REPORT 959

ONE-DIMENSIONAL FLOWS OF AN IMPERFECT DIATOMIC GAS

By A. J. EGERS, Jr.

SUMMARY

With the assumptions that Berthelot's equation of state accounts for molecular size and intermolecular force effects, and that changes in the vibrational heat capacities are given by a Planck term, expressions are developed for analyzing one-dimensional flows of a diatomic gas.

The special cases of flow through normal and oblique shocks in free air at sea level are investigated. It is found that up to a Mach number of 10 the pressure ratio across a normal shock differs by less than 6 percent from its ideal gas value; whereas at Mach numbers above the temperature rise is considerably below and hence the density rise is well above that predicted assuming ideal gas behavior. It is further shown that only the caloric imperfection in air has an appreciable effect on the pressures developed in the shock process considered. The effects of gaseous imperfections on oblique shock flows are studied from the standpoint of their influence on the lift and pressure drag of a flat plate operating at Mach numbers of 10 and 20. The influence is found to be small.

INTRODUCTION

A wide variety of problems in compressible flow has been solved on the assumption that air behaves as an ideal diatomic gas. This assumption is justified, provided the pressure and temperature range of interest is small and near atmospheric. It is an experimental fact, however, that when air is subjected to large changes in state at pressures and temperatures far removed from atmospheric, it ceases to obey the simple gas law and exhibits other properties not characteristic of an ideal gas. Consequently, flow processes in which air is subjected to these extreme conditions can be expected to depart from perfect gas behavior. It is known that such flows will be encountered in hypersonic wind tunnels and by aircraft flying at high supersonic airspeeds; hence, the nature and extent of this departure have become important considerations in aerodynamics.

Classical theories and experiments have shown that three properties of a real gas first cause it to exhibit characteristics unlike those of an ideal gas. These properties may be classified as thermal and caloric imperfections. Thermal imperfections in the form of intermolecular forces and molecular size effects are significantly manifest at low temperatures and high pressures. Changes in the vibrational heat capacities become an important caloric imperfection at relatively high temperatures. Circumstances under which effects of molecular dissociation and/or electronic excitation become important (e.g., temperatures appreciably above 5000° R) may be neglected for the present. Insofar as gases in equilibrium are concerned, it is usually sufficient to account for intermolecular force and molecular size effects with additional terms in the equation of state. Similarly, changes in the vibrational heat capacities of the molecules may be accounted for with a function of temperature in the expressions for the specific heats.

Tsien (reference 1) investigated the effects of gaseous imperfections on air flows using Van der Waals' state equation. Approximate solutions to the one-dimensional isentropic and normal shock equations were obtained. (Tsien points out two very early papers of limited scope on the subject by A. Busemann and W. J. Walker.) The Joule-Thomson effect was neglected in Tsien's analysis, however, thus introducing some error. Donaldson (reference 2) observed this error and found that the differential equations of motion could be integrated to yield one-dimensional isentropic flow equations, exact to the accuracy of Van der Waals' equation. A comparison of results obtained with these equations and the flow equations for a perfect gas indicated that appreciable error would be made if the latter expressions were used to predict aerodynamic phenomena involving high temperatures or high pressures.

A matter considered by Kantrowitz (reference 3) is the inability of a gas composed of polyatomic molecules to instantaneously adjust its internal energy to temperature changes at high temperatures. This time lag in equilibrium partition of energy occurs primarily in the vibrational energies of the molecules which, unlike the translational and rotational energies, require many collisions per molecule to become fully adjusted to a new temperature. As pointed out by Kantrowitz, for rapidly accelerating flows the resulting heat-capacity lag causes an entropy increase and hence a total-head decrease in a gas. The net effect may be made negligible, however, by decreasing the rate of change of temperature of the fluid with time. In the special case of flow through a normal shock wave, Bethe and Teller (reference 4) found that heat-capacity-lag effects caused the thickness of the shock to increase. (The wave is considered to extend over that portion of the fluid in which equilibrium partition of energy does not prevail.) As the Mach number upstream of the wave increases, however, the shock tends rapidly toward a sharp discontinuity. It may also be observed that, although heat-capacity lag influences flow within the shock, it does not alter the magnitude of the

---

1 This error is reported to have been subsequently corrected; however, the author is unaware of the publication.
entropy increase across the shock, as this is independent of the mechanism by which available energy is dissipated within the wave. These observations are important for they lend support to the simplifying assumptions that moderately accelerating flows may be treated as isentropic except in the presence of a shock wave, in which case the wave may be treated as a discontinuity and the properties on both sides calculated as if there were no heat-capacity lag.

In the present paper, one-dimensional flow equations are obtained with the aid of Berthelot's equation of state. This equation, rather than Van der Waals', is employed in order that somewhat better estimates of intermolecular force effects may be obtained. It is assumed that caloric imperfections may be accounted for with a Planck term in the expressions for the specific heats. The analysis covers both isentropic and plane-shock flows. Within the limitations of the assumptions, both exact and approximate flow equations are developed. The approximate expressions provide explicit solutions for all the important flow parameters, and are designed to utilize data available on the theoretical behavior of an ideal diatomic gas. (See, e.g., reference 5.)

