be transformed by use of the relationships:

$$\begin{aligned} \int \lambda_i \frac{\partial f_i}{\partial t} d\vec{u}_i &= \frac{\partial}{\partial t} \int \lambda_i f_i d\vec{u}_i - \int f_i \frac{\partial \lambda_i}{\partial t} d\vec{u}_i \\ &= \frac{\partial (N_i \bar{\lambda}_i)}{\partial t} - N_i \frac{\partial \bar{\lambda}_i}{\partial t} \quad (24) \end{aligned}$$

$$\begin{aligned} \int \lambda_i u_{ix} \frac{\partial f_i}{\partial x} d\vec{u}_i &= \frac{\partial}{\partial x} \int \lambda_i u_{ix} f_i d\vec{u}_i - \int f_i u_{ix} \frac{\partial \lambda_i}{\partial x} d\vec{u}_i \\ &= \frac{\partial}{\partial x} (N_i \overline{\lambda_i u_{ix}}) - N_i u_{ix} \frac{\partial \bar{\lambda}_i}{\partial x} \quad (25) \end{aligned}$$

$$\begin{aligned}
\int \lambda_i \frac{\partial f_i}{\partial u_{ix}} d\vec{u}_i &= \iint [\lambda_i f_i]_{u_{ix}=-\infty}^{u_{ix}=\infty} du_{iy} du_{iz} - \\
&\int f_i \frac{\partial \lambda_i}{\partial u_{ix}} d\vec{u}_i \\
&= -N_i \frac{\partial \bar{\lambda}_i}{\partial u_{ix}} \quad (26)
\end{aligned}$$

Where only the x components are written for (25) and (26), and the term $(\lambda_i f_i)$ is assumed to diminish rapidly for large u_i , the transformed equation is then,

$$\begin{aligned}
\frac{\partial N_i \bar{\lambda}_i}{\partial t} + (\nabla \cdot N_i \bar{\lambda}_i \bar{u}_i) - N_i \left[\frac{\partial \lambda_i}{\partial t} + (\bar{u}_i \cdot \nabla \lambda_i) + \right. \\
\left. \left(\frac{\bar{x}_i}{m_i} \cdot \nabla_{\bar{u}_i} \lambda_i \right) \right] \\
= \sum_j \iiint \lambda_i (f'_i f'_j - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_j d\vec{u}_i \quad (27)
\end{aligned}$$

As written, this last equation is not of any particular use for just any λ_i , due to the almost insurmountable integrals. However, as masses of individual molecules are not changed in a collision,

$$\iiint m_i (f'_i f'_j - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_j d\vec{u}_i = 0 \quad (28)$$

In fact for any conservative property λ_i , such as mass, momentum, and energy, which is conserved in a collision,

$$\sum_i \iiint \lambda_i (f'_i f'_j - f_i f_j) g_{ij} db db d\epsilon d\vec{u}_j d\vec{u}_i = 0 \quad (29)$$

Thus the general equation of change, (27), can be simplified by eliminating the entire right hand side when λ_i is m_i , $m_i \vec{C}_i$, or $\frac{1}{2} m_i \vec{C}_i^2$. A proof of the passing to zero for (28) and (29) is given in Appendix C.

Utilizing the validity of (28) and (29), a set of equations may be obtained by letting λ_i represent, in turn, each of the summational invariants mass, momentum, and energy, after which the resulting expression is summed over i .

Taking first $\lambda_i = m_i$ and applying it to the above procedure, it is found that

$$\frac{\partial N_i}{\partial t} + (\nabla \cdot N_i \vec{u}_i) = 0 \quad (30)$$

or, using the definitions of velocities,

$$\frac{\partial N_i}{\partial t} + [\nabla \cdot N_i (\vec{u}_0 + \vec{C}_i)] = 0 \quad (31)$$

These two expressions are two different ways of expressing the "continuity equation" for the i^{th} chemical species in the case of no reaction. When the i^{th} molecule is being formed, as the result of chemical reaction, then (31) can be put in a different form

$$\frac{D N_i}{Dt} = - N_i (\nabla \cdot \vec{u}_0) - (\nabla \cdot N_i \vec{C}_i) + B_i \quad (32)$$

in which B_i , is a statement of the rate of formation of the i^{th} chemical species per unit volume per unit time, and the substantial (Eulerian) derivative, $\frac{D}{Dt}$, is the time rate of change with respect

to an element of fluid moving with the stream velocity $\vec{u}_0$.

For the entire mixture, the corresponding continuity equation is obtained from multiplying by m_i and summing over all i , to give

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + (\vec{u}_0 \cdot \nabla \rho) = -\rho (\nabla \cdot \vec{u}_0) \quad (33)$$

whether the mixture is reactive or not.

In physical terms, an interpretation of (32) shows that the number density of species i may change because of the expansion of the fluid, diffusion processes, and due to either the production or elimination of species i by chemical reaction. In the case of the mixture, the mass density, ρ , only changes because the volume of the fluid element is changing.

When $\lambda_i = m_i \bar{c}_i$ and the ensuing expression is summed over i , there results

$$\sum_i m_i \left[\frac{\partial (N_i \bar{c}_i)}{\partial t} + (\nabla \cdot N_i \vec{u}_i \bar{c}_i) - N_i \frac{\partial \bar{c}_i}{\partial t} - N_i (\vec{u}_i \cdot \nabla \bar{c}_i) - \frac{N_i}{m_i} (\vec{x}_i \cdot \nabla_{u_i} \bar{c}_i) \right] = 0 \quad (34)$$

Utilizing the definitions of velocities and of the pressure tensor this reduces to the "equation of motion,"

$$\frac{D \vec{u}_0}{Dt} = \frac{\partial \vec{u}_0}{\partial t} + (\vec{u}_0 \cdot \nabla \vec{u}_0) = -\frac{1}{\rho} (\nabla \cdot \mathbb{P}) + \frac{1}{\rho} \sum_i N_i \vec{x}_i \quad (35)$$

where $\vec{r}$ and $\vec{u}_i$ are the independent variables of differentiation. This equation shows that the velocity of the fluid element varies because of the gradient of the pressure tensor and be-

cause of the external forces acting on the individual species.

To obtain the conservation of energy equation, set

$\lambda_i = \frac{1}{2} m_i \bar{c}_i^2$, and in a manner identical to above, there is obtained from the general change equation

$$\sum_i \frac{1}{2} m_i \left[\frac{\partial (N_i \bar{c}_i^2)}{\partial t} + (\nabla \cdot N_i \vec{u}_i \bar{c}_i^2) - N_i \left(\frac{\partial \bar{c}_i^2}{\partial t} \right) - N_i (\vec{u}_i \cdot \nabla \bar{c}_i^2) - \left(\frac{\vec{x}_i}{m_i} \cdot \nabla_{u_i} \bar{c}_i^2 \right) \right] = 0 \quad (36)$$

Using the heat flux vector of (22), and the pressure tensor, this last equation, (36) reduces to

$$\begin{aligned} \frac{\partial (\rho e)}{\partial t} + (\nabla \cdot \rho e \vec{u}_0) + (\nabla \cdot \vec{q}) + (\vec{P} \cdot \nabla \vec{u}_0) \\ - \sum_i N_i (\vec{x}_i \cdot \vec{\bar{c}}_i) = 0 \end{aligned} \quad (37)$$

where e is the internal energy per unit mass, and is defined by

$$e = \frac{1}{\rho} \sum_i \frac{1}{2} N_i m_i \bar{c}_i^2 \quad (38)$$

This represents the total internal energy (intrinsic energy) of a unit mass of gas moving with a reference frame velocity of $\vec{u}_0$; thus the kinetic energy and potential energy of flow is not included in e .

Applying equation of continuity (33) to (37) it may be written

$$\begin{aligned} \rho \frac{De}{Dt} = \rho \frac{\partial e}{\partial t} + \rho (\vec{u}_0 \cdot \nabla e) = - (\nabla \cdot \vec{q}) - (\vec{P} \cdot \nabla \vec{u}_0) + \\ \sum_i N_i (\vec{x}_i \cdot \vec{\bar{c}}_i) \end{aligned} \quad (39)$$

Here, a physical interpretation shows that the internal energy changes due to: the first term on the right of (39) represents the change due to energy flux, the second term is the change due to pV - work and viscous effects, and the third term describes the change due to the work which the diffusing molecules do to overcome external forces.

This system of equations is basically the Navier-Stokes equations, generalized to include more than one component and chemical reactions. Application of them is valid as long as gradients of velocity, concentration, temperature, and pressure are such that a continuum condition is approximated, or "point properties" are possible. When the gradients are linear and the gas is non-reacting, the above equations of change then reduce directly to the Navier-Stokes equation.

Most gas dynamic theory is based on empirically determined bulk properties, while a development, such as above, based on kinetic theory, attempts to predict the dynamics of a gas on the basis of molecular mechanics. Kinetic theory is capable, in theory, of establishing a complete description of motion of a gas from knowledge of inter-molecular forces within the gas and at its boundaries. Furthermore, kinetic theory theoretically can explain transport processes, that is, to furnish general relations between stress and rate of strain and between heat flux and temperature gradient. However, at the present state of our knowledge of molecular properties, it is still necessary to rely on simpler approximations and linearized relationships; so that theory beyond the general expressions becomes quite formidable.

In addition to the above dynamic equation of change, it is desirable to have an equation to describe the rate of change of extensive properties in a fluid. Let these extensive properties per unit mass be designated by a common symbol g .

Consider the rate of change of g within a finite region of space, δ , which is bounded by a surface such that each point of this surface is moving with the local flow velocity of the gas, $\vec{u}_0$. Within this region, g will change for two reasons: (i) because of reversible flow of g across the bounding surface, and (ii) because of irreversible production of g within the region. Let $\vec{\gamma}$ be the flux representing the reversible flow of g , and Γ the rate of irreversible production of g . In terms of these quantities, the equation of change of g in integral form is

$$\frac{d}{dt} \int_{\delta} \rho g d\vec{r} = - \int_{\delta} \vec{\gamma} \cdot d\vec{S} + \int_{\delta} \Gamma d\vec{r} \quad (40)$$

where $\int_{\delta} d\vec{S}$ indicates an integration over the surface of the region

δ under consideration.

Performing the indicated differentiation, equation (40) becomes

$$\int_{\delta} \frac{\partial}{\partial t} (\rho g) d\vec{r} + \int_{\delta} \rho g (\vec{u}_0 \cdot d\vec{S}) = - \int_{\delta} \vec{\gamma} \cdot d\vec{S} + \int_{\delta} \Gamma d\vec{r} \quad (41)$$

Then applying Gauss's Theorem,

$$\int_{\delta} \left[\frac{\partial}{\partial t} (\rho g) + (\nabla \cdot \rho g \vec{u}_0) + (\nabla \cdot \vec{\gamma}) - \Gamma \right] d\vec{r} = 0 \quad (42)$$

By the development of this expression, it is true for any region in space, therefore

$$\frac{\partial}{\partial t} (\rho g) + (\nabla \cdot \rho g \vec{u}_0) = -(\nabla \cdot \vec{\gamma}) + \Gamma \quad (43)$$

and from the equation of continuity, (33),

$$\frac{\partial}{\partial t} (\rho g) + (\rho \vec{u}_0 \cdot \nabla g) = -(\nabla \cdot \vec{\gamma}) + \Gamma \quad (44)$$

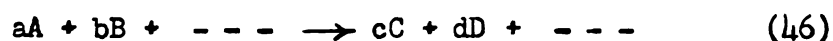
This is the "equation of change of g ", in differential form. Expressed in terms of the substantial derivative, this last equation becomes,

$$\rho \frac{Dg}{Dt} = -(\nabla \cdot \vec{\gamma}) + \Gamma \quad (45)$$

The dynamic equations of change can be applied to this equation to give expressions for $\vec{\gamma}$ and Γ in terms of transport properties and flux vectors. However, as pointed out above, it is extremely difficult, if not impossible, to obtain these expressions in workable form and it is necessary to introduce sufficient simplifications to make the relationships commensurate with present knowledge of physical data.

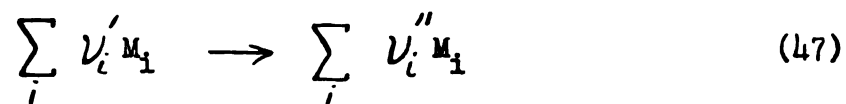
Reaction Kinetics

A one-step chemical reaction, in which reactants are directly forming products, can be written



in which there are a moles of component A reacting with b moles of component B , etc., to form products consisting of c moles of component

C, d moles of component D, etc. To write all reactions in this form would become cumbersome and unwieldy, so a more compact notation will be employed. The stoichiometric relation describing a one-step chemical reaction of arbitrary complexity may be represented by the reaction equation



where the terms ν_i' and ν_i'' represent respectively the stoichiometric coefficients of the reactants and products. For any chemical compound M_i which does not appear as a reactant then $\nu_i' = 0$, and likewise if a compound is not formed then $\nu_i'' = 0$. In a general sense, (47) can adequately describe all possible chemical reactions.

In accordance with the Law of Mass Action, the rate of disappearance of a chemical species is proportional to the products of the concentration of the reacting chemical species, each concentration being raised to a power equal to the corresponding stoichiometric coefficient. For the chemical compound represented by the symbol M_i , concentration will be noted by $[M_i]$, with the units of mole/ft³. Thus

$$\text{reaction rate} \propto \prod_i [M_i]^{\nu_i'} \quad (48)$$

is the Law of Mass Action in symbolic form. Introducing a proportionality factor k_j , called the specific reaction rate constant or coefficient, (48), becomes

$$\text{reaction rate} = k_j \prod_i [M_i]^{\nu_i'} \quad (49)$$

As presented here, (49) is for a homogeneous system and for a given chemical reaction the specific reaction rate k_j is independent of concentration $[M_i]$, depending only on temperature.

In general, k_j can be expressed in the form accredited to Arrhenius,

$$k_j = A e^{-\frac{E}{RT}} \quad (50)$$

where A , the frequency factor, is a quantity that is independent of or varies relatively little with the temperature and E , the activation energy, is the difference in heat content between the activated and inert molecules. Provided that the temperature range is not large, the quantities A and E can be taken as constant. It may thus be assumed that k_j is an empirically determined coefficient which depends only on the temperature for a given chemical reaction. Further discussion of k_j will appear later.

