Properties of the Hugoniot function

By ROBERT D. COWAN
Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico

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SUMMARY

Differentiation of the Hugoniot function

$$H(p,v) = E(p,v)-E(p_0,v_0)+\tfrac{1}{2}(p+p_0)(v-v_0)$$

and use of the first and second laws of thermodynamics leads to the relation $dH = T\,dS+dA$, where dA is the element of area in the (p,v) plane swept out (in a counter-clockwise direction) by the line segment $(p_0,v_0)\to(p,v)$ as the point (p,v) is moved from some point (p_1,v_1) to a neighbouring point (p_1+dp_1,v_1+dv_1). This relation, together with rather general assumptions regarding the shape of the isentropic curves $dS = 0$ for the material behind the shock, makes possible the geometrical derivation of a number of properties of the function H and of the Hugoniot curves $dH = 0$.

1. INTRODUCTION

The laws of conservation of mass, momentum, and energy lead to the following relation (first derived by Hugoniot (1889); see also Courant & Friedrichs (1948), pp. 116–146 and 204–218) which must be satisfied across any shock front:

$$E-E_0 = \tfrac{1}{2}(p+p_0)(v_0-v), \tag{1}$$

where p_0, v_0, and E_0 are the pressure, specific volume, and specific internal energy of the material ahead of the shock front, and p, v, and E are the values of these quantities behind the shock front. (E and E_0 must, of course, be referred to the same energy zero—for example, the energy of the elements in the ideal-gas state at zero temperature.) If the equation of state of the material behind the shock is known so that E and p can be found for any state, then (1) defines all states which can be reached from (p_0,v_0,E_0) by means of a single shock. The locus of all such states can be represented as a curve in the p–v plane, known as the Hugoniot curve.

Even without knowing the equation of state in detail, it is possible to derive several important qualitative properties of the Hugoniot curve on the basis of certain rather general equation-of-state characteristics. This problem has been discussed at length by Bethe (1942) and by Weyl (1949) for the case in which the materials behind and ahead of the shock are chemically identical, and by Courant & Friedrichs (1948) also in the case in which the shock induces a chemical reaction (as in the detonation of explosives). However, though the assumed equation-of-state characteristics are essentially of a geometrical nature (in terms of the p–v plane), the treatments of the above authors are primarily analytical. The result is that one does not readily obtain much of a feeling for the geometrical relations between the original assumptions and the final deductions. The treatment given below is basically geometrical, and the writer has found it quite useful in dealing with several problems which he has encountered, two of which are mentioned at the end of the paper. Many of the properties discussed below are well known, but are included for the sake of completeness; the proofs given serve to illustrate the simplicity of the geometrical approach.

Two of the basic assumptions made by Courant & Friedrichs in treating the reaction case are rather obscure; these points are cleared up in the discussion following equation (2) and Property 15.

2. Assumptions

It is assumed that there is no external electromagnetic field present, which might affect the problem in the case of shock-induced ionization. The state of the material behind the shock (which may be a mixture of several compounds) is then described completely by the internal energy function $E = E(S, v, n_i)$, where S is the specific entropy and n_i the number of moles of compound i per gram of mixture. The difference in internal energy between two neighbouring states is

$$dE = T\,dS - p\,dv + \sum \mu_i\,dn_i, \tag{2}$$

where μ_i is the chemical potential of the ith component. It is assumed that any shock-induced reaction takes place rather rapidly, and we shall consider only those states which occur to the rear of the reaction zone, where the material is essentially in chemical equilibrium. The term $\sum \mu_i\,dn_i$ in (2) is then zero, the change in internal energy becomes simply

$$dE = T\,dS - p\,dv, \tag{3}$$

and the internal energy can be considered as a function of S and v only. Assuming further that

$$(\partial p/\partial S)_v > 0 \tag{4}$$

so that no two isentropic curves ever cross, the energy can be considered as a single-valued function of pressure and volume

$$E = E(p, v), \tag{5}$$

which will be supposed to be everywhere continuous with continuous derivatives. (Assumption (4) is invalid for water between 0° and 4° C, and for phase changes generally.) Finally, it is assumed that all isentropes have negative slope and positive curvature:

$$(\partial p/\partial v)_S < 0, \tag{6}$$

$$(\partial^2 p/\partial v^2)_S > 0. \tag{7}$$

These two conditions are satisfied rather generally; they have been investigated at some length by Bethe (1942) for substances not reacting chemically and shown to be valid usually except at some phase transformations[†]. However, (7) is occasionally violated in the case of chemically reacting substances.

From (3) and (4) it follows that

$$(\partial E/\partial p)_v = T(\partial S/\partial p)_v > 0. \tag{8}$$

Since (4) and (6) imply

$$(\partial S/\partial v)_p > 0, \tag{9}$$

it follows from (3) that

$$(\partial E/\partial v)_p > -p. \tag{10}$$

In some cases for $p > p_0$ and $v < v_0$ (which will be mentioned specifically below), the stronger condition

$$(\partial E/\partial v)_p > -\tfrac{1}{2}(p+p_0) \tag{11 a}$$

or (from (3))

$$(\partial S/\partial v)_p > \tfrac{1}{2}(p-p_0)/T \tag{11 b}$$

will be assumed to hold, and in other cases, the still stronger condition

$$(\partial E/\partial v)_p > 0 \tag{12 a}$$

or

$$(\partial S/\partial v)_p > p/T \tag{12 b}$$

will be applied. Even this last inequality (which, with (8), is equivalent to $(\partial p/\partial v)_E < 0$) has been shown by Bethe to be usually valid except at some phase transformations.

