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Report on "The Theory of Shock Waves for an Arbitrary Equation of State"

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Serial No. 237

NATIONAL DEFENSE RESEARCH COMMITTEE

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OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

DIVISION B
Section B-1*

Report on "The Theory of Shock Waves for an Arbitrary Equation of State" (OD-03)

(1) Endorsement from E. B. Wilson, Jr., Chairman, Subsection B-1-B, to G. B. Kistiakowsky, Chairman, Section B-1. Forwarding report and noting:

> "This report deals with the general conditions for the existence of shock waves in any medium. It includes theorems concerning the relations between the velocities of infinitesimal waves and shock waves, between the entropy, pressure, and volume changes, and so forth. It should be of interest in the theoretical treatment of shock waves in air, water, metals, or other materials."

(2) Endorsement from G. B. Kistiakowsky, Chairman, Section B-1 to Roger Adams, Chairman, Division B. Forwarding report and concurring with above.

(3) Twenty-four copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee.

Roger Adams

* Now Divisiton 8, NDRC.

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ON THE THEORY OF SHOCK WAVES FOR AN ARBITRARY EQUATION OF STATE

by H. A. Bethe

Abstract

The fundamental equations of the hydrodynamic theory of one-dimensional shock waves — that is, the equations of conservation of mass, of momentum, and of energy — are developed. These are used to calculate the velocity, mass-velocity, temperature, and pressure rise in shock waves in air and in water. With one additional equation, they suffice to permit a calculation of detonation velocities in gaseous and in solid explosives. Predictions of detonation velocity as a function of loading density are thereby achieved, accurate to a few percent. Pressures, temperatures, and mass-velocities inside the explosive are also computed. The question of the rarefaction wave following the detonation front in the explosive is investigated. The initial velocity, pressure, and so forth, of the shock wave produced at the end of a stick of explosive are calculated successfully. The dying away of shock waves, problems of reflection, and so forth, are also discussed briefly.

I. INTRODUCTION

The theory of shock waves thus far has been developed mainly for ideal gases. Even for these, the question of the stability of shock waves has received little attention. Recently the problem of shock waves in water has gained much practical importance. Therefore it seems worthwhile to investigate the properties of shock waves under conditions as general as possible.

1. Equation of state, notations, assumptions

We shall consider a material characterized by a certain equation of state

$$p = p(V,T), \qquad (1)$$

where p is the pressure, V the specific volume, and T the absolute temperature. We shall assume that p is a unique function of V and T. This will certainly be fulfilled if thermodynamic equilibrium is es-

tablished behind the shock wave. Moreover, it will also be fulfilled if there are always the same deviations from equilibrium.

The most important example of such "regular" deviations from equilibrium is the nonoccurrence of phase changes in shock waves in cases where they would be demanded by the phase diagram: For instance, Kirkwood has shown that water behind a violent shock wave (pressure about 10,000 atm or higher) would transform into ice VII if thermodynamical equilibrium were established. However, as Kirkwood has pointed out, this will almost certainly not happen since the relaxation time for crystallization is probably many times longer than the duration of a shock condensation. In a case like this, we shall use the (metastable) continuation of the equation of state for liquid water to higher pressures.

For reasons to be explained subsequently, we must quite generally exclude phase changes from our theory (see Secs. 13 and 14). The function $p(V,T)$ will, therefore, in general refer to that phase in which the material existed before the arrival of the shock wave, even if this phase becomes metastable at the density and temperature reached behind the shock wave. The justification for this procedure is the above-mentioned fact that the relaxation time of the phase change will be long enough to preserve the metastable state behind the shock wave. No assumption about the relaxation time is required when the density and temperature behind the shock wave turn out to lie above their critical values. Then this state can be reached without a phase transition, both from the ordinary liquid and from the gaseous state.[1]

Besides p, V, and T, we shall use the energy E and the entropy S, both quantities per gram of the substance. If we agree in which phase the material is to be, its state can be described uniquely by E and V, or by S and V; for example, the pressure is a unique function of S and V. The variables S and V will turn out to be especially convenient.

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[1] The transition of solids to states of extremely high temperatures and high densities will, in general, not involve any difficulties either, although there is probably no critical point for a solid (see Secs. 7 and 14).

Pressure and specific volume, on the other hand, are not a suitable pair of independent variables because they do not always define the state of the substance uniquely. Thus water at 1 atm pressure will occupy the same specific volume below and above 4°C. Ice I at a few atmospheres and 0°C has the same specific volume as liquid water at about 150°C and the same pressure. Both these facts are, of course, consequences of the negative expansion coefficient of water. A negative expansion coefficient is not often found for substances other than water, and even for water the expansion coefficient becomes positive at higher pressures or temperatures. However, we wish to keep our considerations general and therefore admit both signs of the expansion coefficient — including, of course, the possibility of a positive coefficient for certain values of V and T, and a negative coefficient for other values.

We shall find in the following that certain assumptions must be made concerning the equation of state in order to prove the existence and uniqueness of the solutions of Hugoniot's shock-wave equations. The most important of these conditions (see Sec. 3) is

$$(\partial^2 p/\partial V^2)_S > 0 . \qquad (I)$$

Since $-(\partial p/\partial V)_S$ is the adiabatic compression modulus, condition (I) means that this modulus must increase with increasing compression. Condition (I) is very plausible; its validity will be investigated in detail in Sec. 12. It will be shown that for all single-phase systems the condition is very well fulfilled. Only in extreme cases, as for a gas at a pressure of 10^{-44} atm (!), the condition is violated for certain temperatures.

On the other hand, condition (I) is violated for most phase changes (Sec. 13). Only for evaporation and condensation does condition (I) remain true. But for the theory of compressional waves, which forms the main problem of this paper, only phase transformations between condensed phases, that is, from liquid to solid, or from one solid phase to another, would be of interest. For these

transitions condition (I) is in general violated. This is the reason for excluding phase transitions from our theory. If phase changes could take place sufficiently rapidly to occur in shock waves, the violation of condition (I) at the phase boundary would have serious consequences for the structure and stability of the shock waves (Sec. 14).

The second requirement for our theory is

$$-V\left(\frac{\partial p}{\partial E}\right)_V > -2 \qquad \text{(II)}$$

This is only a sufficient, not a necessary, condition in the general proof that compressional waves correspond to an increase of entropy (Sec. 5). Condition (II) is of course fulfilled whenever the substance expands with increasing temperature (at constant pressure). But it is also fulfilled for a small negative expansion coefficient; for example, for liquid water at 0°C, the left-hand side of condition (II) is −0.015. For melting ice I, $V(\partial p/\partial E)_V$ seems to go down to just about the critical value, namely, −2.1. Calculations for water and ice will be given in Sec. 15. We believe that condition (II) is valid for all substances in practically all states.

Conditions (I) and (II) are sufficient for the general proof of the existence and uniqueness of the solutions of the shock equation. However, in proving the stability of shock waves against breaking up in any way (Sec. 11), we also use the inequality

$$(\partial p/\partial V)_E < 0, \qquad \text{(III)}$$

which again is only a sufficient, not a necessary, condition of stability. Condition (III) is obviously fulfilled for ideal gases for which constant energy is equivalent to constant temperature. We have also found it to be valid for all one-phase systems we have investigated (Sec. 16). However, it can be shown that condition (III) breaks down again for some phase transformations, namely, if the energy and entropy change in opposite directions.

2. The shock equations

We shall denote by the subscript 1 the quantities referring to the "undisturbed" substance in front of the shock wave, by 2 those referring

to the material behind the shock wave. The velocity of the material relative to the shock wave will be u. V, E, S, p are volume, energy, entropy, and pressure, the first three quantities per gram. By ΔV, Δp, and so forth we denote the change of volume, pressure, and so forth, namely,

$$\Delta p = p_2 - p_1 , \quad \Delta V = V_2 - V_1 , \text{ and so forth.} \tag{2}$$

The conservation laws for mass, momentum, and energy are, respectively,

$$\frac{u_1}{V_1} = \frac{u_2}{V_2} , \tag{3}$$

$$p_1 + \frac{u_1^2}{V_1} = p_2 + \frac{u_2^2}{V_2} , \tag{4}$$

$$E_1 + p_1 V_1 + \tfrac{1}{2}u_1^2 = E_2 + p_2 V_2 + \tfrac{1}{2}u_2^2 . \tag{5}$$

It is convenient to transform Eq. (4) by use of Eq. (3). We obtain

$$\left.\begin{aligned} \Delta p = p_2 - p_1 &= \frac{u_1^2}{V_1} - \frac{u_2^2}{V_2} = \frac{u_1}{V_1}(u_1 - u_2) \\ &= \frac{u_1^2}{V_1}\left(1 - \frac{V_2}{V_1}\right) = -\frac{u_1^2}{V_1^2}\Delta V , \end{aligned}\right\} \tag{4a}$$

or

$$-\frac{\Delta p}{\Delta V} = \frac{u_1^2}{V_1^2} = \frac{u_2^2}{V_2^2} . \tag{6}$$

Similarly, Eq. (5) may be transformed:

$$\Delta E = E_2 - E_1 = p_1 V_1 - p_2 V_2 + \tfrac{1}{2}\left(u_1^2 - u_2^2\right) . \tag{5a}$$

Now we have from Eq. (4a)

$$u_1^2 - u_2^2 = (u_1 + u_2)\Delta p \frac{V_1}{u_1}.$$

and, using Eq. (3),

$$u_1^2 - u_2^2 = \Delta p(V_1 + V_2). \qquad (7)$$

Inserting into Eq. (5a),

$$-\frac{\Delta E}{\Delta V} = \frac{1}{2}(p_1 + p_2). \qquad (8)$$

This is the famous Hugoniot equation. It will be noted that the equation no longer contains the velocities u_1 or u_2, but that it is an equation between thermodynamic quantities only. It is, therefore, most suitable for a determination of the possible "final" states of the material behind the shock wave, when the "initial" state (state 1), in front of the shock wave, is given. For a given V_1, E_1, p_1 and given V_2, Eq. (8) gives a linear relation between E_2 and p_2. Another relation between the same quantities is provided by the equation of state. At the intersection of these two relations (if such an intersection exists) we find the possible "final" state of the material for the given value of V_2. This makes it easy to determine all possible final states for a given initial state. Having determined p_2 and V_2, we can immediately find the corresponding velocities u_1 and u_2 from Eq. (6).

