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Ionization of air produced by strong shocks

Howard Sajon Joyner

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IONIZATION OF AIR PRODUCED BY STRONG SHOCKS

by

HOWARD SAJON JOYNER, 1939-

A DISSERTATION

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ABSTRACT

This dissertation provides theoretical predictions along with experimental results for electron concentrations behind a shock as a function of Mach number over a range from 11 to 20 using a combustion driven shock tube operating in air. These theoretical predictions represent an upper bound for chemical equilibrium. The model for air was 78.0880% nitrogen, 20.949% oxygen, 0.0300% carbon dioxide, 0.9300% argon, 0.0025% neon, and 0.0005% helium. Also the theory of a double diaphragm shock tube with corresponding pressure ratio vs. Mach number relationships is provided. A computer program using iterative techniques for a succinct presentation covering the modifications and deviations from the perfect gas theory for most simple mixtures of test gases is included. This program utilizes the latest available equilibrium constants for various gases. Also, this dissertation describes a technique which allows the electron concentration to be continuously monitored as a shock wave passes.

The author designed and built the instrumentation for the operation of the shock tube and the monitoring of the electron concentration. This instrumentation included a high pressure gas handling system, velocity measurement techniques, and a laser interferometer for electron concentration measurements. To provide uniform monochromatic light across the beam, a continuously working Helium-Neon laser with a spatial filter was employed. The number of electrons per cubic centimeter behind the shock was measured at Mach numbers of 17.6 and 18.1. The data obtained did not represent accurate quantitative values of electron concentrations due to the unknown composition of the test gas. However, the experimental results demonstrated the reproducibility of the data with the system used.
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Financial support for two years came from the Space Sciences Research Center and one year from teaching in the Mechanical Engineering Department.

I also wish to acknowledge the continued encouragement and understanding of my parents who gave me perseverance. Also the support of my wife cannot go unmentioned.

H.S.J. August, 1969
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USEFUL CONSTANTS

c_s = 1135.4 ft/sec = 0.346 mm/μsec (Air at T = 535°R)
e = 4.8028x10^{-10} esu
h = 6.625x10^{-27} erg sec
k = 1.3804x10^{-16} erg/K = 8.6167x10^{-5} eV/K
m_e = 9.1083x10^{-28} gm
P_{atm} = 1 atm. = 14.7 lb_f/in^2 = 760 torr
R = 1545 ft-lb_f/lb-mole-R = 1.9872 cal/mole-K = 82.057 cm^3 atm/mole-K
R = 53.34 ft-lb_f/lb_m-R (Air)
W = 28.967 gm/mole (Air)
γ = 1.404 (Air)
ρ_{atm} = 2.51x10^{-3} lb_f sec^2/ft^4 = 0.0807 lb_m/ft^3 = 1.2937x10^{-3} gm/cm^3 (Air)

The nomenclature for these constants is located on page five.
I. INTRODUCTION

1.1 Shock Tubes

The earliest conception of producing shock waves by bursting a diaphragm in a tube is attributed to P. Vielle [1] in 1899. It was not until World War II that the interest in shock tube phenomena produced considerable investigation of shock waves. Payman and Shepherd [2] in 1940 described the essential features of the modern bursting diaphragm shock tube.

The first shock tube to be used in this country was constructed at Princeton and is described by G. T. Reynolds [3]. By 1950 shock tubes were used for conducting experiments in shock waves throughout the country.

1.2 Applications of Shock Tubes

Shock tube research has opened the avenues to the resolution of many problems associated with explosives. For example, the destructive overpressure experienced at great distances from atomic detonations can be simulated. The study of gas dynamics at high velocities, the properties of gases at high temperatures, and the kinetics of processes occurring behind shock waves are important in connection with the problem of the motion of bodies with supersonic velocities. These studies can be described in three categories: 1. Aerothermodynamics, which is concerned with the thermodynamic properties of gases at high temperatures and their equations of state. 2. Chemical physics, which deals with relaxation phenomena relating to translation, rotation, vibration, electronic excitation, dissociation, chemical reactions, and ionization. 3. Radiation physics, which is related to the measurement of the emission and absorption
spectra of gases from molecules, atoms, and ions. Information from shock tube studies is gained for all of the above categories.

Perfect gas relationships for shock waves have been developed [4] and verified. With the ability to produce shock waves with higher and higher Mach numbers, deviations from perfect gas considerations become evident. These deviations are primarily due to dissociation and ionization of the gases used in the shock tube studies. Horton and Menard [5] have developed a computer program for computing these deviations using statistical mechanics. The Model for air used by them was O₂ - 20.95%, N₂ - 78.08%, and Ar - 0.97%.

Determination of electron concentrations due to ionization is generally accomplished by means of recording changes in the index of refraction of the test gas. For low electron concentrations the maximum electron densities which are accessible by microwave techniques are of the order of \(10^{14}\) electrons per cubic centimeter; at higher densities the electromagnetic wave is totally reflected.

Optical interferometry has been used to give absolute measurement of electron concentrations. Its ability to resolve high speed phenomena was limited, until recently, by two conflicting requirements; namely, that a small enough light source so that the fringe contrast would be adequate and of a large enough source to provide sufficient light to the detectors. The laser removes the compromise caused by these difficulties by providing a source of parallel light with extreme brightness. Until recently, the laser has had limitations in that the spatial distribution over the face of the light beam was neither uniform nor continuous with time. Pulsed lasers limit the phenomenological observation of the shock front to about 20 nanoseconds with the use of a Kerr cell. Triggering of
the pulsed laser, the Kerr Cell, and the detection devices provides undue difficulties.

Modifications of the gas dynamic equations for the shock tube due to double diaphragm techniques and area changes have been developed [6]. However, no succinct theory covering perfect gas deviations and modifications of the gas dynamic equations for diatomic and polyatomic gases has been developed or verified.

1.3 Purpose of Dissertation

Kolb and Griem [7] presented a survey of theoretical predictions and experimental results for the behavior of shocked gases for a range of initial conditions. These, however, only cover cases for gases other than air in the Mach number range of 15 to 20 and for air in the Mach number range up to 13. Tevelow [8] discussed shock-ionized air in the Mach number range from 8 to 12 for air and Sobolev, et. al., [9] presented data for air in the Mach number range from 6 to 8. It should be pointed out that at these low Mach numbers dissociation and ionization do not play an important part in the properties of air. For single gases in the higher Mach number range, dissociation and ionization can be considered with little difficulty. In the case of air, however, chemical reactions play an important role and greatly complicate the theoretical description of the shocked gas.

Funahashi and Takeda [10] reported data obtained by microwave probe measurements for air in an electromagnetically driven T-type shock tube over a Mach number range of 15 to 25 for pressures of one and two torr. Lin, Neal, and Fyfe [31] measured electron concentrations in a Mach number range of 14 to 20 for pressures of 0.02 torr using microwave
reflection and magnetic probe techniques in a 24 inch diameter shock tube.
Lin and Teare [29] predicted the electron concentration vs. Mach number in
the range from 12 to 26 for 21% oxygen and 79% nitrogen air model mixtures.
Horton and Menard [5] presented electron concentration calculations for
Mach numbers up to 30 using their air model in a statistical mechanical
approach.

It was the purpose of this dissertation to theoretically expand the
model used for air and to provide theoretical predictions of electron
concentrations vs. Mach number in a range from 11 to 20 based on the
assumption that the chemical reactions of dissociation and ionization
are carried out to completion. An additional purpose was to design and
develop a system for monitoring the electron concentration behind a nor-
mal shock without the use of probes inserted into the flow field.
II THEORY

2.1 Nomenclature

A(x) cross-sectional area
a one half of the amplitude of the interference fringes
b coefficient used to linearize dissociation equations
c, cs speed of sound
c₀ speed of light
Cₚ specific heat for constant pressure
Cᵥ specific heat for constant volume
D dissociation energy
d optical distance between mirrors
E_D weighted dissociation energy
e charge on one electron
G gain factor
g statistical weight
h enthalpy per unit mass
h_p Planck's constant
I trial one
J quantum number for total angular momentum
K Gladstone-Dale constant
K_a dissociation equilibrium constant
K_x ionization equilibrium constant
k Boltzmann's constant
L virtual image
M Mach number
mₑ mass of the electron
ṁ mass flow rate
Δm fringe shift
n  index of refraction
n_e  electron concentration
n_g  total number of moles
n_x  moles of component gas
P_s  point source
P  pressure
R  gas constant for a unit mole of gas
R  gas constant for a unit mass of gas
T  temperature
t  time
t_o  thickness of optical substance
u_i  internal energy per unit mass
u  velocity
v  velocity of shock front
w  velocity of shock front relative to shock tube
W  molecular weight
x  distance along tube
x_i  fraction of gas ionized
α  polarizability
α_d  fraction of original molecules dissociated
γ  ratio of specific heats
δ  phase difference
λ  wavelength
θ  divergence angle
ν  reaction balancing coefficient
ρ  density
ω  frequency of interacting radiation
ω_p  plasma frequency
2.2 One Dimensional Compressible Fluid Flow

The equations of motion are derived assuming that the fluid is continuous, homogeneous, and isotropic. Additionally, it is assumed that the fluid is perfect (i.e., intermolecular forces and molecular size are negligible), that the internal energy of the fluid is a function of temperature only, and that the specific heats are independent of temperature. Furthermore, it is assumed that the fluid is in thermodynamic equilibrium and the body forces are negligible.

Four basic equations are essential to describing the motion of a fluid through a tube. Consider the following diagram:

The equations developed here use the Eulerian method in which the origin of coordinates is fixed in space and the state of motion is described at a particular fixed point \( x \) at time \( t \).

The tube has a cross-sectional area \( A(x) \) which is a specific function of \( x \) and the cross-section changes sufficiently slowly for the flow to be essentially one-dimensional. Let the density of the gas be \( \rho(x,t) \) and its velocity be \( u(x,t) \), then the mass of gas flowing into the volume \( Adx \) at \( x \) in time \( dt \) is \( \rho u Adt \). The mass flowing out of the volume in the same time is
\[ [\rho u A + \frac{\partial}{\partial x} (\rho u A) \, dx] \, dt. \]

Hence, the net increase of mass in the volume is \(-\frac{\partial}{\partial x} (\rho u A) dx \, dt\). The increase in mass also may be represented as \(A \frac{\partial \rho}{\partial t} \, dx \, dt\). The resulting equation for the conservation of mass is then:

\[ A \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho u A) = 0. \] (1)

Neglecting wall friction and equating the rate of change in momentum of the fluid element to the net force acting on it, the momentum equation is derived. The net horizontal force in the x-direction is

\[ P A - \left[ P A + \frac{\partial (P A)}{\partial x} \, dx \right] + \left[ P + \frac{\partial P}{\partial x} \, dx \right] dA \]

\[ = - P \frac{\partial A}{\partial x} \, dx - A \frac{\partial P}{\partial x} \, dx + P dA + \frac{\partial P}{\partial x} \, dx \, dA. \]

Neglecting second order terms, the net force becomes

\[-A \frac{\partial P}{\partial x} \, dx.\]

The mass \(\rho A dx\) of fluid will move a distance \(udt\) in time \(dt\).

The velocity at time \(t\) was \(u\) and at time \(t+dt\) the velocity is \(u + \frac{\partial u}{\partial x} \, u dt + \frac{\partial u}{\partial t} \, dt\). Consequently, the change of momentum is

\[ \rho A dx \left[ u + \frac{\partial u}{\partial x} \, u dt + \frac{\partial u}{\partial t} \, dt - u \right] \]

or the rate of change of momentum is

\[ \rho A dx \left[ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right]. \]

Equating this rate of change of momentum to the net force, the momentum equation follows:

\[ \frac{u}{t} + u \frac{\partial u}{\partial x} = - \frac{1}{\rho} \frac{\partial P}{\partial x}. \] (2)
From equation (1) the time independent equation is
\[ \rho u \frac{\partial A}{\partial x} + \rho A \frac{\partial u}{\partial x} + A \frac{\partial P}{\partial x} = 0. \]

Dividing by \( \rho Au \),
\[ \frac{1}{A} \frac{\partial A}{\partial x} + \frac{1}{u} \frac{\partial u}{\partial x} + \frac{1}{\rho} \frac{\partial P}{\partial x} = 0. \]

For a tube of constant cross-section \( \frac{\partial A}{\partial x} = 0 \), then the equation for the conservation of mass becomes
\[ \frac{1}{u} \frac{\partial u}{\partial x} + \frac{1}{\rho} \frac{\partial P}{\partial x} = 0. \] (3)

The time independent part of equation (2) gives
\[ \frac{\partial u}{\partial x} = - \frac{1}{\rho} \frac{\partial P}{\partial x}. \] (4)

Combining (3) and (4)
\[ \frac{1}{u^2 \rho} \frac{\partial P}{\partial x} = \frac{1}{\rho} \frac{\partial P}{\partial x} \text{ or } u^2 = \frac{\partial P}{\partial \rho}. \] (5)

When referred to the undisturbed fluid state, equation (5) may be written \( \frac{\partial P}{\partial \rho} \rho \) and it represents the square of the speed of sound, \( c_s^2 \). This derivative is at constant entropy because the variations in pressure and temperature are vanishingly small and consequently the process is nearly reversible. Also, the speed of the process with the smallness of the temperature variation makes the process nearly adiabatic. In the limit the process may be considered isentropic.

The equation of state for a perfect gas is
\[ P = \rho RT. \] (6)

For an isentropic process, \( P/\rho \gamma = \text{constant} \). Taking the logarithmic derivative yields
\[ \frac{dP}{P} = \gamma \frac{d\rho}{\rho}. \] (7)
Rewriting, \( \frac{\partial \rho}{\partial p} \rho = \gamma p \), which is just the speed of sound squared. Applying the equation of state (6),

\[ c_s^2 = \frac{\gamma p}{\rho} = \gamma RT \quad (8) \]

2.3 Shock Tubes

The shock tube produces essentially a plane shock wave by the sudden bursting of a diaphragm separating a gas at a high pressure from one at low pressure. The shock wave travels with a Mach number, \( M_1 = u_1/c_1 \), and starts a flow at Mach number \( M_2 = u_2/c_2 \) behind the shock wave. This flow is assumed to be isentropic. A simple shock tube is illustrated in the following diagram:

\[ P_3 = \text{contact zone pressure} \quad P_2 = \text{pressure behind shock} \]

\[ P_4 \quad P_3 = P_2 \quad P_1 \]

\[ T_4 \quad T_3 \quad T_1 \]

[diagram showing pressure and temperature profiles]
The driver gas is contained in the high pressure side and the shock wave travels into the experimental gas which is in the low pressure side. The experimental gas and the driver gas make contact at a surface just behind the shock front when the diaphragm bursts. The pressure distribution is shown in (b) and the temperature distribution is shown in (c). The wave diagram for the single diaphragm shock tube is shown in the following:

2.3.1 Shock Relationships in Perfect Gases

Consider the following figure which sets forth the gas parameters in the regions of interest in a shock wave. \( P, \rho, \) and \( T \) are the pressure,
density, and temperature of the gas and \( v \) is the velocity of the gas molecules relative to the shock tube. In the case when \( v_1 = 0 \), the test gas is stationary. \( w_s \) is the velocity of the shock front relative to the tube. For convenience, consider the gas in motion entering with relative velocity \( u_1 \) such that the shock front is stationary. Then the following relations hold:

\[
\begin{align*}
  u_1 &= w_s - v_1 \\
  u_2 &= w_s - v_2
\end{align*}
\]  

For the constant cross-section tube the time independent equation for conservation of mass (1) becomes

\[
\rho_1 u_1 = \rho_2 u_2.
\]  

Now the mass flow rate is \( \dot{m} = \rho A u \), and equation (4) gives \( \frac{dP}{pu} = -\rho A \frac{du}{u} \). Combining the mass flow rate and equation (4) with equation (10) yields \( \dot{m}_A \frac{dP}{A} \). Upon integrating,

\[
\begin{align*}
  P_2 - P_1 &= -\frac{\dot{m}}{A} (u_2 - u_1).
\end{align*}
\]  

(11)
Since $A$ is constant, substituting the mass flow rate into (11) gives

$$p_2 + \rho_2 u_2^2 = p_1 + \rho_1 u_1^2. \quad (12)$$

If there is no heat transfer involved, then the steady flow energy equation may be written

$$h + \frac{u_2^2}{2} = h_0 \quad (a \text{ constant}). \quad (13)$$

Across the shock, the energy equation becomes

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2}. \quad (14)$$

The enthalpy, by definition, is for a perfect gas

$$h_1 = u_1 + p_1 v_1 = u_1 + R_1 T \quad (15)$$

where $u_1$ is the internal energy and $R_1$ is the gas constant for a unit mass of gas.