It is assumed throughout that $p_0 > 0$.

3. Definitions

In order to investigate the properties of the Hugoniot curve defined by (1), it is convenient to define the so-called Hugoniot function

$$H(p,v) \equiv E(p,v) - E(p_0,v_0) - \tfrac{1}{2}(p+p_0)(v_0-v), \tag{13}$$

where $E(p_0, v_0)$ is the internal energy which the material behind the shock would have if it were returned (always under conditions of thermodynamic and chemical equilibrium) to the pressure and specific volume (p_0, v_0) of the unshocked material. By assumption (5), H is a single-valued, continuous, and differentiable function of p and v. In terms of the Hugoniot function, the Hugoniot relation (1) becomes

$$H = E_0(p_0,v_0) - E(p_0,v_0) = \text{constant}. \tag{14}$$

[†] The inequality examined by Bethe is actually

$$(\partial p/\partial v)_E \equiv (\partial p/\partial v)_S + (p/T)(\partial p/\partial S)_v < 0,$$

which is less general than (6) if (4) holds. (However, Bethe's third assumption $(\partial p/\partial S)_v > -2T/v$ is more general than (4).)

Thus the Hugoniot curve is a curve of constant H, the constant value being zero if the shock induces no chemical reaction (or a reaction such as dissociation or ionization for which the shocked material can be returned reversibly and spontaneously to the original state of the unshocked material), and the constant being greater or less than zero if a reaction is induced which is exothermic or endothermic, respectively. (Note that if the unshocked material is, for example, a complicated organic high explosive in a condensed phase, it may be impossible to reduce to p_0 the pressure of the reaction products at volume v_0 even by reducing the temperature to absolute zero, so that $E(p_0, v_0)$ is undefined. In this case, the zero-temperature isotherm passes above the point (p_0, v_0), and $H(p, v)$ must be defined in terms of say $E(T=0, v_0)$ or $E(T=0, p=0)$ instead of $E(p_0, v_0)$. However, this only changes the value of the constant in (14), and requires no essential revision in the discussion below for Hugoniot curves H = constant > 0. It is convenient to suppose that $E(p_0, v_0)$ does exist so as to permit simultaneous treatment of the cases H = constant $\gtreqless 0$.)

The differential of the Hugoniot function (13) is, on using (3),

$$\begin{aligned} dH &= dE+\tfrac{1}{2}\{(p+p_0)\,dv+(v-v_0)\,dp\} \\ &= T\,dS+\tfrac{1}{2}\{-(p-p_0)\,dv+(v-v_0)\,dp\}. \end{aligned} \tag{15}$$

This is the expression used by Weyl (1949) in his analytical discussion of the problem. However, it is much more convenient for a geometrical treatment to write (15) in the form (Cowan 1953)

$$dH = T\,dS+dA, \tag{16}$$

where dA is the area swept out in the p–v plane by the radius vector $(p_0, v_0) \rightarrow (p, v)$ in moving from the point (p, v) to the point $(p+dp, v+dv)$, dA being positive if the radius vector moves in a counter-clockwise direction. That the final term in (15) is the element of area just defined can be seen by noting that this term is just half the alternating (two-dimensional vector) product of the vectors $(v-v_0, p-p_0)$ and (dv, dp), or alternatively by introducing polar coordinates

$$v-v_0 = r\cos\theta, \qquad p-p_0 = r\sin\theta$$

which show that this term is

$$\tfrac{1}{2}r^2\,d\theta = dA. \tag{17}$$

It may be pointed out that although dH is a perfect differential, neither $T\,dS$ nor dA is one. Equation (16) is in fact quite similar to (3), both $p\,dv$ and dA being elements of area in the p–v plane—the one in Cartesian, the other in polar coordinates.

It will be convenient in the discussion below to speak in terms of a coordinate system with origin at (p_0, v_0) and so we introduce the coordinates $p^* = p-p_0$, $v^* = v-v_0$. The isentropic curve which passes through the origin will be denoted by S_0, and the tangent line to S_0 at the origin will be called T_{S_0}. For each isentrope S lying above S_0, then, as a consequence of assumptions (6) and (7), there exist exactly one point on S in the second quadrant and one point on S in the fourth quadrant at which a straight line through the origin is tangent to S. The locus of all such points of tangency will be denoted by LT, and can be seen to be a continuous curve which is tangent to S_0 at the origin, but otherwise lies entirely above S_0 (figure 1). Because of assumptions (4) and (7), any straight line through the origin cuts LT in at most one point, and it is evident from the definition that entropy increases monotonically in travelling along LT outward from the origin in either direction.