SYMBOLS

- $a$: local speed of sound, feet per second
- $A$: nozzle cross-sectional area, square feet
- $b$: molecular size constant, cubic feet per slug
- $c$: intermolecular force constant, $\text{R} \text{ feet to the fifth per slug}$, second squared
- $c_p$: specific heat at constant pressure, foot-pounds per slug, $\text{R}$
- $c_v$: specific heat at constant volume, foot-pounds per slug, $\text{R}$
- $e$: base of natural logarithms, 2.718...
- $\ln e$: logarithm to base $e$
- $M$: Mach number (ratio of local velocity to local velocity of sound)
- $P$: absolute pressure, pounds per square foot
- $R$: gas constant ($1715 \text{ ft-lb per slug} \text{ R}$ for air), foot-pounds per slug $\text{R}$
- $T$: absolute temperature, $\text{R}$
- $u$: internal energy, foot-pounds per slug
- $V$: local velocity, feet per second
- $v$: specific volume ($\frac{1}{\rho}$) cubic feet per slug
- $w$: external work performed, foot-pounds per slug
- $\gamma$: ratio of specific heats ($c_p/c_v$)
- $\rho$: mass density, slugs per cubic foot
- $\theta$: molecular vibrational energy constant, $\text{R}$

SUBSCRIPTS

- $s$: stagnation conditions
- $i$: conditions upstream of shock wave
- $d$: conditions downstream of shock wave
- $i$: ideal gas quantities

SUPERSCRIPTS

- *: quantities at the nozzle throat
- ′: quantum-mechanical functions

ANALYSIS

It will be assumed throughout the analysis that the gas exhibits no heat-capacity lag. Shock-free flows are considered isentropic, and flow through plane shock waves is assumed to be adiabatic. Justification for the first two assumptions is discussed in the Introduction. The extent to which plane shock processes, particularly at high Mach numbers, deviate from adiabatic behavior is left for future investigation.

Berthelot’s equation of state is employed in two forms, depending upon the desired range of applicability. In the development of equations for investigating flows over a wide range of Mach numbers, temperatures, and pressures, the state equation is used in its exact form

$$P = \frac{\rho RT}{1 - b\rho} \frac{c_p^3}{T}$$

where $b$ is the molecular size constant and $c$ is the intermolecular force constant. It will be noted that equation (1) differs from Van der Waals' equation by a factor of $1/T$ in the intermolecular force term. The introduction of this factor yields a variation of intermolecular force with temperature which is in accordance with experiment. (See, e.g., reference 6.) Thus, as pointed out in reference 7, close agreement between theoretical and experimental values of compressibility of gases is obtained.

In the derivation of approximate flow equations an expression of the form

$$P = \rho RT \left( 1 + b\rho - \frac{c_p^3}{RT^2} \right)$$

is employed. This equation is, of course, a first-order approximation to equation (1).

FLOW OF A DIATOMIC GAS OBEYING BERTHELOT'S EQUATION OF STATE

Isentropic flow of a Berthelot gas may be studied with the aids of the differential isentropic expansion equation,

$$du + dw = \left( \frac{\partial u}{\partial v} \right)_{\gamma} d\left( \frac{1}{\rho} \right) + \left( \frac{\partial u}{\partial T} \right)_{\rho} dT + Pd\left( \frac{1}{\rho} \right) = 0$$

where

$$\left( \frac{\partial u}{\partial v} \right)_{\gamma} = c_v$$

and the Joule-Thomson effect is given by

$$\left( \frac{\partial u}{\partial P} \right)_\rho = T \left( \frac{\partial P}{\partial T} \right)_\rho - P = \frac{2c_p^2}{T}$$

Combining these expressions and substituting the value of $P$ from equation (1) yields

$$c_v dT - \frac{c}{T} d\rho - \frac{RT}{\rho (1 - b\rho)} d\rho = 0$$

Now the differential expression for $c_v$ is

$$\left( \frac{\partial c_v}{\partial v} \right)_\gamma = T \left( \frac{\partial P}{\partial T} \right)_\rho$$.
which, upon substituting from equation (1), may be integrated to give

\[ \frac{dS}{T} = c_s' \left( 1 + (\gamma - 1) \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta(T)} - 1}{[1 - e^{\theta(T)}]^2} \right) \]  

(7)

where \( c_s' \) is a function which describes the quantum-mechanical variations of \( c_s \) with temperature. The second term on the right of equation (6) represents the effects of gaseous imperfections on \( c_s \).

The function chosen for \( c_s' \) is determined by the molecular structure of the gas under consideration and the temperature range over which accurate predictions of \( c_s' \) are desired. For aerodynamic purposes, diatomic gases are of primary interest. The important temperature range extends from liquefaction temperatures to several thousand degrees Rankine. A relatively simple function may be written for \( c_s' \) in this case, as the number of translational and rotational degrees of freedom is constant, and only the variation with temperature of the vibrational heat capacity need be considered. This function is

\[ c_s' = c_t \left( 1 + (\gamma - 1) \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta(T)} - 1}{[1 - e^{\theta(T)}]^2} \right) \]  

(7)

The second term in the brackets, essentially a Planck term, accounts for the vibrational contribution to the specific heat at constant volume. The assumption is that the molecules of the gas behave like linear harmonic oscillators insofar as the vibrational degrees of freedom are concerned. (See reference 8.)