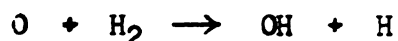
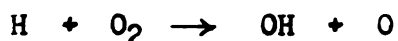
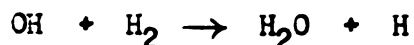
All specific reaction rate constants will be symbolized as k_j , with $j = f$ for forward reactions and $j = b$ for backward or reverse reactions. A forward reaction is one in which the reactants appear on the left hand side of the chemical equation and products on the right hand side, while backward reactions are the reverse.

Net rates of change of the chemical components are the only observable results of a chemical reaction. From (47) the net rate of production of M_i is

$$\begin{aligned} \frac{dn_i}{dt} &= (\nu_i'' - \nu_i') \text{ (Reaction Rate)} \\ &= (\nu_i'' - \nu_i') k_f \prod_i [M_i]^{\nu_i'} \end{aligned} \quad (51)$$

as ν_i'' moles of M_i are formed for every ν_i' moles of M_i used up in the reaction.

The law of mass action, as expressed by (51), may be applied, in a meaningful way, only to elementary reaction steps which describe the correct reaction mechanism. For a number of simple chemical processes, a plausible reaction mechanism has been deduced by chemical kineticists, but for the most part, only intelligent conjectures can be made by the kineticists regarding probable reaction mechanism. Detailed studies¹ show that the production of H_2O from H_2 and O_2 involves, among others, the following elementary steps,



to each of which the law of mass action applies, and for each of which there is a specific reaction rate.

The stoichiometric coefficients for elementary reaction give information about the number of moles reacting, not about the weights or volumes changing. As a function of time, the number of moles of reactants will decrease asymptotically toward a limiting value (not necessarily zero) whereas the number of moles of product species will increase asymptotically toward a limiting value.

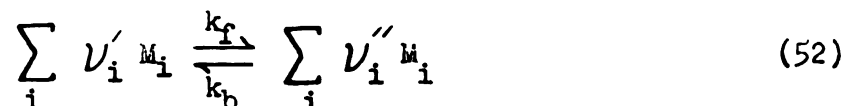
Experimental chemical kinetics is a science of considerable complexity because very large observable effects are frequently brought

¹Lewis, B. and G. von Elbe, Combustion, Flames, and Explosion of Gases, Academic Press, Inc., New York, 1951.

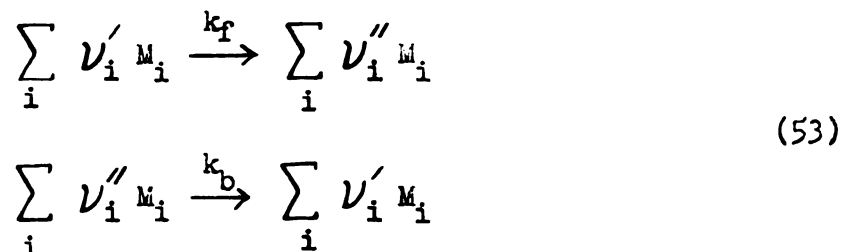
about by uncontrolled factors such as minute concentration of impurities, surface effects, etc. The absolute precision of even the best-known rate constants is low. Due to the temperature dependence of k_j , it is necessary to have extremely precise values of E to yield a reliable prediction for the change of k_j with temperature. Most observed data on k_j are restricted to a relatively narrow temperature range, in which the results can be fitted equally well by a number of different rate laws, and thus extrapolation of known values to higher temperatures are almost always uncertain by an order of magnitude or more.

Chemical reactions can proceed in both the forward direction (reactants forming products, rate constant k_f) and in the reverse direction (reaction products forming the reactants, rate constant k_b), both of which are essentially single-step reactions. At thermodynamic equilibrium, there is no net change in composition, which means that k_f and k_b must be related through this equilibrium constant, K_c , expressed in terms of the ratio of the concentrations raised to appropriate powers.

A general set of opposing chemical reactions may be expressed by



which may be written in terms of single-step reactions as



where the appropriate rate constants are indicated explicitly over the arrows. For simultaneous chemical reactions, the basic rate law of (51) must be applied to each reaction step and $\frac{dn_i}{dt}$ represents the sum of the changes produced by the individual simultaneous reaction steps. For the reaction symbolized by (52)

$$\frac{dn_i}{dt} = (\nu_i'' - \nu_i') k_f \prod_i [M_i]^{\nu_i'} - (\nu_i'' - \nu_i') k_b \prod_i [M_i]^{\nu_i''} \quad (54)$$

At chemical equilibrium

$$\frac{dn_i}{dt} = 0, \quad [M_i] = [M_{i,e}] \quad (55)$$

where $[M_{i,e}]$ denotes the chemical equilibrium concentration for species M_i . From (54) and (55) it follows that

$$\frac{k_f}{k_b} = \prod_i [M_i]^{\nu_i'' - \nu_i'} \equiv K_c \quad (56)$$

in which K_c represents the usual equilibrium constant defined in terms of concentration ratios. This gives a relation between the kinetic parameters and the thermodynamic equilibrium constant, K_c , which can be determined quite accurately by quantum-statistical calculations from molecular properties or by experimental means. Utilizing this relationship (54) can be rewritten as

$$\frac{dn_i}{dt} = (\nu_i'' - \nu_i') k_f \prod_i [M_i]^{\nu_i'} \left[1 - \left(\frac{1}{K_c} \right) \prod_i [M_i]^{\nu_i'' - \nu_i'} \right] \quad (57)$$

Assuming the validity of the ideal gas law, transformations can be made to obtain relations equivalent to (56) and (57) by replacing concentration with partial pressures, mole fractions, weight fractions, etc. At the high temperatures and relatively low pressures involved in the flow of products of combustion through ducts and nozzles, the ideal gas law is a very good approximation. For the ideal gas, the equation of state may be written

$$[M_{i,e}] = \frac{p_{i,e}}{RT} \quad (58)$$

where $p_{i,e}$ is the equilibrium partial pressure of the chemical species identified by M_i and R is the molar gas constant. Typical units would be concentration in moles/ft³, and partial pressures in atmospheres.

When the equilibrium constant K_p is defined by the relation

$$K_p = \prod_i (p_{i,e})^{\nu_i'' - \nu_i'} \quad (59)$$

then from (56), (57), and (59), it can be seen that

$$\frac{k_f}{k_b} = K_c = K_p (RT)^{-\Delta \nu} \quad (60)$$

where

$$\Delta \nu = \sum_i (\nu_i'' - \nu_i') \quad (61)$$

For ideal gases the equilibrium mole fraction of species i , $X_{i,e}$, is given by the relation

$$x_{i,e} = \frac{p_{i,e}}{p_T} = \frac{[M_{i,e}]}{[M_T]} \quad (62)$$

where p_T is the total pressure, $\sum_i p_{i,e}$, and $[M_T]$ is the total number of moles per unit volume of gas mixture, $\sum_i [M_{i,e}]$. From (59) and (60)

$$\frac{k_f}{k_b} = K_c = K_p (RT)^{-\Delta \nu} = K_x \left(\frac{p_T}{RT}\right)^{\Delta \nu} = K_x [M_T]^{\Delta \nu} \quad (63)$$

in which

$$K_x = \prod_i (x_{i,e})^{\nu_i'' - \nu_i'} \quad (64)$$

Also, for an ideal gas equilibrium mass of species i per unit volume, $\rho_{i,e}$, is

$$\rho_{i,e} = \left(\frac{p_{i,e}}{RT}\right) W_i = [M_{i,e}] W_i \quad (65)$$

where W_i represents the molecular weight of species i . The equilibrium weight fraction of species i , $\gamma_{i,e}$, is then

$$\gamma_{i,e} = \frac{\rho_{i,e}}{\rho_e} \quad (66)$$

in which ρ_e denotes the equilibrium density of the fluid mixture.

Combining the above relations

$$\begin{aligned} \frac{k_f}{k_b} &= K_c = K_p (RT)^{-\Delta \nu} = K_x \left(\frac{p_T}{RT}\right)^{\Delta \nu} \\ &= K_x F_W^{-1} \rho_e^{\Delta \nu} = K_p F_W^{-1} \end{aligned} \quad (67)$$

when

$$K_p = \prod_i (\rho_{i,e})^{\nu_i'' - \nu_i'} \quad (68)$$

$$F_W = \prod_i (w_i)^{\nu_i'' - \nu_i'} \quad (69)$$

and

$$K_\gamma = \prod_i (\gamma_{i,e})^{\nu_i'' - \nu_i'} \quad (70)$$

Only when $\Delta \nu = 0$ are k_f/k_b , K_c , K_p , and F_W dimensionless parameters; however, the equilibrium constants defined in terms of mole fraction, K_x , or in terms of weight fractions, K_γ , are always dimensionless. For use in equation (57), all of the expressions given in (67) to (70) are equivalent since the group

$$k_b/k_f \prod_i [M_i]^{\nu_i'' - \nu_i'}$$

is always dimensionless.

Defining a set of quantities K_c^* , K_p^* , K_x^* , K_ρ^* , and K_γ^* , analogous to the equilibrium constants, except that concentrations, partial pressures, etc. refer to the prevailing local concentrations, partial pressures, etc., rather than to equilibrium, for the local conditions at T and P_T , then

$$\begin{aligned} k_b/k_f \prod_i [M_i]^{\nu_i'' - \nu_i'} &= \frac{K_c^*}{K_c} = \frac{K_p^*}{K_p} = \frac{K_x^*}{K_x} \\ &= \frac{K_\rho^*}{K_\rho} = \frac{K_\gamma^*}{K_\gamma} = \frac{K}{K} \end{aligned} \quad (71)$$

Utilizing the above definitions, a set of equivalent expressions can be written for the net rate of production of a chemical species:

$$\begin{aligned}
 \frac{dn_i}{dt} &= (\nu_i'' - \nu_i') k_f \left(1 - \frac{K^*}{K}\right) \prod_i [M_i]^{\nu_i'} \\
 &= (\nu_i'' - \nu_i') k_f (RT)^{-\ell} \left(1 - \frac{K^*}{K}\right) \prod_i (p_c)^{\nu_i'} , \quad \ell = \sum_i \nu_i' \\
 &= (\nu_i'' - \nu_i') k_f [M_T]^\ell \left(1 - \frac{K^*}{K}\right) \prod_i (x_i)^{\nu_i'} \\
 &= (\nu_i'' - \nu_i') k_f \left(1 - \frac{K^*}{K}\right) \prod_i \left(\frac{\rho_i}{w_i}\right)^{\nu_i'} \\
 &= (\nu_i'' - \nu_i') k_f \left(1 - \frac{K^*}{K}\right) \rho^\ell \prod_i \left(\frac{\gamma_i}{w_i}\right)^{\nu_i'} \quad (72)
 \end{aligned}$$

Where the quantities p_i , x_i , ρ_i , and γ_i denote, respectively, partial pressure, mole fraction, mass per unit volume, and weight fraction of species i if the concentration of species i is $[M_i]$.

The starred quantities defined above refer to a situation in which equilibrium conditions do not exist at a given point in the system, at least not relative to the existing temperature and pressure at that point. Such parameters are not to be interpreted as indicating a pseudo-equilibrium, but rather as a measure of deviation from equilibrium. In an article by Penner,¹ on the flow of reactive gases, he

¹Penner, S. S., Jour. of Chem. Physics, Vol. 19, No. 7, July 1951.

points out how such relations may be used for "near-equilibrium" flow conditions, if the deviations from true equilibrium are of small order.

Chemical reactions were discussed above in terms of reaction rates and the equilibrium constant, dwelling primarily on "how fast" a reaction might proceed and what the change in concentration might be with respect to time, the implication being that the reaction would, or most certainly could, attain a condition of equilibrium if sufficient time were available.

In flow systems there is always the possibility that sufficient time will not be available for the reaction to go to completion, attain an equilibrium state, or the reaction may be intentionally stopped at some arbitrary point, and it is desirable to know just how far the reaction has actually progressed. The amount of energy liberated, the change in concentrations of the components, and many other properties will depend on how far the reaction proceeds. To facilitate keeping track of the amount of reaction progress, it is desirable at this time to introduce a reaction coordinate, ξ , which will be used to indicate the amount of change. This is similar to the parameter introduced by DeDonder and referred to as the "extent of reaction."

Considering a system in which no transfer of matter takes place between the system and its surroundings, a "closed system," the masses of the various components can vary only as a result of spontaneous chemical reactions occurring within the system. For the single reaction symbolized in general form as



where ν_i'' and ν_i' are the stoichiometric coefficients of the reactants and products respectively. A sign convention will be applied in which the stoichiometric coefficients of the components formed, ν_i'' , as the reaction proceeds to the right are positive, while for the components consumed ν_i' will be taken as negative. This will permit dropping the superscript and using only the subscript i to denote the i^{th} component.

Increase in mass of component i which is being formed in the reaction is proportional to its molecular weight, W_i , and to its stoichiometric coefficient, ν_i , in the reaction. Therefore,

$$\begin{array}{rcl} m_1 - m_1^0 & = & \nu_1 W_1 \xi \\ \text{---} & & \text{---} \\ m_i - m_i^0 & = & \nu_i W_i \xi \end{array} \quad (73)$$

in which m_i^0 refers to the initial masses of the i^{th} components at time zero, when the extent of reaction, ξ , is also zero. Initial states are in this way defined by $\xi = 0$; and a state of $\xi = 1$ corresponds to the conversion of $\nu_1' \dots \nu_i'$ moles of $M_1 \dots M_i$ reactants to $\nu_1'' \dots \nu_i''$ moles of $M_1 \dots M_i$ products. When a system goes from state $\xi = 0$ to $\xi = 1$ it is said to have completed "one equivalent of reaction."

According to the "principle of conservation of mass," the total mass of a system remains constant in the course of time, and upon summing over all the equations of (73), there results

$$\sum_i \nu_i W_i = 0 \quad (74)$$

This is the stoichiometric equation for the reaction written.

In equations (73), for a closed system in which only one reaction is occurring, the variables $m_1 \dots m_i$ can be replaced by the variables ξ and $m_1^0 \dots m_i^0$. Then the thermodynamic state of a system for which $m_1^0 \dots m_i^0$ are given can be determined by two physical parameters, i.e., T and P , and a single chemical variable ξ .