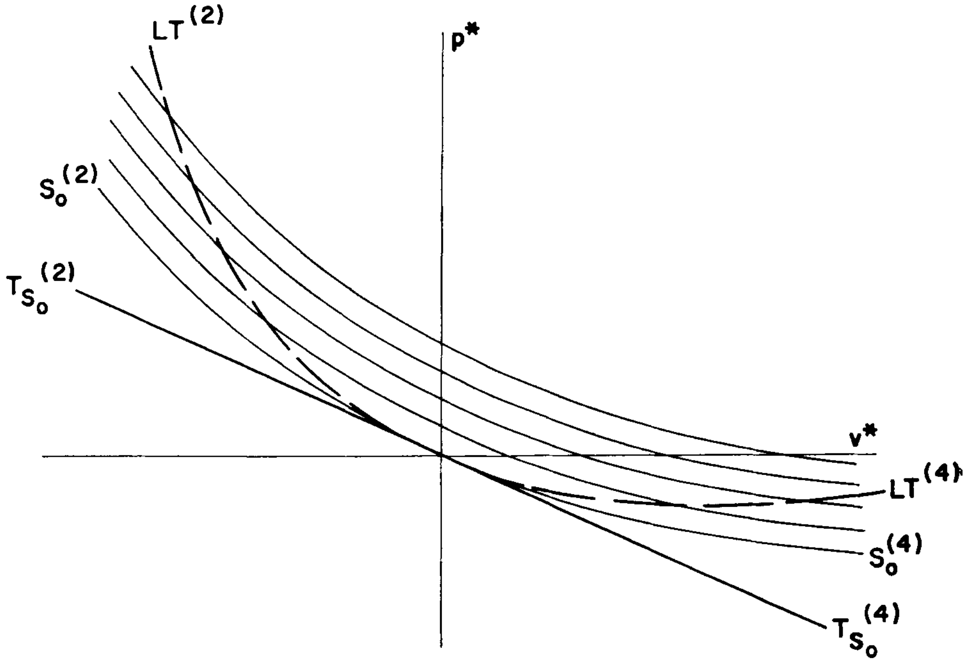

Figure 1. The isentrope S_0, the tangent to S_0 at the origin T_{S_0}, and the locus LT of all points at which a ray through the origin is tangent to an isentrope.

The curves LT, S_0, and T_{S_0} each pass through the origin but are otherwise confined to the second and fourth quadrants. The portions of these curves lying in the second and fourth quadrants will be denoted by the superscripts (2) and (4), respectively.

It should, of course, be kept in mind that the region of the (p^*, v^*)-plane in which H is defined is bounded from below by the zero-temperature isotherm. This (along with any regions in which the assumptions (3) to (7) are invalid) may introduce certain limitations on the validity of some of the statements made below.

4. PROPERTIES OF THE HUGONIOT FUNCTION

General properties of $H(p^*, v^*)$

PROPERTY 1. $H(0,0) = 0$, by definition.

PROPERTY 2. For $p^* < 0$, $(\partial H/\partial v)_p > 0$; for $v^* > 0$, $(\partial H/\partial p)_v > 0$.

Travelling to the right along an isobar $p^* < 0$ or upward along an isochor $v^* > 0$, both dS and dA are positive, and hence $dH > 0$ from (16).

PROPERTY 2′. Wherever condition (11) is satisfied, $(\partial H/\partial v)_p > 0$ even though $p^* > 0$.

This follows immediately from (15).

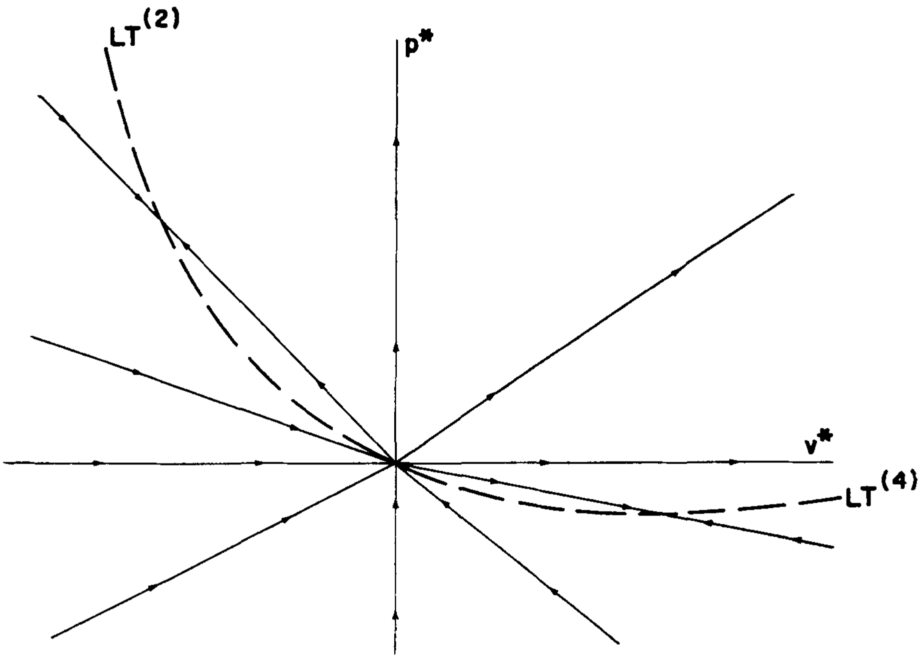

Figure 2. On any straight line through the origin, H increases away from the origin on the first-quadrant side of LT and increases toward the origin on the third-quadrant side of LT (Property 3).

PROPERTY 3. On any ray through the origin travelling away from the origin, $dH > 0$ on the first-quadrant side of LT and $dH < 0$ on the third-quadrant side of LT (figure 2). Thus H passes through a maximum at LT.

On such a ray, $dA = 0$, and hence from (16), $dH = T\,dS$. The qualitative behaviour of H is thus identical to that of S and follows immediately from the definition of LT.

PROPERTY 4. Travelling along an isentrope in the direction of increasing pressure, $dH > 0$ on the first-quadrant side of LT and $dH < 0$ on the third-quadrant side of LT (figure 3). Thus H passes through a minimum at $LT^{(4)}$ and through a maximum at $LT^{(2)}$.

Along an isentrope, $dS = 0$, and hence $dH = dA$.