II. GENERAL THEORY FOR ORDINARY SUBSTANCES[2]

3. Small shock waves

Equations (6) and (8) are obviously generalizations of the equations for infinitesimal (sound) waves. Equation (8) goes over, for infinitesimal changes, into

$$\frac{\partial E}{\partial V} = - p \, , \tag{9}$$

which is the condition for an adiabatic change of state. Equation (6) then takes the form

$$u_1^2 = u_2^2 = - V^2 \left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial p}{\partial \rho}\right)_S \, , \tag{10}$$

where ρ is the density. The right-hand side is the well-known expression for the square of the velocity of sound; that is, the material moves with respect to the "infinitesimal shock wave" with the velocity of sound, and this is, of course, also the velocity of the wave relative to the material.

We shall now consider shock waves of finite, but still very small, amplitude. We choose volume and entropy as independent variables, and expand ΔE and p_2, in Eq. (8), in powers of ΔV and ΔS. Retaining only those powers that will turn out to be relevant, we find

$$\Delta E = \left(\frac{\partial E}{\partial V}\right)_S \Delta V + \frac{1}{2}\left(\frac{\partial^2 E}{\partial V^2}\right)_S \Delta V^2 + \frac{1}{6}\left(\frac{\partial^3 E}{\partial V^3}\right)_S \Delta V^3 + \ldots + \left(\frac{\partial E}{\partial S}\right)_V \Delta S + \ldots \tag{11a}$$

All derivatives are to be taken at the original volume and entropy, V_1 and S_1. Remembering the thermodynamic relations

$$\left(\frac{\partial E}{\partial V}\right)_S = - p \tag{11}$$

and

$$\left(\frac{\partial E}{\partial S}\right)_V = T \, , \tag{12}$$

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[2] That is, substances fulfilling conditions (I) to (III) of Sec. 1.

we find

$$-\frac{\Delta E}{\Delta V} = p + \frac{1}{2}\left(\frac{\partial p}{\partial V}\right)_S \Delta V + \frac{1}{6}\left(\frac{\partial^2 p}{\partial V^2}\right)_S \Delta V^2 + \ldots - T\frac{\Delta S}{\Delta V} + \ldots \quad (12a)$$

Likewise, since $p = p_1$,

$$\frac{1}{2}(p_1 + p_2) = p + \frac{1}{2}\left(\frac{\partial p}{\partial V}\right)_S \Delta V + \frac{1}{4}\left(\frac{\partial^2 p}{\partial V^2}\right)_S \Delta V^2 + \ldots + \frac{1}{2}\left(\frac{\partial p}{\partial S}\right)_V \Delta S + \ldots \quad (12b)$$

The last term in Eq. (12b) is negligible compared with the last term in Eq. (12a) since ΔV is assumed to be small. Comparison of Eqs. (12a) and (12b), which must be equal according to Eq. (8), shows that the two first terms are identical, and therefore

$$\Delta S = S_2 - S_1 = -\left(\frac{\partial^2 p}{\partial V^2}\right)_S \frac{\Delta V^3}{12T}, \quad (13)$$

neglecting higher powers of ΔV.

We have assumed that the shock wave moves into material 1, which is thereby converted into material 2. If the shock wave is to be thermodynamically stable, the entropy must increase in this process; that is, ΔS must be positive. For a compressive wave, $\Delta V = V_2 - V_1$ is negative; if at the same time ΔS is to be positive, we must have [see Eq. (13)]

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_S > 0 \quad (I)$$

This condition seems to be fulfilled for all substances as long as only one phase is present (Sec. 12). At phase boundaries condition (I) is usually violated (Sec. 13). Therefore, if a phase change has time to occur, rarefaction waves might be stable and compression waves unstable, a case discussed in detail in Sec. 14.

As was already mentioned in Sec. 1, phase changes usually cannot occur because of the long time required for them. We can therefore

consider condition (I) quite generally as valid. In any case, we shall assume it to be valid in the main part of this paper (Secs. 3 to 11).

If condition (I) is valid, then Eq. (13) shows that compressive shock waves of small amplitude ΔV are thermodynamically stable since the entropy is greater behind the wave than in front of it. On the other hand, rarefaction waves (positive ΔV) cannot have a finite amplitude because the entropy would decrease in that case. Therefore, in any substance obeying condition (I) rarefaction waves will dissolve into trains of infinitesimal waves, a behavior well known from ideal gases. All these statements have been proven for only small ΔV -- small enough to make the higher powers of ΔV negligible in Eqs. (12a,b). The general proof will be given in Sec. 4.

We have also shown in Eq. (13) that the entropy change is proportional to the third power of the volume change. This is understandable since we have seen that in first approximation the entropy is unchanged [See Eq. (9)]. Moreover, ΔS must be proportional to an odd power of ΔV because, when the states 1 and 2 are interchanged, the sign of both ΔS and ΔV must change. The third-power relation is thus the simplest possible.

We shall now calculate the velocity of the shock wave relative to the two media, u_1 and u_2. For this purpose, we evaluate the left-hand side of Eq. (6):

$$-\frac{\Delta p}{\Delta V} = -\left(\frac{\partial p}{\partial V}\right)_{S,1} - \frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_{S,1} \Delta V + \cdots , \qquad (14)$$

where we have neglected terms of order ΔV^2 and of order $\Delta S/\Delta V$, which is also proportional to ΔV^2 [see Eq. (13)]. The subscript 1 means that the derivatives are to be taken at $V = V_1$, $S = S_1$. Now

$$-\left(\frac{\partial p}{\partial V}\right)_{S,1} = \frac{a_1^2}{V_1^2} , \qquad (14a)$$

where a_1 is the velocity of sound in the medium in front of the shock

wave, and $(\partial^2 p/\partial V^2)_S$ is positive (condition I). Using Eq. (6), we find then

$$u_1^2 = a_1^2 + \frac{1}{2} V^2 \left(\frac{\partial^2 p}{\partial V^2}\right)_S (V_1 - V_2) + \ldots . \qquad (15)$$

Therefore, if state 2 is denser than state 1, $V_1 > V_2$ and

$$u_1 > a_1 . \qquad (15a)$$

In other words, the shock-wave velocity in the medium of smaller density (medium 1) is greater than the velocity of sound in that medium. Conversely, relative to the denser medium, 2, the shock wave moves more slowly than sound. The general proof of these theorems for arbitrarily large pressure change $p_2 - p_1$ will be given in Sec. 9.

4. General proof of the increase of entropy for compression waves

We now admit arbitrarily large changes of the variables of state V, p, E, and S. We shall keep the "initial state" V_1, S_1 fixed and consider all possible "final" states V_2, S_2 which satisfy the shock equation, Eq. (8), and the equation of state.

We shall prove in this section that in any compression wave the entropy must increase, whatever the amount of the compression, whereas in the last section this theorem was proved only for small shock waves. Let $V_1 > V_2$ and let the states 1 and 2 be connected by the shock equation, Eq. (8), namely

$$E_2 - E_1 = \frac{1}{2}(p_2 + p_1)(V_1 - V_2) \qquad (16)$$

Now let us consider that state 1', which has the same specific volume as state 1 but the same entropy as state 2. Its energy is related to that of state 2 by the thermodynamic relation, Eq. (11), which gives upon integration

$$E_2 - E_1' = \int_{V_1}^{V_2} p\, dV . \qquad (17)$$

the integral to be taken along the adiabatic passing through the states 2 and 1. Now the equation of state has already been assumed to fulfill the condition

$$(\partial^2 p/\partial V^2)_S > 0 \ . \qquad \text{(I)}$$

Therefore, if V and p are used as coordinates, the adiabatic from 2 to 1' will lie below the straight line joining 2 and 1'. Explicitly,

$$p(V,S_2) < p_2 + (p_1' - p_2)\frac{V - V_2}{V_1 - V_2} \qquad \text{if } V_2 < V < V_1 \ . \qquad (18)$$

Integration of Eq. (17) gives

$$E_2 - E_1' < \tfrac{1}{2}(p_1' + p_2)(V_1 - V_2) \ . \qquad (18a)$$

Subtracting Eq. (16) from Eq. (18a) yields

$$E_1 - E_1' < \tfrac{1}{2}(p_1' - p_1)(V_1 - V_2) \ . \qquad (19)$$

We are now going to prove that E_1 must be smaller than E_1'. For this purpose let us assume that the reverse is the case, that is, $E_1 - E_1' > 0$. Then, since $V_1 > V_2$ by assumption, Eq. (19) requires that $p_1' > p_1$. This means that, for fixed volume $V = V_1$, the pressure must decrease with increasing energy (and temperature). This requires a negative expansion coefficient (see Sec. 1), which in itself is quite possible.