Differentiating equations (73) with respect to time, noting that the initial masses are constant, gives

$$\begin{aligned} \frac{dm_1}{dt} &= \nu_1 w_1 \frac{d\xi}{dt} \\ &\text{-----} \\ \frac{dm_i}{dt} &= \nu_i w_i \frac{d\xi}{dt} \end{aligned} \quad (75)$$

or

$$\frac{dm_1}{\nu_1 w_1} = \frac{dm_2}{\nu_2 w_2} = \dots = \frac{dm_i}{\nu_i w_i} = d\xi \quad (76)$$

Rather than defining the chemical state of the system in terms of masses, it is usually better to employ the number of moles of the various components, $n_1 \dots n_i$. Then equation (73) becomes

$$\begin{aligned} n_1 - n_1^0 &= \nu_1 \xi \\ &\text{-----} \\ n_i - n_i^0 &= \nu_i \xi \end{aligned} \quad (77)$$

where the original number of moles $n_1^0 \dots n_i^0$ refer to $t = 0$.

Differentiating results in

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_i}{\nu_i} = d\xi \quad (78)$$

Mole fractions of any component can be given by

$$x_i = \frac{n_i}{\sum_i n_i} = \frac{n_i^0 + \nu_i \xi}{\sum_i n_i^0 + \xi \sum_i \nu_i} = \frac{n_i^0 + \nu_i \xi}{n^0 + \xi \nu}$$

where $\nu = \sum_i \nu_i$.

Normally the system being studied will undergo a series of simultaneous independent reactions, rather than a single reaction as considered above. Here "independent" has the same connotation as in the mathematical sense, in that a series of reactions is described as independent if no one of the stoichiometric equations can be derived from the others by linear combination. For such a set of r reactions (74) would become

$$\begin{array}{rcl} \sum_i \nu_{i,1} w_i & = & 0 \\ \text{---} & & \text{---} \\ \sum_i \nu_{i,r} w_i & = & 0 \end{array} \quad (79)$$

where $\nu_{i,1}$ and $\nu_{i,r}$ represent respectively the stoichiometric coefficients of the i^{th} component in the 1^{st} to r^{th} reaction.

Written in more compact form (79) becomes

$$\sum_i \nu_{i,\tau} w_i = 0 \quad (\tau = 1, 2, \dots, r) \quad (80)$$

and (76) may now be written as

$$\frac{d_{\tau} m_1}{\nu_{1,\tau} W_1} = \frac{d_{\tau} m_2}{\nu_{2,\tau} W_2} = \dots = \frac{d_{\tau} m_i}{\nu_{i,\tau} W_i} = d\xi_{\tau} \quad (81)$$

Likewise (78) becomes

$$\frac{d_{\tau} n_1}{\nu_{1,\tau}} = \frac{d_{\tau} n_2}{\nu_{2,\tau}} = \dots = \frac{d_{\tau} n_i}{\nu_{i,\tau}} = d\xi_{\tau} \quad (82)$$

The symbol $d_{\tau} n_i$ represents the change in the number of moles of the i^{th} component in the time dt resulting from the τ^{th} reaction. The total change in n_i as a result of all the r^{th} reactions is

$$dn_i = d_1 n_i + d_2 n_i + \dots + d_r n_i = \sum_{\tau} d_{\tau} n_i \quad (83)$$

or

$$\frac{dn_i}{dt} = \sum_{\tau} \nu_{i,\tau} \frac{d\xi_{\tau}}{dt} \quad (84)$$

In this last expression the relation of rate of change of with respect to time is known as the reaction velocity and will be written as

$$\mathcal{V}_{\tau} \equiv \frac{d\xi(t)_{\tau}}{dt} \quad (85)$$

It is the ratio of the change (positive, zero, or negative) in the extent of reaction during the interval of time dt (always positive) in which this change takes place.

The rate of consumption or production of moles of components can be expressed in terms of the reaction velocity, as by (78) and (84).

$$\frac{dn_i}{dt} = \nu_i \mathcal{N} \quad (\text{Single reaction}) \quad (86)$$

$$\frac{dn_i}{dt} = \sum_{\tau} \nu_{i,\tau} \mathcal{N}_{\tau} \quad (\text{Multiple reaction})$$

In terms of the actual masses of the components

$$\frac{dm_i}{dt} = \sum_{\tau} \nu_{i,\tau} W_i \mathcal{N}_{\tau} \quad (87)$$

By definition, molar concentration is

$$[M_i] = \frac{n_i}{\text{Vol.}} \quad (88)$$

Differentiating this with respect to time gives

$$\frac{d[M_i]}{dt} = [\dot{M}_i] = \frac{1}{V} \frac{dn_i}{dt} - \frac{n_i}{V^2} \frac{dV}{dt} \quad (89)$$

and from (78)

$$[\dot{M}_i] = \frac{\nu_i}{V} \frac{d\xi}{dt} - \frac{n_i}{V^2} \frac{dV}{dt} \quad (90)$$

or

$$[\dot{M}_i] = \frac{\nu_i}{V} \mathcal{N} - \frac{n_i}{V^2} \frac{dV}{dt} \quad (91)$$

which gives the change in concentration for each component in a single reaction.

Extending this last equation to a multiple reaction, the combined change in concentration for any i^{th} component that might appear in more than one reaction, results in

$$[\dot{M}_i] = \sum_r \left(\frac{v_{i,r}}{v} N_r - \frac{n_{i,r}}{v^2} \frac{dv}{dt} \right) \quad (92)$$

which shows that the concentration changes because the number of moles are changing and also, because there may be a change of volume resulting from the reaction. Volume change in this case is attributable directly to the reaction, being a function of the state equation, and not to the spatial volume change connected with container dimension change.

Reactive Flow

Now that the general theory for the flow of a reactive gas mixture has been developed, the next step is to express these relationships in a form applicable to the conditions set forth in the assignment of the problem. This will entail introducing the relevant assumptions to reduce the general equations to ones which can be solved simultaneously, commensurate with available data and boundary conditions.

With the flow restricted to a one-dimensional path, all of the space derivatives become functions only of the axial dimension y , there being no changes in the radial directions. Thus, in any plane normal to the y -axis, there are no changes in properties which are functions of position over that plane, i.e., no gradients are permitted to exist in the plane. Likewise, in this plane normal to the axis, there will be no changes relative to time in those properties which are independent of the effects of chemical reaction, which includes overall density, total internal energy, and total pressure.

Even though these are properties which change with a chemical reaction, and are thus a function of time, the concept of steady-state flow can be applied to the overall flow. It will simply mean that the reaction rates are independent of time, being functions of position, and the properties which are affected by a reaction will be affected in the same manner, relative to time, at any position in the flow device. The reaction rates, which are functions of temperature for a given reaction, are dependent on position only in that temperature is changing along the flow path and is thus a function of position.

The equations of change give a set of equations which describe the bulk properties of the flow as it proceeds through a varying area device. In the one-dimensional analysis, in which the boundaries of the channel are surfaces of revolution, described by a relation $f(x,z) = y$, the following procedure is used to reduce the time independent equation.

Consider a plane normal to the y -axis and let S be that portion of the plane contained within the intersection with the $f(x,z) = y$ surface. If $\vec{F}(\vec{r})$ is a vector field which on the surface $f(x,z) = y$ is tangent to the surface, then

$$\iint_S (\nabla \cdot \vec{F}(\vec{r})) \, dx \, dz = \frac{d}{dy} \iint_S F_y \, dx \, dz \quad (93)$$

where F_y is the y component of $\vec{F}$.

In steady state, the three dimensional continuity equation, (33), is

$$\rho (\nabla \cdot \vec{u}_0) = 0 \quad (94)$$

In the nozzle, the velocity is either zero or tangent to the walls, and (93) may be applied to give,

$$\frac{d}{dy} \iint_S \rho u_{0y} \, dx \, dz = 0$$

which, upon integrating with respect to y , gives

$$\iint_S u_{0y} \, dx \, dz = \text{Constant} \quad (95)$$

Noting that the density and velocity are uniform over any cross-section, (94) can be written

$$\rho_y u_{0y} A_y = \dot{m} = \text{Constant} \quad (96)$$

where w is the mass flow rate, a constant. Since in one dimension it is unnecessary to carry the notation that density, area, and velocity are functions of that dimension, it is permissible to write

$$\rho u_0 A = w \quad (97)$$

A one dimensional conservation of energy equation can be obtained in a similar manner. Starting with equation (35), and multiplying it by $\rho \vec{u}_0$, after which the result is added to equation (39), there results

$$[\rho \vec{u}_0 \cdot \nabla (e + 1/2 u_0^2)] + [\nabla \cdot (\mathcal{P} \cdot \vec{u}_0)] + [\nabla \cdot \vec{q}] = 0 \quad (98)$$

Using the continuity equation, as is given by (94), this becomes,

$$[\nabla \cdot (e + 1/2 u_0^2) \rho \vec{u}_0] + [\nabla \cdot (\mathcal{P} \cdot \vec{u}_0)] + [\nabla \cdot \vec{q}] = 0 \quad (99)$$

When this equation is integrated over the normal plane, with the assumption of no side wall effects and no heat transfer with the walls, the results is

$$(e + 1/2 u_0^2) \rho u_0 A + \rho u_0 A = \text{Constant} \quad (100)$$

Dividing by $\rho u_0 A$, a constant, gives the familiar energy balance equation,

$$h + 1/2 u_0^2 = \text{Constant} \quad (101)$$

or in differential form

$$dh + u_0 du_0 = 0 \quad (102)$$

In like manner, the momentum conservation equation is obtained from (35), in the form

$$u_0 du_0 + 1/\rho dp = 0 \quad (103)$$

These equations, (97), (102, and (103), describe the change of time-independent properties of the flowing fluid, along with the equation of state. Reference is sometimes made to them as bulk equations, since they are common to the entire mass flowing at any point in the nozzle.

Perhaps the most important of the relationships available through the equation of change is that for the conservation of chemical species, (32). It was found to be

$$\frac{Dn_i}{Dt} = -N_i (\nabla \cdot \vec{u}_0) - (\nabla \cdot N_i \vec{C}_i) + B_i \quad (32)$$

For reactive systems, this is not a time-independent relation, since the change in concentration of the i^{th} species is directly dependent on the amount of time available for the specific reaction to take place. Thus,

$$\frac{Dn_i}{Dt} = [\dot{M}_i] \quad (104)$$

where $[\dot{M}_i]$ is defined by (92). For gases at relatively high temperatures and low pressures, flowing through a nozzle, the diffusion velocity term may be neglected, since the average molecular linear velocity is approximately equal to the free stream velocity. This will reduce equation (32) to

$$\frac{Dn_i}{Dt} = [\dot{M}_i] = -N_i (\nabla \cdot \vec{u}_0) + B_i \quad (105)$$

and comparison to (91) shows that

$$B_i = \frac{\nu_i}{V} \mathcal{N} \quad (106)$$

In the case of a multiple reaction, then the continuity equation for any species, in one dimension, is thus

$$[\dot{M}_1] = \sum_{\tau} \frac{V_{1,\tau}}{V} N_{\tau} - N_1 \frac{du_0}{dy} \quad (107)$$

which gives the change in concentration, with respect to time, of the i^{th} species as a result of chemical reaction and change in volume of the system.

Equilibrium composition in a mixture of reactive gases can be obtained from thermodynamic data and from the total amounts of each chemical species concerned, as pointed out above in the section on chemical kinetics. It is not desirable to approach equilibrium composition by means of reaction rates, because for true equilibrium to exist it is mandatory that either the reaction rate constant or the time factor approach a value of infinity. A great deal of analytical and experimental work has been done on equilibrium states, resulting in considerable data and tables. For example, Brinkley and Lewis¹ worked out a very extensive program, suitable for electronic calculation, to determine equilibrium compositions at various temperatures and pressures for the reaction products resulting from the combustion of air and a $C_n H_{2n}$ fuel. This program was used by the General Electric Company to compile some rather comprehensive tables.²

¹Brinkley, S. R. and B. Lewis, The Thermodynamics of Combustion Gases: General Considerations, Bureau of Mines, RI 4806, 1952.

²Powell, H. N. and S. N. Suci, Properties of Combustion Gases, Vol. I and II, McGraw-Hill, 1956.

As in the case of the composition, the thermodynamic properties of gases are point functions of the atomic composition, temperature, and pressure or volume. However, for the energy quantities, there is the requirement of a base point. The choice of this point is entirely arbitrary, but once the choice is made, all thermodynamic quantities must be referred to it. Two bases frequently used are the system stable at ambient temperature (300°K, 530°R) and at a pressure of one atmosphere, and the system hypothetically stable at 0° absolute and one atmosphere. As a majority of the available information on enthalpies, entropies, etc. is given relative to this latter base, it will be employed henceforth.

The determination of enthalpy and internal energy for the equilibrium composition at various temperatures and pressures may be considered in two parts. The first is that due to the heat or energy of reaction at the base temperature, from the standard composition, at base temperatures, to the equilibrium composition at the temperature T . Secondly, is the change in enthalpy or internal energy, in heating this mixture from the base temperature, to the temperature T , plus the effects in going from the perfect gas state, at one atmosphere, to the pressure or density under consideration. These relations can be expressed in equation form as

$$H = \sum_i n_i (\Delta H_f^\circ)_i + \sum_i n_i (H_T^\circ - H_0^\circ)_i + n \int_{p_0}^P \left(\frac{\partial H}{\partial p} \right)_T dp \quad (108)$$

and

$$E = \sum_i n_i (\Delta E_f^\circ)_i + \sum_i n_i (E_T^\circ - E_0^\circ)_i + N \int_{V^0}^V \left(\frac{\partial E}{\partial V} \right)_T dV \quad (109)$$

Where n_i is the number of moles of species i , present at temperature T , and ΔH_f° or ΔE_f° is the heat or energy of formation of the i^{th} species at 0° absolute, from the elements at 0° absolute. The term $(H_T^\circ - H_0^\circ)$, or $(E_T^\circ - E_0^\circ)$, is the integral of the specific heat of species i from 0° to temperature T . It might be noted as an advantage of the base 0° absolute that $\Delta H_f^\circ = \Delta E_f^\circ$ and $H_0^\circ = E_0^\circ$.

In the base of a perfect gas, the last terms in the above equations, which correct for change of enthalpy or internal energy with pressure or volume changes, are equal to zero. For the general case, these terms are given by

$$\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p \quad (110)$$

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad (111)$$

Numerical values would then be obtained from the applicable equation of state, if other than a perfect gas.

Entropy tables are available for the standard state at a pressure of one atmosphere for many substances.^{1,2} Using these values,

¹Rossini, F. D. et al, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, 1952.