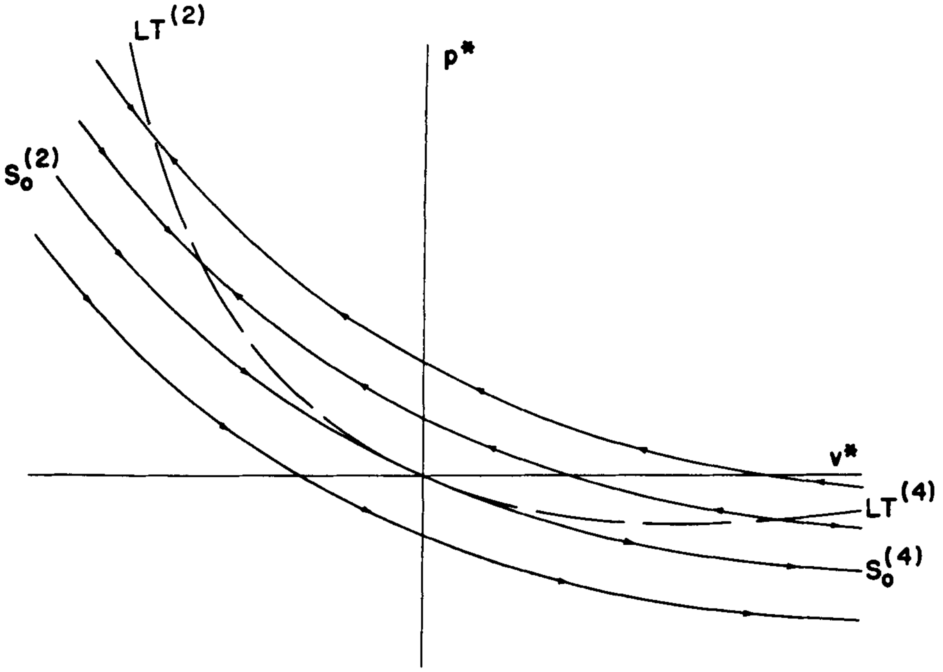

Figure 3. On an isentrope, H increases in the direction of increasing pressure on the first-quadrant side of LT and increases in the direction of decreasing pressure on the third-quadrant side of LT (Property 4).

PROPERTY 5. Except for the origin, $H > 0$ on LT and on $S_0^{(4)}$ and $H < 0$ on $S_0^{(2)}$ and T_{S_0}. Travelling away from the origin, $dH > 0$ on $LT^{(4)}$ and $S_0^{(4)}$ and $dH < 0$ on $S_0^{(2)}$, $T_{S_0}^{(2)}$ and $T_{S_0}^{(4)}$.

The statements regarding $LT^{(2)}$ and T_{S_0} follow from Properties 1 and 3, and those regarding S_0 from Properties 1 and 4. Travelling away from the origin on $LT^{(4)}$, both dS and dA are positive and hence $dH > 0$. Note, however, that a similar statement cannot be made on $LT^{(2)}$ since dS and dA have opposite signs; $H > 0$ on $LT^{(2)}$, but does not necessarily increase monotonically in a direction away from the origin—see the discussion following Property 15.

Properties of the curve $H = 0$

In the case of a shock which includes no chemical reaction (in the sense described in § 3), the possible thermodynamic states behind the shock are those for which $H = 0$; such states are thus of considerable physical interest.

Property 6. There exists a continuous curve $H = 0$ (denoted by H_0 for brevity) which passes through the origin O, but is otherwise confined to the second quadrant between $LT^{(2)}$ and $S_0^{(2)}$ and to the fourth quadrant between $S_0^{(4)}$ and $T_{S_0}^{(4)}$. For any point P on $S_0^{(2)}$, the ray $O \rightarrow P$ cuts H_0 in exactly one point; for P on $S_0^{(4)}$, $O \rightarrow P$ cuts H_0 in at most one point and a vertical or a horizontal line through P cuts H_0 in exactly one point.

It is evident from Properties 3 and 5 that $H > 0$ on the first-quadrant side of $LT^{(2)}$ and $S_0^{(4)}$, and $H < 0$ on the third-quadrant side of $S_0^{(2)}$ and $T_{S_0}^{(4)}$. Thus any points for which $H = 0$ must lie in the portions of the second and fourth quadrants stated above. For any point P on $S_0^{(2)}$, the ray $O \rightarrow P$ cuts $LT^{(2)}$ in exactly one point Q; since the values of H at P and Q are less than and greater than zero, respectively (Property 5), and since H increases monotonically from P to Q (Property 3), the line segment $P \rightarrow Q$ contains exactly one point at which $H = 0$. Similarly, for any point P on $S_0^{(4)}$ (where $H > 0$), a vertical or a horizontal line through P intersects T_{S_0} at a point Q (where $H < 0$)[†], and by Property 2 there exists exactly one point between P and Q at which $H = 0$. Continuity of the curve H_0 follows from that of the curve S_0 and that of the function (13). For P on $S_0^{(4)}$, $O \rightarrow P$ cuts H_0 in at most one point by Property 3.

Note that there is nothing which precludes the possibility of maxima and minima in volume along $H_0^{(2)}$; Bethe has, in fact, discussed phenomena (molecular rotation, vibration, dissociation, ionization) which tend to produce just such effects. The question of pressure maxima and minima on $H_0^{(2)}$ is dealt with in Property 10 below[‡].

Property 7. $H > 0$ on the first-quadrant side of the curve H_0, and $H < 0$ on the third-quadrant side of H_0.

This is evident from the statements made in proving Property 6.

Property 8. As a point P moves along H_0 in the direction from fourth to second quadrant, the straight line through O and P turns continuously clockwise with no stationary values of its slope.