However, Eq. (19) requires also that the decrease of pressure with energy should exceed a certain amount. It is most convenient to divide both sides of Eq. (19) by $\frac{1}{2}(E_1 - E_1')$, which has been assumed to be positive; then we get

$$-\frac{p_1 - p_1'}{E_1 - E_1'}(V_1 - V_2) > 2 \ , \qquad (19a)$$

or

$$-\overline{(\partial p/\partial E)}_V (V_1 - V_2) > 2 . \qquad (20)$$

where $\overline{(\partial p/\partial E)}_V$ denotes the average of the derivative between E_1' and E_1. If $V_1 - V_2$ is small, Eq. (20) can certainly not be fulfilled so that our original assumption, $E_1 > E_1'$, is proved to be wrong for this case, in agreement with our results in Sec. 3. However, for larger volume changes we can assert that Eq. (20) is false only if $(\partial p/\partial E)_V$ is limited in absolute value. A certainly sufficient condition is

$$V\left(\frac{\partial p}{\partial E}\right)_V > -2 \qquad (II)$$

everywhere, because if condition (II) is fulfilled, then Eq. (20) is certainly false, since $V_1 - V_2$ is smaller than V_1. It will be proved in Sec. 15 that condition (II) is very well fulfilled even for water. The only exception we have found (Sec. 15) is melting ice I, but in this case also condition (I) is violated. We believe that condition (II) is probably fulfilled for all substances for which condition (I) is satisfied, and at least for all one-phase systems. If condition (II) is valid, we have shown that E_1 must be smaller than E_1'. Since, at constant volume, the entropy increases together with the energy, S_1' must be greater than S_1. But S_1' is equal to S_2 by definition. Therefore we have proved that

$$S_2 > S_1 \quad \text{if} \quad V_2 < V_1 . \qquad (21)$$

The denser state bounding a shock wave has a greater entropy than the state of smaller density. Hence compressional shock waves are always accompanied by an increase in entropy and are therefore thermodynamically stable. Rarefaction waves of finite amplitude are always unstable.

These results are valid for any substance with any arbitrary equation of state, and for any change of the specific volume and of the

pressure in the shock wave, provided only conditions (I) and (II) are fulfilled.

5. Existence of solutions

Let again $V_2 < V_1$. Then if there is a solution of the shock equations for a given value of V_2, we have shown in the preceding section that $S_2 > S_1$. We ask now whether or not there actually exists a solution for a given V_2 and given "initial" state V_1, E_1.

For fixed V_2, V_1, and E_1, the shock equation, Eq. (8),

$$E_2 - E_1 = \tfrac{1}{2}(p_2 + p_1)(V_1 - V_2) , \qquad (16)$$

is represented by a straight line in a p_2, E_2-diagram. The equation of state, again for the same V_2, is represented by another curve in this diagram, in general not a straight line. The solution (or solutions) of the shock equation, if any, is given by the intersection of the two curves. We shall examine the existence of such intersections by investigating, at two points p_2, which of the two curves lies higher.

(a). Take the state of volume V_2, which has the same entropy as state 1; let us call it p_2', E_2'. Then, in analogy to Eqs. (17) and (18a), we have

$$E_2' - E_1 = \int_{V_2}^{V_1} p\,dV < \tfrac{1}{2}(p_1 + p_2')(V_1 - V_2) . \qquad (22)$$

Denoting by $\tilde{E}_2'$ the value of the energy obtained from the shock equation, Eq. (16), for $p_2 = p_2'$, we see that

$$E_2' < \tilde{E}_2' . \qquad (22a)$$

In words: For the pressure p_2' the equation of state gives a lower energy than the shock equation.

(b). Take a state of extremely high energy (temperature) and of specific volume V_2. The high temperature will cause all molecules to dissociate completely into nuclei and electrons, and the kinetic energy

of their thermal motion will be large compared with their coulomb interaction. Therefore the substance, whatever it may be, will behave as an ideal monatomic gas (more accurately, as a mixture of such gases — namely, the gas of nuclei and the electron gas). For any monatomic gas, we have the relation

$$E = \frac{3}{2} pV , \tag{23}$$

which remains valid even when the gas is partly or wholly degenerate. Therefore if p_2'' denotes some very high pressure and E_2'' and $\tilde{E}_2''$ are the energies corresponding to p_2'' according to the equation of state and the shock equation, respectively, we have

$$E_2'' = \frac{3}{2} p_2'' V_2 , \tag{23a}$$

$$\tilde{E}_2'' = \tfrac{1}{2} p_2''(V_1 - V_2) . \tag{23b}$$

Therefore

$$\left.\begin{aligned} &E_2'' > \tilde{E}_2'' \quad \text{if } V_2 > \tfrac{1}{4} V_1 , \\ &\text{and} \\ &E_2'' < \tilde{E}_2'' \quad \text{if } V_2 < \tfrac{1}{4} V_1 . \end{aligned}\right\} \tag{24}$$

Since $E_2' < \tilde{E}_2'$ [Eq. (22a)], we find that for $V_2 > \frac{1}{4} V_1$ there must be at least one intersection of the curves representing the equation of state and the shock equation. If there is more than one intersection, the number of intersections must be odd. Therefore for any specific volume greater than one-quarter of the original volume, there must be at least one solution, and always an odd number of solutions, of the shock equations.

For any small value of the specific volume, $V_2 < \frac{1}{4} V_1$, there need not be any solution, or, if there are solutions, their number must be even. We are now going to show that for all real substances there will be at least two solutions for volumes V_2 between $\frac{1}{4} V_1$ and a certain, smaller value V_0. The simplest example is an ideal gas which is

not monatomic. If we use the abbreviation

$$\beta = \frac{E}{pV} , \tag{25}$$

it is shown in the ordinary theory of shock waves in ideal gases that the gas may be compressed down to a specific volume

$$V_{2\ min} = \frac{V_1}{2\beta + 1} . \tag{25a}$$

The constant β has, at low temperatures, the value 2.5 for diatomic gases and higher values for polyatomic gases. Inserting the value 2.5 into Eq. (25a) we find the well-known result that diatomic gases may be compressed in shock waves to one sixth of their original volume.

However, much greater compressions are found to be possible when the vibration of the molecule and, especially, its dissociation and ionization are considered. When these processes take place the energy content increases tremendously, and β may easily reach values of 6 or 7.[3] According to Eq. (25a) the density of the gas behind the shock wave may thus be as much as 15 times the original density. Even higher values may be expected for polyatomic gases. If the temperature behind the shock wave is very much higher than that in front, it can easily be shown that, for a given β, V_2 has very nearly the value of Eq. (25a).

The temperature region in which β has high values is likely to be quite extensive because when the dissociation is completed, ionization will follow and will affect first the outer, then successively the inner electron shells. However, at still higher temperatures, when ionization is almost complete, β must decrease again and must finally reach the value 1.5 for monatomic gases, because then the nuclei and electrons may be considered as free particles with small interaction.

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[3] See a paper by H. A. Bethe and E. Teller, published by the Ballistic Laboratory at the Aberdeen Proving Ground in 1940, which gives the energy content of air up to 5000°, and new calculations by H. A. Bethe and J. F. Whitney in which the temperature range is ex-

We thus find that any gas will have a certain maximum β which will be reached at some temperature in the dissociation or ionization region, probably when both processes are already well along, that is, at temperatures of about 10,000°. Correspondingly, for a given initial state, V_2 will have a minimum,

$$V_{2\,\min} \approx \frac{V_1}{2\beta_{\max} + 1}, \tag{25b}$$

which is certainly less than $\frac{1}{4}V_1$; thus there will be at least two solutions for every value of V_2 between $V_{2\,\min}$ and $\frac{1}{4}V_1$.

Our considerations are not restricted to di- and poly-atomic gases. Monatomic gases will also be subject to ionization, and are only distinguished by having the same value of β at low and at very high temperatures. Further, if we start from a condensed system the compression will not become very large so long as the system is a true fluid or solid. But, as the temperature behind the shock wave increases, the substance will become quasi-gaseous (the transformation takes place above the critical density and therefore does not lead to a real gas) and the transition to this state will give rise to phenomena similar to dissociation and ionization. The latter processes themselves will also occur, at higher temperatures.

It can, of course, not be predicted in general whether or not there will be only two solutions for a given V_2. It may happen that β, as a function of temperature, has several maxima. This will occur, for example, if two dissociation or ionization processes occur at widely different temperatures. Ordinary air is an example of this behavior, having one maximum due to dissociation near 8000°, and another, due to ionization, near 20,000°. Then V_2 will have two (or even more) minima, and one (or more) maxima in between. In general the maxima of V_2 will be smaller than $\frac{1}{4}V_1$, because β must be at least 1.5 at any temperature, and V_2 is close to the value of Eq. (25a). Therefore there is, in general, only one solution for every V_2 between $\frac{1}{4}V_1$ and V_1. In Fig. 2 we shall give some examples of possible shock curves (see Sec. 8).