An expression governing isentropic expansion of an imperfect diatomic gas may now be obtained by substituting equations (5) and (7) into equation (5) and integrating from stagnation to static states. Since

\[ d \left( \frac{P}{T} \right) = \frac{T d\rho - 2 \rho dT}{T^2} \]

there results the relation

\[ c_s \ln \left( \frac{T}{T_0} \right) + R \ln \frac{\rho_0 (1 - b \rho)}{\rho (1 - b \rho_0)} - c_s \left( \frac{\rho T}{T_0} - \frac{\rho_0}{T_0} \right) + R \ln \left[ \frac{\rho_0 (1 - b \rho)}{\rho (1 - b \rho_0)} \right] = \]

(8)

In order to determine the Mach number of a stream, it is necessary to find the velocity of flow and speed of sound in the stream. These quantities may be found by employing the one-dimensional energy equation,

\[ du + d(P\nu) + \nu dV = \left( \frac{\partial u}{\partial T} \right)_{\rho} \left( \frac{1}{\rho} \right) dt + \left( \frac{\partial u}{\partial T} \right)_{\rho} \left( \frac{F}{\rho} \right) + \nu dV = 0 \]

(9)

Substituting equations (1), (4), (6), and (7) into equation (9) and integrating from stagnation to static temperature and density yields the velocity

\[ V = \left[ c_t \left( T_0 - T \right) + \frac{R \theta}{[1 - e^{\theta(T)}]} \right] \left( 1 + 2c \left( \frac{T}{T_0} - \frac{\rho_0}{\rho} \right) + \frac{P_0 - P}{\rho_0 - \rho} \right) \]

(10)

The corresponding speed of sound is determined by substituting equations (1), (5), (6), and (7) into the general equation

\[ a^2 = \frac{dP}{d\rho} = \left( \frac{\theta}{\rho} \right) + \left( \frac{\theta}{\rho} \right) \frac{dT}{d\rho} \]

The resulting expression is

\[ a^2 = \frac{RT}{(1 - b \rho)^2} - 2c + \frac{\rho T \left[ \frac{c_t}{\rho_0} + \frac{R}{\rho (1 - b \rho)} \right]}{1 + (\gamma - 1) \left[ \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta(T)} - 1}{[1 - e^{\theta(T)}]^2} + \frac{2c \rho}{R T^2} \right]} \]

(11)

Combining equations (10) and (11) yields the following equation for the Mach number

\[ M^2 = \left[ \frac{1}{\gamma - 1} \left( \frac{P}{P_0} \right)^2 \left( \frac{\theta}{T} \right)^2 \left( \frac{1}{1 - e^{\theta(T)}} \right)^2 \right] + \frac{1}{1 + (\gamma - 1) \left( \frac{\theta}{T} \right)^2 \left( \frac{1}{1 - e^{\theta(T)}} \right)^2 + \frac{2c \rho}{R T^2}} \]

(12)

The specific heats and the ratio of specific heats are readily obtainable for a diatomic gas obeying Berthelot's state equation. The specific heat at constant volume \( c_v \) is found by substituting equation (7) into equation (6), thus yielding

\[ c_v = c_t \left[ 1 + (\gamma - 1) \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta(T)} - 1}{[1 - e^{\theta(T)}]^2} + \frac{2c \rho}{R T^2} \right] \]

(13)

The specific heat at constant pressure \( c_p \) is obtained by substituting equations (1) and (13) into the reciprocity relation

\[ c_p = c_v - T \left( \frac{\partial P/\partial T}{\partial P/\partial \rho} \right)_\rho \]

and setting

\[ c_{t \rho} = c_{p \rho} - R \]

(14)
The resulting expression for \( c_p \) is

\[
 c_p = c_{p_1} \left[ 1 + \frac{\gamma - 1}{\gamma} \left\{ \left( \frac{\gamma}{T} \right)^{\frac{2}{\gamma - 1}} \frac{e^{\frac{4\theta T}{T}}}{1 - e^{\frac{4\theta T}{T}}} \left[ 1 + \frac{\frac{2b_p}{1-b_p} + \frac{c_p}{2RT_1}}{\frac{1}{(1-b_p)^2} \frac{2c_p}{RT_1}} \right] \right\} \right] \quad (15)
\]

The ratio of specific heats \( \gamma \) follows directly, of course, from equations (13) and (15) and may be written

\[
 \gamma = \gamma_1 \frac{1 + \frac{\gamma - 1}{\gamma} \left\{ \left( \frac{\gamma}{T} \right)^{\frac{2}{\gamma - 1}} \frac{e^{\frac{4\theta T}{T}}}{1 - e^{\frac{4\theta T}{T}}} \left[ 1 + \frac{\frac{2b_p}{1-b_p} + \frac{c_p}{2RT_1}}{\frac{1}{(1-b_p)^2} \frac{2c_p}{RT_1}} \right] \right\}}{1 + (\gamma_1 - 1) \left\{ \left( \frac{\theta}{T} \right)^{\frac{2}{\gamma - 1}} \frac{e^{\frac{4\theta T}{T}}}{1 - e^{\frac{4\theta T}{T}}} \left[ 1 + \frac{\frac{2b_p}{1-b_p} + \frac{c_p}{2RT_1}}{\frac{1}{(1-b_p)^2} \frac{2c_p}{RT_1}} \right] \right\}} \quad (16)
\]

A matter of special interest in the study of channel flows is the variation of Mach number with cross-sectional area of the channel. The relation between these two quantities is most conveniently determined from the ratio of cross-sectional area at the sonic velocity station (the station of minimum area for any gas, as pointed out by Tsien) to cross-sectional area at a station of arbitrary Mach number. The continuity equation yields this ratio in the form

\[
 A = A_0 \left( \frac{\rho}{\rho_0} \right)^{\frac{a}{\gamma}} \quad (17)
\]

With the aid of this equation and equations (1), (8), (11), and (12), the area ratio corresponding to a particular Mach number may be determined from a knowledge of the ideal gas specific heats, characteristic constants of the gas (i.e., \( b, c, \) and \( d \)), and, for example, the stagnation conditions. In general, however, this computation cannot be carried out entirely analytically. For example, it is seen from equation (8) that none of the variables can be explicitly determined; hence, a final solution for any single variable must be obtained graphically or by equivalent means.