²Hilsenrath, J. et al, Tables of Thermal Properties of Gases, National Bureau of Standards Circular 564, 1955.

the entropy of a mixture is given by,

$$S^{\circ} = \sum_i n_i S_i^{\circ} - n R \sum_i X_i \ln X_i, \quad X_i = \frac{n_i}{n} \quad (112)$$

In many cases, the above tables may not have entropy information, but instead the free-energy function will be tabulated. By use of the relation $F = H - TS$, the entropy can be determined by

$$S^{\circ} = \frac{1}{T} \sum_i n_i (H_T^{\circ} - H_0^{\circ})_i - \sum_i n_i \left(\frac{F^{\circ} - H_0^{\circ}}{T} \right)_i - n R \sum_i X_i \ln X_i \quad (113)$$

In both cases, the term $n R \sum_i X_i \ln X_i$ is the entropy of mixing all of the components, each originally present at one atmosphere to give the mixture at one atmosphere.

To obtain the entropy at the desired pressure or volume, there must be added to the above relationships, the change of entropy with pressure or volume change. This is given in general by

$$S - S^{\circ} = - \int_{p^{\circ}}^p \left(\frac{\partial V}{\partial T} \right)_p dp = \int_{V^{\circ}}^V \left(\frac{\partial p}{\partial T} \right)_V dV \quad (114)$$

Which in the case of a perfect or ideal gas, becomes

$$S - S^{\circ} = - n R \ln \frac{p}{p^{\circ}} = n R \ln \frac{V}{V^{\circ}} \quad (115)$$

Heat capacities can be found in equation form by applying the definition of C_p and C_v to equations (108) and (109) respectively.

This leads to the expressions,

$$\begin{aligned}
C_p = \left(\frac{\partial H}{\partial T} \right)_p &= \sum_i \left(\frac{\partial n_i}{\partial T} \right)_p (\Delta H_f^\circ)_i + \sum_i \left(\frac{\partial n_i}{\partial T} \right)_p (H_T^\circ - H_o^\circ)_i \\
&+ \sum_i n_i \left(\frac{\partial (H_T^\circ - H_o^\circ)_i}{\partial T} \right)_p - n T \int_{p^o}^p \left(\frac{\partial^2 v}{\partial T^2} \right)_p dp \quad (116)
\end{aligned}$$

and

$$\begin{aligned}
C_v = \left(\frac{\partial E}{\partial T} \right)_v &= \sum_i \left(\frac{\partial n_i}{\partial T} \right)_v (\Delta E_f^\circ)_i + \sum_i \left(\frac{\partial n_i}{\partial T} \right)_v (E_T^\circ - E_o^\circ)_i \\
&+ \sum_i n_i \left(\frac{\partial (E_T^\circ - E_o^\circ)_i}{\partial T} \right)_v - n T \int_{v^o}^v \left(\frac{\partial^2 p}{\partial T^2} \right)_v dv \quad (117)
\end{aligned}$$

The first two terms, in the above equations, give the heat involved in the changes in composition, the third terms give the perfect gas value of the heat capacity at constant composition, and the last terms give the effect due to deviation from the perfect gas criteria.

One other thermodynamic property which is often useful, in the flow application, is the velocity of sound. This is given by

$$a^2 = \left(\frac{\partial p}{\partial \rho} \right)_s \quad (118)$$

which reduces to

$$a^2 = \frac{C_p}{C_v} \left(\frac{\partial p}{\partial \rho} \right)_T \quad (119)$$

The quantities C_p and C_v would be obtained from equation (116) and (117) respectively, and the last term from the equation of state.

All of the developments above were made on a basis of equilibrium. However, the same equation could be directly applied to the condition of frozen flow or constant composition. This would only require that those terms involving derivatives of n_i be set equal to zero.

For the situation of chemical reaction during adiabatic-frictionless flow, unlike the condition of equilibrium chemical re-association, is non-isentropic because the chemical composition is not a unique function of the equation of state of the gas. The energy equation governing such flow, is given by equation (102)

$$dh + u_0 \, d u_0 = 0 \quad (102)$$

which may be equated to equation (103), for the conservation of momentum, to give

$$dh = \frac{dp}{\rho} \quad (120)$$

Upon applying the equation of state for a perfect gas, and for the total mass, shows that,

$$dH = \frac{n R T}{p} \, dp \quad (121)$$

Taking the expression for the enthalpy function as given by equation (108), and writing it for a perfect gas, there results,

$$H = \sum_i n_i (\Delta H_{f_{T_0}})_i + \sum_i n_i \int_{T_0}^T C_{p_i} \, dT \quad (122)$$

For which the derivative would reduce to

$$dH = \sum_i (\Delta H_f)_i \, d n_i + \sum_i n_i C_{p_i} \, dT \quad (123)$$

where now the term $(\Delta H_f)_i$ is the enthalpy of formation at the temperature of the gas.

Now the energy equation may be rewritten by combining (121) with (123) as

$$\sum_i (\Delta H_f)_i \frac{dn_i}{dT} dT + \sum_i n_i C_{p_i} dT = \frac{n R T}{p} dp \quad (124)$$

Dividing through by nT , and indicating $\sum_i n_i C_{p_i} = C_p'$, an average specific heat of the mixture, results in

$$\sum_i \frac{(\Delta H_f)_i}{n_i} \frac{dn_i}{dT} dT + \frac{C_p'}{n} \frac{dT}{T} = R \frac{dp}{p} \quad (125)$$

This equation is not integrable, as n_i can not be expressed as a unique function of the state of the gas, due to its dependence on time. However, for a fixed geometry, as would normally be the case in application, the parameters T and P can be related to the velocity and hence to the time. Knowledge of the reaction rates of the various chemical reactions occurring would permit a solution when (dn_i/dT) is expressed as $(dn_i/dt)(dt/dT)$, because these last derivatives can be expressed analytically. This would transform (125) to the form

$$\sum_i \frac{(\Delta H_f)_i}{n_i} \frac{dn_i}{dt} \frac{dt}{dT} \frac{dT}{T} + \frac{C_p'}{n} \frac{dT}{T} = R \frac{dp}{p} \quad (126)$$

Even though this last expression can be written in analytical form, the complexity of the (dn_i/dt) term makes a solution practically impossible. The most satisfactory way of handling such expressions is by some means of numerical integration applicable to electronic com-

putation. Even then it is desirable to express the $(d n_i/dT)$ quantity as a constant over a given temperature increment and to proceed in a step-wise fashion. This is even more practical when the relative order of accuracy to which the reaction rates are known at high temperature is considered.

CALCULATION PROCEDURE

As indicated in the Assignment of the Problem, the second part of this study is to examine a flow situation along frozen, equilibrium, and reactive paths. For each of the three cases, identical initial conditions will prevail and the nozzle configuration will be the same, that given in Appendix A. The initial composition of the flowing liquid is assumed to be that of equilibrium for ten atmospheres of pressure and a temperature of 5000°R , as given by Powell and Suci¹, for the products of combustion of a C_nH_{2n} - Air mixture. In terms of the mole fractions, X_i , this composition is:

Component	X_i
A	8.4925×10^{-3}
CO	3.5233×10^{-2}
CO ₂	9.2249×10^{-2}
H ₂	6.5445×10^{-3}
H ₂ O	1.1532×10^{-1}
N ₂	7.0671×10^{-1}
O ₂	1.3720×10^{-2}
O	1.9636×10^{-3}
OH	8.7612×10^{-3}
H	1.9307×10^{-3}
NO	8.9587×10^{-3}
N	1.1214×10^{-4}

¹Powell and Suci, op.cit.

One additional initial condition is that the fluid enters the nozzle section with a velocity of 320 feet per second. This is approximately ten percent of the expected velocity at the throat of the nozzle.

Assumptions which pertain to the overall flow, for all three processes, are:

1. Steady flow
2. Adiabaticity
3. Non-viscous fluid
4. One-dimensionality
5. No external forces
6. $p = \rho RT$

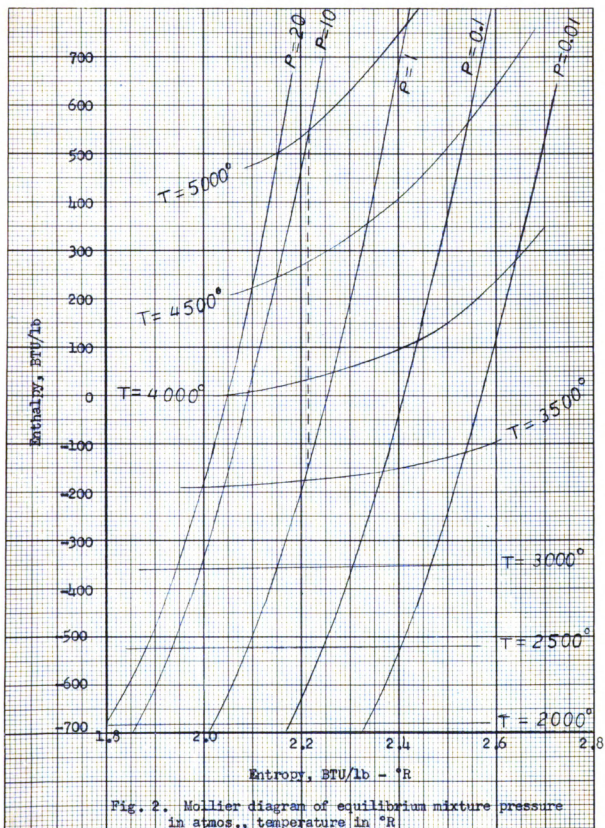
These are consistent with the development of the theory, and thus permits its use directly.

Equilibrium Path

As already indicated, Powell and Suciu,¹ have machine tabulated some of the equilibrium properties as functions of temperature and pressure. Sufficient data are available to permit the construction of an enthalpy-entropy diagram, with isothermal and isobaric lines. Such a plot was constructed on coordinates large enough that values could be read to an accuracy comparable with that of the tabulated data.

Figure 2 is a reduced version of the working graph. From the $h-s$ diagram, it is possible to find the pressures and enthalpies corresponding to given temperatures, along the equilibrium path. In ac-

¹Ibid.



cordance with the assumptions indicated above, an equilibrium path is the same as a constant entropy path, and is so indicated in Fig. 2 .

After the pressures corresponding to given temperatures are known, the equation of state is used to obtain values of density, ρ .

$$\rho = \frac{P W}{R T} \quad (127)$$

where W is the molecular weight of the mixture and is given by

$$W = \sum_i X_i W_i \quad (128)$$

in which W_i is the molecular weight of the i^{th} species.

At the same time that pressure values are obtained from the h - S diagram, values of enthalpy may also be found. Rather than using scale values of enthalpy, the change in enthalpy from that of the initial state, was determined and tabulated. With the changes in enthalpy, Δh , values of velocity may be calculated from

$$u^2 = u_{\text{initial}}^2 + 2 \Delta h \quad (129)$$

According to equation (97), for the condition of steady flow, $w = \text{constant}$,

$$\rho u = \frac{W}{A} \quad (130)$$

and, as the initial value of ρu is given, a dimensionless ratio of areas may be established. This is

$$\frac{A_{\alpha}}{A} = \frac{\rho u}{\rho_{\alpha} u_{\alpha}} \quad (131)$$

where the subscript α refers to initial conditions. Plotting A_{α} / A

against temperature, Fig. 4, shows a maximum which is the throat of the nozzle, A_α/A_t .

Maximum flow rate is controlled by the throat conditions, and it is thus desirable to refer certain parameters to the throat of the nozzle for purposes of comparison. For this reason, the dimensionless ratio A/A_t is tabulated along with other properties. This ratio comes from:

$$A/A_t = A/A_\alpha \times \frac{A_\alpha}{A_t} \quad (132)$$

Frozen Path

Frozen flow differs from equilibrium flow primarily in that the former, by definition, implies a departure from chemical equilibrium. In spite of the imposed conditions that frozen flow is adiabatic, frictionless, etc., irreversibilities are implicit somewhere in the process. For chemically reactive systems the entropy, in general, is not defined by T , P , and R alone; only for an equilibrium system is entropy uniquely defined by T , P , and R . Thus, a frozen path can be reversible and isentropic only within the special framework of infinitely rapid flow processes (or infinitely slow reaction rate). At the end of such a "frozen" expansion, irreversible and exothermic recombination, reactions would take place with an increase in entropy; the entropy of the final equilibrium state being greater than the entropy of an equilibrium path expansion of the same pressure ratio. In fact, the entropy increase would be a function of this pressure ratio.

On the basis of this hypothesis, that the only cause of entropy change is that resulting from a pressure change, equation (115) which is

$$S - S^0 = -nR \ln \frac{P}{P^0} \quad (115)$$

must be satisfied at every state of the fluid. But along the flow path

$$\begin{aligned} S - S^0 &= -nR \ln \frac{P_\alpha}{P^0} \\ S_1 - S_1^0 &= -nR \ln \frac{P_1}{P^0} \\ &\text{-----} \\ S_x - S_x^0 &= -nR \ln \frac{P_x}{P^0} \end{aligned} \quad (133)$$

where subscript x represents any arbitrary point, and since

$$S_\alpha = S_1 = \text{-----} = S_x \quad (134)$$

then,

$$S_\alpha^0 = S_x^0 + nR \ln \frac{P_\alpha}{P_x} \quad (135)$$

For the mixture,

$$\frac{S^0}{n} = \sum_i x_i S_i^0 \quad (136)$$

and writing (133) in a more compact form, gives

$$\ln P_x = \ln P_\alpha - \left[\sum_i x_i \left(\frac{S_i^0}{R} \right)_{T_\alpha} - \sum_i x_i \left(\frac{S_i^0}{R} \right)_{T_x} \right] \quad (137)$$

Using this last expression, the pressure P_x can be calculated for a chosen T_x , when the $\frac{S_1^0}{R}$ values are known. The $\frac{S_1^0}{R}$ quantities have been tabulated, as functions of temperature, by Powell and Suci¹ from data available in the Bureau of Standards Circular 500,² or they may be calculated from the same reference, from the relationship

$$\frac{S_1^0}{R} = \frac{H_1^0 - F_1^0}{RT} \quad (138)$$

The values of pressure in Table II were calculated from (137) in temperature steps of 100 degrees. By its definition, frozen flow requires that X_i be constant all along the path, as must the molecular weight, w . Once the pressure, P_x , is obtained for a given temperature, T_x , application of the equation of state gives the density, ρ_x .

$$\rho_x = \frac{P_x w}{R T_x} \quad (139)$$

Enthalpy change, as tabulated in Table II, comes from the relationship

$$h_x = \frac{RT_x}{w} \sum_i X_i \left(\frac{H_i^0}{RT} \right)_{T_x} \quad (140)$$

again making use of the tabulated quantity $\frac{H_i^0}{RT}$. Here the term H_i^0

¹Ibid.