The most important result, however, is that there is at least one solution for $V_2 > \frac{1}{4}V_1$, and at least two between $\frac{1}{4}V_1$ and some smaller

value, $V_{2\,min}$. In general, the minimum of V_2 occurs at very high temperature.

6. The shock curve.

It is convenient to consider all the solutions of the shock equation, Eq. (8), for a given "initial" state V_1, E_1, including both those with $V_2 < V_1$ and $V_2 > V_1$. The former group (compressed states) will occur behind shock waves propagating into a medium which is in state 1; the latter group (expanded states, $V_2 > V_1$) will occur in front of shock waves behind which the state of the medium is given by V_1, E_1.

We are going to show now that all the solutions of the shock equation must lie on a continuous curve in the V,E-diagram which we shall denote as the "shock curve". For this purpose we consider two solutions of the shock equation whose specific volume differs by the small amount dV. Then we have, by differentiation of Eq. (8) with respect to the quantities defining state 2,

$$2\,dE = -(p_1 + p_2)\,dV - (V_2 - V_1)\,dp \quad . \tag{26}$$

Now the equation of state gives the pressure as a unique function of V and E; therefore we may write

$$dp = \left(\frac{\partial p}{\partial E}\right)_V dE + \left(\frac{\partial p}{\partial V}\right)_E dV \quad , \tag{27}$$

where the derivatives are again unique functions of V and E, determined by the equation of state of the substance. Inserting into Eq. (26), we get

$$\frac{dE}{dV} = -\frac{p_1 + p_2 + (V_2 - V_1)(\partial p/\partial V)_E}{2 + (V_2 - V_1)(\partial p/\partial E)_V} = f(V_2, E_2) \quad . \tag{28}$$

The derivatives $\partial p/\partial E$ and $\partial p/\partial V$ are to be taken at V_2, E_2.

Equation (28) is a first-order differential equation for the shock curve. If the equation of state is known, the entire shock curve

can be obtained by integrating Eq. (28) using any standard method. The integration can be started at the point V_1, E_1; at this point Eq. (28) becomes

$$\frac{dE}{dV} = -p_1 , \tag{28a}$$

a relation already given in Eq. (9). Since Eq. (28) is a first-order differential equation, the shock curve cannot end or start anywhere in the V,E-plane. It must therefore either go to infinity or leave the region of definition of the equation of state or be closed. The last alternative will be proved to be impossible in the next section, and it will be shown that the shock curve goes to infinite energy E_2 at $V_2 = \frac{1}{4}V_1$ (see Sec. 5), whereas on the side $V_2 > V_1$ it goes either to zero temperature or to a phase boundary.

If the numerator or the denominator of Eq. (28) becomes zero separately, no difficulty arises. A simultaneous vanishing of both numerator and denominator would give a singular point, but it will be shown in Sec. 7 that the shock curve cannot start or end in singular points.

For many purposes it is more convenient to use the entropy rather than the energy as an independent variable. According to Sec. 4, we have $S_2 > S_1$ for the compressed states ($V_2 < V_1$), and $S_2 < S_1$ for the expanded states ($V_2 > V_1$). Therefore, in a V,S-diagram with V_1, S_1 as the origin, the part of the shock curve containing the compressed states will lie in the second quadrant, that containing the expanded states in the fourth quadrant. The shock curve in the V,S-diagram will be tangent to the V-axis near the origin, according to Eq. (13).

The entropy can be introduced by means of the thermodynamic relation (applied to state 2)

$$T_2 dS = dE + p_2 dV . \tag{29}$$

Inserting this into Eq. (26) gives

$$2T_2 dS = \Delta p dV - \Delta V dp , \tag{30}$$

a most convenient relation. Expressing p as a function of V and S, we may write

$$dp = \left(\frac{\partial p}{\partial V}\right)_S dV + \left(\frac{\partial p}{\partial S}\right)_V dS \qquad (30a)$$

and obtain

$$\frac{dS}{dV} = \frac{\Delta p - \Delta V(\partial p/\partial V)_S}{2T_2 + \Delta V(\partial p/\partial S)_V} \cdot \qquad (31)$$

The denominator of Eq. (31) is the same as that of Eq. (28), except for the factor T_2, because

$$(\partial E/\partial S)_V = T \ , \qquad (31a)$$

For positive ΔV (expanded states), the denominator can never become zero if condition II is fulfilled by the equation of state. Therefore, on the side of expanded states, the shock curve must go monotonically to greater specific volumes. For compressed states ($\Delta V < 0$), the denominator may easily become zero; this corresponds to a minimum (or maximum) of the specific volume. We have shown at the end of the last section that for all real substances there exists at least one minimum of V_2 for a given V_1 and that this minimum occurs at rather high temperatures (about $10{,}000^\circ$).

The numerator of Eq. (31) may be written

$$\Delta V \left[\frac{\Delta p}{\Delta V} - \left(\frac{\partial p}{\partial V}\right)_S\right] . \qquad (31b)$$

Therefore, if dS/dV were zero anywhere on the shock curve (which, as we are going to show in the next section, does not occur except for $\Delta V = 0$), we should have $\Delta p/\Delta V = (\partial p/\partial V)_S$. Physically, this would mean [See Eq. (6)] that the shock-wave velocity relative to the medium behind the shock wave,

$$u_2 = V_2 \sqrt{-\frac{\Delta p}{\Delta V}} \ , \qquad (31c)$$

becomes equal to the sound velocity in that medium,

$$a_2 = V_2 \sqrt{-\left(\frac{\partial p}{\partial V}\right)_S} \,. \tag{31d}$$

It should be remarked that while dS/dV is well defined by Eq. (31) for any values of V and S, it need not be continuous. For a mixture of two phases, $(\partial p/\partial V)_S$ will have a different (greater) value than for the pure phases (Sec. 13); hence dS/dV will in general have a discontinuity, and S(V) a kink where phase transitions begin or are completed. However, as was pointed out repeatedly, most phase changes must be excluded from our theory because condition (I) is violated.

7. Proof of the monotonic behavior of the entropy

In this section we shall prove the central theorem of the theory, namely: If the state in front of the shock wave (V_1, S_1) is given, there is one and only one solution of the shock equations for any given value of the entropy, S_2 behind the shock wave $(S_1 < S_2 < \infty)$.

If the state behind the shock wave is given (V_1, S_1) and if phase changes are excluded, there is one and only one solution of the shock equations for any given value of the entropy S_2 in front of the wave, S_2 being larger than a certain S_B where the state S_B lies on a phase boundary and S_B is a function of V_1, S_1.

The main problem is to show that there is only one solution; then from the considerations of Sec. 6 it can be proved easily that there is actually one. To prove the main statement we shall show that the assumption of two solutions with the same entropy leads to a contradiction.

Suppose we have two solutions, denoted by subscripts 2 and 3, which have the same entropy,

$$S_2 = S_3 \,. \tag{32}$$

Without loss of generality, we can assume that

$$V_3 > V_2 \,. \tag{32a}$$

Since both solutions fulfill the shock equation, Eq. (8), for the same initial state V_1, p_1, E_1, we have

$$2(E_2 - E_1) = (p_2 + p_1)(V_1 - V_2) , \tag{32b}$$

$$2(E_3 - E_1) = (p_3 + p_1)(V_1 - V_3) . \tag{32c}$$

Therefore

$$2(E_2 - E_3) = (p_2 - p_3)(V_1 - V_2) + (p_3 + p_1)(V_3 - V_2) . \tag{33}$$

Since $S_2 = S_3$, we have in analogy to Eq. (18a)

$$2(E_2 - E_3) = 2\int_{V_2}^{V_3} p\,dV < (p_2 + p_3)(V_3 - V_2) . \tag{33a}$$

Subtracting Eq. (33) from Eq. (33a), we obtain

$$(p_2 - p_1)(V_3 - V_2) + (p_2 - p_3)(V_2 - V_1) > 0 . \tag{34}$$

Since $V_3 > V_2$, we may divide this inequality by $V_3 - V_2$ and obtain

$$p_1 - p_2 < \frac{p_2 - p_3}{V_3 - V_2} (V_2 - V_1) , \tag{34a}$$

which holds irrespective of the sign of $p_1 - p_2$. Adding $p_2 - p_3$ to both sides, we obtain the corresponding equation

$$p_1 - p_3 < \frac{p_2 - p_3}{V_3 - V_2} (V_3 - V_1) . \tag{34b}$$

We can now deduce inequalities for the energy by inserting relations (34a,b) into Eqs. (32b,c). To obtain results independent of the sign of $V_1 - V_2$ or $V_1 - V_3$, we divide Eqs. (32b,c) by these quantities

and get

$$2\,\frac{E_1 - E_2}{V_2 - V_1} = p_1 + p_2 < 2p_2 + \frac{p_2 - p_3}{V_3 - V_2}\,(V_2 - V_1)\,, \tag{35}$$

$$2\,\frac{E_3 - E_1}{V_1 - V_3} = p_1 + p_3 < 2p_3 + \frac{p_2 - p_3}{V_3 - V_2}\,(V_3 - V_1)\,. \tag{35a}$$