Now $h = h(P,T)$; hence,

$$dh = \left(\frac{\partial h}{\partial P}\right)_T dP + \left(\frac{\partial h}{\partial T}\right)_P dT \quad (16)$$

and from (15) $h$ is a function of temperature only, therefore $\left(\frac{\partial h}{\partial P}\right)_T = 0$.

From the definition $C_p = \left(\frac{\partial h}{\partial T}\right)_P$, equation (16) becomes $dh = C_p dT$ or

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT. \quad \text{We have assumed that } C_p \text{ and } C_v \text{ are constant and independent of temperature. Hence, } h_2 - h_1 = C_p (T_2 - T_1) \text{ and from combining this with equation (14)}$$

$$T_2 - T_1 = \frac{u_1^2}{2C_p} - \frac{u_2^2}{2C_p}. \quad (17)$$

Recall that $c_s^2 = \gamma RT$, $\gamma = C_p/C_v$, and $R = C_v(\gamma - 1)$. After applying these relationships, $c_s^2 = \gamma C_v(\gamma - 1)T$; and equation (17) becomes
\[
T_2 - T_1 = \frac{u_1^2}{c_1^2} \frac{\gamma (\gamma - 1) C_v}{2 C_p} T_1 - \frac{u_2^2}{c_2^2} \frac{\gamma (\gamma - 1) C_v}{2 C_p} T_2
\]
\[
T_2 [1 + \frac{M_2^2 (\gamma - 1)}{2}] = T_1 [1 + \frac{M_1^2 (\gamma - 1)}{2}]
\]

\[
\frac{T_2}{T_1} = \frac{1 + \frac{M_2^2 \gamma - 1}{2}}{1 + \frac{M_1^2 \gamma - 1}{2}}
\]

Here \(M = u/c\). This is the equation for the Fanno line in terms of \(T\) and \(M\). From the perfect gas law, \(T_2/T_1 = P_2 \rho_1 / P_1 \rho_2\) and from the equation for conservation of mass, \(\rho_1 u_1 = \rho_2 u_2\); hence, \(T_2/T_1 = P_2 u_2 / P_1 u_1\). Using the definition of \(M\) and the formula for the speed of sound for perfect gas, the temperature ratio becomes \(T_2/T_1 = [P_2 M_2 / P_1 M_1]\). Therefore, 

\[
\frac{T_2}{T_1} = (P_2 M_2 / P_1 M_1)^2
\]

Combining equations (18) and (19) yields

\[
P_2 / P_1 = (M_1 / M_2) \sqrt{[1 + \frac{(\gamma - 1)}{2} M_1^2]/[1 + \frac{(\gamma - 1)}{2} M_2^2]}
\]

Equation (20) is just the Fanno line in terms of \(P\) and \(M\).

To obtain a relation between \(M_1\) and \(M_2\), it is convenient to reduce the quantity \(c^*\) as a common reference sound speed for both \(M_1\) and \(M_2\) and the quantity \(M^* = u/c^*\). The asterisk denotes conditions \(M = 1\), but does not apply to \(M^*\). Hence, \(c^* = u^*\) and \(M^*_1 = u_1/c^* = 1/c_1 c^* = M_1 \sqrt{T_1/T^*}\). Now \(M_1^2 M^*_2^2\) can be written \(M_1^2 M^*_2^2 = M_2^2 T_1 / T^*\). \(T_2 / T^*\). \(T^*\) is the temperature at \(M = 1\); hence, from equation (18)
Therefore, \( M^* M^* \) may be expressed as \( 1 + \frac{\gamma - 1}{2} \). Therefore, \( M^* M^* \) may be expressed as

\[
M^* M^* = \frac{M^* M^*}{(1 + \frac{\gamma - 1}{2})(1 + \frac{\gamma - 1}{2})}
\]

The relation between \( M^* \) and \( M^* \) known as the Prandtl equation, is when \( u_1 u_2 = c^* \) and since \( M^* = u/c^* \), \( M^* M^* = 1 \). Thus,

\[
M^* M^* = \frac{(1 + \gamma)^2}{(1 + \frac{\gamma - 1}{2})(1 + \frac{\gamma - 1}{2})} = 1.
\]

Solving for \( M^* \) in terms of \( M^* \),

\[
M^2 = \frac{\gamma^2 - (\gamma - 1/2)^2}{\gamma M^2 - (\gamma - 1/2)}
\]

or

\[
M^2 = \frac{M^2 + \frac{2}{\gamma - 1} M^2 - 1}{\gamma - 1 - 2 M^2}
\]

2.3.1.1 Single Diaphragm Equations

Using the value of \( M^2 \) expressed in equation (22a) in equation (18) the ratio of \( T_2 \) to \( T_1 \) may be written

\[
T_2/T_1 = \left(1 + \frac{\gamma - 1}{2} M^2\right) \left(\gamma M^2 - \frac{\gamma - 1}{2}\right)
\]

or rearranging,
\[
\frac{T_2}{T_1} = \frac{(1 + \frac{Y_1 - 1}{2} M_1^2)\left(\frac{2Y_1 Y_1 - 1}{\gamma_1 - 1} M_1^2 - 1\right)}{(Y_1 + 1)^2 - 2(Y_1 - 1)^2 M_1^2}
\]  \hspace{1cm} (23b)

Similarly, equation (22a) and equation (20) give the ratio of \( P_2 \) to \( P_1 \) as

\[
\frac{P_2}{P_1} = \frac{2Y_1 Y_1 - 1}{Y_1 + 1} M_1^2 - \frac{Y_1 - 1}{Y_1 + 1}
\]  \hspace{1cm} (24)

To complete the shock relations we have from the perfect gas law:

\[
\frac{\rho_2}{\rho_1} = \frac{P_2}{P_1} \frac{T_1}{T_2}.
\]  \hspace{1cm} (25)

Equations (23), (24), and (25) are shown graphically in Figures 1, 2, and 3 for gases of \( \gamma = 1.4 \) and 5/3 corresponding to the cases for air and for monatomic gases, respectively.

We now apply the above equations to stationary shocks. When the gas ahead of the shock is moving, \( v_1 = 0 \), then \( u_1 = u_1 \) and \( M_1 = u_1 / c_1 \). Substituting equations (23) and (24) into (25) yields

\[
\frac{\rho_2}{\rho_1} = \frac{(Y_1 + 1) M_1^2}{(Y_1 - 1) M_1^2 + 2}.
\]  \hspace{1cm} (26)

The foregoing equations are the classical equations governing shock phenomena. They are derived in a slightly different manner than normal and are consistent with the nomenclature used in this dissertation. The shock strength depends upon the pressure ratio across the diaphragm and the physical properties of the two gases used. For a perfect gas this dependence is derived following the method of Resler, Lin, and Kantrowitz [11]. This method is described in the following paragraphs.
Figure 1

Temperature Ratio vs. Mach Number
TEMPERATURE RATIO $T_2/T_1$

$\gamma = 1.404$, $\times \gamma = 1.667$
Figure 2

Pressure Ratio vs. Mach Number
PRESSURE RATIO P2/P1
+ GAMMA=1.404, X GAMMA=1.667
Figure 3

Density Ratio vs. Mach Number
DENSITY RATIO RH02/RH01
+ GAMMA=1.404, X GAMMA=1.667
Applying Newton's second law of motion $F = m \frac{du}{dt}$ to a one-dimensional thickness $dx$ under the action of a sound wave with a velocity $c$, we obtain a form of equation (4), viz.,

$$-dP = \rho c \, du.$$  \hspace{1cm} \text{(27)}

From the relation $Tds = dh$ when $ds = 0$, $dh = \frac{dP}{\rho}$. Now $dh = C \, dT$ hence, $dP = \rho C \, dT$. Dividing by $P$ and using perfect gas law then,

$$\frac{dP}{P} = \frac{C}{\rho} \frac{dT}{RT}.$$  \hspace{1cm} \text{(28)}

Now $c^2 = \gamma RT$; differentiating, $2c \, dc = \gamma R \, dT$, and solving for $dT$ gives

$$dT = \frac{2 \, c \, dc}{\gamma R}.$$  \hspace{1cm} \text{(29)}

Combining equations (27) and (29) gives

$$\frac{2}{\gamma - 1} \, dc + du = 0.$$  \hspace{1cm} \text{(30)}

Integrating equation (30) yields

$$\frac{2}{\gamma - 1} \, c + u = \text{constant}.$$  \hspace{1cm} \text{(31)}

Applying this equation to the figure on page 10 we have,

$$\frac{2}{\gamma _4 - 1} \, c_4 + v_4 = \frac{2}{\gamma _3 - 1} \, c_3 + v_3.$$  \hspace{1cm} \text{(32)}

Now $v_4 = 0$ and $v_3 = v_2$ along with $P_3 = P_2$. For a perfect gas $\gamma _4 = \gamma _3$.

Hence, equation (31) becomes

$$\frac{2}{\gamma _4 - 1} \, c_4 = \frac{2}{\gamma _3 - 1} \, c_3 + v_2.$$  \hspace{1cm} \text{(32)}

For an isentropic process, $\frac{P}{\rho ^{\gamma}} = \text{constant}$. Applying this relationship, the speed of sound relationship, and the properties of a perfect gas yields
Combining equations (32) and (33) gives

\[ \frac{P_4}{P_3} = \frac{P_4}{P_2} = (c_4/c_3) \left(\frac{\gamma_4 - 1}{\gamma_4 - 1}\right). \]  

\[ (33) \]

Combining equations (34) and (35) gives

\[ \frac{P_4}{P_2} = \left(\frac{c_4}{\gamma_4 - 1}\right) \frac{2\gamma_4}{\gamma_4 - 1}. \]  

\[ (34) \]

From the equation of conservation of mass (10), equation (26), and equation (9)

\[ \nu_2 = \frac{2c_1}{\gamma_1 + 1} \left(M_1 - \frac{1}{M_1}\right). \]  

\[ (35) \]

Combining equations (24), (34), and (35) gives

\[ \frac{P_4}{P_1} = \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \left[1 - \frac{\gamma_4 - 1}{\gamma_4 + 1} \frac{c_1}{c_4} \left(M_1 - \frac{1}{M_1}\right)\right] \frac{2\gamma_4}{\gamma_4 - 1}. \]  

\[ (36) \]

This equation relates the pressure ratio across the diaphragm to the Mach number. It can be seen that the strongest possible shock occurs when

\[ \nu_2/P_1 \to \infty. \]  

Hence,

\[ 1 - \frac{\gamma_4 - 1}{\gamma_4 + 1} \frac{c_1}{c_4} \left(M_1 - \frac{1}{M_1}\right) \frac{2\gamma_4}{\gamma_4 - 1} \to 0 \]  

or

\[ \frac{1}{c_2} \left(M_1 - \frac{1}{M_1}\right) \to 1, \]  

and when \( M_1 \) is large, \( 1 - \frac{\gamma_4 - 1}{\gamma_4 + 1} \frac{c_1}{c_4} M_1 \to 0 \)

is satisfied as

\[ M_1 + \frac{\gamma_4 + 1}{\gamma_4 - 1} \frac{c_4}{c_1}. \]  

\[ (37) \]

The strongest shocks are thus obtained when the driver gas has a specific heat ratio and a high speed of sound. For these reasons
Low density gas is often used as the driver gas, for example, hydrogen or helium. A plot of $M_1$ vs. $P_4/P_1$ obtained from equation (36) for various values of $c_4/c_1$ is shown in Figure 4, where $\gamma_1 = \gamma_4$.

### 3.1.2 Double Diaphragm Equations

Consider Figures 5 and 6 to obtain the shock relations for a double diaphragm shock tube configuration. From equation (24) for a moving shock

$$\frac{P_4}{P_6} = \frac{2\gamma_6}{\gamma_6+1} \frac{M_2^2}{\gamma_6+1} - \frac{\gamma_6^{-1}}{\gamma_6+1}$$

and

$$\frac{P_2}{P_1} = \frac{2\gamma_1}{\gamma_1+1} \frac{M_1^2}{\gamma_1+1} - \frac{\gamma_1^{-1}}{\gamma_1+1}$$

calling that $v_3 = v_2$ and from equation (35)

$$\frac{v_3}{c_1} = \frac{v_2}{c_1} = \frac{2}{\gamma_1+1} \left( M_1 - \frac{1}{M_1} \right)$$

Likewise:

$$\frac{v_4}{c_6} = \frac{2}{\gamma_6+1} \left( M_6 - \frac{1}{M_6} \right)$$

Using equation (8) with equation (23) yields

$$\frac{c_1}{c_2} = \frac{\gamma_1+1}{\gamma_1+1} \frac{M_1}{\left( \frac{1}{2} \right)^{\gamma_1+1}}$$

Equation (35) becomes, upon dividing by $c_2$,

$$\frac{v_2}{c_2} = \frac{2}{\gamma_1+1} \frac{c_1}{c_2} \left( M_1 - \frac{1}{M_1} \right)$$

Combining equations (42) and (43) yields

$$M_2 = \frac{(M_1^2 - 1)}{\left( \gamma_1 M_1^2 - \frac{\gamma_1-1}{2} - \frac{\gamma_1-1}{2} M_1 + 1 \right)^{\frac{1}{2}}$$

and similarly
Figure 4
Pressure Ratios vs. Mach Number for Various
Ratios of Speeds of Sound, $\gamma_1 = \gamma_4$
LOG P4/P1 VS. MACH NUMBER

+ GAMMA=1.404, X GAMMA=1.667
Figure 5

Pressure Distribution for Double Diaphragm Shock Tube

This figure is not an actual representation of the double diaphragm process, but it shows how the intermediate shock strength relations are computed.

