III. INVESTIGATION OF THE THREE CONDITIONS

In this part of the paper we shall investigate the validity of our three postulates

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

$$V(\partial p/\partial E)_V > -2 , \qquad \text{(II)}$$

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

which we have used throughout in our theory of shock waves (Part II). Of these conditions only the first two are needed in the general proof (up to Sec. 10); the last one is required only to prove the stability of shock waves against any kind of splitting (Sec. 11).

Analysis shows that none of the three conditions is required by any general thermodynamic or statistical argument because it can be shown that for each one of the three conditions there exist some substances for which the condition is violated at certain temperatures and densities. Therefore we can only ascertain the range of validity of the conditions by investigating a sufficient number of different physical states. For all single-phase systems which we have investigated, all three conditions have been found valid by a wide margin. Therefore we believe that they are valid for all single-phase systems of any practical importance.

The cases in which one or more of the conditions are violated all refer to phase transitions. Therefore we had to exclude phase transitions in Part II of this paper. In Secs. 14 and 17 we shall discuss briefly some of the phenomena which might occur if phase transitions could take place in shock waves.

12. The condition $(\partial^2 p/\partial V^2)_S > 0$ for single-phase systems

The simplest equation of state is that of a perfect gas with constant specific heat. Then the adiabatics are given by

$$p = \text{constant} \cdot V^{-\gamma} , \qquad (64)$$

where γ is the ratio of the specific heats, c_p/c_V, and the constant depends only on the entropy. Therefore

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_S = \gamma(\gamma + 1)\,\frac{p}{V^2}\,, \tag{64a}$$

which is certainly positive.

For most other cases it is convenient to express the adiabatic derivative in terms of isothermal derivatives. For any function $f(V,T)$, we have

$$\left(\frac{\partial f}{\partial V}\right)_S = \left(\frac{\partial f}{\partial V}\right)_T - \frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V}\left(\frac{\partial f}{\partial T}\right)_V . \tag{65}$$

Here we may use the thermodynamic relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V , \tag{66}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{c_V}{T}\,, \tag{66a}$$

where c_V is the specific heat at constant volume, a positive definite quantity. Applying Eq. (65) to $f = p$, we find

$$\left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial p}{\partial V}\right)_T - \frac{T}{c_V}\left(\frac{\partial p}{\partial T}\right)_V^2 . \tag{67}$$

Since $(\partial p/\partial V)_T$ is negative, we find that the adiabatic modulus of compression, $-(\partial p/\partial V)_S$, is always greater than the isothermal one. Another differentiation gives

$$\left.\begin{aligned}\left(\frac{\partial^2 p}{\partial V^2}\right)_S &= \frac{\partial^2 p}{\partial V^2} - \frac{2T}{c_V}\frac{\partial p}{\partial T}\frac{\partial^2 p}{\partial V \partial T} + \frac{T}{c_V^2}\left(\frac{\partial p}{\partial T}\right)^2\frac{\partial c_V}{\partial V}\\ &- \frac{T}{c_V}\frac{\partial p}{\partial T}\cdot\left[\frac{\partial^2 p}{\partial V \partial T} - \frac{1}{c_V}\left(\frac{\partial p}{\partial T}\right)^2 + \frac{T}{c_V^2}\left(\frac{\partial p}{\partial T}\right)^2\frac{\partial c_V}{\partial T} - \frac{2T}{c_V}\frac{\partial p}{\partial T}\frac{\partial^2 p}{\partial T^2}\right].\end{aligned}\right\} \tag{67a}$$

On the right-hand side, p and c_V are considered

T; hence $\partial/\partial T$ implies that V is kept constnat, and vice versa. Equation (67a) may be slightly simplified by means of the thermodynamic relation

$$T\,\frac{\partial^2 p}{\partial T^2} = \frac{\partial c_V}{\partial V}\,. \tag{67b}$$