From these inequalities we shall deduce an inequality for the entropy of state 1. We have proved in Sec. 4 that

$$S_1 > S_2 = S_3 \quad \text{if} \quad V_1 < V_2\ (<V_3)\,, \tag{36}$$

$$S_1 < S_2 = S_3 \quad \text{if} \quad V_1 > V_3\ (>V_2)\,. \tag{36a}$$

Now let us consider the state p_1', E_1' which has the volume V_1 but the entropy $S_2 = S_3$. The adiabatic which goes through the three states V_2, p_2, V_3, p_3, and V_1, p_1' is convex in the V,p-diagram according to condition (I) — $(\partial^2 p/\partial V^2)_S > 0$. Therefore, everywhere outside the range from V_2 to V_3 the adiabatic will lie above the straight line joining the points V_2, p_2 and V_3, p_3 (Fig. 1). Expressed in formulas,

$$p(V,S_2) > p_2 + \frac{p_2 - p_3}{V_3 - V_2}\,(V_2 - V) = p_3 + \frac{p_2 - p_3}{V_3 - V_2}\,(V_3 - V) \text{ if } V < V_2 \text{ or } V > V_3. \tag{37}$$

Now it is clear that V_1 must lie outside the range from V_2 to V_3 because the states 2 and 3 must either both be compressed states or both be expanded states [See Eqs. (36), (36a)]. If $V_1 < V_2$, we have, using Eqs. (17) and (37),

$$\left.\begin{aligned} 2(E_1' - E_2) = 2\int_{V_1}^{V_2} p\,dV > 2\int_{V_1}^{V_2}\left[p_2 + \frac{p_2 - p_3}{V_3 - V_2}\,(V_2 - V)\right] dV \\ = \left[2p_2 + \frac{p_2 - p_3}{V_3 - V_2}\,(V_2 - V_1)\right](V_2 - V_1)\,. \end{aligned}\right\} \tag{38}$$

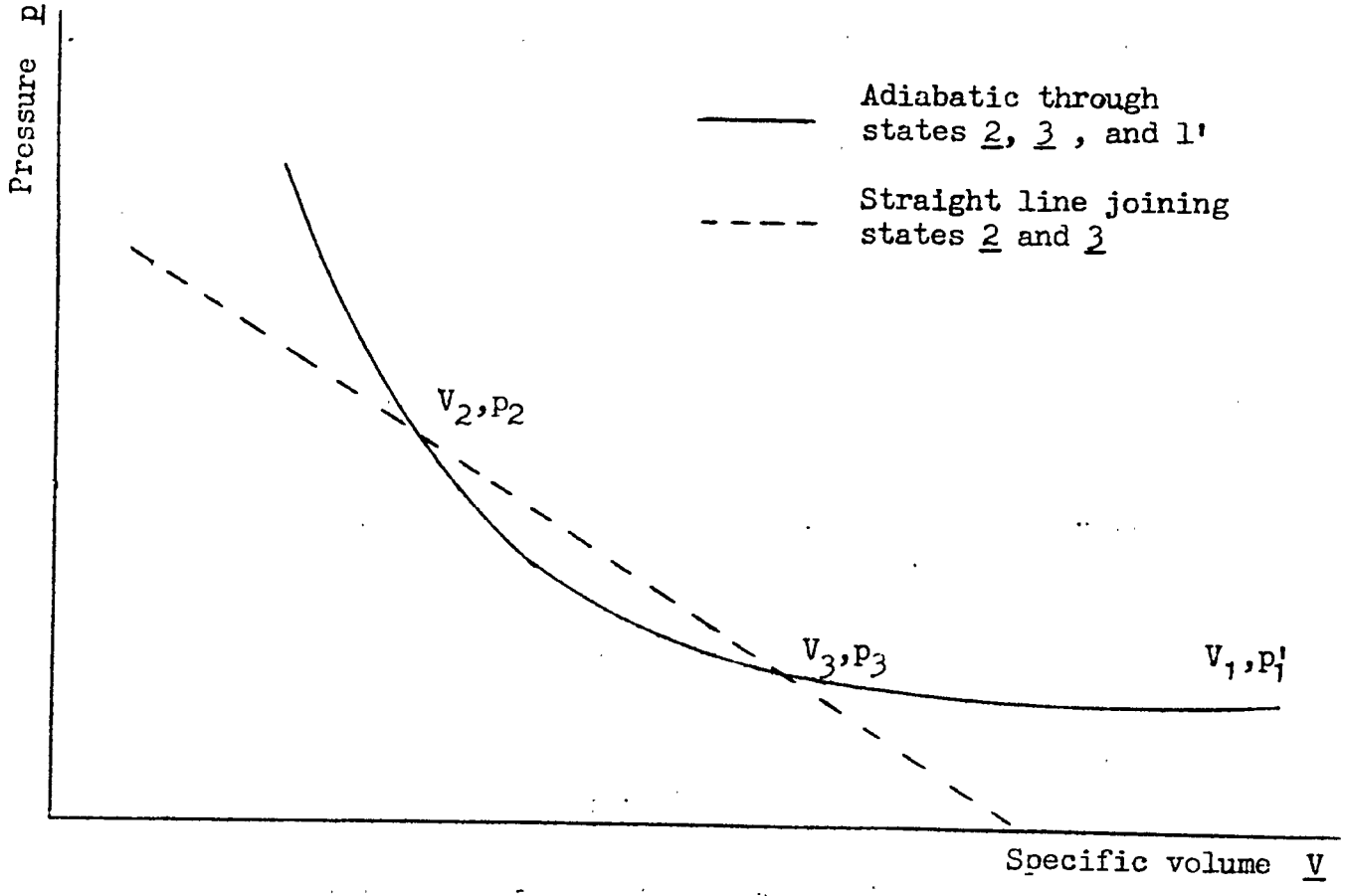


Fig. 1. Specific volume-pressure diagram used in the proof of the central theorem. The adiabatic lies below the straight line between states 2 and 3 (Sec. 4), above it everywhere else (Sec. 7).

Since $V_2 - V_1$ is positive, it follows by comparison with Eq. (35) that

$$E_1' > E_1 , \qquad (39)$$

or, since E_1' and E_1 are states of the same specific volume and since the entropy of state E_1' is S_2,

$$S_2 > S_1 , \qquad (40)$$

Similarly, if $V_1 > V_3$, we calculate the energy E_1' by integration over the part of the adiabatic between V_3 and V_1, rather than V_2 and V_1. We have then, from Eq. (37),

$$\left.\begin{aligned} 2(E_3 - E_1') = 2\int_{V_3}^{V_1} p\,dV > 2\int_{V_3}^{V_1}\left[p_3 + \frac{p_2 - p_3}{V_3 - V_2}(V_3 - V)\right] dV \\ = \left[2p_3 + \frac{p_2 - p_3}{V_3 - V_2}(V_3 - V_1)\right](V_1 - V_3)\,. \end{aligned}\right\} \quad (38a)$$

Since now $V_1 - V_3$ is positive, if follows by comparison with Eq. (35a) that

$$E_1' < E_1 \qquad (39a)$$

and therefore

$$S_2 < S_1\,, \qquad (40a)$$

in contradiction to Eq. (36a), which is applicable to our case.

We have thus obtained a contradiction, both for $V_1 < V_2$ and for $V_1 > V_3$. Therefore our original assumption must be false and we find:

<u>For a given initial state V_1, S_1 there are never two solutions of the shock equation belonging to the same "final" entropy S_2.</u>

<u>The shock curve</u> (Sec. 6) <u>will therefore go monotonically from low S to high S. It cannot have any maximum or minimum</u> because this would imply that the same value of S is taken on at least twice, once on each side of the maximum or minimum. This means also that <u>there cannot be any closed shock curve</u> because such a curve would necessarily have a maximum and a minimum.

Likewise, there cannot be any singularity on the shock curve which is approached in a spiral. If there is any singularity at all, it can at most cause a kink or a cusp in the shock curve, without interrupting the monotonic increase of the entropy.

We have shown in Sec. 6 that the shock curve cannot end anywhere in the V,S-plane but must either be closed or leave the region of definition of V and S, or go to infinity. We have just proved that the curve cannot be closed. The region of definition would extend from 0 to ∞ for both V and S if we considered all phases of the substance. Actually, we have agreed in Sec. 1 to exclude phase changes, firstly since they probably do not occur because of their long relaxation time, and secondly in order to insure the validity of condition (I). If we consider only one phase, for example, the liquid, certain large values of the volume and certain small values of the entropy cannot be reached; we have, therefore, a definite boundary of the phase toward large V and small S. On the other hand, states of high entropy can always be reached without phase change, both from the liquid and from the gas, because high entropy corresponds to temperatures above the critical one. From the solid, states of arbitrarily high S can also be reached by raising the temperature without phase change, it being questionable only whether they are identical with the states obtained by heating the liquid or gas; but metastable phases have explicitly been permitted in our consideration,[4] for the same volumes may be reached by a liquid, and also by a gas above the critical temperature. Summarizing, we find that for compressed states V is limited only by zero and S by infinity, whereas for expanded states the limits are usually given by phase boundaries.

We shall now examine the behavior of the shock curve in the various quadrants. On the side of small V_2 [$<V_1$], we know that the entropy is high, $S_2 > S_1$. We know further that there are states of very high energy and entropy, and of volume $V_2 = \frac{1}{4}V_1$, which satisfy the shock equations, Eqs. (23a,b). It follows that on the high-density

[4] The high temperature-high density state of a solid may consist of an ordered arrangement of the nuclei, with the electrons moving practically freely. Under equilibrium conditions the "lattice of nuclei" will melt at a certain high temperature. In view of the high temperature, this phase change will probably occur rather rapidly. However, as will be shown in Sec. 14, such a phase transition at very high temperature will almost certainly leave our general theory valid.

side the shock curve goes to $S_2 = \infty$ rather than to $V_2 = 0$.