Figure 6

Wave Diagram for Double Diaphragm Shock Tube
$P_5 = \text{contact zone pressure for primary shock}$

$P_4 = \text{pressure behind primary shock}$

$P_3 = \text{contact zone pressure for secondary shock}$

$P_2 = \text{pressure behind secondary shock}$
\[ M_4 = \frac{(M_6^2 - 1)}{[\left(\gamma_6 \frac{M_6^2}{2} - \frac{\gamma_6 - 1}{2}\right) \left(\frac{\gamma_6 - 1}{2}\right) \left(M_6^2 + 1\right)]^{\frac{1}{2}}} \]  (45)

Rearranging equation (33) and equation (31) with \( \gamma_3 = \gamma_4 = \gamma_6 \), gives

\[ \frac{P_4}{P_3} = \frac{c_4}{c_3} = \frac{M_3}{M_4} \quad \frac{v_4}{v_3} = \frac{1 + \frac{\gamma_6 - 1}{2} M_3}{1 + \frac{\gamma_6 - 1}{2} M_4} \]  (46)

Since \( P_2 = P_3 \)

\[ \frac{P_4}{P_3} = \frac{P_4}{P_6} \frac{P_6}{P_{12}} = \frac{1 + \frac{\gamma_6 - 1}{2} M_3}{1 + \frac{\gamma_6 - 1}{2} M_4} \]  (47)

Substitution of equations (38) and (39) into (47) yields

\[ (P_6/P_1) \phi_1 = \phi_2 \]  (48)

where

\[ \phi_1 = \frac{2\gamma_6}{\frac{\gamma_6 + 1}{\gamma_6 + 1} - \frac{\gamma_6 - 1}{\gamma_6 + 1}} \left(1 + \frac{\gamma_6 - 1}{2} M_4\right) \frac{2\gamma_6}{\gamma_6 - 1} \]  (49)

and

\[ \phi_2 = \frac{2\gamma_6}{\frac{\gamma_1 - 1}{\gamma_1 + 1} - \frac{\gamma_1 - 1}{\gamma_1 + 1}} \left(1 + \frac{\gamma_6 - 1}{2} M_4\right) \frac{2\gamma_6}{\gamma_6 - 1} \]  (50)

Equations (40), (41), and (46) combine to give

\[ 1 + \frac{\gamma_6 - 1}{2} M_3 = \left[1 - \frac{\gamma_6 - 1}{2} \frac{\gamma_6 + 1}{\gamma_1 + 1} \frac{c_1}{c_6} \left(M_1 - \frac{1}{M_1}\right) \frac{1}{\phi_3}\right]^{-1} \]  (51)

where

\[ \phi_3 = \left(M_6 - \frac{1}{M_6}\right) \left(1 + \frac{\gamma_6 - 1}{2} M_4\right) / M_4 \]  (52)

For a given value of \( M_6 \), \( M_4 \) is found from equation (45) and hence, \( \phi_1 \) and \( \phi_3 \) can be computed. Equation (48) may now be written with the aid of equations (50) and (51) as

\[ \frac{P_6}{P_1} \phi_1 = \phi_2 = \frac{2\gamma_6}{\frac{\gamma_1 - 1}{\gamma_1 + 1} \frac{M_1^2}{M_1} - \frac{\gamma_1 - 1}{\gamma_1 + 1}} \left[1 - \frac{\gamma_6 - 1}{2} \frac{\gamma_6 + 1}{\gamma_1 + 1} \frac{c_1}{c_6} \left(M_1 - \frac{1}{M_1}\right)\right] \frac{2\gamma_6}{\gamma_6 - 1} \]  (53)
Now \( \frac{P_2}{P_1} = \frac{P_2}{P_6} \cdot \frac{P_6}{P_1} \) and \( M_6 \) can be computed from an equation similar to (36).

Figures 7 and 8 illustrate the results of double diaphragm effects for various overall pressure ratios and a range of values of \( P_6 \) to \( P_1 \) with helium in the primary section, air in the test section and helium and air in the secondary section, respectively. All gases are at room temperature.

### 2.3.1.3 Area Discontinuity

Resler, et al [11] and Henshall [6] have derived a gain factor due to area changes at the diaphragm location to be employed in pressure and temperature calculations. The area ratio and gain factors are both given in terms of a common quantity \( M \). For the second diaphragm location the area ratio equation is

\[
\frac{A_6}{A_1} = \frac{1}{M} \left[ \frac{1 + \frac{\gamma_6-1}{2} M^2}{1 + \frac{\gamma_6-1}{2}} \right]^{\frac{\gamma_6+1}{2(\gamma_6-1)}} \quad (54a)
\]

and the gain equation is

\[
G_{61} = \left[ \left( \frac{1 + \frac{\gamma_6-1}{2} M^2}{1 + \frac{\gamma_6-1}{2}} \right) \left( \frac{1 + \frac{\gamma_6-1}{2}}{1 + \frac{\gamma_6-1}{2} M} \right)^2 \right]^{\frac{\gamma_6}{\gamma_6-1}}. \quad (55a)
\]

Likewise for the first diaphragm location:

\[
\frac{A_7}{A_6} = \frac{1}{M} \left[ \frac{1 + \frac{\gamma_7-1}{2} M^2}{1 + \frac{\gamma_7-1}{2}} \right]^{\frac{\gamma_7+1}{2(\gamma_7-1)}} \quad (54b)
\]

and

\[
G_{76} = \left[ \left( \frac{1 + \frac{\gamma_7-1}{2} M^2}{1 + \frac{\gamma_7-1}{2}} \right) \left( \frac{1 + \frac{\gamma_7-1}{2}}{1 + \frac{\gamma_7-1}{2} M} \right)^2 \right]^{\frac{\gamma_7}{\gamma_7-1}}. \quad (55b)
\]
Figure 7

Double Diaphragm Pressure Ratios for $\gamma = 1.404$
DOUBLE DIAPHRAGM PRESSURE RATIOS

GAMMA=1.404

LOG P6/P1

MACH NUMBER

○ P7/P1=10^0
△ P7/P1=10^1
+ P7/P1=10^2
X P7/P1=10^3
◆ P7/P1=10^4
◆ P7/P1=10^5
Figure 8

Dougle Diaphragm Pressure Ratios for $\gamma = 1.667$
DOUBLE DIAPHRAGM PRESSURE RATIOS
GAMMA=1.667

LOG P6/P1

MACH NUMBER

○ P7/P1=10^0
△ P7/P1=10^1
+ P7/P1=10^2
× P7/P1=10^3
♦ P7/P1=10^4
♦ P7/P1=10^5
The pressure ratio for a single diaphragm shock tube becomes \( G(P_4/P_1) \) while the temperature ratio becomes \( (T_4/T_1) G^{(\gamma-1)/\gamma} \).

Figure 9 shows the area ratio vs. \( G \) for \( \gamma = 1.4 \).

The equations used to compute the ideal shock tube parameters are expressed in section 2.3.1. Figures 10, 11, 12, 13, 14, and 15 take into account area changes for both the single diaphragm and double diaphragm operation of the shock tube facility used in these investigations. Figure 14 and 15 illustrate the increased performance by using an exploding mixture of hydrogen and oxygen buffered by air and helium, respectively.

2.3.2 Deviations from Perfect Shock Tube Theory

The agreement between ideal gas theory and experimental results in shock tubes is very close for low pressure ratios across the diaphragm. As stronger and stronger shock waves are produced by increasing the pressure ratio, the correlation becomes increasingly poor. It is most probable that these deviations are caused by the violation of the assumptions used in the derivations. If the effect of the variations from these assumptions were considered separately, then it should be possible to make approximate corrections to the ideal theory.

2.3.2.1 Shock Relationships for Real Gases

The equations governing the ratios of temperature, pressure, and density for shock conditions must be modified for real gas effects. The flow of a real gas differs from that of a perfect gas for the following significant reasons: a) thermal imperfections, b) caloric imperfections, c) dissociation, and d) ionization effects.
To find the pressure and temperature ratios for area changes at the diaphragm locations, multiply these ratios where no area change exists by the gain factor as indicated on page 36.
Figure 10

Single Diaphragm Shock Tube With Air

in Both Primary and Test Sections
SINGLE DIAPHRAGM SHOCK TUBE

- ○ PRIMARY PRESSURE = 10.0000 PSIA
- ▲ PRIMARY PRESSURE = 100.0000 PSIA
- + PRIMARY PRESSURE = 500.0000 PSIA
- × PRIMARY PRESSURE = 2000.0000 PSIA

LOG TEST SECTION PRESSURE IN PSIA

MACH NUMBER
Figure 11

Single Diaphragm Shock Tube With Helium

in Primary Section and Air in Test Section
SINGLE DIAPHRAGM SHOCK TUBE

- PRIMARY PRESSURE = 10.0000 PSIA
- PRIMARY PRESSURE = 100.0000 PSIA
- PRIMARY PRESSURE = 500.0000 PSIA
- PRIMARY PRESSURE = 2000.0000 PSIA

LOG TEST SECTION PRESSURE IN PSIA

MACH NUMBER
Figure 12
Double Diaphragm Shock Tube Pressure Ratios vs. Mach Number for Helium, Air, and Air in the Primary, Secondary, and Test Sections, Respectively
DOUBLE DIAPHRAGM PRESSURE RATIOS

\[
\begin{align*}
\varnothing P7/P1 &= 10.00 \\
\Delta P7/P1 &= 100.00 \\
\dagger P7/P1 &= 500.00 \\
\times P7/P1 &= 1000.00 \\
\bigcirc P7/P1 &= 2000.00 \\
\bigtriangleup P7/P1 &= 5000.00
\end{align*}
\]
Figure 13
Double Diaphragm Shock Tube Pressure Ratios vs. Mach Number for Helium, Helium, and Air in the Primary, Secondary, and Test Sections, Respectively
DOUBLE DIAPHRAGM PRESSURE RATIOS

- $\circ P7/P1 = 100.00$
- $\triangle P7/P1 = 1000.00$
- $\ast P7/P1 = 5000.00$
- $\times P7/P1 = 10000.00$
- $\diamond P7/P1 = 20000.00$
- $\ast P7/P1 = 50000.00$

LOG $P7/P1$

MACH NUMBER

2 4 6 8 10 12 14 16 18 20
Figure 14
Double Diaphragm Shock Tube Pressure Ratios
vs. Mach Number for $2\text{H}_2 + \text{O}_2$ Combustion, Air, and Air in the Primary, Secondary, and Test Sections, Respectively. $P_7$ is post Combustion Pressure. $P_6$ and $P_1$ are pre-combustion pressures.
DOUBLE DIAPHRAGM PRESSURE RATIOS

\[ \begin{align*}
\odot P7/P1 &= 1272.5720 \\
\triangle P7/P1 &= 221.4766 \\
+ P7/P1 &= 12725.5469 \\
\times P7/P1 &= 19229.7773
\end{align*} \]
Figure 15
Double Diaphragm Shock Tube Pressure Ratios vs. Mach Number for $2H_2 + O_2$ Combustion, Helium, and Air in the Primary, Secondary, and Test Sections, Respectively. $P_7$ is post Combustion Pressure. $P_6$ and $P_1$ are pre-combustion pressures.
DOUBLE DIAPHRAGM PRESSURE RATIOS

\( \frac{\Delta P_7}{P_1} = 1.272.5990 \)
\( \Delta P_7/P_1 = 221.3398 \)
\( +P_7/P_1 = 12725.7344 \)
Thermal imperfections mean that the equation of state for a perfect gas cannot be used to describe the true behavior of the real gas over the entire range of pressure and temperature. Caloric imperfections are caused when the specific heats are not constant. As the temperature range exceeds about 2400°K (4300°R), molecular dissociation of air appears causing variations in specific heats and molecular weight. At higher temperatures, ionization causes more deviations.

In order to give a general treatment, first consider a mixture of perfect gases. The mixture will be homogeneous if all properties are uniform throughout the system when in equilibrium. The enthalpy is now a function of the components of the mixture. A given mass in a volume V will fill it completely and the pressure will adjust accordingly. For a perfect gas, this adjustment is independent of the presence of any other perfect gas in a given volume. Therefore, for a mixture of perfect gases, a partial pressure, \( P_i \), for the \( i \)th component gas will satisfy the perfect gas equation:

\[
P_i = \rho_i R_i T.
\]

The total pressure \( P \) of the mixture is equal to the sum of the partial pressures.

For convenience, consider equations (10), (12), and (14) along with the gas law \( P = \rho \bar{R} T/W \) where \( \bar{R} \) is the universal gas constant and \( W \) is the molecular weight for the component gas in question. Equations (10) and (12) and the gas law yield

\[
\frac{P_2}{P_1} = 1 + \frac{W_1 \rho_1}{\bar{R} T_1} \left( 1 - \frac{\rho_1}{\rho_2} \right).
\]
or \( \frac{P_2}{P_1} = 1 + \gamma_1 \frac{M_2^2}{\rho_2} (1 - \frac{\rho_1}{\rho_2}) \). Equations (10) and (14) give

\[
h_2 - h_1 = \frac{v_1^2}{2} \left( 1 - \frac{\rho_1^2}{\rho_2^2} \right),
\]

while the gas law yields

\[
\frac{P_2}{P_1} = \frac{\rho_2}{\rho_1} \frac{W_1}{W_2} \frac{T_2}{T_1}.
\]

When a polyatomic gas is raised to a sufficiently high temperature for dissociation to occur, a correction must be applied to the perfect gas law to allow for the increase in the number of particles in the gas. If a fraction \( \alpha_d \) of the original molecules have dissociated, the total number of particles in the gas will have been increased by a factor \( 1 + \nu \alpha_d \) where \( \nu \) is the reaction balancing coefficient. The perfect gas law equation becomes

\[
P = (1 + \nu \alpha_d) \rho RT.
\]

At even higher temperatures with ionization, a similar correction is necessary:

\[
P = (1 + \nu \alpha_d) (1 + \nu x_1) \rho RT
\]

where \( x_1 \) is the degree of ionization.

Dissociation and ionization also lead to variations in the specific heat ratios of the gas. The values of the specific heat ratios have been computed [12] for various temperatures and pressures for air.

### 2.3.2.2 Dissociation

Consider an equilibrium of the type \( AB \rightleftharpoons A + B \). The equilibrium concentrations are related by the equilibrium constant

\[
K_\alpha = \frac{[A][B]}{[AB]}
\]
where the brackets indicate the partial pressure of the components at equilibrium. From the relation for partial pressures

$$[AB] + [A] + [B] = P_2$$  (63)

where $P_2$ is the total equilibrium pressure in the shock, the molecular weight $W_2$ of the equilibrium gas mixture is then

$$W_2 = \frac{[AB]}{P_2} W_{AB} + \frac{[A]}{P_2} W_A + \frac{[B]}{P_2} W_B.$$  (64)

The energy involved for the dissociation of a unit mass of gas may be written as

$$\Delta E_D = \frac{[A] D_{AB}}{P_2 W_2}$$  (65)

where $D_{AB}$ is the dissociation energy for one mole of gas $AB$ at initial temperature $T_1$. Hence, equation (58) becomes

$$h_2 - h_1 = \frac{u_1^2}{2} (1 - \frac{\rho_1^2}{\rho_2^2}) - \Delta E_D.$$  (66)

The equilibrium enthalpy per mole of a real dissociated gas is equal to the sum of the enthalpies of the equilibrium chemical components in one mole of the gas at equilibrium temperature $T_2$. This includes molecules, atoms, and free radicals. Hence,

$$h_2 = \left( \frac{[AB]}{P_2} h_{AB} + \frac{[A]}{P_2} h_A + \frac{[B]}{P_2} h_B \right).$$  (67)

For the initial condition when $h_1$ is equal to zero, another relation is needed to obtain a solution to the above equations, viz., the ratio of the components of the reactant gas:

$$\frac{N_A}{N_B} = \frac{[AB] + [A]}{[AB] + [B]}.$$  (68)
Since dissociation is dependent on temperature and pressure, equation (57) cannot be solved exactly and must be solved by an iterative method. It is assumed that the shock speed $u_1$ and the initial temperature and pressure are known. The iterative method is outlined below:

1) A final temperature $T_2$ and pressure $P_2$ is assumed. $P_2$ can be estimated approximately from equation (57) by using the measured value of $u_1$ and assuming a value of $\rho_2/\rho_1$ a little greater than the maximum ideal gas value $(\gamma_1 + 1)/(\gamma_1 - 1)$.