In order to relate the fluid properties on the two sides of a normal shock wave, it is convenient to integrate equation (9), the energy equation, across the wave. The resulting expression is

\[
 \left( \frac{V_1^2 - V_i}{2} \right) + c_i (T_2 - T_i) - \left( \frac{2c_p}{T_2} - \frac{2c_p}{T_1} \right) + \left( \frac{P_2 - P_i}{\rho_2 - \rho_i} \right) \left( \frac{\theta}{T_i} \right)^{\frac{2}{\gamma - 1}} \left[ \left( \frac{\gamma}{T} \right)^{\frac{2}{\gamma - 1}} \frac{e^{\frac{4\theta T}{T}}}{1 - e^{\frac{4\theta T}{T}}} \left[ 1 + \frac{\frac{2b_p}{1-b_p} + \frac{c_p}{2RT_1}}{\frac{1}{(1-b_p)^2} \frac{2c_p}{RT_1}} \right] \right] = 0 \quad (18)
\]

Continuity of flow and conservation of momentum must also be satisfied across the wave. These requirements may be expressed analytically in the familiar forms, respectively,

\[
 \rho_1 \frac{V_i}{2} = \rho_2 V_2 \quad (19)
\]

and

\[
 \rho_1 V_i^2 - \rho_2 V_2^2 = P_2 - P_1 \quad (20)
\]

Equations (18) through (20) provide the additional information necessary to determine the flow through a normal shock wave. Here again, however, final solutions for certain of the unknown flow parameters are most conveniently obtained graphically.

**APPROXIMATE FLOWS OF AN IMPERFECT DIATOMIC GAS**

This part of the study is concerned with first-order deviations of one-dimensional gas flows from the behavior of an ideal gas. With this restriction, explicit solutions can be obtained for all the important flow parameters. Equation (2) will, of course, be employed as the equation of state. A simplification is also allowed in the temperature function for the vibrational contribution to the specific heats, since the specific heats are restricted to vary only in the first order from their ideal gas values. In this case only large values of \( \theta/T \) are considered and the Planck term may be approximated by

\[
 \left( \frac{\theta}{T} \right)^{\frac{2}{\gamma - 1}} \frac{e^{\frac{4\theta T}{T}}}{1 - e^{\frac{4\theta T}{T}}} \approx \left( \frac{\theta}{T} \right)^{\frac{2}{\gamma - 1}} e^{-\frac{\theta T}{T}} \quad (21)
\]

Equation (8) may now be reduced to the form

\[
 \ln \left[ \left( \frac{T}{T_0} \right)^{\gamma - 1} \left( \frac{\rho}{\rho_0} \right) \right] = b_0 \left( \rho_0 - 1 \right) + c_p \left[ \frac{1}{RT_0^2} \left( \frac{T}{T_0} \right)^{\gamma - 1} - 1 \right] + \left( \frac{\theta}{T_0} + 1 \right) e^{-\frac{\theta T_0}{T}} - \left( \frac{\theta}{T_0 + 1} \right) e^{-\frac{\theta T_0}{T}} \quad (22)
\]

This equation can be readily solved for \( \rho/\rho_0 \) in terms of \( T/T_0 \), retaining only terms of the proper order, thus yielding

\[
 \frac{\rho}{\rho_0} = \left( \frac{T}{T_0} \right)^{\gamma - 1} \left[ 1 - b_0 \left( \frac{T}{T_0} \right)^{\gamma - 1} - 1 \right] + c_p R T_0^2 \left( \frac{T}{T_0} \right)^{\gamma - 1} - 1 \]  
\[
 \left( \frac{\theta}{T_0} + 1 \right) e^{-\frac{\theta T_0}{T}} + \left( \frac{\theta}{T_0} \right)^{\frac{2}{\gamma - 1}} e^{-\frac{\theta T_0}{T}} \right] \quad (22)
\]

By solving for \( T/T_0 \) in a similar manner, there is obtained

\[
 T = T_0 \left( \frac{\rho}{\rho_0} \right)^{\gamma - 1} \left[ 1 + \left( \gamma - 1 \right) b_0 \left( \frac{\rho}{\rho_0} - 1 \right) + c_p R T_0^2 \left( \frac{\rho}{\rho_0} \right)^{\gamma - 1} - 1 \right] + \left( \frac{\theta}{T_0} + 1 \right) e^{-\frac{\theta T_0}{T}} + \left( \frac{\theta}{T_0} \right)^{\frac{2}{\gamma - 1}} e^{-\frac{\theta T_0}{T}} \right] \quad (23)
\]
A relation between the pressure and density ratios for isentropic expansion is obtained by combining equation (2) with equation (23). The resulting expression is

\[
\frac{P}{P_0} = \left(\frac{\rho}{\rho_0}\right)^{\gamma_t-2} \frac{c_{p0}}{RT_0} \left[\left(\frac{\rho}{\rho_0}\right)^{\gamma_t-1} - \left(\frac{\rho}{\rho_0}\right)^{-1} \right] e^{-\omega/T_0} \left(\frac{\theta}{T_0}\right)^{\gamma_t-1} + \left(\frac{\theta}{T_0}\right)^{\gamma_t-1} e^{-\omega/T_0}
\]

Equations (22) through (24) are useful for determining the nature and extent of small departures from ideal gas behavior of a diatomic gas undergoing isentropic changes in state.

