In this chapter we shall classify the various types of infinite, plane, steady-state, one-dimensional flows involving exothermic chemical reactions, in which the properties become uniform as \( x \to \pm \infty \). Such a classification provides a framework within which plane deflagration and detonation waves may be investigated. The experimental conditions under which these waves appear are described in Chapters 5 and 6, where detailed analyses of each type of wave are presented.

The Rankine-Hugoniot relations are the equations relating the properties on the upstream and downstream sides of these combustion waves. In this chapter, general Rankine-Hugoniot equations are derived and discussed first; then the Hugoniot curve for a simplified system is studied in detail in order to delineate explicitly the various burning regimes.

Since the major changes in the values of the flow variables in these systems usually take place over a very short distance (in nearly all cases less than a few centimeters; see Sections 5.1.2 and 6.1), in many problems deflagration and detonation waves can be treated as discontinuities (at which heat addition occurs) in the flow equations for an “ideal” (inviscid, nondiffusive, non-heat-conducting, nonreacting) fluid. In such problems, the equations derived in this chapter provide all of the information that is required concerning these waves, except their speed of propagation.

Some other texts discussing the Rankine-Hugoniot equations are listed in [1]–[5].
2.1. GENERAL RANKINE-HUGONIOT EQUATIONS

2.1.1. Derivation of the equations

A coordinate system that is stationary with respect to the wave will be adopted, and it will be assumed that the flow is in the \(+x\) direction and that properties are uniform in planes normal to the \(x\) axis. Upstream conditions (at \(x = -\infty\)) will be identified by the subscript 0, while downstream conditions (at \(x = +\infty\)) are denoted by the subscript \(\infty\). The flow is illustrated schematically in Figure 2.1. Equations (1-26)-(1-29) govern the system.

The continuity equation [equation (1-27)] implies that
\[ \rho_0 v_0 = \rho_\infty v_\infty = m, \]
where \(m\) is the mass flow rate per unit area. Since \(dv/dx\) approaches zero as \(x \to \pm \infty\), equation (1-26) reduces to
\[ \rho_0 v_0^2 + p_0 = \rho_\infty v_\infty^2 + p_\infty \] (momentum conservation). The sequence of states at \(x = \infty\) (with fixed parameters at \(x = -\infty\)) for which equations (1) and (2) are satisfied is often referred to as the Rayleigh line. Since \(q\) is proportional to temperature gradients and concentration gradients, \(q \to 0\) as \(x \to \pm \infty\), and equation (1-28) (the energy equation) implies
\[ h_0 + v_0^2/2 = h_\infty + v_\infty^2/2, \]
where use has been made of equation (1). The species-conservation equations, equation (1-29), provide the additional requirements
\[ w_{i, \infty} = 0, \quad i = 1, \ldots, N, \] and
\[ w_{i, 0} = 0, \quad i = 1, \ldots, N. \]
The equation of state,
\[ f(p_0, \rho_0, T_0, Y_{i,0}) = f(p_\infty, \rho_\infty, T_\infty, Y_{i, \infty}), \]

Zone involving heat conduction, diffusion, reaction, and viscous effects

FIGURE 2.1. Schematic diagram of a deflagration or detonation wave.
and the caloric equation of state,
\[ g(h_0, p_0, T_0, Y_{i,0}) = g(h_\infty, p_\infty, T_\infty, Y_{i,\infty}), \]
constitute further relationships between the initial- and final-flow properties; for ideal-gas mixtures equations (6) and (7), respectively, reduce to equation (1-9) and the relation obtained by substituting equation (1-11) into equation (1-10) \((h = u + p/\rho)\).

In future work it will be convenient to employ modified forms of equations (2) and (3). Since equation (1) implies that
\[ \rho_\infty v_\infty^2 - \rho_0 v_0^2 = m^2 \left( \frac{1}{\rho_\infty} - \frac{1}{\rho_0} \right), \]
equation (2) may be written as
\[ \frac{p_\infty - p_0}{(1/\rho_\infty) - (1/\rho_0)} = -m^2, \]
which defines a straight line (the Rayleigh line) with a negative slope in the \((p_\infty - p_0, 1/\rho_\infty - 1/\rho_0)\) plane. Using equation (1) to express \(v\) in terms of \(m\) and \(\rho\) in equation (3) yields
\[ h_\infty - h_0 = -\frac{1}{2} m^2 \left( \frac{1}{\rho_\infty^2} - \frac{1}{\rho_0^2} \right), \]
which reduces to
\[ h_\infty - h_0 = \frac{1}{2} \left( \frac{1}{\rho_\infty} + \frac{1}{\rho_0} \right) (p_\infty - p_0) \]
when equation (8) is used to eliminate \(m^2\). Equation (9), which is called the Hugoniot equation, is a relationship among thermodynamic properties alone, as velocities have been eliminated.