Then Eq. (67a) becomes

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_S = \frac{\partial^2 p}{\partial V^2} - \frac{3T}{c_V}\frac{\partial p}{\partial T}\frac{\partial^2 p}{\partial V \partial T} + \frac{3T}{c_V^2}\left(\frac{\partial p}{\partial T}\right)^2\frac{\partial c_V}{\partial V} + \frac{T}{c_V^2}\left(\frac{\partial p}{\partial T}\right)^3\left(1 - \frac{T}{c_V}\frac{\partial c_V}{\partial T}\right)\,. \tag{68}$$

From Eq. (68) we can easily get an idea about the terms which might theoretically cause $(\partial^2 p/\partial V^2)_S$ to be negative. Beginning with the last term of Eq. (68), we have the following possibilities:

(a). The specific heat may increase rapidly with the temperature. Then, if $\partial p/\partial T > 0$, which is the normal behavior, the last term of Eq. (68) is negative. It will be large in absolute value if, simultaneously with a large $\partial c_V/\partial T$, we have a small specific heat c_V. This points to low temperatures as the place where $(\partial^2 p/\partial V^2)_S$ might be most likely to become negative. The following cases of rapidly increasing specific heat will be discussed below:

(i) Ideal gases with internal degrees of freedom, such as vibration or electronic excitation.

(ii) Dissociating, but otherwise-ideal, gases (ionization is a special case of dissociation).

(iii) Solids at very low temperature.

In cases (i) and (ii), the first term in Eq. (68) can be shown to be numerically larger than the last one, because c_V is never very small (at least $\frac{3}{2}k$ for monatomic, $\frac{5}{2}k$ for diatomic gases, and so forth). In case (iii), the term with $\partial c_V/\partial V$ is positive and numerically greater than the last term.

(b). The specific heat may decrease with increasing volume, that is, $\partial c_V/\partial V < 0$. This case is realized for a number of liquids. However, from the empirical data it can easily be shown that the thi term in Eq. (68) is usually less than one percent of the first.

(c). The pressure may decrease with the temperature ($\partial p/\partial T < 0$), while the modulus of compression, $-\partial p/\partial V$, increases with T (that is, $\partial^2 p/\partial V \partial T < 0$). Then the second term in Eq. (68) is negative. Water below 4° is an example, but the second term is again less than one percent of the first.

(d). The derivative at constant temperature, $\partial^2 p/\partial V^2$, may be negative. This happens at and near the critical temperature for volumes greater than the critical volume. In this case, the (positive) second term of Eq. (68) more than outweighs the first.

In all cases mentioned, the resulting value of $(\partial^2 p/\partial V^2)_S$ is positive. We shall now discuss the various cases in order.

(a). Specific heat increasing rapidly with temperature. -- (i) Ideal gas with variable specific heat. For an ideal gas, we have

$$pV = RT , \tag{69}$$

$$\frac{\partial p}{\partial T} = \frac{R}{V} > 0 , \tag{69a}$$

$$\frac{\partial c_V}{\partial V} = T \frac{\partial^2 p}{\partial T^2} = 0 . \tag{69b}$$

[See. Eq. (67b)]. Equation (68) becomes

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_S = \frac{p}{V^2}\left[\left(2 + \frac{R}{c_V}\right)\left(1 + \frac{R}{c_V}\right) - \frac{R^2}{c_V^2}\frac{T}{c_V}\frac{dc_V}{dT}\right] . \tag{70}$$

The critical term is obviously the last one. To get an estimate of its value we consider a vibration of the molecules of frequency $\nu = k\Theta/h$. Then the specific heat is

$$\frac{c_V}{R} = \beta + \left(\frac{\Theta}{T}\right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2} , \tag{70a}$$

where βR is the specific heat without the vibration ($\beta = 2.5$ for linear, $\beta = 3$ for nonlinear molecules). The highest value of the last term in Eq. (70) is obtained for $T \approx \frac{1}{4}\,\Theta$; at this temperature the contribution of the oscillation to c_V is about 0.3R, while the derivative, $T\,dc_V/dT$, is about 0.65R. Then, if $\beta = 2.5$, the last term in Eq. (70) becomes −0.030, as against 3.2 for the first term. The negative term is thus only about one percent of the positive one.