2) These values of $T_2$ and $P_2$ are used to evaluate the partial pressures of the chemical constituents and the molecular weight $W_2$ of the shocked gas from equations (63 through 68).

3) $h_2$ and $\Delta E_D$ are computed from equations (67) and (65).

4) Using $T_2$, $P_2$, and the calculated $W_2$, $\rho_2/\rho_1$ is found from equation (59) and using this, the kinetic energy term of equation (66) is evaluated.

5) Compare the quantity $(h_2 - h_1)$ with that computed from equation (66). If the quantity $(h_2 - h_1)$ is greater than that found from equation (66) then the chosen value of $T_2$ is too high, and vice versa.

6) Choose another value of $T_2$ and using the above value of $\rho_2/\rho_1$ evaluate a new $P_2/P_1$ from equation (57). Then repeat the above steps using these values of $T_2$ and $P_2$.

2.3.2.3 Ionization

For the effect of ionization produced in a shock wave, consider the ionization of an atom $A$ to its positive ion $A^+$ and a free electron $e$. 
The equilibrium equation is
\[ A \xrightleftharpoons{\kappa} A^+ + e \]  
(69)
with the equilibrium constant \( K_x \) as
\[ K_x = \frac{[A^+][e]}{[A]} \]  
(70)
Let \( x_i \) equal the fractional amount of gas ionized, then at equilibrium
the total number of moles equals \( 1 - x_i + x_i + x_i = 1 + x_i \). Hence, the mole
fraction for \( A, A^+ \) and \( e \) are \( \frac{1-x_i}{1+x_i}, \frac{x_i}{1+x_i}, \) and \( \frac{x_i}{1+x_i} \), respectively. The partial pressures are then \( P \) times the mole fractions where \( P = [A] + [A^+] + [e] \). Thus, the partial pressures of each constituent at equilibrium is the
product of the mole fraction and the total pressure \( P \).

It can be seen that equation (70) becomes
\[
K_x = \frac{\frac{x_i}{1+x_i} P_2}{\frac{1-x_i}{1+x_i} P_2} = \frac{x_i^2}{1-x_i^2} P_2. 
\]  
(71)

The Saha equation [13] for single ionization is
\[
K_x = \frac{(2 \pi m_e)^{3/2} (kT)^{5/2}}{h^3} \frac{g_e g_{A^+}}{g_A} \exp \left( -I/kT \right) 
\]  
(72)
where \( I \) is the ionization potential of \( A; g_{A^+}, g_A, \) and \( g_e \) are the statistical weights or degeneracies of the ionized atom, the neutral atom, and
the electron, respectively. For the electron \( g_e = 2 \), \( g_{A^+} \) and \( g_A \) equal
\( (2J + 1) \) where \( J \) is the quantum number for the total angular momentum of
the electron in the ground state. Goldberg and Aller [13] list the statistical weights of most atoms.

To correct for the effect of ionization in the final equilibrium
state of the shocked gas, obtain the temperature \( T_2 \) using the
dissociation correction and use that temperature in equation (72) to obtain the equilibrium constant $K$. For a molecular gas, $K_i$ for each constituent must be evaluated. For example, for two species of ionizable atoms $A$ and $B$, these equations will be used:

$$K_A = \frac{[A^+][e]}{[A]} , \quad K_B = \frac{[B^+][e]}{[B]} , \quad [e] = [A^+] + [B^+].$$  \hfill (73)

From the value of $K_i$ obtained, compute $x_i$ from equation (71) using the value of $P_2$ obtained from dissociation data. Next obtain the energy per gram of gas. If this is small compared to the total enthalpy of the equilibrium gas, the effect of ionization is negligible. If it is significant, include the extra term $-\Delta E_i$ on the right hand side of equation (66) and repeat the computation for the equilibrium state as before. This calculation involves the molecular weight $W_2$ and pressure $P_2$ of the gas and must be included in equations (63) and (64).

The results for $T_2/T_1$, $P_2/P_1$, and $\rho_2/\rho_1$ vs Mach number showing the effects of dissociation and ionization are shown in Figures 16, 17, and 18 for a "cold" helium driver in a double diaphragm shock tube. The test section pressure in each case is one atmosphere. The change in slope in Figure 16 at $M \approx 14$ is due to the increased dissociation of $N_2$ at higher temperatures. This effect is more easily noted in Figure 18. The curve for real gases was computed at integral Mach numbers. The program used for these computations is in Appendix A. The gaps in these figures are due to the fact that the computer was unable to detect the small energy differences at those Mach numbers.
Figure 16

Effects of Dissociation and Ionization on Temperature Ratio vs. Mach Number. The ideal gas used a gamma of 1.404 to simulate air while the real case used a mixture of oxygen, nitrogen, carbon dioxide, helium, neon, and argon to simulate air.
TEMPERATURE RATIO $T_2/T_1$
+ IDEAL - REAL

MACH NUMBER

TEMPERATURE RATIO
Figure 17

Effects of Dissociation and Ionization on Pressure Ratio vs. Mach Number. The ideal gas used a gamma of 1.404 to simulate air while the real case used a mixture of oxygen, nitrogen, carbon dioxide, helium, neon, and argon to simulate air.
PRESSURE RATIO $P_2/P_1$

+ IDEAL - REAL

MACH NUMBER

PRESSURE RATIO

0.0 50.0 100.0 150.0 200.0 250.0 300.0 350.0 400.0 450.0 500.0 550.0

2 4 6 8 10 12 14 16 18 20
Figure 18
Effects of Dissociation and Ionization on Density Ratio vs. Mach Number. The ideal gas used a gamma of 1.404 to simulate air while the real case used a mixture of oxygen, nitrogen, carbon dioxide, helium, neon, and argon to simulate air.
DENSITY RATIO RH02/RH01
+ IDEAL - REAL

MACH NUMBER
2.3.3 Real Shock Tube Parameters

In order to employ the method described in the above section for real gas shock tube parameters, the model used to describe air must be established. This then sets forth for consideration a number of possible chemical reactions. Naturally, the more reactions considered, the more complicated are the calculations. However, after considering a given set of reactions in the calculations, it may be that some reactions can be eliminated. The most probable reason for these eliminations is that certain reactions proceed to a very small extent at the temperatures generated in the shock.

2.3.3.1 Dissociation

To proceed with the calculations, the concentration of the chemical species must be established through the theory of chemical reaction equilibrium. This presupposes a knowledge of equilibrium constants for the various reactions considered. If the system involved only two or three chemical reactions, then the equations can be solved simultaneously without too much difficulty. However, in complex systems, solving a large number of independent equations simultaneously becomes almost impossible, and simplifying techniques must be used.

The following procedure is adopted from Kobe and Leland [14], who applied it to combustion problems. For the shock tube application, consider the following reactions in air:

\begin{align*}
(1) \quad & O_2 \Leftrightarrow 20 \\
(2) \quad & N_2 \Leftrightarrow 2N \\
(3) \quad & N_2 + O_2 \Leftrightarrow 2NO \\
(4) \quad & 2CO_2 \Leftrightarrow 2CO + O_2.
\end{align*} 

The inert constituents* are He, Ne, and Ar. Hence, the number of

* A constituent is any identifiable chemical individual which is represented by a distinct formula.
constituent S, is 10. The number of components*, C, of the system is 6 and may be oxygen, nitrogen, carbon dioxide, argon, neon, and helium. Thus, the number of independent equilibrium reactions is \( S - C = 4 \).

These reactions were chosen:

1. \( O_2 + \frac{1}{2} N_2 \rightarrow 2N \)
2. \( N_2 + \frac{1}{2} O_2 \rightarrow NO \)
3. \( \frac{1}{2} O_2 + \frac{1}{2} N_2 \rightarrow NO \)
4. \( CO_2 \rightarrow CO + \frac{1}{2} O_2 \)

The corresponding equilibrium constants are

\[
K_1 = \frac{P^2}{P_{O_2}} \frac{x_{O_2}^2}{x_{O_2}^2} = \frac{n_{O_2}^2}{n_{O_2}^2} \quad K_2 = \frac{P^2}{P_{N_2}} \frac{x_{N_2}^2}{x_{N_2}^2} = \frac{n_{N_2}^2}{n_{N_2}^2} \quad K_3 = \frac{P_{NO}}{P^{\frac{1}{2}}_{O_2} P^{\frac{1}{2}}_{N_2}} \frac{x_{NO} \frac{1}{2}}{x_{O_2} \frac{1}{2} x_{N_2} \frac{1}{2}} = \frac{n_{NO}}{n_{O_2} n_{N_2}} \quad K_4 = \frac{P_{CO_2}}{P_{CO} P_{O_2}} \frac{x_{CO_2} \frac{1}{2}}{x_{CO} \frac{1}{2} x_{O_2} \frac{1}{2}} = \frac{n_{CO_2}^2}{n_{CO_2} n_{O_2}}
\]

where \( P_0 \) represents the partial pressures of atomic oxygen, \( x_0 \) represents the mole fraction of atomic oxygen, and \( n_0 \) represents the number of moles of atomic oxygen, etc.; and \( n_g \) is the total number of moles in the gas phase.

In addition to these equations, we need four more in order to have the same number of equations as unknowns. The most convenient

* A component is one of the smallest number of constituents present which can either react chemically or distribute themselves to produce any possible equilibrium condition of the system.
of these are the material balances on a molal basis and the definition of $n$:

**oxygen balance:**

$$q_{O_2} + 2q_{CO_2} = 2n_0 + 2n_{NO} + 2n_{CO} + 2n_{O_2} + 2n_{CO_2}$$

**nitrogen balance:**

$$q_{N_2} = 2n_{NO} + n_{N_2} + 2n_N$$  \hspace{1cm} (78)

**carbon balance:**

$$q_{CO_2} = n_{CO} + n_{CO_2}$$

**gas phase balance:**

$$n_g = n_{O_2} + n_0 + n_{N_2} + n_N + n_{NO} + n_{CO_2} + n_{CO} + n_{Ar} + n_{Ne} + n_{He}$$

where the $q$'s represent the known number of moles initially present and $n$ the unknown number of moles of a substance at equilibrium.

After the variables of the problem have been determined and a sufficient number of independent equations have been written to relate these variables, the remaining task is the simultaneous solution of these non-linear algebraic equations.

The method used here for solving these equations is Newton's method. It had the advantage that it may be used regardless of the relative magnitude of the concentration variables and it usually converges rapidly.

It is convenient to index the components and derived constituents as follows:

<table>
<thead>
<tr>
<th>component</th>
<th>index $j$</th>
<th>component</th>
<th>index $j$</th>
<th>derived constituent</th>
<th>index $i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>1</td>
<td>$Ar$</td>
<td>4</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>$N_2$</td>
<td>2</td>
<td>$Ne$</td>
<td>5</td>
<td>$N$</td>
<td>8</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>3</td>
<td>$He$</td>
<td>6</td>
<td>$CO$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$NO$</td>
<td>10</td>
</tr>
</tbody>
</table>
Hence, the term \( n_j \) represents the numbered moles of a component and \( n_i \) represents the number of moles of a derived constituent. Thus, the total number of moles \( n_g \) is:

\[
n_g = \sum_{j=1}^{C} n_j + \sum_{i=C+1}^{5} n_i.
\]  

(79)

A matrix is constructed from the detached coefficients of each of the chemical reactions as follows:

\[
\begin{bmatrix}
1 & \text{O}_2 & 1 & 0 & -1 & 1 \\
2 & \text{N}_2 & 0 & 1 & 0 & 1 \\
3 & \text{CO}_2 & 0 & 0 & 2 & 0 \\
4 & \text{Ar} & 0 & 0 & 0 & 0 \\
5 & \text{Ne} & 0 & 0 & 0 & 0 \\
6 & \text{He} & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\]

(80)

Call this matrix \( \nu_{ji} \).

Equations (76) become

\[
\begin{align*}
20 &= \text{O}_2 \\
2N &= \text{N}_2 \\
2\text{NO} &= \text{O}_2 + \text{N}_2 \\
2\text{CO} + \text{O}_2 &= 2\text{CO}_2.
\end{align*}
\]  

(81)

Consider a function \( F \) defined as

\[
F_k = q_k - n_g \sum_j x_j
\]  

(82)

and a function \( G \) defined as

\[
G = 1 - \sum_j x_j
\]  

(83)

where \( j \) equals one through six.
The q's are the original number of moles. These functions may be represented by a Taylor's series expansion about each point \( x_j \) as follows

\[
F_k = F_k(I) + \sum_j \frac{\partial F_k}{\partial x_j} \Delta x_j + \frac{\partial F_k}{\partial n_g} \Delta n_g
\]

(84)

where \( \Delta x_j = x_j - x_j(I) \) and \( I = \) first trial, \( k = \) number of independent equations, and \( j = \) number of components. This is an approximation of a non-linear equation \( F = 0 \). The best values of the correction terms are those which cause \( F_k \) to be equal to zero. Setting \( F_k \) equal to zero in equation (84) gives

\[
F_k(I) = -\sum_j \frac{\partial F_k}{\partial x_j} \Delta x_j - \frac{\partial F_k}{\partial n_g} \Delta n_g
\]

(85)

Also consider \( G \) as

\[
G = G(I) + \frac{1}{n_g} \sum_j \frac{\partial G}{\partial x_j} \Delta x_j.
\]

(86)

Setting \( G = 0 \),

\[
G(I) = -\frac{1}{n_g} \sum_j \frac{\partial G}{\partial x_j} \Delta x_j.
\]

(87)

Call \( \Delta x_j/x_j(I) = b_j \), \( \Delta n = g \), \( A_{kj} = \) coefficients of \( \Delta x_j/x_j(I) \) terms in \( F \), \( B_j = \) coefficients of \( \Delta x_j/x_j(I) \) terms in \( G \) and coefficients of \( \Delta n \) terms in \( F \). Now equations (85) and (87) become

\[
F_k(I) = \sum_j A_{kj} b_j + B_k g
\]

(88)

\[
G(I) = \sum_j B_j b_j.
\]

All of the coefficients of the \( b \) and \( g \) terms in equations (88) may be written directly from the matrix (80) by means of the following definitions:
\[ A_{kj} = n_j + \sum_{i=C+1}^{S} (\nu_{ji})^2 n_i \text{ when } k = j \]  
(89)

\[ A_{kj} = \sum_{i=C+1}^{C} (\nu_{ji})(\nu_{ki}) n_i \text{ when } k \neq j \]  
(90)

and

\[ B_j = \frac{1}{n_g} [n_j + \sum_{i=C+1}^{S} (\nu_{ji}) n_i]. \]  
(91)

Now the functions \( F_{kI} \) and \( G_{I} \) are just the value of the functions initially and are

\[ F_k = q_k - n_g \sum_j x_j, \]

and

\[ G = 1 - \sum_j x_j. \]  
(92)

These functions can be found from the matrix (80) as:

\[ F_k = q_k - n_k - \sum_{i=C+1}^{S} (\nu_{ki}) n_i, \]

and

\[ G = 1 - \frac{1}{n_g} [\frac{C}{n_g} n_j + \sum_{i=C+1}^{S} n_i]. \]  
(93)

Set the quantities in equations (88) equal to the corresponding ones in equations (93) and solve for the \( b \)'s and \( g \). These results now furnish improved values of \( n_j \) terms and \( n_g \) to be used in the next trial:

\[ n_{gII} = n_{gI} + g \]

\[ n_{jII} = (b_j + 1) \frac{n_{gII}}{n_{gI}} n_{jI} \]  
(94)

and \( n_{jII} \) is found from equations (77) using the new values of \( n_{jII} \).