In the vicinity of the origin, H_0 has positive curvature. On the second-quadrant side of the origin, this follows from Property 6 and assumption (7); on the fourth-quadrant side, H_0 cannot have negative curvature because of Property 6, and it cannot have zero curvature because to the second order dS (and hence also dH) is negative going down $T_{S_0}^{(4)}$. Thus Property 8 holds in the vicinity of the origin. Since the line $O \rightarrow P$ cannot cut H_0 in two different points (Property 6), the direction of rotation of $O \rightarrow P$

[†] If Q lies below the zero-temperature isotherm (isentrope), then the line through P must be terminated at the $S = 0$ curve, where H may or may not be negative (Property 4). This indicates the likelihood of an upper limit to volume on H_0. Such a limit indeed exists (as pointed out by Bethe) since the final term in (13) tends to plus infinity with v whereas $E(p, v)$ certainly has a finite lower bound.

[‡] Bethe states that pressure maxima and minima may occur on $H_0^{(4)}$. This is a result of his assumption $(\partial p/\partial S)_v > -2T/v$, which is less restrictive than (4).

can never reverse itself. A point of inflection P at which H_0 is tangent to $O \rightarrow P$ is also impossible, from Properties 3 and 6.

PROPERTY 9. Travelling along H_0 in the direction from fourth to second quadrants, S increases monotonically ($dS > 0$) except for a stationary value at the origin, where ΔS is of the third order in shock strength.

Since $dH = 0$ along H_0, then, from (16) and (17),

$$T\,dS = -dA = -\tfrac{1}{2}r^2\,d\theta.$$

In the vicinity of the origin

$$\tan\theta = \frac{p^*}{v^*} \doteq \left(\frac{\partial p}{\partial v}\right)_H + \frac{1}{2}\left(\frac{\partial^2 p}{\partial v^2}\right)_H v^*$$

and

$$d\tan\theta = \frac{r^2}{v^{*2}}\,d\theta \doteq \frac{1}{2}\left(\frac{\partial^2 p}{\partial v^2}\right)_H dv^*,$$

so that

$$S(v^*) - S(0) \doteq -\frac{1}{12T_0}\left(\frac{\partial^2 p}{\partial v^2}\right)_H (v^*)^3 = -\frac{1}{12T_0}\left(\frac{\partial^2 p}{\partial v^2}\right)_S (v^*)^3 \qquad (18)$$

which is of the third order in v^*†. It may be noted that the change of entropy along H_0 near the origin is directly related to the non-zero curvature of the isentrope S_0. (In fact, if S_0 were a straight line, then along S_0, $dS = dA = 0$ and hence $dH = 0$; thus H_0 would be coincident with S_0 along the entire length of the latter.)

PROPERTY 10. In travelling along $H_0^{(2)}$ away from the origin, the pressure and energy vary as follows: (*a*) if $dv < 0$, then $dp > 0$ and $dE > 0$; (*b*) if $dv > 0$, then $dp > 0$ if and only if the inequality (11) is satisfied on H_0, and $dE > 0$ if the inequality (12) is satisfied on H_0.

If $dv < 0$ in travelling up $H^{(2)}$, then Property 8 implies $dp > 0$, and from (3)

$$dE = T\,dS - p\,dv > 0$$

since $dS > 0$ from Property 9. If $dv > 0$ in travelling up $H_0^{(2)}$, then $T\,dS > 0$ and $-p\,dv < 0$ and nothing definite can be said about the sign of dE. However, if the inequality (11) is satisfied, then $(\partial H/\partial v)_p > 0$ from (15), and this implies $dp > 0$ from Property 7. If the even stronger condition (12) is satisfied, then $dv > 0$ and $dp > 0$ along H_0 imply from (8) and (12) that also $dE > 0$ along H_0. (Note that assumption (12) is a sufficient but not a necessary condition for $dE > 0$.)

Properties of a curve $H = -c$ (c = constant > 0)

Constant-H curves for $H < 0$ are not of great interest since such a curve (which will be denoted by H_-) represents the locus of possible states

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† This expression can also be obtained by direct differentiation of (15) at constant H to give the coefficients $(\partial^{(n)}S/\partial v^{(n)})_H$ in a Taylor series expansion for S.

behind a shock which has induced an endothermic chemical reaction, and such cases are not of much physical importance. The properties of such curves are similar to those of H_0 and will only be summarized briefly.

PROPERTY 11. H_- lies everywhere on the third-quadrant side of H_0; $H > -c$ everywhere on the first-quadrant side of H_- and $H < -c$ everywhere on the other side (Properties 7 and 3). For $p^* < 0$, a horizontal line cuts H_- at most once; for $v^* > 0$, a vertical line cuts H_- at most once (Property 2). Any ray from the origin cuts H_- at most once (Property 3). In travelling along H_- in the direction from fourth to second quadrant, $dA < 0$ and $dS > 0$ (see (16)). On $H_-^{(2)}$, the behaviour of pressure and energy is as described in Property 10.

Properties of a curve $H = +c$ (c = constant > 0)

Constant-H curves for $H > 0$ are of great physical interest since one such curve (which will be denoted by H_+) includes the locus of possible states behind a shock-induced exothermic chemical reaction (as in the detonation of an explosive, either gaseous, liquid, or solid) or behind such a reaction which is not shock-induced (slow combustions or deflagrations); see, for example, Courant & Friedrichs (1948).

PROPERTY 12. H_+ lies everywhere on the first-quadrant side of H_0, or, if H is not defined at the origin, then everywhere above the zero-temperature isentrope. In any case, H_+ is confined to the second, first, and fourth quadrants.

If H is defined at the origin, this follows from Property 7; if not, then it follows from the physical requirement $T > 0$. In addition, it can be shown (Courant & Friedrichs 1948) that the only physically significant parts of H_+ are those in the second and fourth quadrants, and so we shall not consider $H_+^{(1)}$ in any detail.