It might be expected that the negative term in Eq. (70) will become greater if the molecule has several modes of vibration, because each mode will contribute to $T\,dc_V/dT$. However, this effect will be largely offset by the increase of c_V itself. For example, for a molecule having as many as 100 different modes of vibration, all of the same frequency, and having $\beta = 3$, the maximum of the negative term occurs at $T \approx 0.12\Theta$ and has a value of about 0.11, as against 2.7 for the positive term. Only for a molecule with more than 10^{66} (!) vibrational modes all of the same frequency, would the derivative $(\partial^2 p/\partial V^2)_S$ become negative at certain (low) temperatures. From this we see that, <u>while it is in principle possible that postulate (I) is violated</u>, this will never occur as the result of the excitation of vibrations for any real gas. It can easily be seen that the same holds for the excitation of the higher electronic states.

(ii) <u>Dissociation of molecules</u>. In this case, the exact calculation would become exceedingly complicated. We can, however, get a rather good approximation by remembering that the significant term in Eq. (68) is the last one and that this term is greatest when the specific heat rises steeply but is not yet itself very large. This will occur when the degree of dissociation, α, is still very low; in fact, from our calculation we shall find that a value of α less than 1 percent is most favorable. Then we can neglect α compared with 1, but we must, of course, not neglect $T\,\partial\alpha/\partial T$.

When a molecule dissociates into n + 1 atoms, the degree of dissociation is given by

$$\frac{\alpha^{n+1}}{(1-\alpha)V^n} = K(T) = A^n e^{-Q/RT} , \qquad (71)$$

where *K* is the dissociation constant, *Q* the dissociation energy per gram, *R* the gas constant per gram of the molecular gas, and A^n is the ratio of the "*a priori* probabilities" of dissociated and molecular states and depends only slightly on temperature. The numerical value of AV is of the order of 10^4 to 10^8 for ordinary densities and temperatures.

With our assumption, $\alpha << 1$, we have

$$\alpha = (AV)^{\frac{n}{n+1}} e^{-q} , \tag{71a}$$

with

$$q = \frac{Q}{(n+1)RT} . \tag{71b}$$

We shall need the derivatives

$$\frac{\partial\alpha}{\partial V} = \frac{n}{n+1} \frac{\alpha}{V} , \tag{72}$$

$$\frac{\partial\alpha}{\partial T} = q \frac{\alpha}{T} . \tag{72a}$$

Because of the large value of the "*a priori* probability" AV, we get appreciable dissociation already for quite large values of *q*. If we require $(n+1)\alpha \approx 0.001$ to 0.01 (see below) and have $AV = 10^4$ to 10^8, then

$$q = 10 \text{ to } 30 . \tag{72b}$$

The pressure is given by

$$p = \frac{RT}{V} (1 + n\alpha) . \tag{73}$$

The derivatives required in Eq. (68) are, neglecting $n\alpha$ but keeping $qn\alpha$,

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{V^3} . \tag{73c}$$

The specific heat may be written

$$c_V = c_{V,0} + Q \frac{\partial \alpha}{\partial T} , \tag{74}$$

where $c_{V,0}$ is the value of the specific heat if the degree of dissociation does not change, that is, essentially the c_V of the molecule. Putting

$$c_{V,0} = \beta R , \tag{74a}$$

where β is a slowly changing function of the temperature, and using Eq. (71b), we find

$$c_V = R[\beta + (n+1)q^2\alpha] . \tag{75}$$

Therefore

$$\frac{\partial c_V}{\partial V} = \frac{R}{V} nq^2 \alpha , \tag{75a}$$

$$\frac{\partial c_V}{\partial T} = R \left[\frac{d\beta}{dT} + (n+1)\frac{\alpha}{T} q^2(q-2)\right] . \tag{75b}$$

Inserting the results of the previous paragraph into Eq. (68), we obtain, term by term,

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_S = \frac{p}{V^2}\left\{2 + 3\,\frac{(1+nq\alpha)\left(1+\frac{n}{n+1}\,q\alpha\right)}{\beta + (n+1)q^2\alpha} + 3\,\frac{nq^2\alpha(1+nq\alpha)^2}{[\beta + (n+1)q^2\alpha]^2}\right.$$

$$\left. + \frac{(1+nq\alpha)^3}{[\beta + (n+1)q^2\alpha]^2} - \frac{(1+nq\alpha)^3}{[\beta + (n+1)q^2\alpha]^3}\left[T\frac{d\beta}{dT} + (n+1)q^2(q-2)\alpha\right]\right\}. \qquad (76)$$