Isentropic relations will now be obtained between pressure, temperature and density ratios, and the stream Mach number. In order to do this, it is convenient to reduce equation (12) to a form consistent with the first-order approximations. Performing this operation yields

\[
B_1(M) = 2 \left[\left(\frac{P}{P_0}\right)_t - \left(\frac{P}{P_0}\right)_i \right] + \frac{\gamma_t-1}{\gamma_t} \left[\left(\frac{\theta}{T_0}\right)_t - \left(\frac{\theta}{T_0}\right)_i \right]
\]

\[
C_1(M) = \frac{\gamma_t}{\gamma_t-1} \left[\left(\frac{\rho}{\rho_0}\right)_t - \left(\frac{\rho}{\rho_0}\right)_i \right] + 3 \frac{\gamma_t-1}{\gamma_t} \left[\left(\frac{\rho}{\rho_0}\right)_t - \left(\frac{\rho}{\rho_0}\right)_i \right]
\]

\[
D_1 \left(\frac{\theta}{T_0}, M\right) = \frac{\gamma_t-1}{\gamma_t} \left[1 - \frac{\gamma_t}{\gamma_t-1} \left(\frac{\theta}{T_0}\right) \left(\frac{T_0}{T_0}\right)_t \left(\frac{T_0}{T_0}\right)_i - 1\right]
\]

where \((T/T_0)_t\), \((\rho/\rho_0)_t\), and \((P/P_0)_t\) are unique functions of the Mach number \(M\). (These functions and all other ideal gas expressions employed in the analysis are included in Appendix A.) The density and pressure ratios are obtained by substituting equations (23) and (24), respectively into equation (26), thus yielding

\[
\frac{\rho}{\rho_0} = \left(\frac{\rho}{\rho_0}\right)_i \left[1 + B_1(M) \left(\frac{\rho}{\rho_0}\right)_i + C_1(M) \frac{c_{p0}}{RT_0^3} + D_1 \left(\frac{\theta}{T_0}, M\right) \left(\frac{\theta}{T_0}\right) e^{-\omega/T_0}\right]
\]

where

\[
B_1(M) = \frac{\gamma_t}{\gamma_t-1} B_1(M)
\]

\[
C_1(M) = 2 \left[1 - \left(\frac{\rho}{\rho_0}\right)_i \right] + \frac{\gamma_t}{\gamma_t-1} C_1(M)
\]

and

\[
D_1 \left(\frac{\theta}{T_0}, M\right) = \left(\frac{\theta}{T_0}\right)_t \left[1 + D_1 \left(\frac{\theta}{T_0}, M\right) \left(\frac{\theta}{T_0}\right) e^{-\omega/T_0}\right]
\]

Similarly

\[
\frac{P}{P_0} = \left(\frac{P}{P_0}\right)_i \left[1 + B_1(M) \left(\frac{\rho}{\rho_0}\right)_i + C_1(M) \frac{c_{p0}}{RT_0^3} + D_1 \left(\frac{\theta}{T_0}, M\right) \left(\frac{\theta}{T_0}\right) e^{-\omega/T_0}\right]
\]

It may be noted that equations (26), (28), and (30) can be rearranged to give the Mach number in terms of \(T/T_0\), \(\rho/\rho_0\), and \(P/P_0\), respectively.

Expressions for the specific heats and the ratio of specific heats are derived by reducing equations (13), (15), and (16)
to conform to the first-order deviation theory. Performing this operation yields
\[ c_1 = c_1 \left( 1 + \left( \frac{\gamma - 1}{\gamma} \right) \frac{\rho}{T} \right) e^{-\omega T} + \frac{2 \rho T}{R T_0} \] (32)
\[ c_2 = c_2 \left( 1 + \left( \frac{\gamma - 1}{\gamma} \right) \frac{\rho}{T} \right) e^{-\omega T} + \frac{6 \rho T}{R T_0} \] (33)
and
\[ \gamma = \gamma \left( 1 - \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{T}{T_0} \right) e^{-\omega T} + \left( \frac{T}{T_0} \right)^2 \right) \] (34)

It is observed that \( c_1, c_2, \) and \( \gamma \) are independent of molecular size within the limitations of the theory. This fact appreciably simplifies the determination of the characteristic gas constants \( c \) and \( \delta \).

The calculation of cross-sectional area of a nozzle for isentropic expansion of an approximate Berthelot gas can now be made. For this purpose it is convenient to write equation (17) as follows:
\[ \frac{A^*}{A} = \left( \frac{\rho^*}{\rho_0} \right) \left( \frac{a^*}{a_0} \right) M \]

The local speed of sound \( a \) can be obtained directly from equation (11) by retaining only first-order terms, thus
\[ a = \sqrt{\gamma RT} \left[ 1 + \frac{b_1}{T_1} \frac{c_1 p}{R T_0^2} \frac{(\gamma - 1)^2}{2 \gamma} \left( \frac{T_0}{T} \right)^2 e^{-(\omega T)} \right] \] (35)