That the curve does not go to $V_2 = 0$ can be demonstrated in various ways, of which the following may be the simplest. At very small specific volume, the atoms of the substance will be crushed by pressure ionization even at low temperatures since the mean distance between nuclei can be made smaller than the radius of the K-shell. Then the electrons and nuclei form again a perfect though highly degenerate gas. The coulomb energy becomes negligible in the limit of very small specific volume, being proportional to $V^{-1/3}$, while the kinetic energy of the degenerate electrons is proportional to $V^{-2/3}$. As has been mentioned in Sec. 5, the relation

$$E = \frac{3}{2} pV \tag{23}$$

is valid for a degenerate gas just as for a nondegenerate one, provided only the interactions are negligible. But if Eq. (23) is valid then there cannot be any solutions of the shock equation for $V_2 < \frac{1}{4} V_1$ [see Eqs. (23a,b)]. Therefore there is certainly no solution for very small V_2.

On the side of expanded states, $V_2 > V_1$, the entropy S_2 is less than S_1. Now it can easily be seen that there is no solution for very large V_2, for it follows from the fundamental equation, Eq. (8), that for $V_2 \gg V_1$

$$E_2 - E_1 \approx -\frac{1}{2}(p_1 + p_2)V_2 < -\frac{1}{2} p_1 V_2 , \tag{41}$$

which goes to $-\infty$ as V_2 increases. Since there is a lower bound to the energy, no solutions exist for V_2 very large. Therefore the shock curve must leave the range of definition either at $S_2 = 0$ or at a phase boundary. In the latter case, we denote by S_B the value of S_2 reached at the phase boundary.

Thus we have proved:

The shock curve is a continuous curve -- beginning at $S_2 = 0$ (absolute zero temperature) or at a phase boundary and at finite $V_2 > V_1$ and going to $S_2 = \infty$ and $V_2 = \frac{1}{4} V_1$. The

entropy has no maxima and minama. Every solution of the shock equation (for the given phase) lies on this shock curve.

These statements contain the theorem enounced at the beginning of this section — namely, that there is one and only one solution for any value of S_2 greater than S_1. It is possible to arrange all solutions for given V_1, S_1 in a single sequence according to the value of S_2.

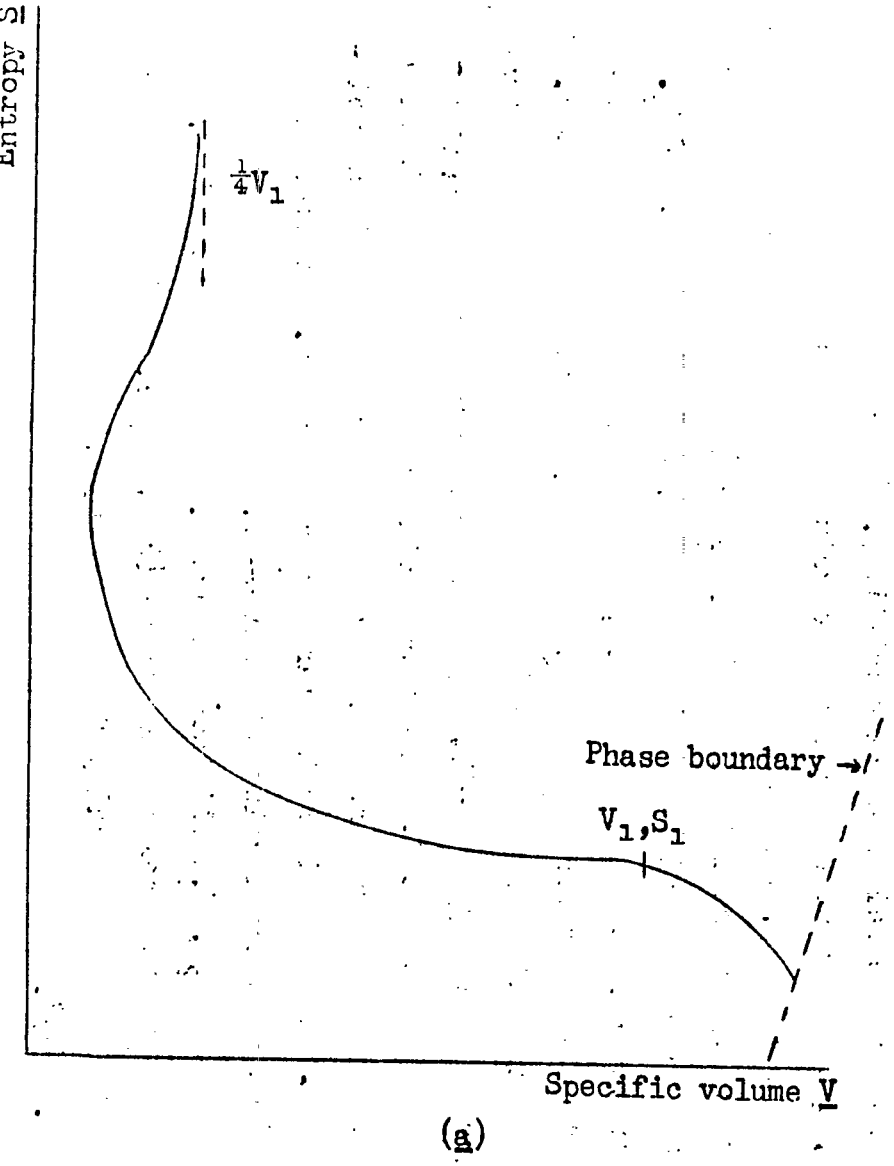
8. Behavior of volume, energy, and pressure on the shock curve

The specific volume V does not show such monotonic behavior as the entropy S. Only for expanded states ($V_2 > V_1$), which are of relatively little interest, can we show that there is at most one solution for any given V_2. This has been done in Sec. 6, by means of Eq. (31a) [see the remarks after Eq. (31a)].

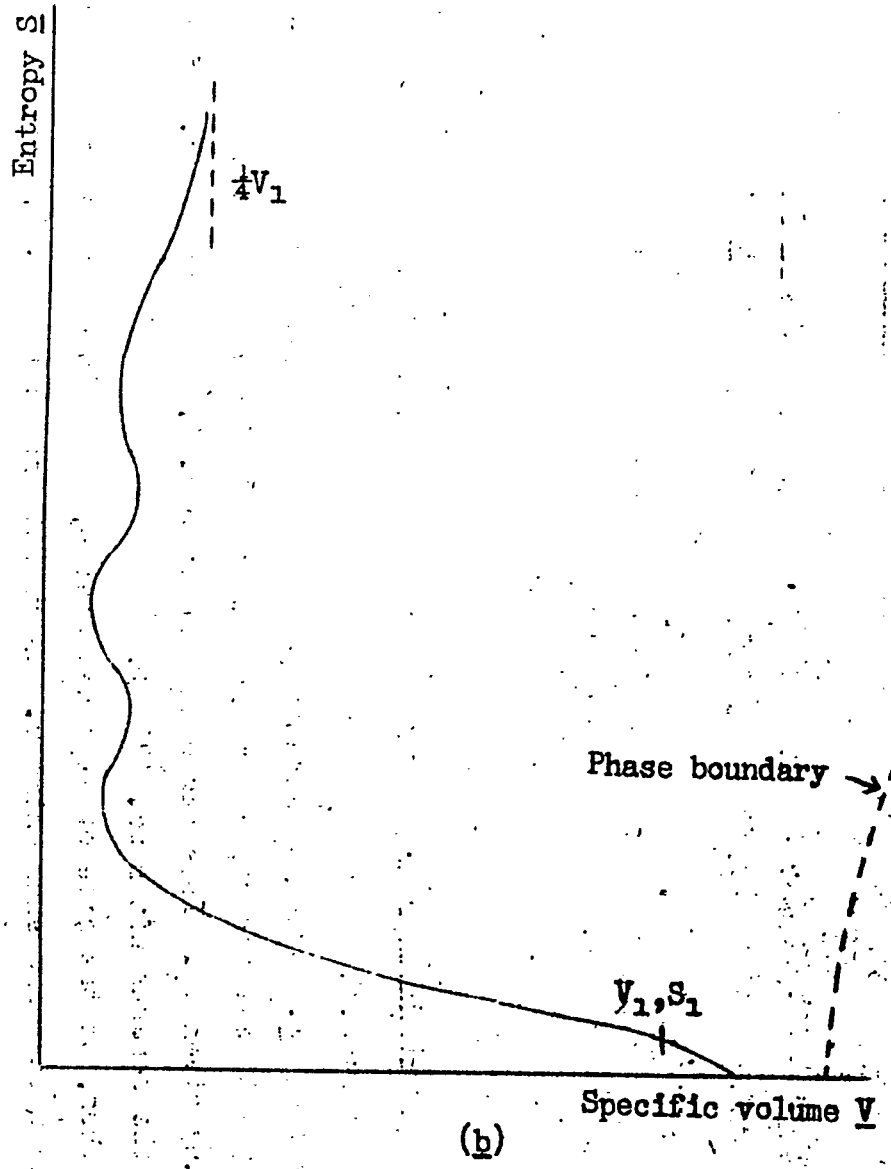
Thus, on the side of expanded states, the volume increases monotonically with decreasing entropy. As we have shown in Sec. 7, the shock curve ends in general on a phase boundary, or possibly on the line $S_2 = 0$, but in any case with a finite volume V_2 which we may denote by V_B. In other words, the possible states in front of a shock wave, behind which the material is in state V_1, S_1, can be ordered in a single sequence of monotonically increasing volume, ranging from V_1 to V_B.