Only the last term is negative, as expected. We know already that the term $T\,d\beta/dT$ is harmless [see case (i)]. The other negative term is largest for large q and relatively small α. It can easily be shown that the maximum of this term, for fixed q [$\gg 1$] and variable α is obtained for

$$(n+1)q^2\alpha \approx \frac{1}{2}\beta\ . \qquad (76a)$$

Then $nq\alpha < \beta/2q$, and the last term of Eq. (76) becomes approximately

$$\frac{\frac{1}{2}\beta\left(q + \frac{3}{2}\beta - 2\right)}{\left(\frac{3}{2}\beta\right)^3} = \frac{4}{27}\,\frac{q + \frac{3}{2}\beta - 2}{\beta^2}\ . \qquad (76b)$$

The highest value which q can take [see Eq. (72b)] is about 30, and this can occur only for large n, in which case β is at least 3, and in most cases very much higher. For $q = 30$, $\beta = 3$, we obtain for the last term of Eq. (76),

$$\text{Last term} = \frac{4}{27}\,\frac{32.5}{9} = 0.54\ , \qquad (76c)$$

while the positive terms become 2.94. The negative term is thus less than one fifth of the positive ones, although we have made conditions most favorable for a large negative term. The value of $(n+1)\alpha$ becomes, with our assumptions, about 0.0017, justifying the neglections made ($n\alpha \ll 1$) and also the value of α used in computing Eq. (72b).

The case of the ionization of monatomic gases may seem of interest because for these β is only 1.5. However, at the same time the *a priori* weight *A* is reduced because of the small mass of the electron. Values of AV between 1 and 10^4 are usual, which, with $(n+1)\alpha = 0.01$, gives *q* between 5 and 14. In the most favorable case this gives about 1 for the negative term in Eq. (76) against about 4 for the positive terms.

As in the case of an ideal gas with variable β, there exists the possibility of negative $(\partial^2 p/\partial V^2)_S$, but only for extreme dilution of the gas. If we consider the ionization of a monatomic gas which is most favorable for negative $(\partial^2 p/\partial V^2)_S$, and if $AV = 10^4$ for 1 atm pressure, we expect $AV = 10^{48}$ for a pressure of 10^{44} atmospheres (!). For this value of AV, and for $(n+1)\alpha = 10^{-4}$, we get $q = 120$, which would make the negative term in Eq. (76) just greater than the positive ones. Thus we see again that $(\partial^2 p/\partial V^2)_S > 0$ is not required on statistical grounds but is very well fulfilled for all experimentally obtainable pressures.

(iii) Solids at very low temperatures. The specific heat is given in good approximation by Debye's relation

$$c_V = a(T/\theta)^3 , \qquad (77)$$

where θ is the Debye temperature and *a* a constant. We have thus a rapid increase of c_V with temperature, and at the same time we can make c_V itself as small as we like, in contrast to the two previous cases where c_V was at least equal to the specific heat of translation and rotation. It seems therefore that the negative term with $\partial c_V/\partial T$, can be made as large as we like compared with the first term in Eq. (68). However, as we shall see, the term with $\partial c_V/\partial V$ saves the inequality $(\partial^2 p/\partial V^2)_S > 0$.

We have from Eq. (77)

$$\frac{T}{c_V}\frac{\partial c_V}{\partial T} = 3 \; ; \qquad (77a)$$

hence the three last terms in Eq. (68) become

$$\frac{T}{c_V^2}\left(\frac{\partial p}{\partial T}\right)^2\left(3\,\frac{\partial c_V}{\partial V} - 2\,\frac{\partial S}{\partial V}\right), \tag{77b}$$

where we have used the thermodynamic relation, Eq. (66). At zero temperature, the entropy is zero for any V; further, we have from Eq. (77) for a given V,

$$S = \int_0^T \frac{c_V}{T}\,dT = \frac{1}{3}c_V\,. \tag{77c}$$

Inserting into Eq. (77b), the term in parentheses becomes

$$\left(3 - \frac{2}{3}\right)\frac{\partial c_V}{\partial V} = -7\,c_V\,\frac{\partial \log\theta}{\partial V}\,, \tag{78}$$

which is certainly positive, because the Debye temperature depends on the strength of the elastic forces and therefore increases upon compression.