²Rossini, F. D., et al, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, 1952.

represents the sensible enthalpy plus the zero heat of formation, through

$$H_1^{\circ} = (H_1^{\circ} - H_{10}^{\circ}) + H_{10}^{\circ} \quad (111)$$

Thus the change in enthalpy, Δh , from the nozzle inlet is

$$\Delta h = h_{\alpha} - h_x = \frac{RT_{\alpha}}{W} \sum_i x_i \left(\frac{H_1^{\circ}}{RT} \right)_T - \frac{RT_x}{W} \sum_i x_i \left(\frac{H_1^{\circ}}{RT} \right)_{T_x} \quad (112)$$

When the Δh values have been obtained, they are then used to determine the corresponding velocity in the same manner as described above for equilibrium flow. Likewise, for the ρu terms and the dimensionless quantities A^{α}/A and A/A_t the procedure outlined above is followed.

The only point along the flow path which can not be calculated, in the sequence indicated above, is that corresponding to the throat position. In order to obtain throat conditions, it is necessary to construct a graph of temperature versus A^{α}/A , Fig. 4, on which the maximum value of A^{α}/A represents throat position. With the temperature found in this manner, then the sequence of calculations may be followed to obtain the remaining quantities.

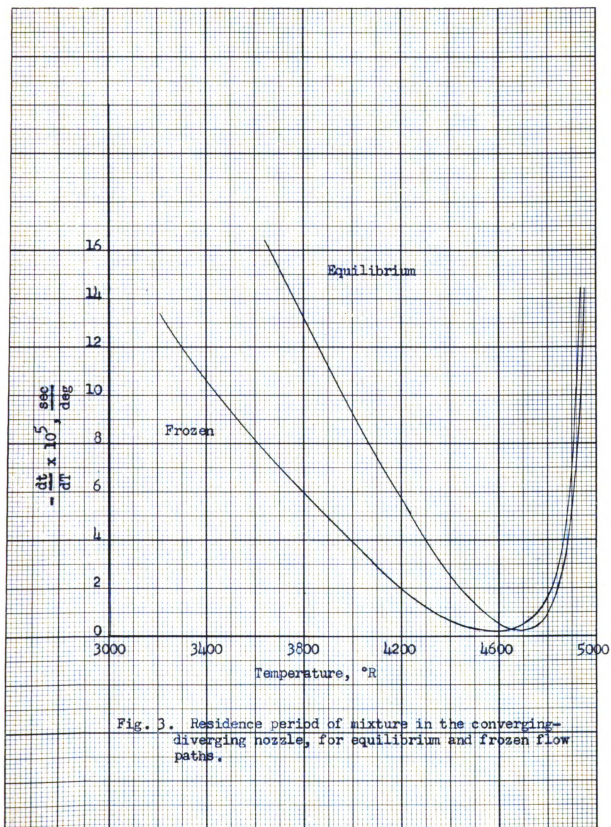
Temperature - time Relationships

Up to this point in the calculations, it is not necessary to specify the exact nozzle dimensions, only to know that the shape is converging-diverging. Nozzle size has no effect on any of the specific values such as pressure, temperature, etc., and not on the ratios such as A^{α}/A or A/A_t . Rather, these terms predict the necessary nozzle

length, once the angles of divergence and convergence are set. This is due to the definitions of equilibrium and frozen flow, which eliminate the necessity of needing to know anything about the period of residence of the flowing fluid in any given section of the nozzle. In the one case, an infinitely short period is satisfactory, and in the other case, even an infinitely long period results in no reaction.

However, in the case of reactive flow, where the reaction rates are finite, it is necessary to know for how long a period the flow will occupy a given state, or be in transit between two states. The actual amount of reaction taking place in any portion of the nozzle will depend on how fast the reaction can occur and how long it is permitted to proceed at this rate. Rate of reaction is primarily a function of temperature, and the available time is dependent on the velocity of the fluid. Neither temperature nor velocity are solely functions of nozzle shape, but are dependent, in part, on the nozzle geometry. Thus, in order to approach a problem involving finite reaction rates, some connection must be established with the nozzle shape and either temperature or velocity.

Using the data obtained from the above equilibrium and frozen path calculations, in conjunction with the nozzle shape described in Appendix A, the rate of change of temperature, with respect to time, may be determined. This was done for various temperatures and resulted in the curves of Fig. 3. These curves represent the limits for this particular flow situation, in that reactive flow with finite reaction rates would be between them.



The procedure for establishing the value of $\frac{\Delta t}{\Delta T}$ for a given temperature consists of first choosing a temperature range centered about the desired temperature. In this case, a one hundred degree ΔT was used. Values of A/A_t are determined for the end point temperature of the ΔT , and then from Fig. 10 the change in length, Δy , is obtained. Likewise, for the same end point temperatures, the change in velocity, Δu , may be found from Fig. 7. Then

$$\frac{\Delta t}{\Delta T} = \frac{\Delta y}{\Delta T} \cdot \frac{\Delta T}{\Delta u} \cdot \frac{1}{\Delta T} \quad (143)$$

This information is used to establish the probable time available for reaction in the study of reactive flow with finite reaction rates.

Flow with Finite Reaction Rate

Fundamentally, the analysis of the flow of a chemically reactive mixture with finite reaction rates, which here will be referred to as "finite" flow, is handled the same as for equilibrium and frozen flow paths, once the bulk enthalpy function is available. However, the collection of suitable information to enable the determination of the enthalpy function is quite a formidable undertaking. Most of the complications arise from lack of knowledge concerning the proper physical description of what takes place, plus a dearth of experimental information in the high temperature range.

In order to determine the bulk enthalpy at any point, it is necessary to know the mixture composition at that point, along with the

pressure and temperature. As the mixture is reactive, it is always tending toward an equilibrium state, with some components being consumed and others formed. The rate of change of each of the i^{th} species being

$$\frac{d n_i}{dt} = \sum_{\tau} \frac{d_{\tau} n_i}{dt}, \quad \tau = 1, 2, \dots, r \quad (144)$$

where τ designates the various reactions. When $d n_i/dt$ is known, then for a certain time increment, the change in number of moles of species i is

$$\Delta n_i = \frac{\Delta n_i}{\Delta t} \cdot \Delta t \quad (145)$$

As shown above, equation (72),

$$\frac{d_{\tau} n_i}{dt} = (\nu_i'' - \nu_i') k_{f\tau} [M_T] \sum_i \nu_i' \left(1 - \frac{K_x^*}{K_x} \right) \prod_i (x_i)^{\nu_i'} \quad (72)$$

gives the time rate of change for a component not in an equilibrium state.

Before this relationship can be applied, it is necessary to know what reactions are occurring, or at least to establish a probable system of reactions. With a mixture such as the one considered here, all of the components are directly involved in reactions, with the exception of the Argon and it is serving as a third-body for collision. Thus, there are a tremendous number of reactions which could be chemically possible.

As a starting point in establishing a workable system of reactions, the following assumptions were made:

- (a) only components appearing in the initial composition would be permitted as either reactants or products
- (b) only two body collisions considered, except where a third body is necessary to carry off momentum.

The first of these assumptions can be justified on the basis that the mixture enters the nozzle in an equilibrium condition, there having been sufficient time for all excited forms to have decayed to the ground state and the most stable composition attained. Should there subsequently be other molecular forms resulting from the reaction, these molecules would be in small concentration. In regards to the second assumption, the probability of triple collisions involving specific bodies is small compared to that for two body collision; and as such, any reaction requiring a triple collision of specific bodies would have only a negligible contribution to the overall system. For those reactions which do require a third body, triple collision, any molecule in the mixture, other than the reacting species, is presumed adequate as the third body. On the basis of these assumptions, there could be twenty-three possible reactions from the eleven reactive components in the entering mixture.

Due to the fact that the initial state is assumed to be one of equilibrium, the relationship given by (72) can not be applied, for one of the requirements of equilibrium is that $\frac{dn_1}{dt} = 0$, which is the case by virtue of $K_X = K_X^*$. To start the analysis, the first position considered is that at an assumed temperature of 4900°R, which would be only a short distance into the nozzle and should be still close to equilibrium. Then (72) may be applied to each reaction at the mean

temperature, 4950°R, and can be assumed to describe the reaction change for the $\Delta T = 100^\circ$. The concentration term $[M_T]$, and the mole fractions X_i are assumed to be those of the initial mixture.

For this first step where no information is available to calculate K_X^* , which is a function of finite composition, the Van't Hoff equation may be used to determine the ratio K_X^*/K_X . This equation gives the change of the equilibrium constant with respect to temperature¹ as

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (146)$$

where

$$\Delta H^\circ = \sum H^\circ_{\text{final}} - \sum H^\circ_{\text{initial}} \quad (147)$$

For the small ΔT , (146) may be written

$$\frac{\Delta (\ln K)}{\Delta T} = \frac{\Delta H^\circ}{RT_1 T_2} \quad (148)$$

and

$$\ln \frac{K}{K^*} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (149)$$

It is only for this first step that such a procedure is necessary to find the K_X^*/K_X ratio, because in later calculations, the finite and equilibrium compositions will be different.

¹Glasstone, S., Thermodynamics for Chemists, (New York: D. Van Nostrand Co., 1955), p. 288.

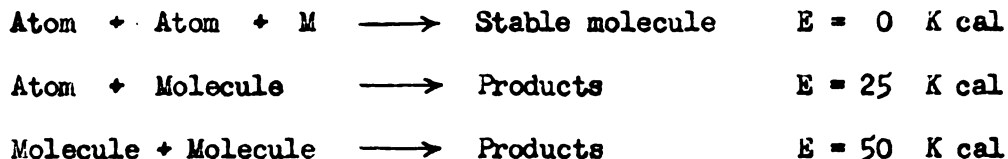
The only remaining term in (72) is the reaction rate, k_{FT} , which is given by the Arrhenius relationship,

$$k = A e^{-\frac{E}{RT}} \quad (50)$$

Practically no specific information is available as to the experimental values of either A or E in the high temperature range; about the highest temperature investigations reported are in the order of 1000°K . For the purpose of this study, the value of A is taken as

$$10^{10} \left(\frac{\text{Mole}}{\text{ft}^3} \right)^{-2} - \text{sec}^{-1}, \text{ as recommended by Glasstone}^1 \text{ and Amdur.}^2$$

The activation energy can also be assumed independent of temperature, but for different types of reactions there will be a different E constant. For this reason, the following values of E were assumed, relative to the type of reaction occurring:



No experimental evidence is available to substantiate the assumed activation energies, at the high temperatures involved, but from low temperature data, these seem to be reasonable mean values. Both E and A are relatively independent of temperature, and using the above assumed data gives values of k comparable to published values for equal temperatures.

¹Glasstone, S., K. J. Laidler, and H. Eyring, The Theory of Rate Processes, (New York: McGraw-Hill, 1941).

²Amdur, I., Journal of American Chemical Society, 60,2347,(1935).

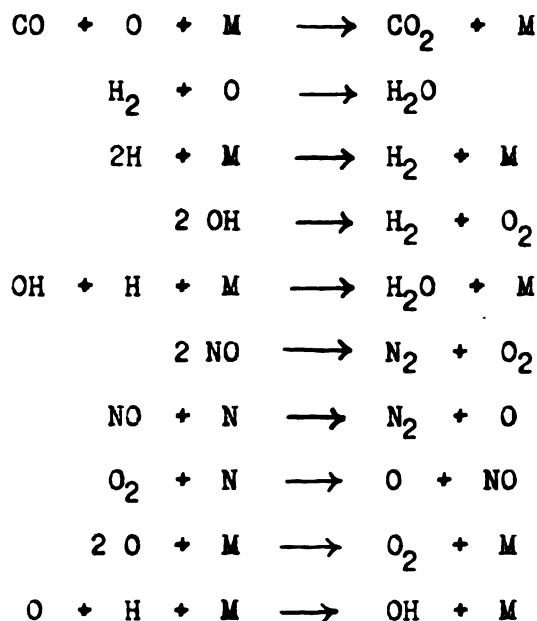
With this information (72) can be applied to each of the reactions, giving the $d_r n_i/dt$ contribution per reaction. It is not necessary to solve $d_r n_i/dt$ for each component in each reaction, since from the reaction coordinate, ξ ,

$$\frac{d \xi_r}{dt} = \frac{1}{\nu_{i,r}} \frac{d_r n_i}{dt} \quad (82)$$

and for the multiple reactions

$$\frac{d n_i}{dt} = \sum_r \nu_{i,r} \frac{d \xi_r}{dt} \quad (84)$$

In this manner the net rate of change of each component is found by summing over all of the reactions, in this case, twenty-three. Examination of the resulting rates of change showed that several of the reactions were relatively slow and the significant effects could be described by a system of ten reactions. These ten reactions, which are assumed for the rest of the study, are:



Contrary to the situations for equilibrium and frozen flow, it is necessary to have a control volume or mass for finite flow in order to know the number of moles of the i^{th} species. For this study, a control volume was chosen equivalent to the volume in the nozzle between y inlet and $y = 0.4$, on the converging side. From the equation of state, with initial conditions, the number of moles of mixture, and each component, may be calculated. In this case there are 6.3604×10^{-5} moles of mixture.

With the initial composition thus established, the change in composition due to reaction may be determined up to $T = 4900^\circ\text{R}$.

This comes from

$$\Delta n_i = \frac{\Delta n_i}{\Delta t} \cdot \frac{\Delta t}{\Delta T} \cdot \Delta T \quad (150)$$

in which the term $\frac{\Delta t}{\Delta T}$ is taken as the mean value between equilibrium and frozen flow at $T = 4950^\circ\text{R}$, as indicated in Fig. 3. Then

$$n_{i \text{ } T_x} = n_{i \text{ } T_\alpha} - \Delta n_i \quad (151)$$

and the moles of mixture is obtained from summing over all i . The new mole fractions at $T = 4900$ are

$$X_{i \text{ } T = 4900} = \left(\frac{n_i}{\sum_i n_i} \right)_{T = 4900} \quad (152)$$

After the X_i are found, the mixture molecular weight and heat capacity are determined through

$$W_{\text{mixture}} = \sum_i W_i X_i \quad (153)$$

and

$$C_p = \sum_i C_{p_i} \quad (154)$$

Sufficient information is thus available to obtain a solution of the energy equation, as given by (126). A solution in this case, results in the pressure of the mixture necessary to satisfy the mixture at the temperature in question. As the left hand side of this relation is a statement of the sensible and latent enthalpies, it also gives the total enthalpy change. The enthalpy change, Δh , may also be calculated from (123).