These \( n_{jII} \) and \( n_{jII} \) values are used to evaluate \( F_{kII} \) and \( G_{II} \) which are substituted back in equations (88) and are solved for the \( b \) and \( g \) terms. The process is repeated in this manner until successive trials are in agreement.
The mole fraction \( x_j \) is just \( n_j / n \) and the corresponding partial pressure \( P_j = x_j P_2 \). It is advisable to check the sum of the partial pressures and verify that it is equal to the total pressure \( P_2 \).

The molecular weight \( W_2 \) is then calculated from

\[
W_2 = \frac{1}{P_2} \sum_j P_j W_j
\]

and the energy needed for the dissociation of a unit mass of gas is then

\[
\Delta E_D = \frac{1}{W_2 P_2} \sum_j P_j D_j
\]

where \( D_j \) is the dissociation energy of the \( j^{\text{th}} \) reaction. Now \( h_2 \) is found from

\[
h_2 = \frac{1}{W_2 P_2} \sum_j P_j h_j.
\]

Using \( T_2, P_2, \) and \( W_2 \) find \( \rho_2 / \rho_1 \) from

\[
\frac{P_2}{P_1} = \frac{\rho_2}{\rho_1} \frac{W_1 T_2}{W_2 T_1}
\]

and use this value of \( \rho_2 / \rho_1 \) in

\[
h_2 - h_1 = \frac{u_1^2}{2} \left[ 1 - \left( \frac{\rho_1}{\rho_2} \right)^2 \right] - \Delta E_D
\]

to evaluate the enthalpy change \( h_2 - h_1 \). Since \( h_1 \) is equal to zero, a comparison between equations (97) and (99) can be made. If the quantity in equation (97) is greater than that of equation (99) then the initial choice of \( T_2 \) is too high. Make a new choice of \( T_2 \) and repeat the procedure as heretofore outlined, doing so until there is agreement.

2.3.3.2 Ionization

After the equilibrium concentrations of the constituents and the temperature have been found, the effect of ionization must be taken into account. Consider the ionization of an atom called A into a positive
ion \( A^+ \) and a free electron \( e \). The equilibrium equation is

\[
A + A^+ + e
\]

with the equilibrium constant \( K_x \) as

\[
K_x = \frac{[A^+][e]}{[A]}
\]

Let \( x \) equal the fractional amount of gas \( A \) ionized, then at equilibrium the total number of moles equal \( 1 - x + x + x = 1 + x \). Hence, the mole fraction for \( A, A^+ \), and \( e \) are \( \frac{1 - x}{1 + x}, \frac{x}{1 + x}, \) and \( \frac{x}{1 + x} \), respectively.

Continuing with the same example, consider the following ionization reactions:

\[
\begin{align*}
1 & \quad 0_2 \leftrightarrow 0_2^+ + e \\
2 & \quad N_2 \leftrightarrow N_2^+ + e \\
3 & \quad CO_2 \leftrightarrow CO_2^+ + e \\
4 & \quad Ar \leftrightarrow Ar^+ + e \\
5 & \quad Ne \leftrightarrow Ne^+ + e \\
6 & \quad He \leftrightarrow He^+ + e \\
7 & \quad O \leftrightarrow O^+ + e \\
8 & \quad N \leftrightarrow N^+ + e \\
9 & \quad CO \leftrightarrow CO^+ + e \\
10 & \quad NO \leftrightarrow NO^+ + e
\end{align*}
\]

The corresponding equilibrium constants are:

\[
\begin{align*}
K_1 &= \frac{P_0^+ P_e}{P_0} = \frac{x_0^+ x_e P_2}{P_2} = \frac{n_0^+ n_e P_2}{n_0 n_g} \\
K_2 &= \frac{P_{N_2^+} P_e}{P_{N_2}} = \frac{x_{N_2^+} x_e P_2}{P_2} = \frac{n_{N_2^+} n_e P_2}{n_{N_2} n_g} \\
K_3 &= \frac{P_{CO_2^+} P_e}{P_{CO_2}} = \frac{x_{CO_2^+} x_e P_2}{x_{CO_2}} = \frac{n_{CO_2^+} n_e P_2}{n_{CO_2} n_g} \\
K_4 &= \frac{P_{Ar^+} P_e}{P_{Ar}} = \frac{x_{Ar^+} x_e P_2}{x_{Ar}} = \frac{n_{Ar^+} n_e P_2}{n_{Ar} n_g} \\
K_5 &= \frac{P_{Ne^+} P_e}{P_{Ne}} = \frac{x_{Ne^+} x_e P_2}{x_{Ne}} = \frac{n_{Ne^+} n_e P_2}{n_{Ne} n_g}
\end{align*}
\]
The values of these equilibrium constants are found from the Saha equation:

\[ K = \exp \left( \frac{-I}{kT} \right) \]

where \( I \) is the ionization potential, \( g_e, g_\pm \), and \( g \) are the statistical weights or degeneracy of the electron, ionized molecule, and neutral molecule, respectively. For the electron \( g_e = 2 \). The following table gives the degeneracies of the atoms and molecules used:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ground State</th>
<th>Statistical Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 3P_2 )</td>
<td>( 2J + 1 ) for atoms</td>
</tr>
<tr>
<td>( 0^+ )</td>
<td>( 4S_{3/2} )</td>
<td>( 2(2S + 1) ) for ( \Sigma ) molecules</td>
</tr>
<tr>
<td>N</td>
<td>( 4S_{3/2} )</td>
<td>( 2(2S + 1) ) for other molecules</td>
</tr>
<tr>
<td>( N^+ )</td>
<td>( 3P_0 )</td>
<td>1</td>
</tr>
<tr>
<td>NO</td>
<td>( 2\pi_{\frac{3}{2}} )</td>
<td>4</td>
</tr>
<tr>
<td>( NO^+ )</td>
<td>( \Sigma^+ )</td>
<td>2</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>( 3\Sigma^- )</td>
<td>3</td>
</tr>
<tr>
<td>(0_2)</td>
<td>(2\pi)</td>
<td>4</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>----</td>
</tr>
<tr>
<td>(N_2)</td>
<td>(1\Gamma^+)</td>
<td>1</td>
</tr>
<tr>
<td>(N_2^+)</td>
<td>(2\pi^+)</td>
<td>2</td>
</tr>
<tr>
<td>(CO)</td>
<td>(1\Sigma^+)</td>
<td>1</td>
</tr>
<tr>
<td>(CO^+)</td>
<td>(2\pi^+)</td>
<td>2</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>(1\Gamma^+)</td>
<td>1</td>
</tr>
<tr>
<td>(CO_2^+)</td>
<td>?</td>
<td>2 (guess)</td>
</tr>
<tr>
<td>(Ar)</td>
<td>(1S_0)</td>
<td>1</td>
</tr>
<tr>
<td>(Ar^+)</td>
<td>(2P_{3/2})</td>
<td>4</td>
</tr>
<tr>
<td>(Ne)</td>
<td>(1S_0)</td>
<td>1</td>
</tr>
<tr>
<td>(Ne^+)</td>
<td>(2P_{3/2})</td>
<td>4</td>
</tr>
<tr>
<td>(He)</td>
<td>(1S_0)</td>
<td>1</td>
</tr>
<tr>
<td>(He^+)</td>
<td>(2S_\frac{3}{2})</td>
<td>2</td>
</tr>
</tbody>
</table>

From the temperature found from dissociation considerations find the equilibrium constants for each reaction. Recalling the mole fractions, the equilibrium constants may be written

\[
K_{x_i} = \frac{x_i}{1+x_i} \frac{p_2}{p_1} \frac{x_i}{1+x_i} \frac{p_2}{p_1} = \frac{x_i^2 p_2}{1-x_i^2}.
\]  

(105)

Next solve for \(x_i\) from (105). These values are used in computing \(\Delta E_i\).

\[
\Delta E_i = \sum_i \left( \frac{x_i}{1+x_i} \frac{I_i}{W_2} \right)
\]  

(106)

Add the term \(-\Delta E_i\) to the right hand side of equation (99) and repeat the equilibrium calculations until close agreement is found.

After agreement has been found, the electron concentration is found from the sum of the fractional amount of gas ionized times the gas concentration for each gas ionized.

\[
n_e = \Sigma x_i n_i
\]  

(107)
Hence, the electron concentration per cubic centimeter is

\[ n_e = \left( \frac{6.024 \times 10^{23}}{22.4 \times 10^3} \right)^{20} \sum_{i=1}^{20} x_i n_i \]  

(108)

A plot of electron concentration vs. Mach number is shown in Figure 19.

Appendix A is a listing of the computer program used to compute the equilibrium concentrations of electrons.

Alpher and White [15, 16, 17] have shown that optical interferometry can be used to measure electron concentrations. The interferometric techniques depend upon changes in the index of refraction of the test gas. The change in index of refraction in turn is due to changes in both neutral and charged particle concentrations.

2.4 Interferometry

Interferometry has been used principally for the measurement of fine structure of spectrum lines, length or displacements in terms of wavelengths of light, and refractive indices. This investigation makes use of measurements in the change of refractive indices. Consider the following diagram. In principle, interferometry
Figure 19

Electron Concentrations vs. Mach Number

Initial Pressure in Test Chamber = 1 torr.
makes use of the information gained from the recombination of two beams which have a common source, S. Beams A and B are obtained by intensity division at plate G₁. One beam passes through the test section and the other beam (optically shorter) is the reference beam. For a monochromatic light source it is not necessary to insert a compensating plate in the shorter traversed beam, but is mandatory when white light is used. The source light must be from an extended source, i.e., it must have a finite width. If the mirrors M₁ and M₂ are exactly perpendicular to each other (optically parallel) as is shown below, a set of circular fringes will appear on a screen placed in the path of the recombined beams.

The intensity distribution of the interference fringes is given by:

\[ I \propto A^2 = 4a^2 \cos^2 \frac{\delta}{2} \]

where \( \delta = \text{phase difference} = \frac{2\pi}{\lambda} 2d \cos \theta \) [18].

If the mirrors are not exactly parallel, fringes will be seen with monochromatic light for path differences not exceeding a few millimeters. This is illustrated in the following diagram. The fringes will be practically straight if \( d \) has a small value. When the
two mirrors intersect optically, the fringes are perfectly straight.

2.4.1 Density and Fringe Shift Relation

If a thickness $t_o$ of a substance having an index of refraction $n$ is introduced into the path of one of the interfering beams in the interferometer, the optical path in this beam is increased because of the fact that light travels more slowly in the substance and consequently has a shorter wavelength. The optical path is now $nt_o$ through the medium, whereas it was practically $t_o$ through the corresponding thickness of air ($n-1$). Thus, the increase in optical path due to insertion of the substance is $(n - 1)t_o$. This will introduce $(n - 1)t_o/\lambda$ extra waves in the path of one beam. If $\Delta m$ equals the number of fringes by which the fringe system is displaced when the substance is placed in the beam, we have $(n - 1)t_o = \Delta m\lambda$.

If the optical path difference between the two beams is varied by a change in the refractive index of the gas in one beam, the fringes will shift through a distance which is directly proportional to this change.
The presence of density gradients causes a fringe pattern to be produced from a uniformly illuminated field; each fringe represents the locus of points for which the optical path distance through the flow is constant.

2.4.2 Dispersion Relation

In order to relate the index of refraction to the electron density, the dispersion relation must be used. Stratton [19] and Margenau [20] have shown that when the mean free path of the electrons is long, the refractive index for electrons is given by: 

\[ n^2 = 1 - \left(\frac{\omega_p}{\omega}\right)^2 \]  

or

\[ n = \left[1 - \left(\frac{\omega_p}{\omega}\right)^2\right]^\frac{1}{2} \]  

where \( \omega_p \) is the plasma frequency, related by \( \omega_p^2 = 4\pi n_e e^2 / m_e \) and \( \omega \) is the observing frequency, related by \( \omega = c \lambda / \lambda \). Expanding equation (109),

\[
\begin{align*}
n &= 1 + \frac{3}{2}(- (\omega_p/\omega)^2) + \frac{1}{2} \left(\frac{\omega - \omega_p}{\omega}\right)^2 \left[1 - (\omega_p/\omega)^2\right] + \ldots \\
&= 1 - \frac{3}{2}(\omega_p/\omega)^2 - 1/8(\omega_p/\omega)^4 - \ldots
\end{align*}
\]

Now, \( \omega_p << \omega \), thus, terms higher than second order are neglected giving:

\[ (n - 1) = \frac{3}{2}(\omega_p/\omega)^2 \]  

Thus, \( (n - 1)_e = -4.48 \times 10^{-14} \frac{n_e \lambda^2}{\lambda}, \) where \( n_e \) is the total number of electrons per cm.\(^3\) and \( \lambda \) is measured in centimeters.

Any change in refractivity of the gas caused by ionization will produce a shift in the fringe system. Hence, the fringe shift expressed in number of fringes is proportional to the variation in refractivity

\[ \Delta m = \Delta(n - 1) \frac{t_o}{\lambda} \]  

Now \( \Delta(n - 1) \) is given by

\[ \Delta(n - 1) = (n - 1)_{\text{plasma}} - (n - 1)_{\text{neutral gas}}. \]
The plasma refractivity can be made up of several components,

\[(n - 1)_{\text{plasma}} = (n - 1)_A + (n - 1)_M + (n - 1)_I + (n - 1)_e + \ldots .\] (113)

The subscripts A, M, and I refer to atoms, molecules, and ions, respectively in the ground state; and e refers to electrons. In addition, there may be contributions from such things as excited states.

For atoms and molecules, the refractivity is given by

\[(n - 1)_{A,M} = \frac{2\pi N_{A,M}}{\alpha_{A,M}}\]  

where \(N\) is the number density of the molecular or atomic species and \(\alpha\) is its polarizability*. The polarizability is a function of wavelength, but in most cases there is little difference between them. This is because optical frequencies are small compared to the natural atomic frequencies. The polarizabilities of the ions are not known in general; however it is not unreasonable to assume that they are of the same order of magnitude as for the neutral species. Although the polarizability of an excited state of an atom, molecule, or ion is expected to be larger than the corresponding species in the ground state, the number density of particles in these excited states is generally so low that the contribution of these particles to the plasma refractivity can be neglected [17].