(b) Specific heat decreasing with increasing volume, liquids and solids at ordinary temperature. -- Here we may use the Tait equation of state

$$p = B(T)\left[e^{(V_0 - V)/\kappa} - e^{(V_0 - V_T)/\kappa}\right], \tag{79}$$

where κ is a certain constant of the dimension of a volume, usually about one-tenth of the volume of the substance, V_T is the volume at temperature T and zero pressure, and V_0 a suitably chosen standard volume (constant). The function B is a function of temperature; in all cases the author is aware of, it increases with T; for water it has a value of about 3000 bars (1 bar ≈ 1 kg/cm^2 ≈ 1 atm).

We have then

$$\frac{\partial^2 p}{\partial V^2} = \frac{B}{\kappa^2}\,e^{(V_0 - V)/\kappa} > 0\,, \tag{79a}$$

$$\frac{\partial^2 p}{\partial V \partial T} = -\frac{1}{\kappa}\frac{dB}{dT}\, e^{(V_o - V)/\kappa} < 0 . \qquad (79b)$$

For all substances with positive expansion coefficient $\partial p/\partial T$ is positive, therefore the first two terms in Eq. (68) are positive. Usually $\partial c_V/\partial T$ is very small so that the last term in parentheses in Eq. (68) is also positive. There remains the term with $\partial c_V/\partial V$. This is "generally assumed to be zero"[5] but may actually be slightly negative, as for[5] CCl_4 and[6] C_6H_6. For CCl_4 at 45°C and 1 atm pressure, we have

$$\partial c_V/\partial V = 9.5 \text{ bar/deg},$$

$$B = 740 \text{ bars},$$

$$dB/dT = 2.2 \text{ bar/deg},$$

$$\kappa = 0.0600 \text{ cm}^3/\text{gm},$$

$$T\,\partial p/\partial T = p + \partial E/\partial V = 3250 \text{ bars},$$

$$c_V = 0.21 \text{ cal/gm-deg} = 8.9 \text{ bar-cm}^3/\text{gm-deg}.$$

Therefore

$$\frac{\partial^2 p}{\partial V^2} = 206{,}000 \quad \text{bar } (\text{gm/cm}^3)^2 ,$$

$$-\frac{3T}{c_V}\frac{\partial p}{\partial T}\frac{\partial^2 p}{\partial V \partial T} = 40{,}000 \quad \text{bar } (\text{gm/cm}^3)^2 ,$$

$$\frac{3T}{c_V^2}\left(\frac{\partial p}{\partial T}\right)^2 \frac{\partial c_V}{\partial V} = -12{,}000 \quad \text{bar } (\text{gm/cm}^3)^2 .$$

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[5] R. E. Gibson and D. H. Loeffler, Journ. Am. Chem. Soc. 63, 898, 1941.

[6] R. E. Gibson and D. H. Loeffler,

The negative term is thus seen to be only about one-seventeenth of the leading (first) term. It is also clear from the nature of the quantity $\partial c_V/\partial V$ that it cannot be very large because otherwise c_V would reach exceedingly high values for high compression.

(c) Pressure decreasing with temperature, water below 4°C. -- Below 4°C, water has a negative $\partial p/\partial T$. The expansion coefficient at 0°C, is[7]

$$(\partial V/\partial T)_p = -3.1 \times 10^{-5} \text{ cm}^3/\text{gm-deg.} \tag{79c}$$

The characteristic pressure B, extrapolated from Ref. 5, is about 2750 bars, while $\kappa = 0.137$ cm^3/gm. Therefore

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{B}{\kappa}\left(\frac{\partial V}{\partial T}\right)_p = -0.62 \text{ bar/deg.} \tag{79d}$$