Hence, substituting equations (28), (29), and (35) into equation (17) in the above form yields for \( A^*/A \),
\[ \frac{A^*}{A} = \left( \frac{\rho^*}{\rho_0} \right) \left( \frac{a^*}{a_0} \right) M \]

where
\[ B_4(M) = \frac{\gamma + 1}{2(\gamma - 1)} \left| B_1(M) - B_1(M^*) \right| \]
\[ C_4(M) = \frac{\gamma + 1}{2(\gamma - 1)} \left| C_1(M) - C_1(M^*) \right| + \frac{\gamma_1 - \gamma_2}{\gamma_1} \left[ \left( \frac{\rho_0}{\rho_0} \right) - \left( \frac{\rho_0}{\rho_0} \right) \right] \]
\[ D_4 \left( \frac{\theta}{T_0}, M \right) = \frac{\gamma + 1}{2(\gamma - 1)} \left[ D_1 \left( \frac{\theta}{T_0}, M \right) - D_1 \left( \frac{\theta}{T_0}, M^* \right) \right] + e^{-(\omega T)} \left[ \left( \frac{T}{T_0} \right)^2 - \frac{1}{2 \gamma} \left( \frac{T_0}{T} \right)^2 \right] \] (37)

and \( (A^*/A) \) is the explicit function of Mach number given in Appendix A.

Flow through a normal shock wave will now be considered. The temperature, density, and pressure ratios across a normal shock wave may be related to the ideal gas expressions for these quantities by simplifying and rewriting equation (18) as follows:
\[ \frac{V_2^2 - V_1^2}{2} = c_1 T_1 \left( 1 - \frac{T_1}{T_2} \right) \left( \frac{\rho_2}{\rho_1} \right) \left( \frac{p_2}{p_1} \right) \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ e^{-(\omega T)} - e^{-(\omega T)} \right] \] (38)

Substituting equations (2), (19), and (20) into equation (38), dividing through by equation (35), and solving for the temperature ratio yields the expression:
\[ \frac{T_2}{T_1} = \frac{T_2}{T_1} \left[ 1 + \frac{1}{G(M)} \right] \left( B_4(M) \left( \frac{\theta}{\theta} \right) \left( \frac{\theta}{\theta} \right) \left( \frac{\theta}{\theta} \right) \right] \]
where
\[ G(M) = 2 \left( \frac{\rho_0}{\rho_0} \right) \left( 1 + \frac{1}{\gamma_1 M^2} \right) \]
\[ B_4(M) = \left( \frac{\rho_0}{\rho_0} \right) + G(M) \left( \frac{T_1}{T_2} \right) \left( \frac{\rho_1}{\rho_1} \right) + \frac{2 \gamma_1}{\gamma_1 - 1} \left( \frac{T_1}{T_2} \right) \left( \frac{\rho_1}{\rho_1} \right) \left( \frac{p_1}{p_1} \right) \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \]
\[ C_4(M) = G(M) \left( \frac{T_1}{T_2} \right) \left( \frac{\rho_1}{\rho_1} \right) + \frac{2 \gamma_1}{\gamma_1 - 1} \left( \frac{T_1}{T_2} \right) \left( \frac{\rho_1}{\rho_1} \right) \left( \frac{p_1}{p_1} \right) \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \]
\[ D_4 \left( \frac{\theta}{T_1}, M \right) = G(M) \left[ \frac{T_1}{T_2} \right] \left( 1 - \left( \frac{\rho_1}{\rho_1} \right) \left( \frac{T_1}{T_2} \right) \right) \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \left( \frac{T_1}{T_2} \right) \left( \frac{\theta}{\theta} \right) \left[ 1 - \left( \frac{p_1}{p_1} \right) \right] \] (40)
In order to obtain the relation for the density ratio \( \rho_2/\rho_1 \), it is convenient to write equation (39) in the form
\[
\frac{T_2}{T_1} = \left(\frac{T_{12}}{T_1}\right) \left(1 + \epsilon_T\right)
\]  
(41)
where \( \epsilon_T \) includes all the first-order correction terms in equation (40). Combining this expression and equations (2), (19), and (35) with equation (38) yields the relation
\[
\frac{\rho_2}{\rho_1} = \left(\frac{\rho_2}{\rho_1}\right) \left[1 - \left(\frac{\rho_2}{\rho_1}\right) - \frac{1}{M_1^2} \left(B_0(M_1) b_{\rho_1} + C_b(M_1) \frac{\rho_o}{RT_1^3} \right) \right] + D_b \left(\frac{\theta}{T_1}, M_1\right) \left(\frac{\theta}{T_1}\right) e^{-(\beta T_1)} - \frac{1}{\gamma_1 - 1} \left(\frac{T_2}{T_1}\right) \epsilon_T
\]
(42)
where
\[
B_0(M_1) = \frac{T_2}{T_1} \left[\frac{1}{\gamma_1 - 1} - \frac{1}{\gamma_1 (\gamma_1 - 1)}\right]
\]
and
\[
C_b(M_1) = \frac{1}{\gamma_1} \left[\frac{T_2}{T_1} - 1\right] + 3 \left[\left(\frac{\rho_o}{\rho_1}\right) - 1\right]
\]
(43)

As with the temperature ratio, it will be convenient to write equation (42) in the form
\[
\frac{\rho_2}{\rho_1} = \left(\frac{\rho_2}{\rho_1}\right) \left[1 - \epsilon_\rho + \epsilon_\rho'\right]
\]
(44)
where \( \epsilon_\rho \) is the sum of all the first-order correction terms. The pressure ratio across a normal shock wave is now obtained by combining equations (19), (20), (35), and (44) to provide the relation
\[
\frac{P_2}{P_1} = \left(\frac{P_2}{P_1}\right) \left[1 + \gamma_1 M_i^2 \left(\frac{P_1}{P_2}\right) \left(\epsilon_\rho + \eta - \gamma_1 \right)\right]
\]
(45)
in which
\[
\eta = -b_{\rho_1} - \frac{cp_o}{RT_1^3} \left(\frac{1}{\gamma_1} + \frac{T_2}{T_1} \right) \left(\frac{\theta}{T_1}\right) e^{-(\beta T_1)}
\]
(46)