The species-conservation equations require further discussion because equations (4) and (5) may not all be independent, and all of the information that can be obtained from equation (1-29) is not contained in equations (4) and (5). From equation (1-8) we see that the mass rate of production of species \(i\) by chemical reactions may be expressed as
\[ w_i = \sum_{k=1}^{M} w_{i,k}, \quad i = 1, \ldots, N, \]
where \(w_{i,k}\) is the mass rate of production of species \(i\) in the \(k\)th reaction and there are \(M\) independent reactions. The convention to be adopted here is slightly different from that for equation (1-8); forward and backward reactions will not be considered separately as is implied by equation (1-8), so that the present \(M\) is half of the previous \(M\), and \(w_{i,k}\) is the difference of two terms of the type appearing inside the summation in equation (1-8). From the stoichiometry of the \(k\)th reaction, it follows that
\[ w_{i,k} = W_k (v'_{i,k} - v''_{i,k}) \omega_k, \quad i = 1, \ldots, N, \quad k = 1, \ldots, M, \]
where \( \omega_k \) (which is independent of \( i \)) is the net rate of the \( k \)th reaction (that is, the difference between the forward rate and the backward rate; see Section B.1.2). Equations (10) and (11) imply that equations (4) and (5) are satisfied when

\[
\omega_{k, \infty} = 0, \quad k = 1, \ldots, M, \tag{12}
\]

and

\[
\omega_{k, 0} = 0, \quad k = 1, \ldots, M, \tag{13}
\]

which may constitute fewer relations than equations (4) and (5), since \( M \leq N \) in general.

However, when \( M < N \) it is possible to derive additional (atom-conservation) conditions from equation (1-29). If \( v_l^{(j)} \) denotes the number of atoms of kind \( j \) in a molecule of kind \( i \), then the fact that atoms are neither created nor destroyed by chemical reactions is expressed by the equation

\[
\sum_{i=1}^{N} v_l^{(j)} w_i / W_i = 0, \quad j = 1, \ldots, L, \tag{14}
\]

where \( L \) is the total number of atoms in the system. Substituting equation (1-29) for \( w_i \) into equation (14) and integrating from \( x = -\infty \) to \( x = +\infty \) yields

\[
\sum_{i=1}^{N} v_l^{(j)} Y_{i, 0} / W_i = \sum_{i=1}^{N} v_l^{(j)} Y_{i, \infty} / W_i, \quad j = 1, \ldots, L, \tag{15}
\]

since \( \rho_0 v_0 = \rho_x v_x \) [equation (1)] and \( V_l \to 0 \) as \( x \to \pm \infty \) (because diffusion velocities are proportional to gradients of the flow properties). Although it may be found that not all of the \( L \) additional relations between the properties at \( x = +\infty \) and those at \( x = -\infty \), given by equation (15), are linearly independent, it will always be true that \( N - M \) of these relations are independent (compare Section A.3.7). Hence equations (12) and (15) provide a total of \( N \) independent relations among the flow properties at \( x = \infty \); there are \( M \) equilibrium conditions and \( N - M \) atom-conservation conditions, just as in the problem of computing equilibrium compositions in closed systems (Appendix A).

### 2.1.2. The cold-boundary difficulty

The restrictions given by equation (13) [or equation (5)] are not fulfilled exactly in deflagration or detonation waves. The combustible mixture approaching from \( x = -\infty \) in Figure 2.1 is not in stable chemical equilibrium; the stable condition is that in which the mixture is composed of products of combustion. The initial mixture is in a metastable state and therefore actually reacts at a small but finite rate. Hence \( \omega_{k, 0} \neq 0 \), but \( \omega_{k, 0} \)
is very small compared with its value in the reaction zone so that, in some sense, equation (13) is satisfied approximately. Furthermore, equation (13) will be satisfied approximately for any initial mixture composition for which the mixture can be contained long enough to support a detonation or deflagration wave. Therefore, equation (13) actually provides no reasonable restriction on the initial conditions and will be omitted from the governing equations. If the problem were formulated in terms of wave propagation in a given combustible mixture, equation (13) would not even arise. However, it appears to be desirable to introduce this "cold-boundary difficulty" at an early stage, thus emphasizing how elementary it is, because the same trouble necessarily arises in studies of detonation structure (Section 6.1.2.2) and of deflagration propagation velocities (Section 5.3.2).

2.1.3. Use of the Rankine-Hugoniot equations

In summary, equations (1), (6)–(9), (12), and (15) comprise the independent relations between upstream and downstream conditions. If all upstream conditions (including \( v_0 \)) were specified, then these \( N + 5 \) equations would determine the downstream flow variables \( v_\infty, \rho_\infty, p_\infty, T_\infty, h_\infty, \) and \( Y_\infty \). Although the initial composition and thermodynamic properties are adjustable experimentally, the propagation velocity \( v_0 \) is not controlled directly but instead is determined by other experimental parameters; in a typical experiment a given mixture in a tube will be ignited, and the velocity at which the combustion wave propagates down the tube will be measured. Therefore, study of combustion waves is facilitated by eliminating \( v_0 \) from as many equations as possible. After the equations that do not contain \( v_0 \) are solved for relations among flow properties downstream, the conditions that fix \( v_0 \) (to be defined in later sections) may be introduced to complete the solution. Equations (1), (6)–(9), (12), and (15) constitute the required forms since velocities appear only in equations (1) and (8) of this set. With \( p_0, p_\infty, T_0, h_0, \) and \( Y_{i,0} \) given, the values of \( T_\infty \) and the chemical equilibrium composition \( (Y_{i,\infty}) \) can be calculated for various values of \( p_\infty \) and \( \rho_\infty \) from equations (6), (12), and (15),* the enthalpy \( h_\infty \) may then be evaluated for these same values of \( \rho_\infty \) and \( p_\infty \) from equation (7), and the result may finally be substituted into the Hugoniot equation, equation (9), in order to determine a curve in the \( (p_\infty, 1/\rho_\infty) \) plane along which the solution must lie regardless of the value of \( v_0 \). The nature of this curve, called the Hugoniot curve, is investigated in the following section. As illustrated in Figure 2.2, the intersection of the Hugoniot curve with the Rayleigh line defined by equation (8) determines the final thermodynamic state, after \( m \) has been obtained from \( v_0 \) for the particular experiment. The value of \( v_\infty \) may then