Monitoring the change in refractivity indicates any change in concentration of the constituents of the test gas. The contribution from electrons is of opposite sign and greater in magnitude [17] from the rest of the components. Therefore,

\[\Delta(n - 1) = (n - 1)_e.\] (114)

*If an atom or molecule is brought into an electric field \(F\), and an electric dipole moment \(P\) is induced in the system, the magnitude of the resulting dipole moment is proportional to that of the field, i.e., \(P = \alpha F\) where \(\alpha\) is the polarizability [21],
Refractivity due to electrons can now be related to fringe shift by

$$\frac{\Delta m \lambda}{t_o} = (n - 1)_e = -4.48 \times 10^{-14} \frac{n_e \lambda^2}{t_o}$$; (115)

in terms of electron concentrations:

$$n_e = \frac{\Delta m}{4.48 \times 10^{-14} \frac{t_o}{\lambda}}.$$ (116)
3.1 Shock Tube

The shock tube used in these studies was designed and built in 1965 for the University of Missouri-Rolla. W. A. Crede [22] has described this facility in his thesis. A photograph of this facility is below.

3.1.1 Physical Dimensions and Associated Components

There are three main sections of this shock tube which makes use of two diaphragms. The following chart gives the basic statistics for the tube.

### 3.1.1.1 Shock Tube Statistics

<table>
<thead>
<tr>
<th>Shock Tube</th>
<th>Overall length</th>
<th>Driver length/diameter</th>
<th>Driver length/ Test section length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>26' 3-1/4&quot;</td>
<td>3</td>
<td>1/9</td>
</tr>
</tbody>
</table>
### 3.1.1.2 Diaphragms

The diaphragms used in these experiments were scribed with cross shaped grooves. These grooves provided nearly consistent diaphragm bursting characteristics. Also, the grooves caused the diaphragms to petal upon breaking. This petaling prevented diaphragm fragments from traveling down the tube which could cause the observation windows to be scratched. Normally the diaphragms are placed with the scribed portion facing down stream, however, greater strength and higher rupture pressures could be obtained by reversing the direction of the scribed side.

For the primary diaphragm material, 0.105 inch thick type 304 stainless steel was used. The following table provides the specifications for the diaphragms used in the experiments:

<table>
<thead>
<tr>
<th>Length</th>
<th>Internal Diameter</th>
<th>Wall Thickness</th>
<th>Maximum Pressure</th>
<th>Material</th>
<th>Weight</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driver</td>
<td>2' 3-1/4&quot;</td>
<td>8&quot;</td>
<td>2-1/2&quot; min.</td>
<td>12,500 psi</td>
<td>1027 lbs.</td>
<td>1232 in.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A-105 Gr II</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary Section</td>
<td>3'</td>
<td>7&quot;</td>
<td>1&quot;</td>
<td>6000 psi</td>
<td>974 lbs.</td>
<td>1383 in.</td>
</tr>
<tr>
<td>Test Section</td>
<td>21'</td>
<td>4-3/8&quot; sq.</td>
<td>5/8&quot;</td>
<td>1000 psi</td>
<td>1933 lbs.</td>
<td>4825 in.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A-240 Tp 304 SS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
stainless steel was used. The scribe depth was 0.030 inches which gave good petaling. The scribe side faced down stream and this arrangement yielded an average bursting pressure of 2500 psi. The secondary diaphragm was made from 0.080 inch thick aluminum. The scribe depth was 0.050 inches with the scribe facing downstream.

3.1.1.3 Windows

The windows used in this study were made from CORNING #7940 Optical grade Fused Silica and were ground flat and parallel to within 1/10 wavelength of the laser light used (6328Å). For a good description of mounting procedures, see West [23].

3.1.2 Driver Techniques

In order to produce strong shock waves in a shock tube, it is necessary to use driver gases with high sonic velocity as shown by equation (37). The driver gas must have a low molecular weight and a high temperature in order to have high sound velocity. Reasonably strong shock waves in air or other gases can be produced by using hydrogen or helium in the driver. To produce stronger shock waves, the hydrogen or helium temperatures must be increased.

3.1.2.1 Heating

Perhaps the simplest method to heat the driver gas is by conduction through the walls of the driver chamber. This method is not used for shock tube operation because of the low strength of most structural materials at elevated temperatures.
Another method is to heat the driver gas directly by heating elements located inside the driver section. The maximum temperature attainable by this method is limited by the allowable temperature of the heating element.

2.2 Constant Volume Combustion

High temperatures may be obtained in the primary driver by burning a stoichiometric mixture of hydrogen and oxygen in an excess of hydrogen or helium. This combustible mixture is used because of comparatively light products of combustion and the high heat of combustion.

Resler, Lin, and Kantrowitz [11] first suggested the possibility of burning a combustible mixture of hydrogen and oxygen in shock tube experiments to produce stronger shock waves than are attainable with a temperature hydrogen or helium. Witliff and Wilson [24] showed that constant volume combustion of a hydrogen-oxygen-helium mixture would produce a driver gas nearly as efficient as the hydrogen-oxygen mixture and was safer to use. Nagamatsu and his associates [25] conducted similar studies using a multiple spark ignition system and found that helium mixtures in the range of 70% to 75% with a balance of stoichiometric hydrogen and oxygen provided detonation-free combustion.

It was decided to use a 70% helium, stoichiometric hydrogen-oxygen mixture in these experiments. Theoretical computations have been made for the constant volume combustion of hydrogen-oxygen-helium...
mixtures over the range of initial pressures and compositions of interest by Benoit [26]. In these calculations dissociation was taken into account.

Figure 20 shows a schematic of the piping system used for gas handling to the shock tube. All components used in relation to the primary section were rated at 20,000 psi. or better as a safety precaution. Also, at appropriate locations, one-way check valves were used. If a power failure occurs a relief valve opens automatically to release any pressure in the primary section. Essentially all valve controls were mounted in the console shown below.

3.1.2.3 Ignition System

An exploding wire technique was used to ignite the mixture of hydrogen and oxygen. Basically, to facilitate this, a bank of capacitors was discharged by means of a thyatron tube through a length of 0.002 inch diameter aluminum wire stretched down the center of the primary section. The maximum power available for this arrangement was 150 joules. Figure 21 shows a diagram of the ignition system, and Figure 22 is a schematic diagram of the triggering amplifier.
Figure 20
Piping of Gas Handling System
Figure 21

Diagram of Ignition System
H.V. power supply

0-5000 volts

1 meg @25 watts

5C22

33\mu\text{h}

100pf

3 \text{ kv}

30K

16\mu\text{f}

5 \text{ kv}

10K

universal trigger

ignition wire
Figure 22

Schematic of Trigger Amplifier
Trig in: 4/450 v

12AT7

10 K 2W

30 K 2W

2M .1/1Kv

12AT7 2D21

+400

10 K 1W

470

430 1W

.01

.01

.1/1Kv

18K 1W -pulse

18K 1W -sync

2K 1W +sync

18K 1W +pulse

D 50 piv or more diode
L Dailco #38 lamp
T1 Thordarson 22R04
T2 Pri.=16 turns #26 nyclad on 1" core
Sec.=32 turns ct. #26 nyclad over primary

50K

.01

50/50

1A sb

117 v AC

100K

2K

100K

18K 1W

1N2094

Jones plug

1N2071

5Y3

1.3K

40/450

1M

18K 1W

1N480

2K 1W

2K 1W

1N480

18K 1W

-24V

normal open
3.2 Schlieren Photograph

Before any meaningful data could be taken with the interferometer, a schlieren photograph of the shock front was made using the technique outlined by West [23]. The light source for this system was a General Radio Type 1538-A electronic stroboscope triggered from the oscilloscope at a delayed time by a pulse from a pressure transducer placed just in front of the observation window. A prism was used to obtain the dominant visible wavelength of the Xenon flash which was then used in the schlieren system. The reason for obtaining a photograph was to determine the profile of the shock front. Shown below is the first schlieren photograph of a shock front taken at the University of Missouri-Rolla's Shock Tube Facility.
3.3 **Instrumentation**

Primarily, the instrumentation of the shock tube facility used in this experiment continuously monitored the change in density as the shock passed the test section windows, measured the initial and final pressures in all three parts of the shock tube, measured the velocity of the shock front, and measured the residual wall temperature.

3.3.1 **Interferometry**

As discussed in section 2.4, interferometry gives a good means of monitoring density changes which are related to electron concentrations.

3.3.1.1 **Optical System**

The interferometer shown in Figure 23 was constructed by the Gaertner Company according to the author's specifications. The Twyman-Green arrangement was chosen mainly for its simplicity and because double sensitivity to changes in gas density is provided by the double passage of one interfering beam through the shock tube. It consisted of one half silvered mirror and two first surface mirrors placed in a tee on optical benches. Light from the source was split by the beam splitter; one beam passed through the shock tube window, and was reflected back from the first mirror. The other beam not passing through the shock tube was reflected back from the second mirror. These two beams then recombined and fell on the detection system.

Each mirror was mounted on a heavy support, gimballed such that the mirror could be rotated around the horizontal and vertical axis of
Figure 23

Diagram of Interferometer
first surface mirror

window

shock tube

first surface mirror

half silvered mirror

laser

d lens

photo cells
the plane of its surface. Also, the second mirror is provided with a translational motion in the direction normal to its surface. The mirrors are one half inch thick, a three by 4-1/2 inches rectangle, and are flat and parallel to 1/10 wavelength.

3.3.1.2 Light Source

The effects of a finite source and the use of white light complicates the analysis and the design of the interferometer considerably. Winkler [27] has studied these problems in detail. Some results of his investigation follow.

As was mentioned in section 2.4.1 the fringe spacing is directly proportional to the wavelength. If white light is used, only the central fringe is distinct. The fringes formed by the various colors of the light separate since their spacing depends on the wavelength.

The effect of a finite source size using monochromatic light is now considered. In order to obtain good resolution a bright light source is required. It should therefore be as large as possible. However, all of the light rays from a finite source cannot be made parallel by a lens. The rays may make as large an angle as \( \pm \omega \) to the central ray where \( \omega = d/2f \). \( d \) is the source diameter and \( f \) is the focal length of the lens.

To overcome the difficulties a laser was used. The laser was a Spectra Physics model 124 with a model 332 spatial filter. The spatial filter eliminated fringe contrast fluctuations experienced by Besse and Kelly [28], and provided an improved method for monitoring the fringe shift.
3.3.1.3 Detection System

The detection system consisted of two photoelectric cells for measurement of the fringe shifts. The detection of the fringe shifts was accomplished by measuring the intensity at two points in the plane of observation. These two points should preferably be spaced 1/4, 3/4, or 5/4 a fringe width apart. An aperture blanked out unwanted reflections.

The two photo diodes originally used in this experiment were Texas Instrument P-N Epitaxial Planer Silicon Laser Detectors, type LSX 900. These diodes were placed as shown in Figure 24 in the detection assembly. A CORNING filter set CS 2-102 was used to filter out any self luminescence in the shock tube and passed a narrow region of the spectrum centered about the laser frequency. A negative lens expanded the interference pattern to a useful size. The signals from the diodes were displayed on a Tektronix model 556 dual beam oscilloscope and recorded with a Polaroid camera attachment. To assure that the diodes were placed (2\(n + 1\))/4 the distance between the fringes, their signals were fed into the x and y inputs of a scope. The optical path was modulated and the Lissajous figure was observed. A circular figure was seen when the inputs of the diodes differed by 1/2\(\pi\) or 90°.

It was found, however, that the photo diodes did not provide a large enough signal to be useful. In their place two RCA 925 vacuum photo cells were used in the same configuration.

3.3.1.4 Alignment of Interferometer

Caution must be maintained throughout the alignment of the interferometer so that the eye is not exposed to direct contact with
Figure 24

Detection Assembly
the laser beam. Looking directly into the beam can cause irreparable damage to the retina. Initially, the alignment was made with one mirror covered while the second mirror and beam splitter was adjusted for beam location on the photo cells. Next, the other mirror was covered and the first mirror aligned.

A screen was placed as indicated in Figure 24 and adjustment of one of the mirrors was made to obtain horizontal fringes.

3.3.2 Velocity Measurement

The measurement of the velocity of the shock front was attempted by the use of two piezoelectric pressure transducers. Kistler model 601A transducers were used with model 566 electrostatic charge amplifiers which fed a Tektronix model 556 dual beam oscilloscope. It was found that electronic noise from the triggering of the explosive mixture in the primary chamber and vibration of the shock tube caused a premature trace on the oscilloscope. After investigating several methods for measurement of the velocity, it was determined that ionization probes as shown in Figure 25 were the most reliable. The scope with a Polaroid camera attached gave a recording of the time difference between pulses from the two ionization probes giving a measure of the shock speed.

3.3.3 Wall Temperature Measurements

The residual temperature of the wall of the test section was measured to determine if appreciable heating of the walls occurred. This information was of interest in view of structural considerations. A thermocouple embedded in stainless steel and mounted flush with the walls was used for this measurement. Figure 26 shows the arrangement of the thermocouple. Experiment showed that there was little temperature change.
Figure 25

Ionization Probes Used for Velocity Measurements
Ionization probes

-300 v

22 meg.

.001

1N34

Ionization Probes

22 meg.

.001

1N34

30K

Output to Cathode Follower
Figure 26

Thermocouple Mounting
to potentiometer

stainless steel jacket

silver solder

stainless steel

thermocouple

wall of shock tube
3.4 Procedure for Operation of Double Diaphragm Shock Tube

Safety is of utmost importance when operating the double diaphragm shock tube with combustion techniques. Since the shock tube utilizes combustion methods, the usual precautions concerning combustible materials must be maintained. Hydrogen and oxygen were used in these series of experiments; therefore, any leaks in the system could produce a dangerous situation. At all times a hydrogen leak detector should be in operation.

The piping system allows the entire shock tube, except the primary section, to be evacuated with a vacuum pump. A one-way valve prevents the primary section from being evacuated; however, a venting valve can be opened to allow any residual gas to escape from that section.

Refer to Figures 20 and 27 for the check list of operational procedures which follow:

1. Determine the Mach number desired.
2. Turn on all electronic equipment.
3. Turn on the air pressure supply for the remote control valve.
4. Place exploding wire into the primary section.
5. Insert the appropriate diaphragms.
6. Open vent valve.
7. Open valves to draw a vacuum in test section and in secondary section.
8. From the desired Mach number, determine the initial pressure needed for combustion constituents from Figures 14 and 15.
Figure 27
Test Equipment Hook up for Double Diaphragm Shock Tube
Tektronix 556

trigger in from velocity sweep

vert in

Photo Cells

trigger in from ignition

vert in

vert in

Kistler Filter 544A100

Kistler 566 Charge Amp.

Kistler 601 Transducer
to ionization probes

Cathode Follower
10. Turn on gases.
11. Fill secondary section to desired pressure with helium.
12. Fill primary section with oxygen to 10% of precombustion pressure.
13. Fill primary section with helium until pressure is 80% of precombustion pressure.
14. Fill primary section with hydrogen until pressure equals precombustion pressure.
15. Purge the lines with helium.
16. Close inlet valve to primary and secondary sections.
17. Fill test section to desired pressure for determined Mach number.
18. Close valves to test section.
19. Check for leaks.
20. Let mixture stand for 30 minutes.
21. Set ionization probe charge amplifier and scope controls to proper ranges for the desired Mach number.
22. Set interference fringe detector scope controls to proper values.
23. Photograph grids of both scopes.
24. Charge the capacitors.
25. Ignite the mixture.
26. Record the residual pressure.
27. Develop the Polaroid print.
28. Open the vent valve.
IV RESULTS AND CONCLUSIONS

4.1 Velocity Measurement

In order to make accurate velocity measurements, two ionization probes spaced three inches apart were used as discussed in section 3.3.2. The pulse from the first probe triggered the scope trace. Both pulses from the probes were recorded giving the time it took for the shock wave to travel the distance of three inches. Hence, the velocity was determined. A photograph of the ionization probe trace is shown below in the upper trace. The lower trace is a record of the primary chamber pressure history. The sudden reduction of pressure indicates when the diaphragm ruptured.