PROPERTY 13. Given any point P on LT, then, according as the value of H at P is less than, equal to, or greater than c, the ray $O \rightarrow P$ cuts H_+ not at all, at the one point P, or at (at most) one point on either side of P. Similarly, the isentrope through P cuts H_+ zero, one, or (at most) two times according as $H(P) \substack{<\\=\\>} c$ if P is on $LT^{(2)}$ or according as $H(P) \substack{>\\=\\<} c$ if P is on $LT^{(4)}$.

These statements follow immediately from Properties 3 and 4. Note the essential difference between these properties of H_+ and the corresponding properties of H_0 and H_-, directly connected with the fact that only H_+ can intersect LT at a point other than the origin (Property 5).

PROPERTY 14. For any point P on $LT^{(4)}$, there exists a continuous curve H_+ through P, which at P is tangent from below to $S_0^{(4)}$ and tangent from above to $O \rightarrow P$; $(\partial^2 p/\partial v^2)_S > (\partial^2 p/\partial v^2)_H > 0$. On $H_+^{(4)}$, the entropy has a maximum value where it crosses $LT^{(4)}$ and decreases monotonically on either side of this point.

The statements regarding tangency follow directly from Properties 4, 3, and 2, and the continuity of the Hugoniot function (13). The entropy maximum follows from the tangency relations, and the absence of any other stationary points in entropy is obvious since only at points on LT can dS and dA be simultaneously zero (see (16)).

The intersection of $H_+^{(4)}$ and $LT^{(4)}$ represents the state of the reaction products for a Chapman–Jouguet deflagration (Courant & Friedrichs 1948).

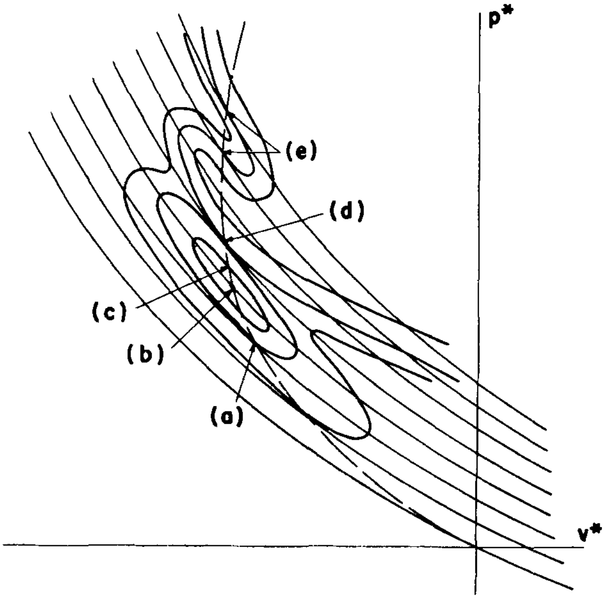

Figure 4. Diagram showing the mutual relation of isentrope, $LT^{(2)}$, and curves H_+ defined by H = constant > 0. Under the assumptions (4) to (10), the relations shown at (*a*), (*b*), (*c*), and (*d*) are possible (Property 15), but those at (*e*) are not (Property 3). Under assumption (11), only (*a*) is possible.

PROPERTY 15. For any point P on $LT^{(2)}$, the constant-H curve, H_+, which passes through P may behave in any of several ways: (*a*) H_+ may be tangent from above to the isentrope through P; (*b*) H_+ may consist of the single point P; (*c*) H_+ may be tangent from below to the ray $O \to P$; (*d*) H_+ may have two branches, one of the form (*a*) and one of the form (*c*). H_+ cannot have a point of inflection at P, behaving as in (*a*) on one side of $LT^{(2)}$ and as in (*c*) on the other side.

At any point P on LT, then along $O \to P$ (or along the isentrope through P) $dS = dA = 0$ and hence $dH = 0$ from (16); thus H_+ must be tangent to $O \to P$ (and to the isentrope S_P). However, H_+ cannot lie in between $O \to P$ and S_P because, travelling away from P on such a curve, $dS < 0$ and $dA < 0$ and hence dH cannot be zero. Thus H_+ must behave as shown at (*a*), (*b*), (*c*), or (*d*) in figure 4. An inflection point at P is not possible; see figure 4 and Property 3.

It is evident from figure 4 (which may be viewed as a contour-map of a three-dimensional (v,p,H) surface) that H_+ has the form (*a*), (*b*), (*c*), or (*d*) according as in travelling up $LT^{(2)}$ H increases, passes through a maximum, decreases, or passes through a minimum, respectively. Thus the necessary and sufficient condition that only the relation (*a*) prevail is that H increase monotonically in travelling up $LT^{(2)}$ (see the discussion following Property 5). Since on $LT^{(2)}$ $(\partial p/\partial v)_H = (\partial p/\partial v)_S < 0$, an equivalent condition is that $(\partial H/\partial p)_v > 0$ or $(\partial H/\partial v)_p > 0$. This last inequality, from (15), is equivalent to (11). *In all the following discussion of the properties of* H_+, *it will be assumed that on* $LT^{(2)}$

$$\left(\frac{\partial E}{\partial v}\right)_p > -\tfrac{1}{2}(p+p_0) \qquad \text{or} \quad \left(\frac{\partial E}{\partial p}\right)_v > \tfrac{1}{2}(v_0-v).$$

Proofs of most of the following statements have already been given or are obvious.

PROPERTY 16. In travelling along $LT^{(2)}$ in the direction away from the origin, $dH > 0$.