* This calculation is similar to the equilibrium-composition computations discussed in Appendix A.
be calculated from equation (1). Variations of this procedure have been programmed in recent years for solution by electronic computers (for example, [6]), which provide accurate Hugoniot curves based on the best values available for thermochemical properties.

2.2. ANALYSIS OF A SIMPLIFIED SYSTEM

2.2.1. Simplification of the Rankine-Hugoniot equations

The essential characteristics of the Hugoniot curve are most easily illustrated by studying a particular simple system. We shall consider an ideal gas mixture in order to assure that equations (1-9)–(1-11) are valid. It will be assumed that for the given initial thermodynamic properties \( p_0, p_0, Y_{i,0}, \) and so on, (1) the final equilibrium composition along the Hugoniot curve is constant (that is, \( Y_{i,\infty} \) are all fixed), (2) the final average molecular weight equals the initial average molecular weight—that is,

\[
\left( \sum_{i=1}^{N} \frac{Y_{i,\infty}}{W_i} \right)^{-1} = \left( \sum_{i=1}^{N} \frac{Y_{i,0}}{W_i} \right)^{-1} \equiv W
\]

—and (3) between the initial temperature \( T_0 \) and any final temperature \( T_{\infty} \) along the Hugoniot curve, the specific heat at constant pressure at the final composition equals the specific heat at constant pressure of the initial mixture—that is,

\[
\sum_{i=1}^{N} Y_{i,\infty} c_{p,i} = \sum_{i=1}^{N} Y_{i,0} c_{p,i,0} \equiv c_p \quad (= \text{constant})
\]

for \( c_{p,i} \) in some \( T \) range including \( T_0 \) and \( T_{\infty} \). The simplest system for which
2.2. Analysis of a Simplified System

Equations (16) and (17) are valid is one in which all species have equal molecular weights \( W_i = W \) for all \( i \) and constant and equal heat capacities \( c_{p,i} = c_p = \text{constant for all} \ i \).

In view of equation (16), equation (1-9) reduces to

\[
\frac{p_\infty}{\rho_\infty T_\infty} = \frac{p_0}{\rho_0 T_0} = \frac{R^0}{W}.
\]

Substituting equation (1-11) into equation (1-10), solving for \( h = u + p/\rho \), and evaluating the result at \( x = -\infty \) and at \( x = +\infty \) yields

\[
h_\infty - h_0 = \sum_{i=1}^{N} (Y_{i,\infty} - Y_{i,0}) h_i^0 + \int_{T_0}^{T_\infty} \left( \sum_{i=1}^{N} Y_{i,\infty} c_{p,i} \right) dT
\]

\[
- \int_{T_0}^{T_\infty} \left( \sum_{i=1}^{N} Y_{i,0} c_{p,i} \right) dT
\]

(19)

after subtraction. The heat of reaction of the mixture may be defined as

\[
q \equiv \sum_{i=1}^{N} \left[ \left( Y_{i,0} - Y_{i,\infty} \right) \left( h_i^0 + \int_{T_0}^{T_\infty} c_{p,i} dT \right) \right],
\]

(20)

which, in view of equation (17), is the total chemical heat released per unit mass of combustible mixture. Substituting equation (20) into equation (19), we obtain

\[
h_\infty - h_0 = -q + \int_{T_0}^{T_\infty} \left( \sum_{i=1}^{N} Y_{i,\infty} c_{p,i} \right) dT = -q + c_p (T_\infty - T_0),
\]

(21)

where use has been made of equation (17) in obtaining the final equality.