Further, $dB/dT \approx 10$ bar/deg (likewise extrapolated), so that [see Eq. (79b)]

$$\partial^2 p/\partial T\partial V \approx -70 \text{ bar-gm/cm}^3\text{-deg.}$$

The second term in Eq. (68) becomes then, with $c_V = 42$ bar-cm^3/gm-deg,

$$-\frac{3T}{c_V}\frac{\partial p}{\partial T}\frac{\partial^2 p}{\partial V\partial T} = -850 \text{ bar } (\text{gm/cm}^3)^2,$$

while the first term

$$\frac{\partial^2 p}{\partial V^2} = \frac{B}{\kappa^2} = 145\,000 \text{ bar } (\text{gm/cm}^3)^2.$$

(d) Derivative at constant temperature, $\partial^2 p/\partial V^2$, negative; neighborhood of the critical point[8]. On the critical isotherm we have $(\partial p/\partial V)_T = 0$ at the critical volume and $(\partial p/\partial V)_T < 0$ for larger

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[7] Dorsey, Properties of ordinary water substance (Reinhold, 1940), p. 231.

[8] I am indebted to Dr. G. Placzek for the calculations reported in this section.

volumes, so that $(\partial^2 p/\partial V^2)_T$ is negative at volumes somewhat above the critical one. This contribution may be compensated by the second term of Eq. (68): $(\partial p/\partial T)_V$ is positive for a gas, and $\partial^2 p/\partial V \partial T$ is negative, that is, the modulus of compression, $-\partial p/\partial V$, increases with T.

The calculation is simplest if we use reduced temperatures, volumes, and pressures, namely,

$$v = \frac{V}{V_c} , \quad \tau = \frac{T}{T_c} , \quad \pi = \frac{p}{p_c} , \tag{80}$$

where V_c, T_c, and p_c are the critical volume, temperature, and pressure. According to Van der Waals' equation,

$$p_c V_c = \frac{3}{8} RT_c , \tag{80a}$$

and the equation itself has the form

$$\pi = \frac{8}{3} \frac{\tau}{v - \frac{1}{3}} - \frac{3}{v^2} . \tag{80b}$$

The derivatives are

$$\left(\frac{\partial^2 \pi}{\partial v^2}\right)_\tau = \frac{16}{3} \frac{\tau}{\left(v - \frac{1}{3}\right)^3} - \frac{18}{v^4} \tag{80c}$$

$$\left(\frac{\partial \pi}{\partial \tau}\right)_v = \frac{8}{3} \frac{1}{v - \frac{1}{3}} , \tag{80d}$$

$$\left(\frac{\partial^2 \pi}{\partial \tau^2}\right)_v = 0 ; \quad \text{therefore [see Eq. (67b)]} \ \frac{\partial c_v}{\partial v} = 0 , \tag{80e}$$

$$\frac{\partial^2 \pi}{\partial v \partial \tau} = - \frac{8}{3} \frac{1}{\left(v - \frac{1}{3}\right)^2} . \tag{80f}$$

Inserting into Eq. (68), we obtain after simplification,

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_S = \frac{16}{3}\frac{p_c}{V_c^2}\frac{1}{\left(v-\frac{1}{3}\right)^3}\left[\tau - \frac{27}{8}\frac{\left(v-\frac{1}{3}\right)^3}{v^4} + \frac{3\tau}{2\beta} + \frac{\tau}{2\beta^2}\right] . \qquad (81)$$

The first two terms in the square bracket arise from $(\partial^2 p/\partial V^2)_T$; the third term in Eq. (81) represents the second term in Eq. (68), and the last one comes from the fourth term in Eq. (68). The third term in Eq. (68) is zero because of the special form of the Van der Waals' equation [see Eq. (80e)]; the last term in Eq. (68) has been assumed to be zero, that is, c_v is assumed to be independent of temperature, and to be given by

$$c_v = \beta R . \qquad (81a)$$

The isothermal derivative, $(\partial^2 p/\partial V^2)_T$, that is, the first two terms in Eq. (81), is negative if

$$\tau < \tau_\ell = \frac{27}{8}\frac{\left(v-\frac{1}{3}\right)^3}{v^4} . \qquad (81b)$$