PROPERTY 17. For any point P on $LT^{(2)}$, there exists a continuous curve H_+ passing through P which is tangent from above to the isentrope through P $((\partial^2 p/\partial v^2)_H > (\partial^2 p/\partial v^2)_S > 0)$ and which meets $LT^{(2)}$ *only* at P. For any point P' on $LT^{(2)}$ between O and P and for any point P'' on $LT^{(2)}$ beyond P, the ray $O \rightarrow P'$ and the isentrope $S_{P'}$ intersect $H_+^{(2)}$ not at all, $O \rightarrow P$ and S_P meet $H_+^{(2)}$ only at P, and $O \rightarrow P''$ and $S_{P''}$ each intersect $H_+^{(2)}$ at most twice (once on either side of $LT^{(2)}$).

PROPERTY 18. In travelling along $H_+^{(2)}$ away from $LT^{(2)}$ in either direction, S increases monotonically with no stationary values except at the point of intersection P of $H_+^{(2)}$ and $LT^{(2)}$, where S is a minimum. For a point Q near P, the difference $S(Q)-S(P)$ is of the second order in $\Delta v = v_Q - v_P$.

Similarly to the derivation of Property 9, one has†

$$\tan\theta \doteq \left(\frac{\partial p}{\partial v}\right)_H + \frac{1}{2}\left(\frac{\partial^2 p}{\partial v^2}\right)_H \frac{(\Delta v)^2}{v^*},$$

and

$$d\tan\theta = \frac{r^2}{v^{*2}}\,d\theta \doteq \left(\frac{\partial^2 p}{\partial v^2}\right)_H \frac{\Delta v}{v^*}\,d(\Delta v),$$

$$S(Q)-S(P) \doteq \frac{(v_0-v)}{4T}\left(\frac{\partial^2 p}{\partial v^2}\right)_H (\Delta v)^2. \tag{19}$$

PROPERTY 19. At the point of intersection of $H_+^{(2)}$ and $LT^{(2)}$, the internal energy increases in the direction of increasing pressure. On the part of $H_+^{(2)}$

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† See the footnote to Property 9.

which lies to the left of $LT^{(2)}$, the behaviour of pressure and energy are as given in Property 10 for $H_0^{(2)}$.

The first statement follows from (3) and (6);

$$(\partial E/\partial p)_H = (\partial E/\partial p)_S = -p(\partial v/\partial p)_S > 0.$$

Proof of the remainder is exactly as that for Property 10.

The intersection of $H^{(2)}$ and $LT^{(2)}$ represents the state of the reaction products for a Chapman–Jouguet detonation (Courant & Friedrichs 1948).

5. Summary and applications

In figure 5 is sketched a series of constant-H curves illustrating the most important properties developed above, assuming that condition (11) holds for $p^* > 0$. These properties—subject to limitations which may arise from the fact that the zero-temperature isotherm does not pass below the origin, or from phase transformations or other causes of violation of assumptions (4) to (10)—are briefly as follows.

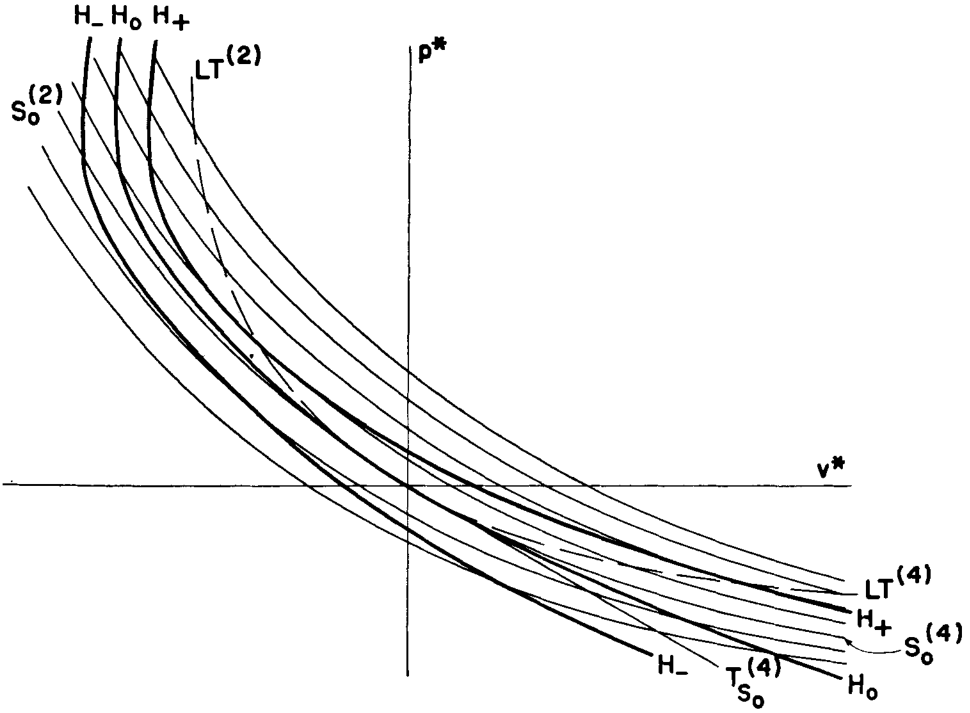

Figure 5. Diagram showing isentropes, the curve LT, and the general form of the constant-H curves assuming conditions (4) through (11) to be valid. (In order to illustrate volume minima on $H^{(2)}$ on the scale of this figure, the upper part of $H_0^{(2)}$ has been drawn in such a way that the requirements of (21) are violated.)