The temperatures \( T_0 \) and \( T_\infty \) may be eliminated from equation (21) by using equation (18). It can be seen that the ratio \( c_p/(R^0/W) \) will enter into the result. Since the specific heat at constant volume is given by \( c_v = c_p - R^0/W \) for an ideal-gas mixture, it follows that \( c_p/(R^0/W) = c_p/(c_p - c_v) = \gamma/(\gamma - 1) \), where \( \gamma \equiv c_p/c_v \) is the specific-heat ratio for the final mixture. Solving equation (18) for \( T_\infty \) and \( T_0 \) and substituting these results into equation (21) therefore yields

\[
h_\infty - h_0 = -q + \frac{\gamma}{\gamma - 1} \left( \frac{p_\infty}{\rho_\infty} - \frac{p_0}{\rho_0} \right).
\]

(22)

Equations (9) and (22) show that the Hugoniot equation may be written in the form

\[
\left( \frac{\gamma}{\gamma - 1} \right) \left( \frac{p_\infty}{\rho_\infty} - \frac{p_0}{\rho_0} \right) - \frac{1}{2} \left( \frac{1}{\rho_\infty} + \frac{1}{\rho_0} \right) (p_\infty - p_0) = q,
\]

(23)

which contains only the known constants \( \gamma, q, p_0, \) and \( p_0 \) in addition to the variables \( p_\infty \) and \( \rho_\infty \). Equation (23) may also be obtained by considering a
one-component ideal gas to which an amount of heat \( q \) (per unit mass) is added externally.

From equation (23) an explicit algebraic expression for \( p_\infty \) as a function of \( \rho_\infty \) along the Hugoniot curve may be obtained. Equations (8) and (23) therefore determine the complete solution for the simplified system.

### 2.2.2. Dimensionless form

The nature of the results will become more transparent if dimensionless variables are introduced. A dimensionless final pressure is the pressure ratio

\[
p = \frac{p_\infty}{p_0}.
\]

A dimensionless final specific volume is the density ratio

\[
v = \frac{\rho_0}{\rho_\infty},
\]

which is also equal to the velocity ratio \( v_\infty/v_0 \) according to equation (1). A dimensionless heat of reaction is

\[
\alpha = \frac{q\rho_0}{p_0},
\]

and a dimensionless mass-flow rate is

\[
\mu = \frac{m_0}{\rho_0}.
\]

It will be observed that \( p, v, \) and \( \mu \) must all be positive for physically acceptable solutions. Multiplying equation (23) by \( \rho_0/p_0 \) yields

\[
\left( \frac{\gamma}{\gamma - 1} \right) (pv - 1) - \frac{1}{2} (v + 1)(p - 1) = \alpha,
\]

the solution of which is

\[
p = \frac{2\alpha + (\gamma + 1)/(\gamma - 1)}{[\gamma + 1]/(\gamma - 1)v - 1} - v.
\]

Dividing equation (8) by \( p_0\rho_0 \) gives

\[
\frac{p - 1}{v - 1} = -\mu.
\]

### 2.2.3. Properties of the Hugoniot curve

The Hugoniot curves given by equation (24) are plotted in Figures 2.3 and 2.4 for \( \gamma = 1.4 \) and \( \gamma = 1.2 \), respectively.* All curves asymptotically approach the lines \( v = (\gamma - 1)/(\gamma + 1) \) and \( p = -(\gamma - 1)/(\gamma + 1) \). Therefore,

* The curves for \( \alpha = 0 \) are of significance in connection with ordinary shock waves.
the entire range of pressure ratio \((0 \leq p \leq \infty)\) may occur, but the specific-volume (or velocity) ratio is restricted to the interval

\[
\frac{\gamma-1}{\gamma+1} \leq \frac{v}{\gamma+1} \leq 2\alpha + \left[\frac{(\gamma+1)}{(\gamma-1)}\right],
\]

with the upper bound corresponding to the limit \(p \to 0\) [see equation (24)].

The intersection between the appropriate Hugoniot curve and the straight line through the point \((1, 1)\) with slope \(-\mu\) [equation (25)] establishes the final state of the system. Since \(\mu > 0\), the slope of this straight line is negative, and end states lying in the two shaded quadrants in Figures 2.3 and 2.4 are physically meaningless. Each Hugoniot curve is therefore divided into two nonoverlapping branches, an upper branch \([1 + (\gamma - 1)\alpha \leq p \leq \infty, \frac{(\gamma-1)}{(\gamma+1)} \leq \frac{v}{\gamma+1} \leq 1;\) see equation (24)] called the **detonation branch** and a lower branch \([0 \leq p \leq 1, 1 + (\gamma - 1)\alpha/\gamma \leq \frac{v}{\gamma+1} \leq 2\alpha + (\gamma + 1)/(\gamma - 1);\) see equation (24)] called the **deflagration branch**. Acceptable end states must lie on one of these two branches. Combustion waves are termed detonation waves or deflagration waves according to the branch of the Hugoniot curve upon which the final condition falls.

**FIGURE 2.3.** Hugoniot diagram from (24) with \(\gamma = 1.4\).
Although this formal distinction is invaluable because of its unambiguity, an understanding of the difference between detonation and deflagration waves is best obtained by contrasting the characteristics of each. Thus (see Figures 2.3 and 2.4), in passing through a detonation wave the gas is slowed down, and its pressure and density increase; however, in going through a deflagration the gas speeds up and expands, and its pressure decreases. Other striking differences between the two types of waves will appear when we discuss wave structures in subsequent chapters (see Sections 5.3 and 6.1).