The maximum of τ_ℓ is obtained for $v = 4/3$ and has the value

$$\tau_{\ell\,\max} = \frac{2187}{2048} = 1.0678 . \qquad (81c)$$

For a given v, the substance is a gas only if τ is greater than a certain τ_g, while for lower temperature we would obtain an unstable state. If the Van der Waals' equation is used, the minimum temperature for $v = 4/3$ is[9]

$$\tau_g(4/3) = 0.9838 . \qquad (81d)$$

For actual gases, τ_g is even higher than the value given by Van der

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[9] From Kuenen, Zustandsgleichung, 1907, p. 94 (according to a table calculated by J. P. Dalton).

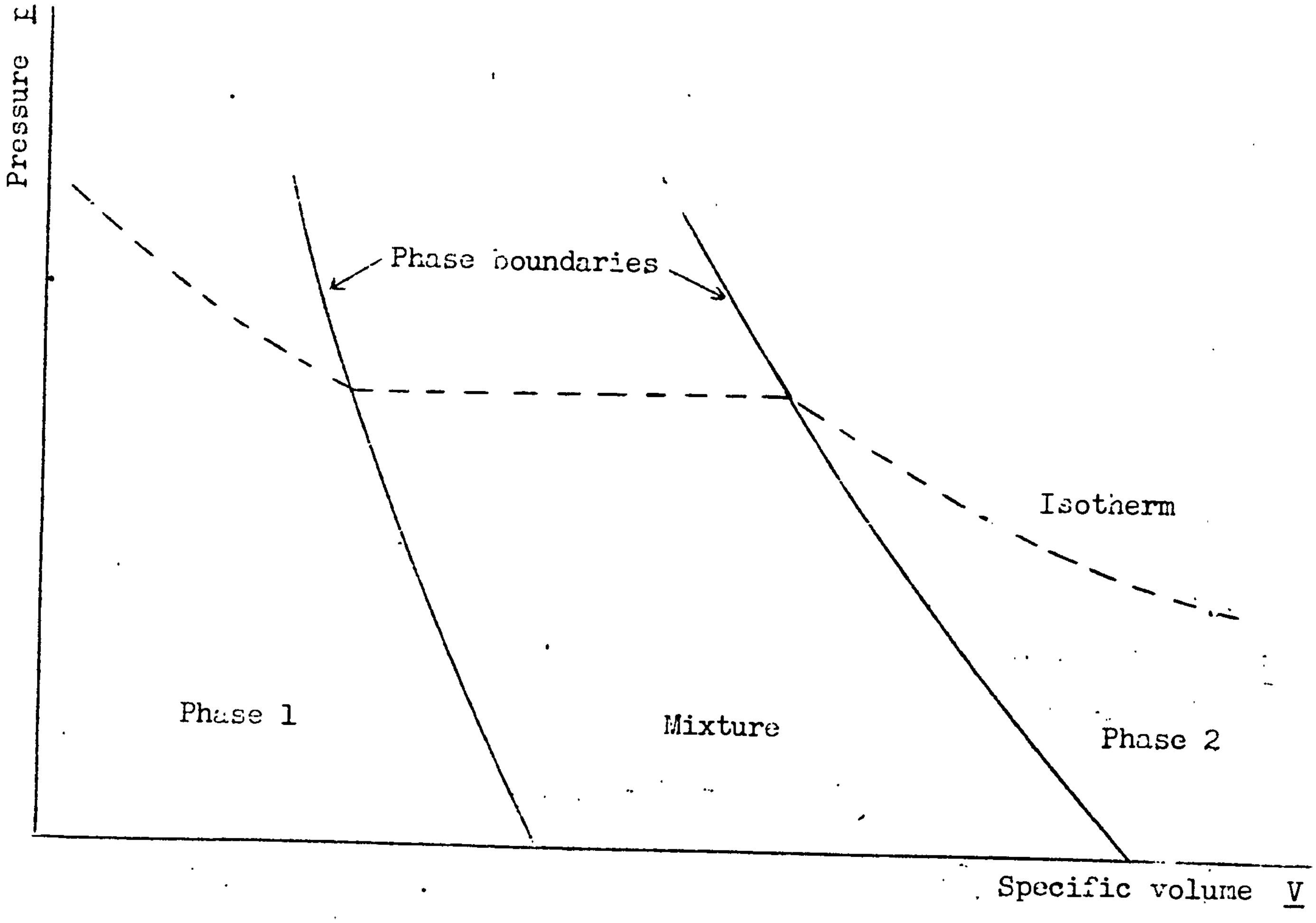


Fig. 3. Diagram of a phase transition.