4.2 Fringe Shaft Measurement

As mentioned in section 3.3.1.3 the two photo cells were separated by \((2n + 1)/4\), the distance between two succeeding fringes. This arrangement allows the determination of the direction of the
fringe shift to be made. If one photo cell was placed on a maxima and the other photo cell was placed as described and to the left of the first photo cell then a fringe shift to the right would cause the first photo cell to decrease in signal while the second photo cell would increase in signal. If the fringe shift were to the left then the first photo cell would decrease in signal, but the second photo cell would also decrease in signal. The signals would behave as expected for being 90° out of phase. Thus, by careful analysis the direction of fringe shift was determined.

An example of the procedure used in this interpretation follows. Consider Figure 28. This figure shows a hypothetical signal response of two photo cells 90° out of phase. The second photo cell leads the first photo cell for a time, then the situation is reversed. Figure 28c shows how this information is interpreted. For each increment of time, for example, one microsecond, both response traces are examined for how many cycles the signal has traced and whether the same relation exists between both traces. When the second photo cell lags the first one, then the direction of the fringe shifts reverses. If both photo cells maintain the same relation to each other throughout the trace, then the number of fringe shifts is simply the number of cycles either photo cell has undergone.

Using equation (116) developed in section 2.4.2, the electron concentration is given by

\[ n_e = 1.64 \times 10^{16} \Delta m \]  

(117)
Figure 28
Hypothetical Signal Response
where \( t_0 = 21.5 \) cm. (twice the width of the shock tube) and \( \lambda = 6328 \) Å.

If the resolution on the \( \Delta m \) measurement is limited to \( \Delta m = 0.05 \) fringes, then the lower limit of electron concentration that is measurable is \( 8.2 \times 10^{14} \) electrons/cm\(^3\).

To apply this technique, for example, to the data for \( M = 17.6 \), consider the following photograph.

The time scale is 20 microseconds per centimeter. At 30 microseconds the two traces began to deviate from each other and did so until 180 microseconds. These points were determined by superposition of one trace on the other. During this interval, the number of cycles either trace made was approximately 0.35 based upon the fact that the amplitude of either trace was a maximum of 2.8 centimeters. This value was determined by measuring the amplitude change as a fringe pattern changed from light to dark. The period of these traces was not constant over a long time as shown by Besse and Kelly [28], but was considered to be so over the time range of interest.
4.3 Comparison of Theory and Experiment

A comparison of theory and experiment for this study is shown in Figure 29 along with the results obtained by other authors. The experimental data of Funahashi and Takeda [10] is somewhat lower than the theoretical prediction of Lin and Teare [29] which was supported by the data of Lin, Neal, and Fyfe [32] while the theoretical prediction of Horton and Menard [5] differs from both sets of data.

Lin and Teare used 21% oxygen and 79% nitrogen as a model for air in their study. For their analysis, they allowed both forward and backward going reactions to occur simultaneously and plotted peak electron concentration vs. Mach number. Horton and Menard used statistical mechanics in their analysis with an air model of 20.95% oxygen, 70.08% nitrogen, and 0.97% argon. They also allowed forward and backward going reactions to occur simultaneously. Due to the fact that it was assumed in this study that all dissociation reactions were completed before ionization was considered, it seems reasonable to assume that the theoretical results obtained represent an upper bound for chemical equilibrium. The air model used in this study consisted of 20.949% oxygen, 78.088% nitrogen, 0.93% argon, 0.03% carbon dioxide, 0.0025% neon, and 0.0005% helium. In view of the fact that the experimental data of Funahashi and Takeda differ from that of Lin, Neal, and Fyfe by 70%, the upper bound theoretical solution would be useful in design when energy dissipation is a requisite of the problem.

Ordinary room air was used as the experimental test gas. Various impurities in the air could cause considerable variation in the electron concentration produced by the shock. Although the composition of the air used was unknown, the experimental results demonstrated the reproducibility of the data with the technique used.
Figure 29

Comparison of Theory and Experiment for Electron Concentration

Theoretical curves: • This study

△ Lin and Teare
○ Horton and Menard

Experimental curves: • This study

□ Funahashi and Takeda
4.4 Errors

The errors encountered in this presentation can be classified into two categories, viz., theoretical and experimental.

4.4.1 Theory

Theoretical predictions of the gas flow properties in a shock tube are usually based on two simplifying assumptions. First, it is assumed that immediately upon bursting the diaphragm, which initially divides the tube into the high pressure chamber and the low pressure channel, a shock and a rarefaction form at the diaphragm position. At this instant and at this position, the shock and the rarefaction are presumed to be plane and fully developed. Second, by assuming that the subsequent flow is one-dimensional, adiabatic, and inviscid interactions with the walls of the tube are neglected.

Possible causes of further deviations from theory are factors such as the dimensions of the tube, the surface roughness and interactions, the geometrical shape of the tube cross-section, the diaphragm material, the stress on the diaphragm at the time of rupture, the manner in which it breaks, the initial mixing of the contact zone, etc. which are not amenable to theoretical analysis. These factors can be grouped into two categories; first, the diaphragm influences the flow in the tube, and second, the shock is attenuated as it propagates by viscous forces.

The diaphragm tends to destroy the one-dimensional character of the shock tube flow. Under the initial pressure differential, the diaphragm tends to bow and as soon as it ruptures the gas flow has a component towards the wall of the shock tube rather than directed only along the axis.
The viscous forces set up by the relative motion between the gas and the tube walls act to decelerate the shock front as it travels down the tube. The boundary layer formed varies in thickness from zero at the shock front to a maximum value at the contact surface.

At low temperatures and moderate densities, the statistical weights are approximated by their ground state values. At elevated temperatures or lower densities, significant population of excited states occurs and the statistical weights must be computed more carefully.

Another important factor in the theoretical model used was the choice of values for equilibrium constants used in the computations. The values used were obtained from Gaydon and Hurle [30] for temperatures up to 4000°C. For temperatures greater than 4000°C values from Hilsenrath, Klein, and Sumida [31] were used. In the temperature range from 3000°C to 4000°C there was good agreement between these two authors. Interpolation was used for values of the equilibrium constants at temperatures between those given in these references. These equilibrium constants of Hilsenrath, Klein, and Sumida were derived from classical thermodynamics and are in agreement with Horton and Menard who derived them using statistical mechanics.

4.4.2 Experiment

Fringe constant is apparently reduced when the optical path changes rapidly because interpretation becomes difficult. This problem is avoided in some experiments by having the test beam of the interferometer non-perpendicular to the shock tube axis. This increases the time required for the shock front to cross the beam and avoids rapid changes in optical length.
Assuming \( F = F(x_i) \) and using the calculus method of propagation of errors one has for a measurement of error:

\[
\frac{\Delta F}{F} = \left[ \sum \frac{\Delta x_i^2}{x_i^2} \right]^{\frac{1}{2}}
\]

(118)

where \( \Delta x_i \) is the uncertainty associated with the quantity \( x_i \).

For these experiments the error in the velocity measurement is due to the uncertainties in the location of the ionization probes and the time interval measurement. Thus, for \( v = \frac{d}{t} \), then

\[
\frac{\Delta v}{v} = \left[ \left( \frac{\Delta d}{d} \right)^2 + \left( \frac{\Delta t}{t} \right)^2 \right]^{\frac{1}{2}}.
\]

The distance between ionization probes is known to within 0.005 inches, and the time can be read to within 0.1 microsecond. Therefore, for the Mach number equal to 20 (approximately 11 microseconds), the probable error in the velocity measurement is

\[
\frac{\Delta v}{v} = \left[ \left( \frac{0.1}{11} \right)^2 + \left( \frac{0.005}{3.00} \right)^2 \right]^{\frac{1}{2}}
\]

which is 0.9 percent or less.

Likewise for the electron concentration measurement the probable error is found from specifying the error in the fringe shift as 0.05 fringes and the error in measuring the optical path through the shock tube as 0.1 cm. For a fringe shift of 0.4 and the optical path length of 21.5 cm., the probable error is 12.5 percent.

4.5 Suggestions for Further Experiments

Further investigations of ionization behind strong shocks should be pursued both in theory and in experimental techniques. It would be desirable to consider all possible dissociation and ionization reactions in both pure air and real air mixtures. It would be helpful to have data using interferometric techniques in the Mach number range of 20 to
30 for both conventional shock tubes and electromagnetically driven shock tubes. Also as a check of the instrumentation techniques, data should be obtained for argon and should be compared to other data available for argon.

For application to re-entry vehicles into a planet's atmosphere, the concentrations of constituents in air mixtures must be well known at various altitudes. To incorporate these varying amounts into theoretical predictions of ionization, the parameter of time (or altitude) must be used in conjunction with those of concentrations.

The next logical step in the investigation would be to consider non-equilibrium kinetics. This would be important in predicting the time histories behind the shock waves. Here not only classical processes should be included, but also energy relaxation processes such as translational and vibrational relaxation, collisional excitation and de-excitation of electronic states, and chemiluminescent processes including those involving electrons should be considered.

Experimental techniques should be used to confirm the theoretical predictions. Diagnostic techniques for monitoring the kinetic processes in addition to the method presented in this dissertation include infrared emission and absorption, electron absorption and scattering, the Hook method (using a spectrometer crossed with an interferometer), and mass spectrometry. Mass spectrometry would determine the actual composition of the test gas used in the experiments. A technique which may be used in the preparation of non-equilibrium distributions is the production of free radicals by shocking unstable molecules.
Along with interest in production of ionized particles is that of controlling the degree of ionization especially in relation to re-entry vehicles. In order to reduce the amount of ionization, energy must be absorbed thus reducing the temperature to below that which ionizes the molecules and atoms in the region of interest. A possible way to do this is to inject molecules of high dissociation and ionization energies in the shock front.
BIBLIOGRAPHY

17. Ibid, p. 162.


APPENDIX A

COMPUTER PROGRAM FOR EQUILIBRIUM COMPUTATIONS

The following is a list of the computer program used to compute the real gas effects for temperature, pressure, and density vs. Mach number. Also, this program computes the electron concentrations vs. Mach number.

The gaps that appear in Figures 16, 17, and 18 for the real gas curves are due to the fact that at Mach numbers in these regions the contributions due to dissociation and ionization are so small that the computer is unable to detect a change of values in the energy terms. It is reasonable to assume, however, that the real curves asymptotically approach the perfect gas curves at low Mach numbers.
Computer nomenclature as encountered.

\( KKK \) = dummy index

\( W1 \) = initial molecular weight of air

\( P1 \) = initial pressure

\( M1 \) = Mach Number

\( G1 \) = Ratio of specific heats

\( T1 \) = initial temperature

\( NNNN \) = number of components

\( NNN \) = number of equilibrium constants

\( T(J,I) \) = temperatures for corresponding equilibrium constants

\( ECON \) = equilibrium constants

\( MK(J) \) = dummy index

\( P21 \) = \( P2/P1 \)

\( P2 \) = pressure after shock

\( RH021 \) = \( RH02/RH01 \)

\( T2 \) = temperature after shock

\( C \) = number of components

\( S \) = number of constituents

\( Q(I) \) = initial molar concentrations of components

\( N(J) \) = molar concentrations of components

\( NU(J,I) \) = matrix of detached coefficients

\( W(J) \) = weights of constituents

\( D(J) \) = dissociation energies

\( JJ \) = number of enthalpy values

\( JJJ \) = number of enthalpies
\( \text{TH}(J,I) = \text{temperature of corresponding enthalpies} \)

\( \text{ENTH} = \text{enthalpies} \)

\( \text{ME}(J) = \text{dummy index} \)

\( \text{G}(J) = \text{statistical weights of atoms} \)

\( \text{GG}(J) = \text{statistical weights of ions} \)

\( \text{IPOT} = \text{ionization potentials} \)

\( \text{COEF} = \text{argument for subroutine KCOEF} \)

\( \text{NG} = \text{total moles} \)

\( \text{EOCON} = \text{specific equilibrium constants} \)

\( \text{AIJBL} = \text{coefficients subroutine} \)

\( \text{FUNG} = \text{function } F_k \text{ subroutine} \)

\( \text{ARG} = \text{argument subroutine} \)

\( \text{SIMO} = \text{subroutine for equation solving} \)

\( \text{NGG} = \text{new value of total moles} \)

\( \text{NN}(J) = \text{new values of constituent concentrations} \)

\( \text{PTOT} = \text{total pressure} \)

\( \text{X}(J) = \text{molar concentrations of constituents} \)

\( \text{H2} = \text{enthalpy} \)

\( \text{C1} = \text{speed of sound} \)

\( \text{H21} = \text{H2/H1} \)

\( \text{GK} = \text{ionization equilibrium constant} \)

\( \text{DELI} = \text{energy increment due to ionization} \)

\( \text{IONCON} = \text{electron concentration} \)
THIS PROGRAM DETERMINES THE ELECTRON CONCENTRATION IN SHOCKED AIR.