2.2.4. Analysis of the detonation branch

It is easily seen from Figure 2.3 or Figure 2.4 that a unique straight line through the point (1, 1) is tangent to the detonation branch of the Hugoniot curve. This can be proven formally by considering the equation

$$\frac{dp}{dv} = \frac{p - 1}{v - 1},$$

(26)
where \( p(v) \) and \( dp/dv \) are evaluated from the Hugoniot equation, equation (24). Equation (26), which states that the slope of the Hugoniot curve equals the slope of the straight line from the Hugoniot curve to the point \((1, 1)\), can be shown to possess only one solution, \((p_+, v_+)\), lying on the detonation branch. This point \((p_+, v_+)\) on the detonation branch is said to be the **upper Chapman-Jouguet point**, and the wave with this end condition (point \(B\) on the Hugoniot curve illustrated in Figure 2.5) is a **Chapman-Jouguet detonation**.

A straight line through the point \((1, 1)\) will not intersect the detonation branch anywhere if the magnitude of its slope is less than that of the tangent line, while it intersects the detonation branch at two points if the magnitude of its slope exceeds that of the tangent line. This is illustrated in Figure 2.5, where typical solutions lying on the detonation branch \(ABC\) are indicated. Equation (25) therefore implies that there is a minimum value of \(\mu\) (that is, a minimum wave speed) for detonations, corresponding to the Chapman-Jouguet end conditions (at point \(B\) in Figure 2.5). When \(\mu\) exceeds its minimum value \(\mu_+\) (that is, at higher wave speeds), there are two possible end states for the detonation, one lying on the line \(AB\) (a **strong detonation**) and the other lying on the line \(BC\) (a **weak detonation**).

The experimental conditions determine whether a strong detonation, a Chapman-Jouguet wave, or a weak detonation will be observed at a given value of \(\mu\). Under most experimental conditions, detonations are Chapman-Jouguet waves; this topic will be discussed more fully in Section 6.2, since the reasoning involves concepts of the structure of the wave.

**FIGURE 2.5.** Schematic diagram depicting the various sections of the Hugoniot curve.
Figure 2.5 shows that as the nomenclature implies, the pressure ratio and the velocity change across a strong detonation exceed those across a weak detonation. The strong detonation with \( p = \infty \) and the isochoric weak detonation \( (v = 1) \), both of which propagate at infinite velocity \( (\mu = \infty) \), represent unattainable limiting cases.

### 2.2.5. Analysis of the deflagration branch

Remarks precisely analogous to those given above for the detonation branch of the Hugoniot curve also apply to the deflagration branch. Figure 2.3, Figure 2.4, or equation (26), shows that a unique straight line through the point \((1, 1)\) is tangent to the deflagration branch \((DEF \text{ in Figure 2.5})\) at a point \((p_-, v_-)\), which is called the 'lower Chapman-Jouguet point' \((\text{point } E \text{ in Figure 2.5})\). A wave with endpoint \(E\) is a Chapman-Jouguet deflagration.

A straight line through the point \((1, 1)\) fails to intersect the deflagration branch if the magnitude of its slope exceeds that of the tangent line, and it intersects the deflagration branch at two points (once on \(DE\) and once on \(EF\)) if its slope is less than that of the tangent line. Hence the Chapman-Jouguet deflagration has the maximum wave speed \( (\mu = \mu_-) \) of all deflagrations. Figure 2.5 clearly shows that this maximum deflagration velocity is less than the minimum detonation velocity \( (\mu_- < \mu_+) \); this result can also be derived from equation (26).

Waves with end states lying along line \(DE\) are weak deflagrations and those with end states on line \(EF\) are strong deflagrations. The pressure and velocity changes across strong deflagrations exceed those across weak deflagrations. Limiting cases are the strong deflagration with \( p = 0 \), which has a finite (nonzero) propagation speed, and the isobaric weak deflagration \( (p = 1) \), which propagates at zero velocity \( (\mu = 0) \).

From considerations of combustion-wave structure, it will be indicated in Section 6.1.3 that strong deflagrations do not occur; hence the physically meaningful section of the deflagration branch of the Hugoniot curve is \(DE\). Most deflagrations are, in fact, nearly isobaric.

### 2.2.6. Properties of Chapman-Jouguet waves

Chapman-Jouguet waves assume a special significance in many systems, particularly those involving detonations. It is therefore of interest to investigate the properties of the Chapman-Jouguet points in greater detail.

Differentiating equation (24) yields

\[
\frac{dp}{dv} = -\frac{[(\gamma + 1)/(\gamma - 1)]p + 1}{[(\gamma + 1)/(\gamma - 1)]v - 1},
\]

Equation (26)
2.2. Analysis of a Simplified System

which may be substituted into equation (26) to obtain

\[ p = v/[(\gamma + 1)v - \gamma] \]  

(27)

at either Chapman-Jouguet point. By using this relation in equation (25), it can be shown that

\[ \mu = \gamma p/v \]  

(28)

at the Chapman-Jouguet points. From the definitions of the dimensionless variables \( \mu, p, \) and \( v, \) the dimensional form of equation (28) is seen to be

\[ m^2 = \gamma p_\infty \rho_\infty, \]  

which implies that

\[ v_\infty = \sqrt{\gamma p_\infty / \rho_\infty} \]  

(29)

[see equation (1)]. Recalling that the speed of sound in an ideal gas is

\[ a_\infty = \sqrt{\gamma p_\infty / \rho_\infty} \]  

(\( s = \) entropy per unit mass), we see that equation (29) implies that the downstream Mach number \( M_\infty \equiv v_\infty / a_\infty \) is unity at both Chapman-Jouguet points. A more thorough analysis shows that the downstream gas velocity relative to the wave exceeds the sound velocity \((M_\infty > 1)\) for weak detonations and strong deflagrations and is less than the sound velocity \((M_\infty < 1)\) for strong detonations and weak deflagrations.