For compressed states ($V_2 < V_1$), there is no restriction on the number of solutions for a given V_2. In fact, we have shown in Sec. 5 that for any real substance there will be at least two solutions for any V_2 between $V_{2\ \min}$ and $\frac{1}{4}V_1$. Typical shock curves in the V,S-diagram are shown in Fig. 2. The (first) minimum of V_2 will ordinarily occur at a rather high temperature at which dissociation of the molecules (or ionization) is rather far advanced for air. It lies at bout 8000°, and has a value of about $\frac{1}{14}V_1$. For higher temperature T_2 (or entropy S_2), V_1 will increase again. For some substances, V_2 will have further maxima and minima [Fig. 2(b)], while for others it may increase monotonically from $V_{2\ \min}$ to the asymptotic value $\frac{1}{4}V_1$ [Fig. 2(a)].

The part of the shock curve between V_1 and $V_{2\ \min}$ is ordinarily



(a)



(b)

Fig. 2. Examples of shock curves in a specific volume-entropy diagram. Both curves approach $= \frac{1}{4}V_1$ asymptotically for large S.

(a) Only one minimum for V. Curve ends for large V on a phase boundary.
(b) Three minima of V. Curve goes to S = 0.

the "main section."

We shall now consider the energy E. We have the thermodynamic relation

$$dE = T_2 dS - p_2 dV , \qquad (29)$$

where, as usual, dE, dS, dV denote small changes of E_2, S_2, V_2, with E_1, S_1, V_1 kept constant. Over the "main section" of the shock curve (see preceding paragraph), dV is negative for positive dS. Therefore dE is positive, that is, the energy increases with increasing S_2.

When V_2 has passed its minimum and S_2 increases further, the second term on the right-hand side of Eq. (29) becomes negative, but, directly behind the minimum of V_2, dV will be small and hence the energy will still increase with S. The same will again be true at extremely high entropy where (Sec. 5) the volume remains almost constant, $V_2 = \frac{1}{4} V_1$. However, in between there may, in principle, be a maximum of E_2 (followed by a minimum at a higher value of S_2). In order to derive the condition for such a maximum, we use the fundamental equation

$$2(E_2 - E_1) = (p_2 + p_1)(V_1 - V_2) \qquad (8)$$

and consider p_2 as a function of E_2 and V_2. Differentiating, we obtain

$$2\,dE = (\partial p/\partial E)_V (V_1 - V_2) dE + (V_1 - V_2)(\partial p/\partial V)_E\, dV - (p_1 + p_2) dV . \qquad (42)$$

Therefore, if dE/dV is to be zero, we must have

$$\left(\frac{\partial p}{\partial V}\right)_E = \frac{p_1 + p_2}{V_1 - V_2} . \qquad (43)$$

The right-hand side is positive for compressed states. Therefore a necessary, though by no means sufficient, condition for the occurrence of a maximum of E_2 is

$$\left(\frac{\partial p}{\partial V}\right)_E > 0 . \qquad (44)$$

Therefore we can exclude the occurence of any energy maximum on the shock curve if we require

$$\left(\frac{\partial p}{\partial V}\right)_E < 0. \qquad \text{(III)}$$

Condition (III) can easily be shown to be satisfied for ideal gases and for dissociating gases. We have not found any exception to it for any one-phase system (Sec. 16). In fact, condition (III) is even fulfilled for most phase transitions for which condition (I) is violated. We believe therefore that condition (III) is generally valid when condition (I) is valid; that is, when our entire theory is justified.

If condition (III) is satisfied, the energy of "compressed states" increases monotonically with the entropy, from E_1 to ∞. For "expanded states" we have shown in the beginning of this section that the volume V_2 increases monotonically with decreasing S_2. Therefore both terms in Eq. (29) are negative, that is, the energy decreases monotonically with decreasing entropy. Therefore we find:

If condition (III) is fulfilled, the energy E_2 increases monotonically with the entropy, along the entire shock curve.

[For the monotonic increase of S, condition (III) need not be fulfilled.] In Sec. 17 we shall discuss what happens if, for some substance, condition (III) should be violated while conditions (I) and (II) are satisfied.

For the pressure, we shall prove first that $\Delta p = p_2 - p_1$ cannot be zero anywhere, except at the "origin," $V_2 = V_1$, $S_2 = S_1$. For compressed states, $V_2 < V_1$, this follows most easily from a relation proved in the next section, Eq. (50), which states that $u_1^2 > a_1^2$ if $V_2 < V_1$. Using this result, we find from Eq. (6)

$$p_2 - p_1 = (V_1 - V_2)\frac{u_1^2}{V_1^2} > 0 \qquad \text{if } V_2 < V_1 . \qquad (45)$$

Since the shock equations are symmetrical in states 1 and 2, it follows

from Eq. (45) that also

$$p_2 < p_1 \qquad \text{if } V_2 > V_1 \,. \tag{45a}$$

Summarizing, we have proved that the material behind a shock wave must have greater density, entropy, energy, and pressure than the material in front of the wave.

Next, we can show that p_2 increases monotonically as the entropy increases from S_1 to ∞ provided the energy also increases monotonically, that is, provided condition (III) is fulfilled. It can be seen immediately that p_2 certainly increases with S_2 as long as V_2 decreases. This follows from Eq. (30), which gives, for negative ΔV,

$$|\Delta V|\, dp = 2T_2 dS - \Delta p\, dV \,. \tag{46}$$

Since Δp is positive (see previous paragraph), it follows that dp must be positive if dS is positive and dV negative. On the other hand, if the volume increases with increasing entropy, we may use Eq. (8), namely,

$$p_2 + p_1 = \frac{2(E_2 - E_1)}{V_1 - V_2} \,. \tag{47}$$

Then, as long as E_2 increases with the entropy, the numerator will increase, the denominator decrease; therefore p_2 will still increase with increasing S_2.

For expanded states very little can be said about p_2 beyond the statement $p_2 < p_1$ [Eq. (45a)]. Equation (30) gives, for positive ΔV and negative Δp,

$$\Delta V dp = -2T_2 dS - |\Delta p|\, dV \,. \tag{48}$$

The first term is positive for decreasing entropy, the second negative, and we do not have much information about their relative magnitude. Therefore p_2 may easily have maxima and minima, for $p_2 < p_1$.

Thus we find that energy and entropy increase monotonically together, being greater than E_1, S_1 for compressed states and smaller than E_1, S_1 for expanded states. The pressure increases monotonically with the entropy for compressed states; for expanded states it need not behave monotonically but will always remain below p_1. The volume increases monotonically with decreasing entropy for expanded states; for compressed states it will in general not decrease monotonically but will always remain smaller than V_1.

9. Relation between velocity and entropy

In Eq. (30) we have shown that

$$2T_2 dS = \Delta p dV - \Delta V dp \qquad (30)$$

if S_2, V_2, p_2 and $S_2 + dS$, $V_2 + dV$, $p_2 + dp$ are both solutions of the shock equation for the same initial state S_1, V_1, p_1. These two neighboring solutions will correspond to different velocities, u_1 and $u_1 + du_1$, of the shock wave relative to medium 1. Differentiating Eq. (6) logarithmically, we get

$$\frac{2\,du_1}{u_1} = \frac{dp}{\Delta p} - \frac{dV}{\Delta V} . \qquad (49)$$

Comparing this with Eq. (30), we find immediately

$$\frac{du_1}{u_1} = -\frac{T_2}{\Delta p \Delta V}\, dS , \qquad (49a)$$

and, multiplying again by Eq. (6),

$$u_1 du_1 = \frac{V_1^2}{\Delta V^2}\, T_2 dS . \qquad (50)$$

By Eq. (50), the velocity change du_1 is uniquely related to dS, the coefficient being positive definite. Therefore, since the entropy increases monotonically on the shock curve from S_B to infinity, the velocity u_1 must also increase monotonically. Moreover, there can be

only one solution of the shock equations for any given value of u_1, but we have not yet shown whether or not a solution will exist for a given u_1.

For $S_2 = S_1$, we have shown already in Sec. 3, Eq. (10), that u_1 is the sound velocity, a_1. For $S_2 > S_1$ (compression waves), Eq. (50) shows that u_1 must be greater than a_1. As S_2 increases, V_2 approaches the value $\frac{1}{4}V_1$ [see Eq. (23)] while p_2 can increase indefinitely; therefore, according to Eq. (6), u_1 will also increase indefinitely. The same conclusion can also be deduced from Eq. (50). Therefore

> For any initial state of the material, V_1, S_1, there exists one and only one solution of the shock equations for any shock-wave velocity, u_1, greater than the velocity of sound in the material, a_1.

For all these solutions, the specific volume V_2 behind the shock wave will be less than that in front, V_1, while pressure, entropy, and energy are higher behind the wave than in front of it. If conditions (I), (II), and (III) are satisfied, pressure, energy, and entropy behind the shock wave are monotonically increasing functions of the shock-wave velocity u_1. In the case of the entropy S_2, this statement is valid even if condition (III) should be violated.