After the Δh and the pressure are known, the remaining quantities are calculated in the same manner, as noted above, for equilibrium and frozen flows.

Finite flow properties for the remainder of the nozzle are calculated in an analogous manner, the major difference being in the application of (72) for $d\tau n_i/dt$. After the first step down the nozzle, the non-equilibrium mole fractions are known and thus K_x^* may be calculated directly, without the necessity of using Van't Hoff's equation. In this case,

$$K_x^* = \prod_i (X_i)^{\nu_i'' - \nu_i'} \quad (155)$$

for the finite composition. The K_x term is given by,

$$K_x = \prod_i (X_{i,e})^{\nu_i'' - \nu_i'} \quad (156)$$

in which $X_{i,e}$ are the equilibrium mole fraction for the same temperature.

PRESENTATION AND DISCUSSION OF RESULTS

Using the reactive gas mixture and method of calculation, as indicated above, an expansion of the mixture is followed through a nozzle with a ten to one pressure differential. As this is a comparative study, the equilibrium path and frozen path are used as the "boundary or limiting" conditions; because they represent a limit in terms of reaction rates and practically all analyses are made on one or the other bases.

Parameters selected for purposes of comparison are:

1. temperature profile
2. pressure distribution
3. density distribution
4. area ratios, relative to nozzle inlet and throat

Values of these parameters, as determined by the indicated calculation procedure, are presented in Tables I, II, and III. Only five points, in addition to the initial conditions, are presented for finite flow. Due to the magnitude of the calculations, it was not practicable to generate more data. Electronic computation is almost mandatory in making a complete analysis, as was done for the data available to equilibrium flow. It is felt that the data computed is representative and while machine calculation would permit considerable refinement, the results would be comparable.

Actual comparison of the three flow paths is shown by means of Figures 4, 5, 6, 7, and 8. Temperature is used as the basis of com-

TABLE I

EQUILIBRIUM FLOW

t °K	P Atmos	Δh BTU/lb	u ft/sec	W $\frac{\text{lb}}{\text{Mol}}$	$\rho \times 10^2$ lb/ft ³	ρ^u lb/ft ² -sec	A α /A	A/A _t	P/P _a
5000	10.00	0	320	28.168	7.715	24.688	1.000	6.176	1.000
4950	9.32	30	1266	28.19	7.267	92.00	3.727	1.657	0.942
4900	8.60	58	1730	28.24	6.778	117.26	4.750	1.300	0.879
4800	7.30	110	2368	28.32	5.898	139.66	5.657	1.092	0.764
4700	6.30	167	2908	28.36	5.206	151.39	6.132	1.007	0.675
4660	5.85	190	3098	28.39	4.992	152.48	6.176	1.000	0.638
4600	5.30	221	3340	28.42	4.484	149.76	6.066	1.018	0.581
4500	4.53	271	3695	28.50	3.929	145.18	5.880	1.050	0.509
4400	3.90	323	4032	28.53	3.463	139.63	5.656	1.092	0.449
4300	3.25	372	4324	28.57	2.957	127.86	5.179	1.193	0.383
4200	2.73	422	4600	28.65	2.550	117.30	4.751	1.300	0.331
4100	2.36	469	4851	28.68	2.261	109.68	4.443	1.390	0.293
4000	1.98	514	5080	28.72	1.947	98.91	4.006	1.542	0.252
3900	1.69	557	5287	28.75	1.706	90.20	3.653	1.690	0.221
3800	1.47	603	5500	28.78	1.525	83.88	3.397	1.818	0.198
3700	1.23	642	5675	28.81	1.312	74.46	3.016	2.048	0.170
3600	1.02	682	5849	28.83	1.119	65.45	2.651	2.330	0.145
3580	1.00	689	5878	28.84	1.103	64.83	2.636	2.352	0.143
3400	0.75	762	6180	28.87	0.872	53.89	2.183	2.829	0.113

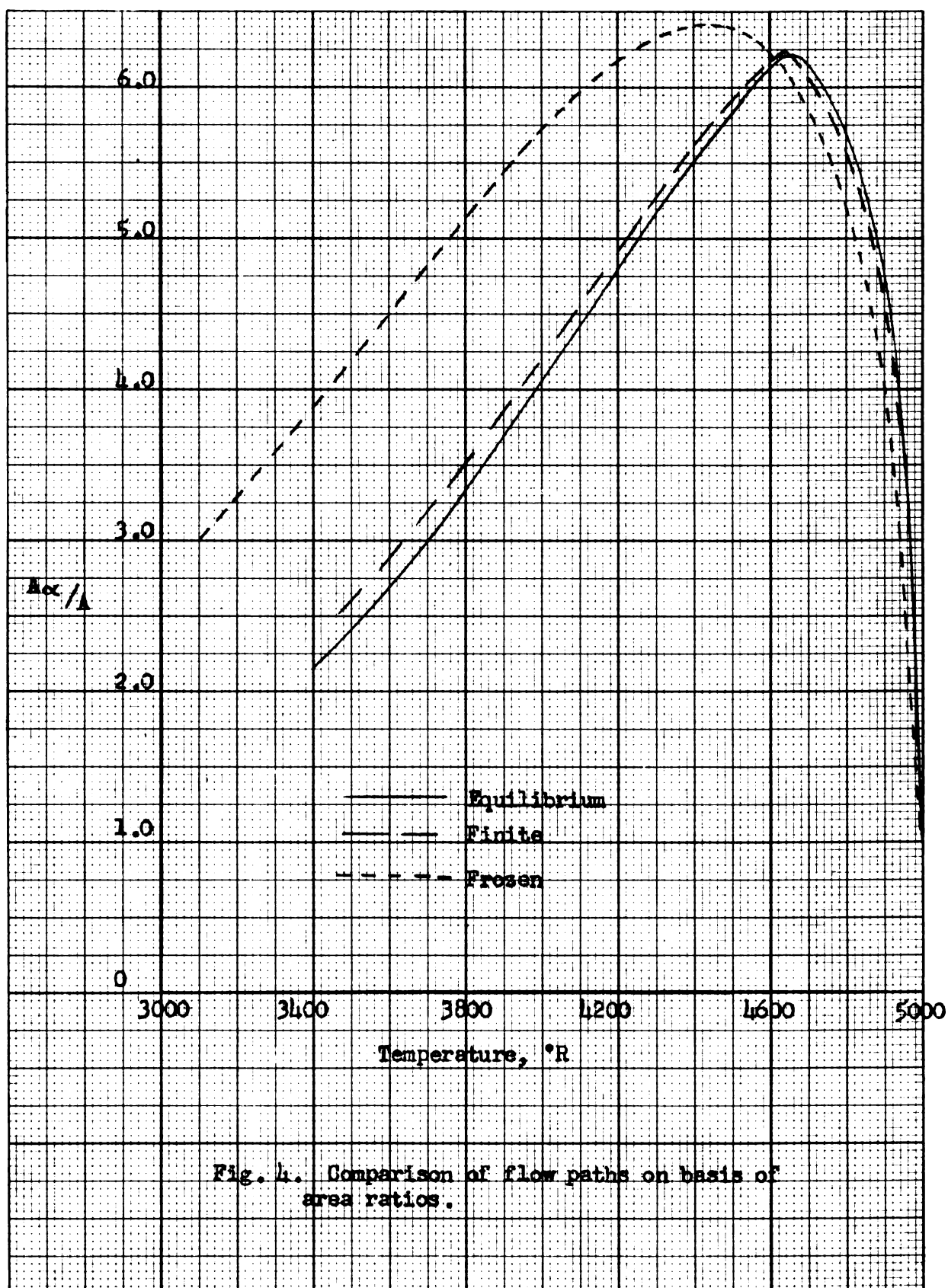
TABLE II
FROZEN FLOW

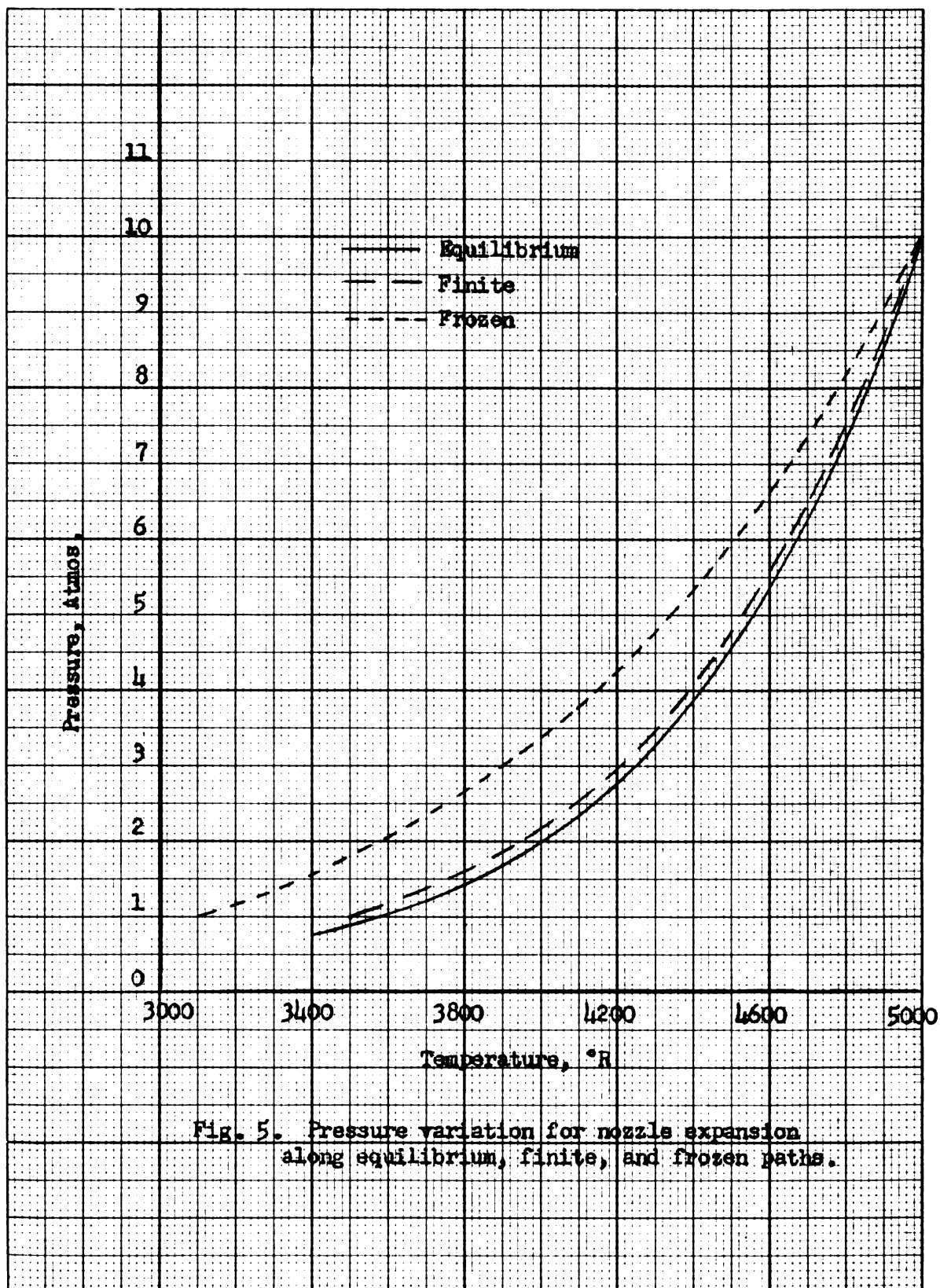
T °R	P Atmos	Δh BTU/lb	u ft/sec	$\rho \times 10^2$ lb/ft ³	ρu lb/ft ² -sec	$A \propto A$	A/A_t	ρ/ρ_a
5000	10.00	00.00	320	7.715	24.688	1.000	6.420	1.000
4900	9.07	34.77	1356	7.417	100.57	4.074	1.576	0.961
4800	8.18	69.26	1888	6.828	128.92	5.222	1.229	0.885
4700	7.40	104.09	2303	6.309	145.29	5.885	1.091	0.818
4600	6.65	138.65	2660	5.792	154.08	6.241	1.029	0.751
4500	5.97	173.15	2959	5.316	157.29	6.371	1.008	0.689
4430	5.51	198.93	3170	5.000	158.50	6.420	1.000	0.648
4400	5.35	207.59	3238	4.872	157.76	6.390	1.005	0.632
4300	4.78	241.91	3493	4.454	155.58	6.302	1.019	0.577
4200	4.26	276.32	3730	4.064	151.59	6.140	1.046	0.527
4100	3.79	310.43	3953	3.704	146.41	5.931	1.082	0.480
4000	3.37	344.54	4163	3.376	140.53	5.692	1.128	0.438
3900	2.98	378.57	4363	3.062	133.58	5.411	1.186	0.397
3800	2.63	412.51	4553	2.773	126.25	5.114	1.255	0.359
3700	2.31	446.37	4738	2.502	118.52	4.801	1.337	0.324
3600	2.03	480.13	4910	2.259	110.93	4.493	1.429	0.293
3500	1.77	513.80	5080	2.026	102.92	4.169	1.540	0.263
3400	1.54	544.13	5232	1.815	94.95	3.846	1.669	0.235
3300	1.34	580.66	5397	1.672	87.81	3.557	1.805	0.211
3200	1.16	613.95	5550	1.452	80.61	3.265	1.966	0.188
3100	1.00	647.11	5697	1.293	73.63	2.983	2.152	0.168