It is also possible to prove that along the Hugoniot curve, the entropy assumes a local minimum value only at the upper Chapman-Jouguet point and a local maximum value only at the lower Chapman-Jouguet point [7] and that along each tangent line given by equation (25) (the Rayleigh line), the entropy assumes a local maximum value at the Chapman-Jouguet point [8].

Explicit expressions for the dimensionless downstream properties (in terms of \( \alpha \) and \( \gamma \)) are easily derived for Chapman-Jouguet waves. For example, if equation (27) is solved for \( v, \) giving

\[ v = \gamma p/[(\gamma + 1)p - 1], \]  

(30)

and this result is substituted into equation (24), then a quadratic equation for \( p \) is obtained, the solution to which is

\[ p_\pm = 1 + \alpha(\gamma - 1)\left\{ 1 \pm \left[ 1 + \frac{2\gamma}{\alpha(\gamma^2 - 1)} \right]^{1/2} \right\}. \]  

(31)

Upper signs correspond to the detonation branch, and lower signs correspond to the deflagration branch. Substitution of equation (31) into equation (30) yields

\[ v_\pm = 1 + \alpha\left(\frac{\gamma - 1}{\gamma}\right)\left\{ 1 \mp \left[ 1 + \frac{2\gamma}{\alpha(\gamma^2 - 1)} \right]^{1/2} \right\}. \]  

(32)
By using equations (31) and (32) in equation (25), we find that

\[
\mu_{\pm} = \gamma + \alpha(\gamma^2 - 1) \left\{ 1 \pm \left[ 1 + \frac{2\gamma}{\alpha(\gamma^2 - 1)} \right]^{1/2} \right\},
\]

(33)

The temperature ratio may be computed from \( T_\infty/T_0 = pv \) [see equation (18)]; the downstream temperature is found to exceed the upstream temperature at both Chapman-Jouguet points.

Equation (33) may be used to compute the initial Mach number for Chapman-Jouguet waves. The result is

\[
M_{0,\pm} = \left[ 1 + \frac{\alpha(\gamma^2 - 1)}{2\gamma} \right]^{1/2} \pm \left[ \frac{\alpha(\gamma^2 - 1)}{2\gamma} \right]^{1/2},
\]

(34)

since \( M_0 \equiv v_0/a_0 = v_0/\sqrt{\gamma p_0/\rho_0} = \sqrt{\mu/\gamma} \) from equation (1) and the definition of \( \mu \). Equation (34) shows that both \( M_{0,+} \) and \( M_{0,-} \) approach unity as the heat-release parameter \( \alpha \) goes to zero, while \( M_{0,+} \rightarrow \infty \) and \( M_{0,-} \rightarrow 0 \) as \( \alpha \rightarrow \infty \). According to equation (34), the initial Mach number always exceeds unity for Chapman-Jouguet detonations and lies between zero and unity for Chapman-Jouguet deflagrations. Since the Chapman-Jouguet waves correspond to the minimum propagation speed for detonations and the maximum propagation speed for deflagrations, we conclude that all detonations propagate at supersonic velocities and all deflagrations propagate at subsonic velocities.

\[\text{FIGURE 2.6. The dependence of the properties of Chapman-Jouguet waves upon the dimensionless heat-release parameter } \alpha, \text{ as determined by equations (31)–(34) with } \gamma = 1.3.\]
2.3. Extensions of the Results to Arbitrary Systems

Numerical values of the parameters for Chapman-Jouguet waves are plotted in Figure 2.6 as functions of the dimensionless heat-release parameter \( \alpha \) for \( \gamma = 1.3 \). A representative value of \( \alpha \) is \( \alpha = 30 \), for which Figure 2.6 shows that, approximately, \( p_+ = 20 \), \( v_+ = 0.58 \), \( (T_m/T_0)_+ = 12.5 \), and \( M_{0+} = 5.8 \) (giving \( v_0 \approx 1000 \text{ m/s} \)) at the upper Chapman-Jouguet point, while \( p_- = 0.46 \), \( v_- = 15.4 \), \( (T_m/T_0)_- = 7 \), and \( M_{0-} = 0.17 \) at the lower Chapman-Jouguet point. In accordance with our earlier discussion, these numbers are typical of experimentally observed detonations but unrealistic for deflagrations.