The additional information needed to define the flow through a normal shock wave is the Mach number \( M_2 \) on the downstream side of the wave. This Mach number may be obtained with the continuity equation
\[
\frac{M_2}{M_1} = \left(\frac{M_2}{M_1}\right) \left(1 + \epsilon_\eta - \epsilon_\rho\right)
\]
(47)

where
\[
\epsilon_\eta = -\frac{\gamma_1}{2} b_{\rho_1} \left[1 - \left(\frac{\rho_2}{\rho_1}\right)\right] + \frac{T_1}{\gamma_1} \frac{cp_o}{RT_1^3} \left[1 - \left(\frac{\rho_o}{\rho_1}\right)\right] \left(\frac{T_2}{T_1}\right) e^{-(\beta T_1)} - \frac{1}{\gamma_1 - 1} \left(\frac{T_2}{T_1}\right) \epsilon_T
\]
(48)

Stagnation conditions downstream of the wave may be related to stagnation conditions upstream of the wave with the three identities
\[
\frac{P_2}{P_1} = \left(\frac{P_2}{P_1}\right) \left(\frac{P_1}{P_0}\right) \left(\frac{P_0}{P_2}\right)
\]
(49)
and
\[
\frac{\rho_2}{\rho_1} = \left(\frac{\rho_2}{\rho_1}\right) \left(\frac{\rho_o}{\rho_1}\right) \left(\frac{\rho_o}{\rho_2}\right)
\]
(50)

\[
\frac{T_2}{T_1} = \left(\frac{T_2}{T_1}\right) \left(\frac{T_1}{T_0}\right) \left(\frac{T_0}{T_2}\right)
\]
(51)
in which all terms of the right-hand members are given in previously developed expressions.

It is important to note that the normal shock expressions are applicable to the study of oblique shock flows. For example, equations (39) through (44) may be employed directly by substituting \( M_1 \sin \beta \) for \( M_1 \) wherever it occurs. In order to determine \( M_2 \), however, it is convenient to have a relation between the wave angle \( \beta \) and the stream deflection angle \( \delta \). This relation may be obtained by combining the momentum and continuity equations for flow through an oblique shock (reference 9) to yield the expression
\[
\frac{P_2}{P_1} - 1 = \frac{b_{\rho_1}}{\rho_1} \cot \beta \cot \delta + 1
\]
(52)
which may be written
\[
\cot \delta = \tan \beta \left[\gamma_1 M_i^2 (1 - \eta) \left(\frac{P_2}{P_1}\right) - 1\right]
\]
(53)

The complex manner in which gaseous imperfections influence general one-dimensional-flow processes precludes the detailed consideration, here, of more than two flows of aerodynamic interest. Before discussing these flows, it may be worth while to establish more definitely the conditions under which imperfections in air can alter its dynamical behavior from that predicted on the assumption that ideal gas laws are obeyed. These conditions are easily deduced from the

\section*{DISCUSSION AND CONCLUSIONS}

The complex manner in which gaseous imperfections influence general one-dimensional-flow processes precludes the detailed consideration, here, of more than two flows of aerodynamic interest. Before discussing these flows, it may be worth while to establish more definitely the conditions under which imperfections in air can alter its dynamical behavior from that predicted on the assumption that ideal gas laws are obeyed. These conditions are easily deduced from the
equations employed in the analysis and a knowledge of the characteristic gas constants. They may be summarized as follows:

1. The occurrence of temperatures in excess of 800° R, in which case the specific heats change appreciably.
2. The occurrence of densities in excess of 10 times sea level atmospheric, in which case the molecules occupy an appreciable fraction of the available volume.
3. The occurrence of sufficiently high pressures and low temperatures to cause the intermolecular forces to be appreciable.

One additional observation should be made concerning the integrated effect of these phenomena on a particular flow process. This is that the several imperfections frequently counteract each other (note, e.g., the state equation and equations (24), (26), and (27)), and thus alter certain flow parameters only slightly from their ideal gas values.

The special cases of flow through normal and oblique shocks in free air (NACA standard atmospheric conditions at sea level) will now be considered. The pressure and temperature ratios across a normal shock have been calculated for Mach numbers from 1 to 10 using equations (1), (11), (18), (19), and (20). In this case the terms containing \( b \) and \( c \) are extremely small (it is easily shown that they could, in fact, be neglected), and it is sufficiently accurate to use the values for these constants given in Appendix B.

The pressure rise so determined is shown in figure 1 as a function of Mach number, and it is seen that it differs by less than 6 percent from the ideal gas value up to the maximum Mach number of 10. This behavior might be anticipated from the ideal gas equation for the pressure ratio (Appendix A) which is relatively insensitive to variations in \( \gamma \) at high Mach numbers. The corresponding temperature rise across a normal shock is illustrated in figure 2. Here it is observed that the effect of increase in specific heats appreciably reduces the temperature ratio below the ideal gas value at the higher Mach numbers.