THE METHOD USED FOR THIS CALCULATION IS OUTLINED IN "IONIZATION OF AIR PRODUCED BY STRONG SHOCKS", BY H.S. JOYNER

THE DATA IS READ IN THE FOLLOWING ORDER WITH INDICATED FORMATS:

1. INITIAL PRESSURE, MACH NUMBER, RATIO OF SPECIFIC HEATS, AND INITIAL TEMPERATURE. (4F10.4)
2. NUMBER OF DISSOCIATION EQUILIBRIUM CONSTANTS. (I4)
3. NUMBER OF KNOWN EQUILIBRIUM CONSTANTS VS. TEMPERATURE. (I4)
4. TEMPERATURE AND CORRESPONDING EQUILIBRIUM CONSTANT (2E18.8)
5. NUMBER OF CONSTITUENTS OF AIR (I4)
6. INITIAL CONCENTRATION OF CONSTITUENTS OF AIR (6F10.4)
7. MATRIX OF DETACHED COEFFICIENTS (4F10.4)
8. MOLECULAR WEIGHTS OF CONSTITUENTS (10F7.2)
9. DISSOCIATION ENERGIES IN K-CAL/MOLE (4F10.4)
10. NUMBER OF ENTHALPY VALUES (I4)
11. NUMBER OF KNOWN ENTHALpies VS. TEMPERATURE (I4)
12. TEMPERATURE AND CORRESPONDING ENTHALPIES (2E18.8)
13. STATISTICAL WEIGHS OF NEUTRAL AND IONIZED SPECIES (2E18.8)
14. IONIZATION POTENTIALS IN EV (2E18.8)

DIMENSION COEF(20),ECON(10,20),T(10,20), EQCON(10),A(7,7),B(7),
1Q(6),P(6),X(10),P(10),DIS(50),ECOF(30),D(10),ENTH(10,30),H(10),
2W(10),G(10),GG(10),ALPHA(10),AMTION(10),TH(10,30)
REAL MK(10),M1,N(10),NU(6,10),NG,NN(10),NGG,ME(10),
1ICON(10),IPOT(10),IONCON
INTEGER C,CC,S
WRITE (3,400)
KKK=0
W1=28.98

INITIAL CONDITIONS ARE READ IN HERE
READ (1,102) P1,M1,G1,T1

DISSOCIATION EQUILIBRIUM DATA IS READ HERE
READ (1,100) NNNN
DO 10 J=1,NNNN
READ (1,10C) NNN
READ (1,101) (T(J,I),ECON(J,I),I=1,NNN)
MK(J)=NNN
10 CONTINUE

C
C FINAL PRESSURE AND TEMPERATURE ARE FOUND HERE ALONG WITH DENSITY RATIO.
C
P21=(2.0*G1*M1**2-G1+1.0)/(G1+1.0)
P2=P1*P21
RH021=(G1+1.0)*M1**2/((G1-1.0)*M1**2+2.0)+1.0
RH012=1.0/RH021
T2=P21*RH012*T1
WRITE (3,500) P1,P1,T2

35 READ (1,100) C
CC=C+1
S=10

C
C INITIAL CONSTITUENT CONCENTRATIONS ARE READ HERE.
READ (1,103) (N(I),I=1,C)
Q(1)=N(1)
Q(2)=N(2)
Q(3)=N(3)
Q(4)=N(4)
Q(5)=N(5)
Q(6)=N(6)
DO 45 I=1,S
DO 45 J=1,C
NU(J,I)=0.0
45 CONTINUE

C
C THE MATRIX OF DETached coefficients IS READ HERE.
READ (1,102) ((NU(J,I),I=CC,S),J=1,C)

C
C THE MOLECULAR weights ARE READ HERE.
READ (1,104) (W(J),J=1,S)
THE DISSOCIATION ENERGIES IN K-CALS/MOLE ARE READ HERE.
READ (1,102) (D(J),J=1,4)

ENTHALPY DATA IS READ IN HERE.
READ (1,100) JJ
DO 75 J=1,JJ
READ (1,100) JJJ
READ (1,101) (TH(J,I),ENTH(J,I),I=1,JJJ)
ME(J)=JJJ
75 CONTINUE

THE STATISTICAL WEIGHTS OF THE ATOM AND ION ARE READ IN HERE.
READ (1,101) (G(J),GG(J),J=1,S)

THE IONIZATION POTENTIAL IN EV IS READ IN HERE.
READ (1,105) (IPOT(J),J=1,S)

THE EQUILIBRIUM CONSTANT FOR FINAL TEMPERATURE IS FOUND HERE.
36 DO 30 J=1,NNNN
    DO 37 I=1,NNN
    COEF(I)=ECON(J,I)
37 CONTINUE
    CALL KCOEF(T,COEF,ME,J,T2,EQCON)
30 CONTINUE
N(1)=Q(1)
N(2)=Q(2)
N(3)=Q(3)
N(4)=Q(4)
N(5)=Q(5)
N(6)=Q(6)
NG=0.0
DO 40 I=1,C
    NG=NG+N(I)
40 CONTINUE
C DERIVED CONSTITUENT CONCENTRATIONS ARE COMPUTED HERE.

41 N(7)=SQRT(EQCON(1)*N(1)*NG/P2)
   N(8)=SQRT(EQCON(2)*N(2)*NG/P2)
   N(9)=EQCON(4)*N(3)*NG/SQRT(N(1)*P2)
   N(10)=EQCON(3)*SQRT(N(1)*N(2))

C COEFFICIENTS OF SIMULTANEOUS EQUATIONS ARE DETERMINED HERE.
   CALL AIJBJ(N,NU,C,CC,S,A,B,NG)
   CALL FUNG(N,Q,F,NU,C,CC,S,G,NG)
   CALL ARG(B,F,G,C)
   CALL SIMQ(A,B,7,KS)
   NGG=NG+8(7)

C THE EQUILIBRIUM CONSTITUENT CONCENTRATIONS ARE COMPUTED HERE.
   DO 50 J=1,C
   NN(J)=B(J)+1.0)*NG*NN(J)/NG
50 CONTINUE

C ITERATION CONTINUES UNTIL AGREEMENT IS WITHIN 1/2 PERCENT OF
C PREVIOUS VALUE.
   IF (ABS((N(1)-NN(1))*100.0/N(1)).LT.0.5) GO TO 56
   DO 55 J=1,C
   N(J)=NN(J)
55 CONTINUE
   NG=NGG
   GO TO 41
56 DO 59 J=1,C
   N(J)=NN(J)
59 CONTINUE
   NG=NGG
   W2=0.0
   PTOT=0.0

C PARTIAL PRESSURES OF CONSTITUENTS ARE DETERMINED ALONG WITH FINAL
C WEIGHT.
   DO 65 J=1,S
\[ X(J) = \frac{N(J)}{NG} \]
\[ P(J) = X(J) * P2 \]
\[ P_{TOT} = P_{TOT} + P(J) \]
\[ W2 = W2 + P(J) * W(J) \]

65 CONTINUE
\[ W2 = W2 / P2 \]

C A MORE ACCURATE VALUE OF DENSITY RATIO IS FOUND.
\[ \text{RH012} = \frac{W1 * T2 * P1}{(W2 * T1 * P2)} \]
IF (RH012 .LT. 1.0) GO TO 66
\[ \text{RH012} = 0.99999 \]

66 CONTINUE
\[ \text{RH021} = 1.0 / \text{RH012} \]

C POTENTIAL ENERGY CONTRIBUTION FOR ENTHALPY DUE TO DISSOCIATION IS COMPUTED.
\[ \text{DELED} = \frac{P(7) * D(1) / 2.0 + P(8) * D(2) / 2.0 + P(9) * D(3) + P(10) * D(4)}{2.0} \]
\[ \text{DELED} = \frac{\text{DELED}}{(W2 * P2)} \]

C ENTHALPIES FOR THE CONSTITUENTS ARE COMPUTED HERE.
DO 85 J = 1, JJ
DO 86 I = 1, JJJ
\[ \text{ECOF}(I) = \text{ENTH}(J, I) \]
86 CONTINUE
CALL DISCOF(TH, ECOF, ME, J, T2, H)
85 CONTINUE

C THE TOTAL ENTHALPY FOR THE DISSOCIATING GAS IS COMPUTED HERE.
\[ H2 = 0.0 \]
DO 90 J = 1, S
\[ H2 = H2 + P(J) * H(J) \]
90 CONTINUE
\[ H2 = H2 / (W2 * P2) \]
\[ C1 = \sqrt{G1 * 32.17 * 1545.0 * T1 * 9.0 / (28.98 * 5.0)} \]

C THE AVAILABLE THERMAL ENERGY IS COMPUTED HERE.
H21=((M1*C1)**2/2.0)*(1.0-RHO12**2)*2.21E-08-DELED
IF (KKK.EQ.1) GO TO 200
C
C IF GOOD AGREEMENT IS FOUND THE PROGRAM PROCEEDS TO THE IONIZATION
C CONSIDERATION; IF NOT, THE FINAL TEMPERATURE IS REDUCED AND A NEW
C ENTHALPY IS FOUND.
IF(H2.LT.H21) GO TO 200
T2=T2-25.0
P2=P1*(1.0+(G1*M1**2)*(1.0-RHO12))
GO TO 36
200 KKK=1
RHO12=(T2*P1*W1)/(T1*P2*W2)
C
C THE IONIZATION EQUILIBRIUM CONSTANTS ARE DETERMINED HERE.
DO 95 J=1,S
GK=-23053.0*IPOT(J)/(4.573*T2)+(5.0/2.0)*ALOG10(T2)-6.49+ALOG10(12.0*GG(J)/G(J))
ICON(J)=10.0**GK
X(J)=SQRT(ICON(J)/(P2+ICON(J)))
95 CONTINUE
C
C THE POTENTIAL ENERGY FOR ENTHALPY DUE TO IONIZATION IS COMPUTED
C HERE.
CALL DELEI(X,S,W2,DELI,IPOT)
H21=H21-DELI
C
C IF GOOD AGREEMENT IS FOUND THE PROGRAM PROCEEDS TO THE ELECTRON
C CONCENTRATION CALCULATION; IF NOT, THE FINAL TEMPERATURE IS REDUCED
C AND A NEW ENTHALPY IS FOUND.
IF(H2.LT.H21) GO TO 250
T2=T2-25.0
GO TO 36
C
C THE ELECTRON CONCENTRATION IN NUMBER OF ELECTRONS PER CUBIC CENTI-
C METER IS FOUND HERE.
250 SUM=0.0
DO 98 J=1,S
  SUM=SUM+X(J)*N(J)
98 CONTINUE
  RH021=1.0/RH012
  IONCON=SUM/100.0
  IONCON=IONCON*6.023E+23/22.4E+03
  WRITE (3,501) T2
  WRITE (3,511) P2,RH021
  WRITE (3,502)
  WRITE (3,503)
  WRITE (3,504) N
  WRITE (3,505) IONCON
  WRITE (3,506)
100 FORMAT (I4)
101 FORMAT (2E18.8)
102 FORMAT (4F10.4)
103 FORMAT (6F10.4)
104 FORMAT (10F7.2)
105 FORMAT (E18.8)
400 FORMAT ('*1')
500 FORMAT (1X,'FOR A TEST SECTION PRESSURE OF ','F6.3,' ATMOS. AND MAC
1H NUMBER OF ','F6.3,' THE IDEAL TEMPERATURE IS ','F8.1,' DEGREES KEL
2VIN',/)
501 FORMAT (1X,'AFTER DISSOCIATION AND IONIZATION HAVE BEEN TAKEN INTO
1 CONSIDERATION, THE FINAL EQUILIBRIUM TEMPERATURE IS ','F7.1')
511 FORMAT (1X,'WITH A FINAL PRESSURE BEHIND THE SHOCK FRONT OF ','
1F6.2,' ATMOS., AND A FINAL DENSITY RATIO OF ','F6.2,/)
502 FORMAT(1X,'THE FINAL EQUILIBRIUM CONCENTRATION OF THE COMPONENTS A
1RE:')
503 FORMAT (6X,'O2',10X,'N2',10X,'CO2',10X,'A',10X,'NE',10X,'HE',11X,
1'O',11X,'N',10X,'CO',10X,'NO')
504 FORMAT (4X,F6.2,9F12.2,/)  
505 FORMAT(1X,'THE ELECTRON CONCENTRATION IS ','E9.4,' ELECTRONS PER CU
1BIC CENTIMETER')
506 FORMAT ('*1')
9999 CALL EXIT
SUBROUTINE KCOEF(T, COEF, MK, J, T2, EQCON)
DIMENSION T(10, 20), COEF(20), EQCON(10)
REAL MK(10)
JJ = MK(J) + 0.99999
DO 5 I = 1, JJ
T(J, I) = 1000.0 / T(J, I)
5 CONTINUE
T2 = 1000.0 / T2
DO 6 I = 1, JJ
IF (T(J, I) - T2) 8, 7, 6
7 EQCON(J) = COEF(I)
GO TO 10
8 N = I - 1
GO TO 9
6 CONTINUE
9 EQCON(J) = (COEF(N + 1) - COEF(N)) * (T(J, N) - T2) / (T(J, N) - T(J, N + 1)) + COEF(N)
10 IF (J .LT. 3) GO TO 11
EQCON(J) = EQCON(J) * 2.0
11 EQCON(J) = 10.0 ** EQCON(J)
T2 = 1000.0 / T2
DO 12 I = 1, JJ
T(J, I) = 1000.0 / T(J, I)
12 CONTINUE
RETURN
END

SUBROUTINE AIJBK(N, NU, C, CC, S, A, B, NG)
DIMENSION A(7, 7), B(7)
REAL N(10), NU(6, 10), NG
INTEGER C, CC, S
SUMNJ = 0.0
DO 30 J = 1, C
SUMA = 0.0
DO 40 I = CC, S
SUMA = SUMA + (NU(J, I) ** 2) * N(I)
40 CONTINUE
A(J,J) = N(J) + SUMAJJ

30 CONTINUE
DO 50 J = 1, C
DO 60 JJ = 1, C
IF (JJ .EQ. J) GO TO 60
A(J, JJ) = 0.0
DO 70 I = CC, S
A(J, JJ) = A(J, JJ) + NU(J, I) * NU(JJ, I) * N(I)
70 CONTINUE
60 CONTINUE
50 CONTINUE

SUMBJ = 0.0
DO 80 J = 1, C
DO 90 I = CC, S
SUMBJ = SUMBJ + NU(J, I) * N(I)
90 CONTINUE
B(J) = (N(J) + SUMBJ) / NG
80 CONTINUE
DO 100 J = 1, C
A(J, 7) = B(J)
A(7, J) = B(J)
100 CONTINUE
A(7, 7) = 0.0
RETURN
END

SUBROUTINE FUNG(N, Q, F, NU, C, CC, S, G, NG)
DIMENSION Q(6), F(6)
REAL N(10), NU(6, 10), NG
INTEGER C, CC, S
DO 10 J = 1, C
D = 0.0
DO 20 I = CC, S
F(J) = Q(J) - N(J) - (D + NU(J, I) * N(I))
D = D + NU(J, I) * N(I)
20 CONTINUE
10 CONTINUE
SUMNJ=0.0
DO 30 J=1,C
   SUMNJ=SUMNJ+N(J)
30 CONTINUE
SUMNI=0.0
DO 40 I=CC,S
   SUMNI=SUMNI+N(I)
40 CONTINUE
G=1.0-(SUMNJ+SUMNI)/NG
RETURN
END
SUBROUTINE ARG(B,F,G,C)
DIMENSION B(7),F(6)
INTEGER C,CC
DO 10 J=1,C
   B(J)=F(J)
10 CONTINUE
B(7)=G
RETURN
END
SUBROUTINE DISCOF(TH,ECOF,ME,J,T2,H)
DIMENSION ECOF(30),H(10),TH(10,30)
REAL ME(10)
M=ME(J)
DO 6 I=1,M
   IF (TH(J,I)-T2) 6,7,8
7 H(J)=ECOF(I)
   GO TO 10
6 CONTINUE
H(J)=(ECOF(N+1)-ECOF(N))*TH(J,N)-T2)/(TH(J,N)-TH(J,N+1))+ECOF(N)
10 CONTINUE
RETURN
END
SUBROUTINE DELEI(X,S,W2,DELI,IP)
DIMENSION X(10)
REAL IPOT(10)
INTEGER S
DELI=0.0
DO 10 J=1,S
DELI=DELI+X(J)*IPOT(J)*23.053/(W2*(X(J)+1.0))
10 CONTINUE
RETURN
END
VITA

Howard Sajon Joyner was born June 6, 1939, in Ft. Worth, Texas, the son of Howard W. and Arista A. Joyner. Upon graduating from Arlington High School, Arlington, Texas, in June, 1957, he received a cooperative scholarship with Chance Vought, Inc., Dallas, Texas, and entered Arlington State College.

In September, 1960, he entered The University of Texas at Austin and was awarded the B.S. degree in Physics in June, 1962, and the M.A. degree in January, 1964. While at the University he was employed as a Research Assistant in the Physics of Metastable Systems Laboratory sponsored by the Propulsion Science Division, Air Force Office of Scientific Research.

After employment with General Dynamics/Ft. Worth as a Nuclear Engineer, he entered the Graduate School of the University of Missouri at Rolla in September, 1964. As a Research Fellow at the Graduate Center for Materials Research of the Space Science Research Center of The University of Missouri he received the M.S. degree in Physics in January, 1967.

In 1969 he was selected to be listed in Who's Who in the South and Southwest. On June 15, 1969, he was married to Mary Ellen Yankoff.

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