2.3. EXTENSION OF THE RESULTS TO ARBITRARY SYSTEMS

2.3.1. Range of validity of the results of Section 2.2

More-general analyses than those given in the preceding section show that the qualitative properties of the Hugoniot curve derived in Section 2.2 remain valid for all the systems that fall within the framework of the equations presented in Section 2.1. Many quantitative results obtained in Section 2.2 are also of general validity; only some equations and certain limits on inequalities will require modification. The expressions which must be changed are those that involve \( c_1 \) explicitly, since the single parameter \( c_1 \) is not sufficient to characterize the behavior of arbitrary multicomponent mixtures. We shall briefly discuss the most important complication that arises in attempting to extend our results, and then we shall summarize most of the properties of arbitrary Hugoniot curves by means of a table.

2.3.2. Frozen versus equilibrium sound speeds

It was shown in Section 2.2 that the downstream Mach number is unity for Chapman-Jouguet waves. When interpreted correctly, this result applies to any combustible gas mixture. However, a possible source of ambiguity for multicomponent systems is the fact that more than one sound speed \( a \) can be defined.* Since there are \( N + 2 \) independent thermodynamic variables in an \( N \)-component gas mixture, \( N \) parameters besides \( s \) must be specified as constants in computing \( \partial p/\partial \rho \) to evaluate \( a^2 \).†

A frozen (constant-composition) sound speed may be defined as

\[
a_f = \left[ (\partial p/\partial \rho)_s, Y_{i(1,\ldots,N)} \right]^{1/2}
\]

* The subscript \( \infty \) is suppressed in this section for the sake of clarity in notation. It is understood that we are always referring to downstream conditions here.
† If \( s \) is the entropy per unit mass, then actually only \( N - 1 \) independent intensive parameters must be specified because \( p, \rho, \) and \( a \) are intensive properties that are independent of the size of the system.
(\(Y_i \equiv \) mass fraction of chemical species \(i\)), and an \textbf{equilibrium sound speed}
may be defined as
\[
a_e = \left[\frac{\partial \rho}{\partial \rho}\right]_{\epsilon = \epsilon_i, Y_i = Y_i, (\rho, s)}^{1/2},
\]
where \(Y_i, \epsilon(\rho, s)\) represents the equilibrium mass fraction of species \(i\) at the
given \(\rho\) and \(s\) in a mixture at the specified overall atomic composition
[equation (15)]. The subscript notation \(Y_i = Y_i, \epsilon(\rho, s)\) means that \(Y_i\) is to
be set equal to its equilibrium function of \(\rho\) and \(s\) [which is determined by
equation (12)] in computing the partial derivative. Since \(a_f \geq a_e\) in general,*
the problem is to determine which (if either) of these appears in the definition
of \(M\) for which \(M = 1\) at the Chapman-Jouguet points.

Since the Hugoniot curve is an equilibrium curve, it might be expected
that the Chapman-Jouguet tangency condition would lead to \(M = 1\) with
\(M\) defined in terms of \(a_e\). The rigorous analysis given in the following para-
graph supports this guess; the downstream gas velocity relative to the wave
equals the equilibrium sound speed at the Chapman-Jouguet points. Using
\(M = 1\) to define the Chapman-Jouguet point, with the \(M\) based on \(a_f\) instead
of \(a_e\), may lead to overestimates of the computed Chapman-Jouguet detonation-propagation velocities, which are comparable with the errors in the
most accurate experimental measurements of this parameter (about one
part in \(10^3\)).† Further information on this topic may be found in [9] and in
some of the references quoted therein (see also Section 6.2.4).

\textbf{2.3.3. Proof that} \(v_\infty = a_{e, \infty}\) \textbf{at the Chapman-Jouguet points}

For a small change along the general Hugoniot curve [equation (9)],
we find by differentiation that
\[
dh_e = \frac{1}{2} \left( \frac{1}{\rho_\infty} + \frac{1}{\rho_0} \right) dp_e + \frac{1}{2} \left( p_\infty - p_0 \right) d\left( \frac{1}{\rho_\infty} \right). \tag{35}
\]

* This is a consequence of the fact that thermodynamically unstable equilibria are not
attainable in natural processes. For example, if only one chemical reaction can occur in the
system under consideration, then straightforward thermodynamic calculations show that
\[
a_f^2 - a_e^2 = \left( \frac{\rho}{V} \right) \left[ \frac{\partial \epsilon}{\partial \rho} \right]_{\eta = \eta_i, \epsilon(\rho, s)}^{1/2} \left\{ \frac{\partial}{\partial \epsilon} \left[ \sum_{i=1}^{N} \mu_i (v_i' - v_i) \right] \right\}_{S, V},
\]
where \(\epsilon\) is the reaction progress variable defined in equation (A-19), other symbols are defined
in Appendix A, and the partial derivatives are taken in a closed system (of entropy \(S\) and volume
\(V\)). Since the factors preceding the brace on the right-hand side of this relation are intrinsically
positive, the sign of \(a_f^2 - a_e^2\) is the same as the sign of the last factor, [which equals \((\partial^2 U/\partial \epsilon^2)_{S, V}\)
\((U \equiv \) internal energy)]. The reasoning following equation (A-20) implies that a small distur-
bance will cause the system to move away from the equilibrium point if this last factor is negative.