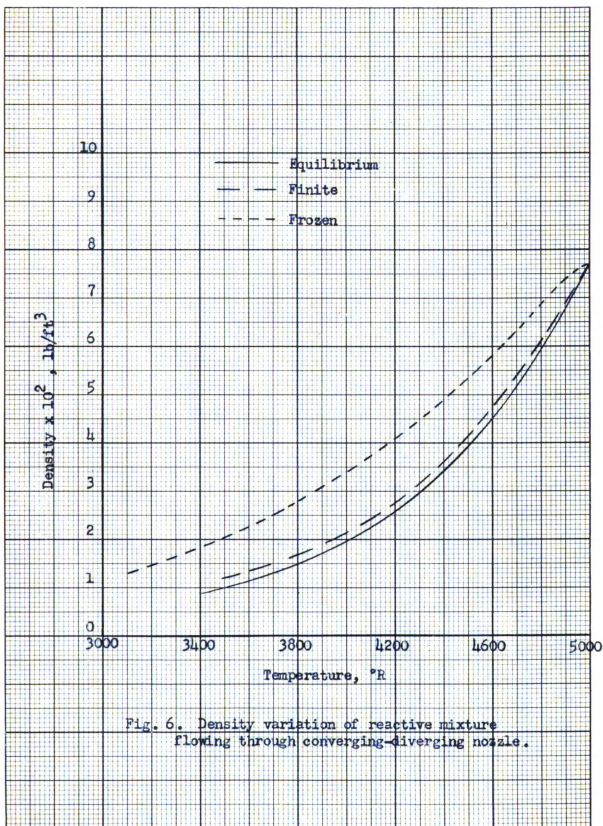
TABLE III

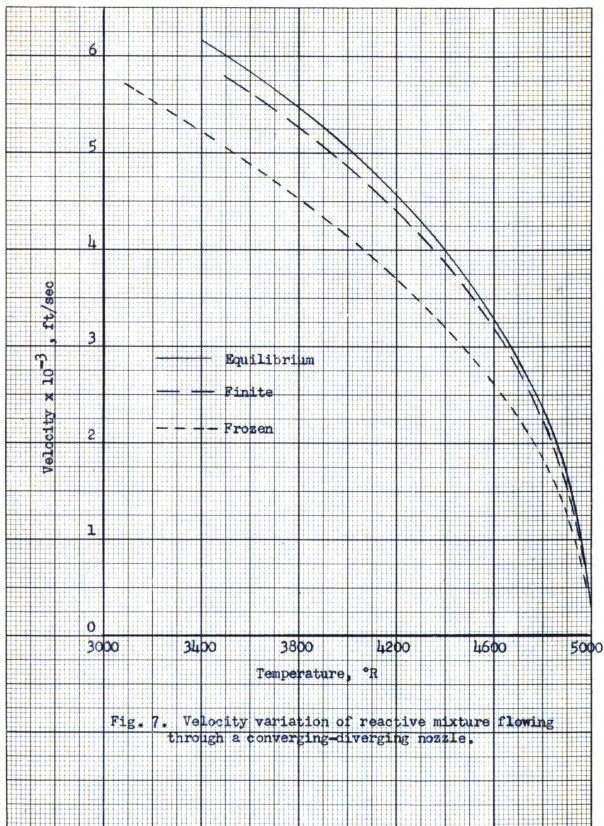
FINITE FLOW

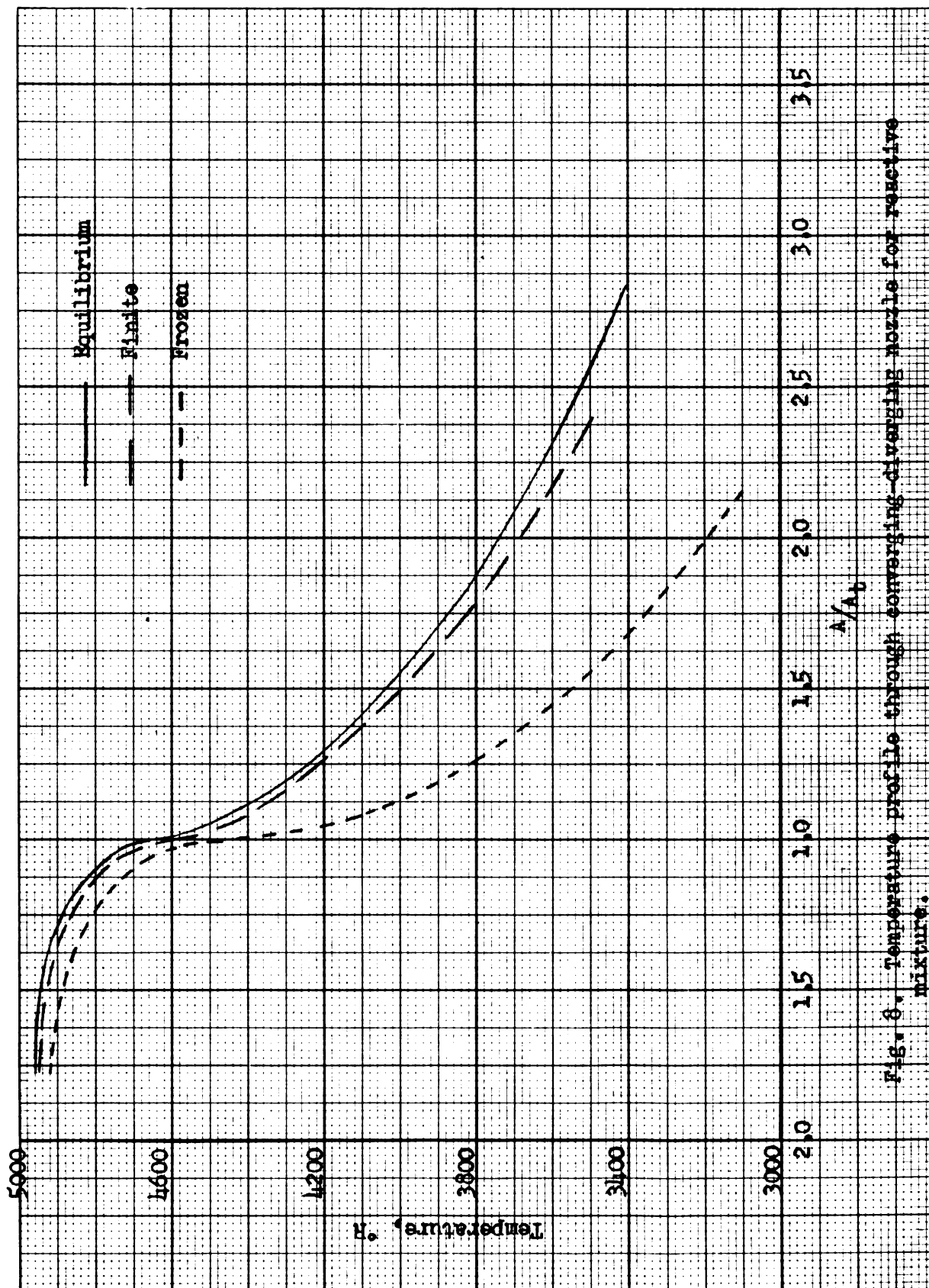
T °R	P Atmos	C _p BTU/lb _m °R	W lb _m /MOL	Δh BTU/lb _m	u ft/sec	$\rho \times 10^2$ lb _m /ft ³	ρu^2 lb/ft ² -sec	A α/A	A/A _t
5000	10.00	0.36	28.168	0.0	320	7.715	24.688	1.000	6.220
4900	8.65	0.349	28.20	55.5	1690	6.822	115.29	4.669	1.332
4700	6.40	0.347	28.36	156.6	2816	5.290	148.97	6.03	1.032
4300	3.40	0.344	28.49	347.6	4181	3.095	129.40	5.271	1.160
3900	1.85	0.3411	28.675	514.34	5091	1.863	94.85	3.842	1.619
3500	0.985	0.337	28.80	669.26	5790	1.107	64.10	2.596	2.395











parison in constructing the curves of each of the figures; not because temperature has a special significance in the dynamics of nozzle flow, but due to influence on the reaction kinetics.

The most significant feature brought out in this study is the nearness of the finite flow path to the equilibrium path throughout the entire length of the nozzle. There is a gradual tendency for the finite flow to deviate from the ideal equilibrium flow, but it appears that this tendency is not as severe as sometimes assumed. Bray¹ investigated a so-called "Ideal Dissociating Gas" and concluded that the gas would act like a frozen mixture shortly after the throat of a nozzle. Heims² reported from the study of "air" flow through a nozzle, with a mixture consisting, initially, of undissociated nitrogen and partially dissociated oxygen, that the flow path would be located approximately mid-way between the equilibrium and frozen paths.

As the flow proceeds down the nozzle, there is a reduction of temperature, which reduces the reaction rate constant through its exponential term; and at the same time, the velocity is increasing, which decreases the time available for reactions. Both of these effects tend to decrease the amount of net reaction. However, as these two effects are driving the mixture away from equilibrium composition, the ratio of free energy functions, expressed as K^*/K , acts as a potential to restore equilibrium. It is the net effect of these three forces which will ultimately predict the finite path location.

¹Bray, K. N. C., op. cit.

²Heims, S. P., op. cit.

An examination of Table IV, where compositions are compared at the same temperature and pressure, shows that some of the mixture constituents tend to remain very close to equilibrium while others deviate quite appreciably. This comes about from the complex system of reactions involved in the recombination process, each of which has its own activation energy and collision frequency factor. Thus, the gross mixture properties are made up of the contributions of the individual reactions making up the entire system, some of which may be near equilibrium and some near frozen paths. It is the gross properties which are being compared in this study.

If the nozzle used in the above calculations was designed on the basis of frozen flow analysis, as is the current practice in industry, it would have to be of sufficient length to satisfy the area ratios for the converging and diverging section. Finite flow analysis shows that such a nozzle would be about 2% too long in the converging section and 11% too short in the diverging section, for a pressure ratio of ten to one. The designed nozzle would be expected to have a mass flow rate of 3.46 pounds per second, but with finite flow it would only carry 3.358 pounds per second. In addition, there would be a higher temperature and pressure distribution than predicted by the design.

The effect of having too long a converging section would be negligible, only wasted material, but the short diverging section would cause an under-expansion of the flow and would result in a shock at the exit. This would represent a loss of nozzle effectiveness, be it measured in terms of velocity, thrust, or impulse. On the basis of

TABLE
COMPOSITIONS, X_1 ,

T, °R	A	CO	CO ₂	H ₂	H ₂ O	N ₂
5000	8.493 3	3.523 2	9.225 2	6.545 3	1.153 1	7.067 1
4900	8.512 3	3.304 2	9.505 2	5.901 3	1.161 1	7.088 1
	8.511 3	3.335 2	9.458 2	5.820 3	1.160 1	7.087 1
4700	8.553 3	2.641 2	1.019 1	4.874 3	1.200 1	7.122 1
	8.543 3	2.848 2	1.002 1	5.047 3	1.215 1	7.118 1
4300	8.622 3	1.562 2	1.130 1	3.015 3	1.238 1	7.205 1
	8.604 3	1.843 2	1.103 1	2.881 3	1.257 1	7.163 1
3900	8.672 3	7.985 3	1.223 1	1.500 3	1.275 1	7.258 1
	8.662 3	9.576 3	1.192 1	1.681 3	1.265 1	7.240 1
3500	8.699 3	3.970 3	1.263 1	7.560 4	1.294 1	7.282 1
	8.678 3	6.894 3	1.203 1	1.031 3	1.290 1	7.274 1

Note: 8.493 3 means 0.008493

IV

EQUILIBRIUM AND FINITE FLOW

O ₂	O	OH	H	NO	N	
1.372 2	1.964 3	8.761 3	1.931 3	8.959 3	1.121 4	
1.275 2	1.620 3	7.750 3	1.620 3	8.105 3	8.785 5	Equil.
1.294 2	1.726 3	8.023 3	8.353 4	8.558 3	9.930 5	Finite
1.132 2	1.085 3	6.005 3	1.215 3	6.202 3	5.245 5	Equil.
1.144 2	1.107 3	5.379 3	1.107 3	7.246 3	7.278 5	Finite
6.935 3	4.240 4	3.210 3	4.615 4	3.290 3	1.515 5	Equil.
7.757 3	8.707 4	4.749 3	4.116 4	3.688 3	1.890 5	Finite
3.354 3	9.740 5	1.285 3	1.263 4	1.490 3	2.950 6	Equil.
4.217 3	8.403 4	3.139 3	1.964 4	1.696 3	6.342 6	Finite
1.310 3	1.783 5	6.140 4	2.150 5	7.367 4	3.355 7	Equil.
2.484 3	4.936 5	2.882 3	2.707 5	1.169 3	5.477 7	Finite

specific thrust, design would indicate a value of 171 pound-force-second per pound mass, while the finite flow would result in a specific impulse of 165 pound-force-second per pound mass. This represents a decrease of 3.5 percent in design performance. Had the nozzle design been based on finite flow analysis, the expected thrust would be 170.1 pound-force-second per pound mass, an increase of some 3.7 percent over that developed in a frozen flow designed nozzle. These values are based on the assumptions as set up for the study, and show only the effects of neglecting recombination reactions with their potential energy release.

All of the results of calculation presented here are valid within the frame of reference, as prescribed by the initial assumption, that the nozzle is frictionless, adiabatic, etc. As the purpose of this study is to investigate one specific phenomenon, it is felt that the simplification permitted by these assumptions, is justified. The eventual goal in nozzle design should be to include all of the possible deviations from ideality, but the analyses of individual effects should prove to be a most useful adjunct to the overall understanding of nozzle problems. With the increase interest in rocketry and jet propulsion, it is necessary that chemical thermodynamics become a part of fluid dynamic theory.

Until a great deal more experimental data and electronic calculating equipment are available, it appears that the recommended form of flow analysis, for design purposes, should be based on an equilibrium path. With access to tabulated information, such as that of Powell and

Suciu¹ and of the Bureau of Standards,² an equilibrium analysis is no more difficult than a frozen analysis.

Based on results obtained from this study, the following conclusions may be drawn:

1. When a high temperature mixture of reactive gases is expanded through a converging-diverging nozzle, the thermodynamic path followed approximates an equilibrium path, when the mixture is initially in a state of equilibrium.
2. Deviation from the equilibrium path increases with decreasing pressure, but at a decreasing rate.
3. Nozzle performance, based on a finite reaction rate design, was found to be 3 percent better than for a comparable frozen flow design.
4. The effects of chemical reaction should be included before expecting the results to accurately describe the best performance a properly-designed nozzle might have.

¹Powell, H. N. and S. N. Suciu, op. cit.

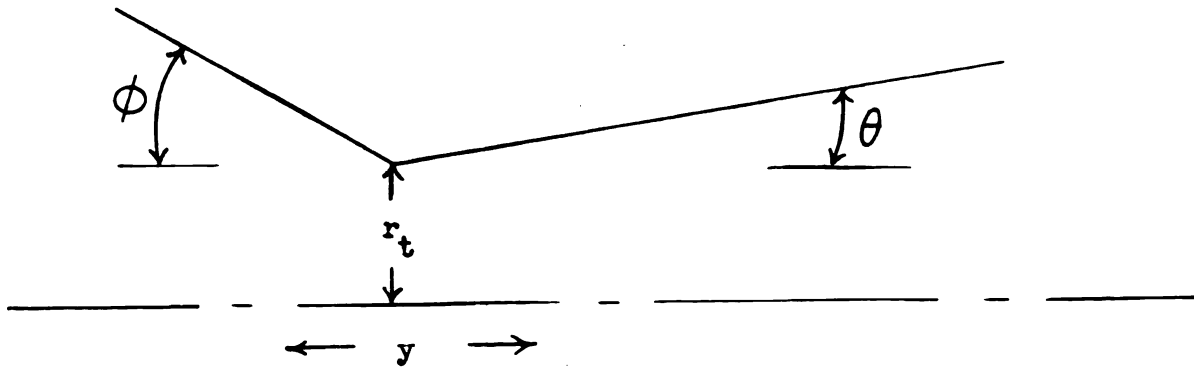
²Rossini, F. D., et al, op. cit.