The (p^*, v^*)-plane can be thought of as divided into three parts by the half-line $(v^* = 0, p^* < 0)$, and by the curves $LT^{(2)}$ and $LT^{(4)}$, the loci of all possible Chapman–Jouguet states for exothermic detonations and deflagrations, respectively. No constant-H curve has pressure maxima or minima anywhere, nor volume maxima or minima for $v^* > 0$. No constant-H curve is cut by a straight line through the origin nor by an isentropic curve more than once in each of the three regions of the (p^*, v^*)-plane. The curve $H = 0$ passes through the origin, in the second quadrant lies between $LT^{(2)}$ and $S_0^{(2)}$, and in the fourth quadrant lies between $S_0^{(4)}$ and $T_{S_0}^{(4)}$. Above and to the right of any constant-H curve $H = c$, the value of H is greater than c; on the other side of this curve, H is less than c. Travelling up $H = 0$ in the direction from fourth to second quadrant, the entropy increases monotonically except for a point of inflection at the origin. Travelling up a curve $H =$ constant < 0, $dS > 0$ everywhere. A curve $H =$ constant > 0 in general crosses both $LT^{(4)}$ and $LT^{(2)}$; in travelling up this curve, starting below $LT^{(4)}$, entropy increases monotonically until it reaches a maximum value at $LT^{(4)}$, then decreases monotonically to a minimum value at $LT^{(2)}$, after which it again increases monotonically.

Two applications of the properties developed above will be given. Both pertain to the curve $H_0^{(2)}$ (the case in which the shock produces no chemical reaction), and serve to elaborate on certain characteristics of this curve.

1. The equation of state of a gas may be written in the form

$$E = pv/(\gamma - 1). \tag{20}$$

In the case of a monatomic ideal gas, $\gamma = 5/3$ for all p and v; the effect of excitation and ionization in a real gas is to increase E for given p and v and thus produce an effective value of γ which is less than 5/3. Thus for a point (p, v) which lies on the Hugoniot curve for the ideal gas, it is seen from (13) that $H > 0$ for the real gas. From Property 7, it follows that the Hugoniot curve for the real gas lies to the left of (or below) the ideal-gas curve. At very high pressures, the real gas is completely ionized and the potential energy becomes negligible relative to the kinetic energy, so that the equation of state of the real gas becomes identical with that of the ideal one and, consequently, the two Hugoniot curves also become identical; the possibility of a volume minimum on the Hugionot curve of the real gas (due to ionization, etc., as mentioned earlier) is thus evident.

2. For a certain problem which the author once encountered, it was important to know for an arbitrary point (p_1, v_1) on $H_0^{(2)}$ whether the isentrope through this point intersected the chord $(p_0, v_0) \rightarrow (p_1, v_1)$ or lay everywhere above it. It is immediately evident from Property 6 that the former is the case. In fact, the point of intersection is closer to (p_0, v_0) than to (p_1, v_1) as can be seen in the following way. In figure 6, S_1 is the isentrope through (p_1, v_1) and (p_2, v_2) is the point on S_1 for which $p_2 = p_0$. Then from the Hugoniot relation (1)

$$E_1 - E_0 = \tfrac{1}{2}(p - p_0)(v_0 - v_1) + p_0(v_0 - v_1),$$

and from (3)

$$E_2 - E_1 = -\int_{v_1}^{v_2} p_{S_1}\, dv,$$

so that

$$E_2 - E_0 = A_1 - A_2 - p_0(v_2 - v_0), \tag{21}$$

where A_1 and A_2 are the shaded areas in figure 6. From assumption (10), it follows that $A_1 > A_2$. Thus it may be seen that not only does $H_0^{(2)}$ lie between $LT^{(2)}$ and $S_0^{(2)}$, but tends to lie closer to the latter than to the former (see figure 5).

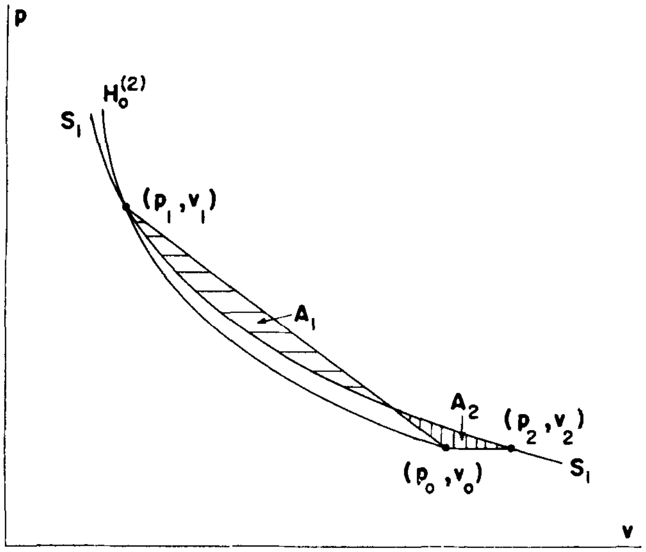

Figure 6. Relation of the Hugoniot chord $(p_0, v_0) \to (p_1, v_1)$ to the isentrope through (p_1, v_1); the area A_1 is greater than the area A_2.

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REFERENCES

BETHE, H. A. 1942 The theory of shock waves for an arbitrary equation of state, *OSRD Report* no. 545 (unclassified).

COURANT, R. & FRIEDRICHS, K. O. 1948 *Supersonic Flow and Shock Waves.* New York: Interscience.

COWAN, R. D. 1953 *Phys. Rev.* **92,** 1079 (A).

HUGONIOT, H. 1889 *J. Éc. polyt. Paris* **58,** 1.

WEYL, H. 1949 *Comm. Pure Appl. Math.* **2,** 103.