† Methods for computing Chapman-Jouguet detonation velocities are given in [1], [2],
[6], [10], and [11], for example.
2.3. Extensions of the Results to Arbitrary Systems

The tangent to the Hugoniot curve is a straight line through the point \((p_0, 1/\rho_0)\) provided that, in equation (35),

\[
\frac{dp_\infty}{d(1/\rho_\infty)} = \frac{p_\infty - p_0}{1/\rho_\infty - 1/\rho_0}.
\]  

(36)

Using equation (36) to eliminate \(d(1/\rho_\infty)\) from equation (35), we obtain the expression

\[
dh_\infty = \frac{1}{\rho_\infty} dp_\infty.
\]  

(37)

Since the entropy change along the Hugoniot curve \([at Y_{i,\infty} = Y_{i,e,\infty}(\rho_\infty, s_\infty)\] for \(i = 1, \ldots, N\)] is given by the thermodynamic relationship

\[
T_\infty ds_\infty = dh_\infty - \left(\frac{1}{\rho_\infty}\right) dp_\infty,
\]  

(38)

equation (37) implies that

\[
ds_\infty = 0
\]  

(39)

at the Chapman-Jouguet points along the Hugoniot curve. Hence, in equation (36),

\[
\frac{dp_\infty}{d(1/\rho_\infty)} = \left[\frac{\partial p_\infty}{\partial(1/\rho_\infty)}\right]_{s_\infty, Y_{i,\infty} = Y_{i,e,\infty}(\rho_\infty, s_\infty)(i = 1, \ldots, N)}.
\]  

(40)

Equations (8) and (36) show that

\[
\frac{dp_\infty}{d(1/\rho_\infty)} = -m^2 = -(\rho_\infty v_\infty)^2,
\]  

(41)

where the last equality follows from equation (1). Equations (40) and (41) finally yield

\[
v^2_\infty = (\partial p_\infty/\partial \rho_\infty)_{s_\infty, Y_{i,\infty} = Y_{i,e,\infty}(\rho_\infty, s_\infty)(i = 1, \ldots, N)},
\]  

(42)

which states that \(v_\infty = a_{v,\infty}\) at the Chapman-Jouguet points as desired.

This analysis is illustrative of the type of reasoning required when the assumptions of Section 2.2 are inapplicable.

2.3.4. Summary of the properties of Hugoniot curves

Table 2.1 summarizes many of the properties of Hugoniot curves. In the table, quantities identified by the subscripts +, −, 1, max, and min are fixed constants, determined by the initial state of the mixture. The quantities

* Terms corresponding to \(\sum_{i=1}^{Y} \mu_i dN_i\) in equation (A-5) do not appear in equation (38) because the condition of chemical equilibrium [equation (A-16) with the equality sign] implies that these terms are zero in the present case.
<table>
<thead>
<tr>
<th>Strong detonations</th>
<th>Upper Chapman-Jouguet point</th>
<th>Weak detonations</th>
<th>Weak deflagrations</th>
<th>Lower Chapman-Jouguet point</th>
<th>Strong deflagrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section in Fig. 2-5</td>
<td>Line A-B</td>
<td>p_+ &lt; p &lt; \infty</td>
<td>p = p_+ \quad (p_+ &gt; 1)</td>
<td>p_- &lt; p &lt; 1</td>
<td>0 &lt; p &lt; p_- \quad (p_- &lt; 1)</td>
</tr>
<tr>
<td>Pressure ratio p = (p_\infty/p_0)</td>
<td>v_{\text{min}} &lt; v &lt; v_+ \quad (v_{\text{min}} &gt; 0)</td>
<td>v = v_+ \quad (v_+ &lt; 1)</td>
<td>v_1 &lt; v &lt; v_- \quad (v_1 &gt; 1)</td>
<td>v = v_- \quad (v_- &gt; 1)</td>
<td>v_- &lt; v &lt; v_{\text{max}} \quad (v_{\text{max}} &lt; \infty)</td>
</tr>
<tr>
<td>Velocity and density ratios v = (v_{\infty}/v_0) = (p_0/p_\infty)</td>
<td>M_{0+} &lt; M_0 &lt; \infty</td>
<td>M_0 = M_{0+} \quad (M_{0+} &gt; 1)</td>
<td>0 &lt; M_0 &lt; M_{0-}</td>
<td>M_0 = M_{0-} \quad (M_{0-} &lt; 1)</td>
<td>M_{0-} &lt; M_0 &lt; M_{0-} \quad (M_{0-} &gt; 0)</td>
</tr>
<tr>
<td>Propagation Mach number M_0 \equiv (v_0/a_{\infty})</td>
<td>Downstream Mach number M_\infty \equiv (v_\infty/a_{\infty})</td>
<td>Remarks</td>
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with subscripts + and − are given by equations (31)–(34) only under the restrictive conditions imposed in Section 2.2. The quantity \( M_0 \) is based on the chemically frozen sound speed in the initial mixture, and \( M_\infty \) is based on the equilibrium sound speed in the final mixture. The limits for all of the inequalities except those in parentheses are intended to represent greatest lower bounds or least upper bounds. With this information, Table 2.1 should become self-explanatory.

REFERENCES