For $S_2 < S_1$ (expanded states; for their physical meaning, see beginning of Sec. 6), u_1 must be smaller than the velocity of sound, a_1. As S_2 decreases, u_1 will also decrease. However, when S_2 becomes equal to S_B (phase boundary) or even equal to zero, u_1 will certainly not vanish -- because V_2 is finite, as shown in Sec. 8, and p_2 must be smaller than p_1 [see Eq. 45(a)]. Therefore Eq. (6) gives

$$\frac{u_1^2}{V_1^2} = \frac{p_1 - p_2}{V_2 - V_1} > 0 \qquad \text{for } S_2 = S_B . \qquad (51)$$

Let us denote the value of u_1 for $S_2 = S_B$ (or 0), by u_{1B}.

Then we find: For given V_1, S_1 there is one and only one solution for every u_1 between u_{1B} and a_1. These solutions correspond

to $V_2 > V_1$, $p_2 < p_1$, $E_2 < E_1$, and $S_2 < S_1$, and represent those states which may exist in front of a shock wave when the material behind the wave is in state V_1, S_1. For $u_1 < u_{1B}$, there is no solution of the shock equations.

The result which will be most important for the stability considerations (Secs. 10, 11) is this:

> The velocity of a shock wave with respect to the material in front of it (less-dense material) is always greater than the sound velocity in that material; the velocity relative to the material behind the wave (denser material) is always less than the corresponding sound velocity.

10. Stability of shock waves against splitting into waves moving in the same direction

Consider a shock wave which is preceded or followed by infinitesimal waves, either compression or rarefaction waves. Since infinitesimal waves move with the velocity of sound of the medium, the shock wave will, according to the last theorem of Sec. 9, move faster than the infinitesimal waves in front of it and more slowly than those behind it. Therefore the shock wave will catch up with the sound waves preceding it and will be overtaken by the sound waves following it.

Now consider two shock waves moving in the same direction. With respect to the material between the two waves, the "front" shock wave will move more slowly than sound, the "rear" shock wave faster than sound. Therefore the rear shock wave will overtake the front shock wave.

The same will be true for any arrangement of waves moving in the same direction, however many shock waves and infinitesimal waves it may contain. Each shock wave in the system will move faster than the wave preceding it and more slowly than the wave following it, and there is therefore always a tendency toward combination of waves. We shall now prove the stability of a single shock wave against splitting into several waves moving in the same direction. Let the shock wave be at $x = 0$ at time $t = 0$. If the wave splits at this instant, all the

partial waves must start from the same point, x = 0. But, according to our discussion, the "preceding" waves move more slowly than those "following" them, which is obviously impossible if they all start from the same point.

No shock wave can split into "partial" waves traveling in the same direction, whether these partial waves be shock waves or infinitesimal ones.

Quite generally, it is impossible that a shock wave and any other wave start from the same point at the same time in the same direction. There can only be either a shock wave or a train of infinitesimal rarefaction waves.

11. Stability against any splitting

The result of Sec. 10 still leaves the possibility open that a shock wave may split spontaneously into two shock waves moving in opposite directions (instead of the shock wave moving opposite to the direction of the original shock wave, we may substitute a train of infinitesimal rarefaction waves). In addition to the two shock waves, as von Neumann has pointed out, there will in general exist a discontinuity of the density (and entropy) which is stationary with respect to the material and remains at the material point where the splitting of the original shock wave has occurred. The pressure is continuous at this point.

Let O be the original shock wave, A that shock wave which after the split moves in the same direction as O (which we call "to the right"), C the wave which moves "to the left," and B the stationary discontinuity of density. Further, let 1 be the material to the right of wave O or A which is as yet unaffected by the shock waves; 2 the material between A and B; 3 that between B and C; and 4 that behind C or, originally, behind O.

Then materials 4 and 1 must be connected by the shock equations since they are originally separated by shock wave O. Thus

$$2(E_4 - E_1) = (p_4 + p_1)(V_1 - V_4) , \qquad (52)$$

and

$$\frac{u_{01}^2}{V_1^2} = \frac{u_{04}^2}{V_4^2} = \frac{p_4 - p_1}{V_1 - V_4}, \tag{53}$$

where u_{01} and u_{04} denote the velocity of the shock wave 0 relative to the media 1 and 4, respectively. Medium 4, then, moves to the right relative to medium 1 with the velocity

$$v = u_{01} - u_{04}. \tag{54}$$

This velocity must, of course, remain unchanged after the split of the shock wave.

Materials 2 and 1 must also be connected by the shock equations because wave A must obviously be a shock wave rather than a rarefaction wave. Consequently,

$$2(E_2 - E_1) = (p_2 + p_1)(V_1 - V_2), \tag{55}$$

$$\frac{u_{A1}^2}{V_1^2} = \frac{u_{A2}^2}{V_2^2} = \frac{p_2 - p_1}{V_1 - V_2}, \tag{55a}$$

and the velocity of 2 with respect to 1 will be

$$v_2 = u_{A1} - u_{A2} \tag{55b}$$

toward the right.

Materials 3 and 2 have the same pressure and velocity,

$$\left.\begin{aligned} p_3 &= p_2, \\ v_3 &= v_2, \end{aligned}\right\} \tag{55c}$$

while there is no condition on V_3 or V_2 or on E_3 or E_2. We have

be a shock wave or a rarefaction wave. We shall not use the detailed theory of that wave but only the following simple consideration. If u_{C3} and u_{C4} are the velocities of wave C relative to the media 3 and 4, then, since wave C moves to the left relative to the material, the velocity to the right of medium 4 relative to 3 will be

$$v_4 - v_3 = u_{C4} - u_{C3} . \tag{56}$$

Using Eqs. (55b,c), we get for the velocity to the right of medium 4 relative to medium 1

$$v_4 = u_{A1} - u_{A2} + u_{C4} - u_{C3} . \tag{56a}$$

This quantity must be equal to the velocity v given by Eq. (54), that is,

$$u_{O1} - u_{O4} = u_{A1} - u_{A2} + u_{C4} - u_{C3} . \tag{57}$$

This will be the fundamental equation of the theory.

Now we have from Eq. (3)

$$\frac{u_{C4}}{u_{C3}} = \frac{V_4}{V_3} . \tag{58}$$

Therefore

(a). If wave C is a compression wave,

$$p_2 = p_3 > p_4 . \tag{59}$$

Therefore, according to Sec. 8,

$$V_4 > V_3 ;$$

and, according to Eq. (58),

$$u_{C4} > u_{C3} .$$

Inserting this into Eq. (57) gives

$$u_{O1} - u_{O4} > u_{A1} - u_{A2} . \tag{59a}$$

(b). If wave C is a rarefaction wave,

$$p_2 < p_4 , \tag{60}$$

- we obtain by a similar reasoning

$$u_{01} - u_{04} < u_{A1} - u_{A2} . \tag{60a}$$

Equations (59a) and (60a) are in a convenient form since they require the comparison of two solutions of the shock equation belonging to the same initial state, 1. From Eq. (53) we find

$$(u_{01} - u_{04})^2 = (p_4 - p_1)(V_1 - V_4) , \tag{61}$$

and similarly

$$(u_{A1} - u_{A2})^2 = (p_2 - p_1)(V_1 - V_2) . \tag{61a}$$

Obviously, Eqs. (59) to (61) are completely symmetrical with respect to states 2 and 4; therefore we can assume without loss of generality that $p_4 > p_2$, that is, Eq. (60). Then Eq. (60a) must hold, and therefore we find from Eqs. (61) and (61a) the condition for solit:

$$(p_4 - p_1)(V_1 - V_4) < (p_2 - p_1)(V_1 - V_2) . \tag{62}$$

Since $p_4 > p_2$, Eq. (62) is obviously impossible if

$$V_4 < V_2 . \tag{62a}$$

However, Eq. (62a) follows automatically from $p_4 > p_2$ as long as both states, 2 and 4, lie on a part of the shock curve on which the volume decreases with increasing entropy, for example, on the "main section" (Sec. 8). For most substances, this main section probably covers all temperatures up to about 10,000° (Sec. 8).

However, at very high temperatures, which may still be experimentally accessible, V_2 increases with increasing entropy (Sec. 8) while p_2 continues to increase. Then Eq. (62a) does not hold but is reversed,

that is, $V_4 > V_2$. In this case, we have certainly

$$2p_1(V_1 - V_4) < 2p_1(V_1 - V_2) \ . \tag{62b}$$

Adding this inequality to Eq. (62) and using the fundamental shock equations (52) and (55), we get the condition

$$E_4 < E_2 \ , \tag{63}$$

which is necessary but not sufficient for the split of the original shock wave. (It is almost sufficient since $p_1 \ll p_2$ beyond the minimum of the volume.) Now, as we have shown in Sec. 8, the energy will increase monotonically with the pressure if the material fulfills condition (III). Then Eq. (63) can certainly not be fulfilled for $p_4 > p_2$. Thus we find:

A shock wave can never split in a material whose equation of state fulfills the three conditions (I), (II), (III).

As these conditions appear to be valid for practically all materials, as long as there are no phase transitions, we have proved the complete stability of one-dimensional shock waves in all ordinary materials.