In view of the fact that the changes with temperature of the specific heats of air do not strongly influence the pressure rise across a normal shock, up to Mach numbers of 10, it follows that corresponding pressure effects in flow through oblique shocks will also be small, provided the Mach number of the component of velocity normal to the wave is below 10. This suggests, within the limitations observed, that the effect of variable specific heats on those aerodynamic

---

**Figure 1.** Variation of pressure ratio across a normal shock wave with Mach number. (Initial state—NACA standard atmosphere at sea level.)

**Figure 2.** Variation of temperature ratio across a normal shock wave with Mach number. (Initial state—NACA standard atmosphere at sea level.)
characteristics essentially independent of viscosity may be small for some shapes. (Epstein’s findings in reference 11, concerning hypersonic flows about bodies, pertain to much higher Mach numbers than those considered here.) The extent to which this is correct has been investigated for the simplest shape, a flat plate. Pressures on the upper surface of the plate were determined, assuming Prandtl-Meyer flow about the leading edge, and pressures on the lower surface were found with equations (45) (replacing \( M_i \) with \( M_i \sin \beta \)) and (52). These data and the corresponding lift and pressure drag coefficients of the plate were calculated for Mach numbers of 10 and 20, and for angles of attack from 0° to 24° and 13°, respectively. A comparison of the coefficients with those obtained assuming ideal gas flow over both the lower and upper surfaces showed that the effect of variable specific heats is very small. (For example, the force coefficients are smaller in the case of the imperfect gas but never by more than 3 percent, even at the highest angles of attack.) This result is not justification for assuming ideal gas behavior to calculate the high Mach number aerodynamic characteristics of arbitrary shapes, other effects such as specific heat lag being neglected; but it does indicate that the assumption is justifiable for certain shapes on which the important pressure forces are obtained through oblique or normal shock compression.

Ames Aeronautical Laboratory,
National Advisory Committee for Aeronautics,
APPENDIX A

IDEAL GAS EQUATIONS

The following are ideal gas equations used in the analysis of approximate flows of an imperfect diatomic gas:

ISENTROPIC FLOW EQUATIONS

\[
\left( \frac{P}{P_0} \right) = \left( \frac{\rho}{\rho_0} \right)^{-\gamma} = \left( 1 + \gamma - 1 \frac{1}{2} M^2 \right)^{-\frac{1}{\gamma-1}}
\]

\[
\left( \frac{\rho}{\rho_0} \right) = \left( \frac{T}{T_0} \right)^{-\frac{1}{\gamma-1}} = \left( 1 + \gamma - 1 \frac{1}{2} M^2 \right)^{-\frac{1}{\gamma-1}}
\]

\[
\left( \frac{T}{T_0} \right) = \left( \frac{P}{P_0} \right)^{\frac{1}{\gamma-1}} = \left( 1 + \gamma - 1 \frac{1}{2} M^2 \right)^{\frac{1}{1-\gamma}}
\]

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

APPENDIX B

DETERMINATION OF CHARACTERISTIC GAS CONSTANTS FOR AIR

Numerical values for the characteristic gas constants \( b \) and \( c \) may be determined from a knowledge of the critical pressure and temperature of a gas. Values determined in this manner are, however, generally less accurate in a particular range of temperatures and pressures than is desired. Consequently, it is often advantageous to fix \( b \) and \( c \) such that theoretical and experimental values of the primary parameters \( c_p, \gamma \) and compressibility (i.e., \( P/\rho \)) are in good agreement in the range of interest. This method is the more suitable of the two for most aerodynamic studies as the variations in pressure and temperature are limited; hence, it has been employed in this paper to determine \( b \) and \( c \), as well as \( \theta \), for air. It is sufficient for the illustrative applications presented here to determine the former constants only for the approximate flow equations. Separate values of \( \theta \) are found for the exact and approximate Planck terms.

As pointed out previously (note the development of approximate expressions for \( c_p, c_v, \) and \( \gamma \)), it is a simple matter to obtain the characteristic gas constants appearing in the approximate flow equations. In this example, \( c \) and \( \theta \) were chosen first to give agreement between experimental and theoretical values of \( c_p \) and \( \gamma \), the latter values being calculated from equations (33) and (34), respectively. Data on the variation of these quantities with pressure and temperature at high temperatures were obtained from references 12 through 19. A comparison of these data with theory, setting

\[ c = 2.25 \times 10^8 \text{ ft}^2/\text{slug, sec}^2 \text{ and } \theta = 5800 \text{ R, is shown in figures 3 and 4 for pressures of 0 and } 144 \times 10^5 \text{ pounds per square foot absolute. The agreement is observed to be good up to temperatures of } 3000 \text{ R. Using equations (15) and (16) to calculate } c_p \text{ and } \gamma, \text{ respectively, and a value of } \theta = 5500 \text{ R, it is seen that at zero pressure excellent agreement with the correlated data is obtained up to } 5000 \text{ R. The approximate theory was then checked at low temperatures with experimental values of } \gamma \text{ given in reference 20. At temperatures above liquefaction and pressures up to 25 atmospheres, the difference between theoretical and experimental values of } \gamma \text{ was found not to exceed 3 percent.}

![Figure 3](image-url)

![Figure 4](image-url)
The molecular size constant $b$ was chosen to yield good agreement between theoretical and experimental values of compressibility of air. The theoretical values were calculated from equation (2), and the experimental data were obtained from reference 21. In general, it was found that using $b = 0.485$ ft$^3$/slug and the previously determined value of $c$, equation (2) predicts the compressibility of air to within 2-percent error at pressures from 0 to 150 atmospheres, and temperatures from liquefaction to 850° R. (The deviation from ideal gas behavior is small above this temperature at the pressures indicated.)

REFERENCES