APPENDIX

APPENDIX A

NOZZLE CONFIGURATION

The nozzle shape assumed for purposes of this study is that of two truncated cones, placed small end to small end. In the convergent section, the angle of convergence, ϕ , is taken as 30° , while in the divergent section, the angle of divergence, θ , is $7\frac{1}{2}^\circ$.



Each cone of the nozzle may be defined by an equation,

$$r_y = r_t + y \frac{dr}{dy} = r_t + y \tan \angle$$

in which y is positive to the left, for the converging section and the $\angle$ is ϕ ; y is positive to the right for the diverging section and the angle is θ .

A dimensionless ratio of the area at any point y to that at the throat, A/A_t , is given by

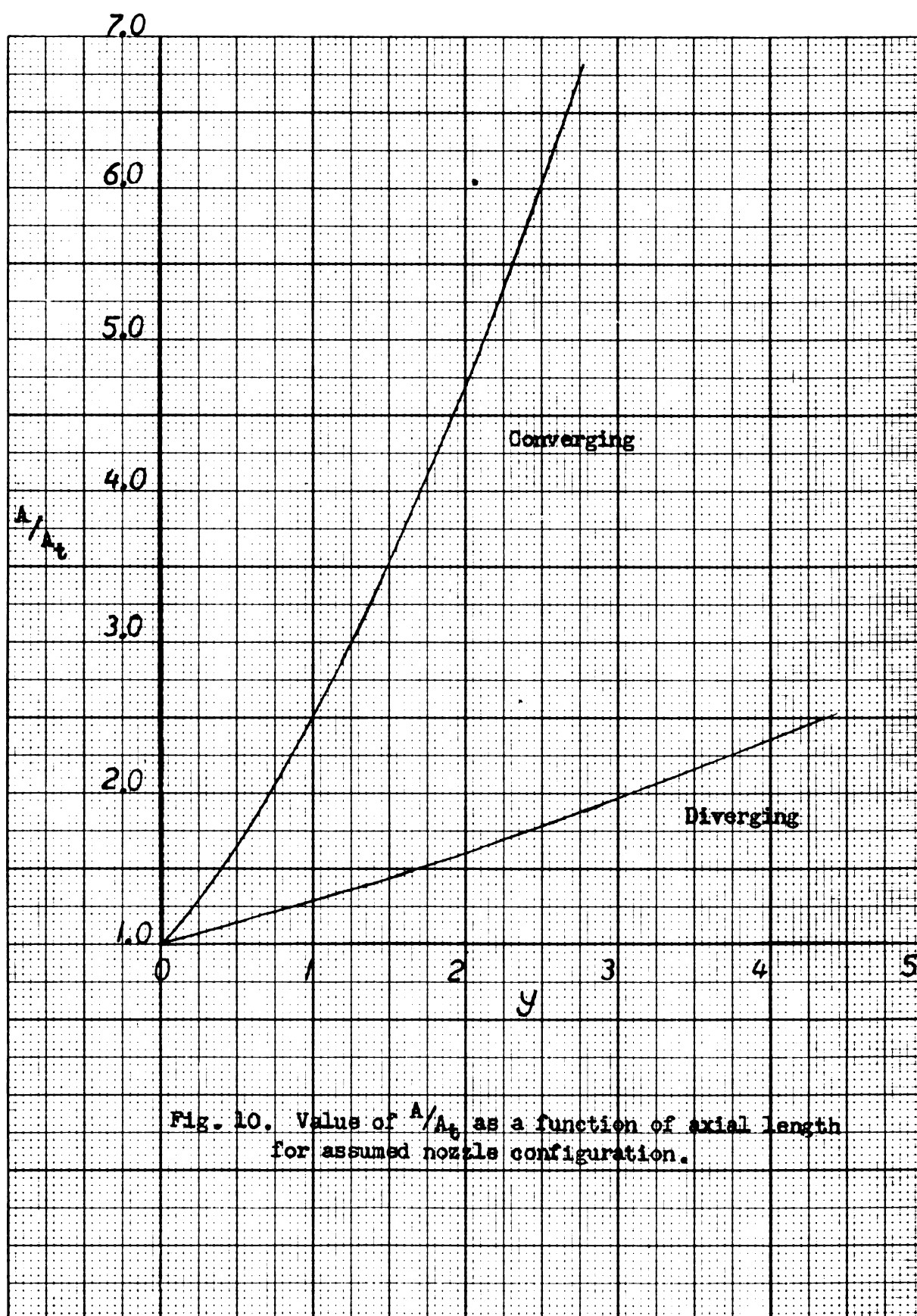
$$A/A_t = \left(\frac{r}{r_t} \right)^2 = \left(\frac{r_t + y \tan \angle}{r_t} \right)^2 = \left(1 + \frac{y}{r_t} \tan \angle \right)^2$$

Table A-1 contains a tabulation of some of the properties of A/A_t for various y , based on a throat radius of unity. Fig. 9 shows the configuration of such a nozzle. Fig. 10 shows the relationships of Table A-1.

TABLE A - 1

NOZZLE GEOMETRY RELATIONSHIPS

Converging, $\phi = 30^\circ$					Diverging, $\theta = 7\ 1/2^\circ$				
y	$y \tan \phi$	$1 + y \tan \phi$	A/A_t	y	$y \tan \theta$	$1 + y \tan \theta$	A/A_t	y	A/A_t
0.0	0.0000	1.0000	1.000	0.0	0.0000	1.0000	1.000	0.0	1.000
0.1	0.0577	1.0577	1.119	0.1	0.0132	1.0132	1.027	0.1	1.027
0.2	0.1155	1.1155	1.244	0.2	0.0263	1.0263	1.053	0.2	1.053
0.3	0.1732	1.1732	1.376	0.3	0.0395	1.0395	1.081	0.3	1.081
0.4	0.2309	1.2309	1.515	0.4	0.0527	1.0527	1.108	0.4	1.108
0.5	0.2887	1.2887	1.661	0.5	0.0658	1.0658	1.136	0.5	1.136
0.6	0.3464	1.3464	1.813	0.6	0.0790	1.0790	1.164	0.6	1.164
0.7	0.4041	1.4041	1.971	0.7	0.0922	1.0922	1.193	0.7	1.193
0.8	0.4619	1.4619	2.137	0.8	0.1053	1.1053	1.222	0.8	1.222
0.9	0.5196	1.5196	2.309	0.9	0.1185	1.1185	1.251	0.9	1.251
1.0	0.5774	1.5774	2.488	1.0	0.1317	1.1317	1.281	1.0	1.281
1.2	0.6928	1.6928	2.866	1.2	0.1580	1.1580	1.341	1.2	1.341
1.4	0.8083	1.8083	3.269	1.4	0.1843	1.1843	1.403	1.4	1.403
1.6	0.9238	1.9238	3.701	1.6	0.2106	1.2106	1.467	1.6	1.467
1.8	1.0392	2.0392	4.158	1.8	0.2370	1.2370	1.530	1.8	1.530
2.0	1.1547	2.1547	4.643	2.0	0.2633	1.2633	1.596	2.0	1.596
2.2	1.2720	2.2720	5.154	2.2	0.2896	1.2896	1.663	2.2	1.663
2.4	1.3856	2.3856	5.691	2.4	0.3160	1.3160	1.732	2.4	1.732
2.6	1.5011	2.5011	6.256	2.6	0.3423	1.3423	1.802	2.6	1.802
2.8	1.6166	2.6166	6.847	2.8	0.3686	1.3686	1.873	2.8	1.873
				3.0	0.3950	1.3950	1.946	3.0	1.946
				3.5	0.4608	1.4608	2.134	3.5	2.134
				4.0	0.5266	1.5266	2.331	4.0	2.331
				4.5	0.5924	1.5924	2.536	4.5	2.536



APPENDIX B

BOLTZMANN TERMS

The terms of equation (2) may best be explained by means of Fig. B-1.¹

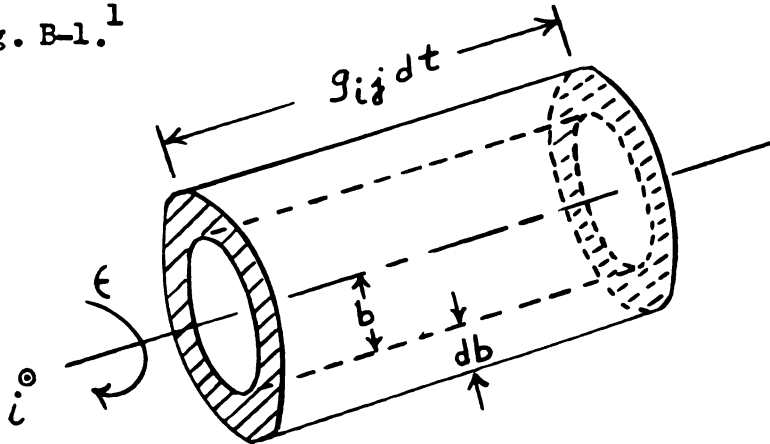


Fig. B-1. Collisions of molecules of type "j" with one molecule of type "i"

This equation is an expression relating the various molecular forces and momenta involved in the collision of moving molecules of type "j" with a fixed molecule of type "i". To find the probability that an "i" molecule, located at position $\vec{r}$, with velocity $\vec{u}_i$, will experience an impact with a molecule of type "j", in the time interval dt , with the impact parameter in a range db about b . The impact parameter b is the distance of closest approach of the two molecules if they continued to move in straight lines with their initial velocities. The relative velocities of the two types of molecules is given by the difference $|\vec{u}_j - \vec{u}_i|$ and is noted as g_{ij} , ($g_{ij} = g_{ji}$).

¹Rossins, F. D., High Speed Aerodynamics and Jet Propulsion, Vol. I, (Princeton, N. J.: Princeton University Press), 1954.

During a short interval of time dt , any molecule of type "j", which is located in the cylinder of base $b db d\epsilon$ and height $g_{ij} dt$, will undergo a collision with molecule i . The probable number of molecules of type "j" in this cylinder is

$$f_j(\vec{r}, \vec{u}, t) g_{ij} b db d\epsilon dt$$

Then the total number of collisions experienced by this molecule i , with molecules of type "j", is obtained by summing over all the number of collisions characterized by all values of the parameter b and ϵ and all the relative velocities g_{ij} . The result is

$$dt \iiint f_j(\vec{r}, \vec{u}, t) g_{ij} b db d\epsilon d\vec{u}_j$$

Since the probable number of i molecules in the volume element $d\vec{r}$ about $\vec{r}$ with velocities in the range $d\vec{u}_i$ about $\vec{u}_i$ is

$f_i(\vec{r}, \vec{u}, t) d\vec{r} d\vec{u}$, it follows that a collision parameter $\Gamma_{ij}^{(-)}$ is

$$\Gamma_{ij}^{(-)} = \iiint f_i f_g g_{ij} b db d\epsilon d\vec{u}_j$$

By similar reasoning, another collision parameter for conditions after a collision, $\Gamma_{ij}^{(+)}$, is given by

$$\Gamma_{ij}^{(+)} = \iiint f_i' f_j' g_{ij} b db d\epsilon d\vec{u}_j$$

where the primes refer to post-collision properties and the equalities

$$\begin{aligned} b &= b' \\ g_{ij} &= g_{ij}' \\ d\vec{u}_i d\vec{u}_j &= d\vec{u}_i' d\vec{u}_j' \end{aligned}$$

are assumed to hold.

It was on the basis of these parameters and relationships that the Boltzmann equation, in the form (2), was derived. The term $\vec{X}_1$ represents an external force acting on the molecules, which is a function of position and time.

APPENDIX C

VALIDITY OF EQUATIONS (28) AND (29)

The integral

$$\iiint \lambda_i (f_i' f_j' - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j$$

is equivalent to the integral written in terms of inverse encounters, i.e., where different symbols are used to indicate the variables of integration. Thus

$$\iiint \lambda_i' (f_i f_j - f_i' f_j') g_{ij}' b' d\epsilon d\vec{u}_i' d\vec{u}_j'$$

It has already been shown that

$$g_{ij} = g_{ij}', \quad b = b', \quad \text{and} \quad d\vec{u}_i d\vec{u}_j = d\vec{u}_i' d\vec{u}_j'$$

which permits rewriting the above equation to

$$- \iiint \lambda_i (f_i' f_j' - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j$$

As the integrals are equal, they are also each equal to one-half the sum of the two. Such an operation gives

$$\begin{aligned} & \iiint \lambda_i (f_i' f_j' - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j \\ &= 1/2 \iiint (\lambda_i - \lambda_i') (f_i' f_j' - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j \end{aligned}$$

When $\lambda_i = m_i$ the validity is immediately established; for $(\lambda_i - \lambda'_i) = 0$ indicates that the individual masses of the molecules are conserved in an encounter.

However, the last equation may be summed over both i and j , after which the dummy indices are interchanged to give the identity

$$\begin{aligned} & \frac{1}{2} \sum_{ij} \iiint (\lambda_i - \lambda'_i) (f'_i f'_j - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j \\ &= \frac{1}{2} \sum_{ij} \iiint (\lambda_j - \lambda'_j) (f'_i f'_j - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j \end{aligned}$$

Whereupon,

$$\begin{aligned} & \sum_{ij} \iiint \lambda_i (f'_i f'_j - f_i f_j) g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j \\ &= \frac{1}{4} \sum_{ij} \iiint (\lambda_i + \lambda_j - \lambda'_i - \lambda'_j) (f'_i f'_j - f_i f_j) \\ & \quad g_{ij} b db d\epsilon d\vec{u}_i d\vec{u}_j \end{aligned}$$

The invariants of an encounter are then defined by the vanishing of the term $(\lambda_i + \lambda_j - \lambda'_i - \lambda'_j)$, or those properties which make (28) and (29) equal to zero. Properties which are conserved in an encounter are thus: mass of the individual molecule m_i , momentum $m_i \vec{C}_i$, and kinetic energy $\frac{1}{2} m_i C_i^2$.

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BIBLIOGRAPHY

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