Of course $(\partial^2 p/\partial V^2)_S$ will also have discontinuities at the two boundaries, and we wish to find out the sign of these discontinuities. In the pure phase 1, we have from Eq. (67)

$$\left(\frac{\partial p}{\partial V}\right)_{S,1} = \left(\frac{\partial p}{\partial V}\right)_{T,1} - \frac{T}{c_{V,1}} \left(\frac{\partial p}{\partial T}\right)^2_{V,1} . \qquad (82)$$

In the two-phase region, p is a function of T only and is independent of V. Therefore

$$\left(\frac{\partial p}{\partial V}\right)_{SM} = - \frac{T}{c_{VM}} \left(\frac{dp}{dT}\right)^2 , \qquad (82a)$$

where the subscript M refers to the mixture of the two phases, and total derivatives, like dp/dT, refer to the phase boundary. The Clapeyron equation gives

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_2 - S_1}{V_2 - V_1} , \tag{82b}$$

where ΔS and ΔV are the differences of entropy and volume between the two phases at the temperature T.

The quantity most difficult to calculate is c_{VM}. If the volume of the mixture is to be kept constant while the temperature changes, the concentration of the two phases must change. If x is the concentration of phase 2, the volume of the mixture is

$$V = xV_2 + (1 - x)V_1 , \tag{83}$$

where V_2 and V_1 are the volumes of the pure phases. Therefore, if the volume is to remain constant with change of temperature, we have

$$\frac{dV_1}{dT} + x\frac{d\Delta V}{dT} + \frac{dx}{dT}\Delta V = 0 . \tag{83a}$$

Since we want to consider a state near the phase boundary, x is negligible. Then the specific heat of the mixture becomes

$$c_{VM} = \left(\frac{\partial E}{\partial T}\right)_V = \frac{dE_1}{dT} + \frac{dx}{dT}\Delta E = \frac{dE_1}{dT} - \frac{\Delta E}{\Delta V}\frac{dV_1}{dT} . \tag{84}$$

The derivative dE_1/dT can be expressed as follows:

$$\frac{dE_1}{dT} = \left(\frac{\partial E}{\partial T}\right)_{V,1} + \left(\frac{\partial E}{\partial V}\right)_{T,1}\frac{dV_1}{dT} . \tag{84a}$$

Using the thermodynamic relations

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{84b}$$

and

$$T\Delta S = \Delta E + p\Delta V \,, \tag{84c}$$

and remembering Eq. (82b), Eq. (84) becomes

$$c_{VM} = c_{V,1} + T\,\frac{dV_1}{dT}\left[\left(\frac{\partial p}{\partial T}\right)_{V,1} - \frac{dp}{dT}\right] . \tag{84d}$$

Now, in analogy to Eq. (84a), we have

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial T}\right)_{V,1} + \left(\frac{\partial p}{\partial V}\right)_{T,1}\frac{dV_1}{dT} \,; \tag{84e}$$

therefore Eq. (84d) reduces to

$$c_{VM} = c_{V,1} - T\left(\frac{\partial p}{\partial V}\right)_{T,1}\left(\frac{dV_1}{dT}\right)^2 . \tag{85}$$

Since $(\partial p/\partial V)_T$ is always negative, Eq. (85) shows that the specific heat of the mixture, near the boundary, is always greater than that of the adjacent pure phase.

Now let us calculate the difference between the values of $(\partial p/\partial V)_S$ for pure phase and mixture, or rather this difference multiplied by c_{VM},

$$c_{VM}\left[\left(\frac{\partial p}{\partial V}\right)_{SM} - \left(\frac{\partial p}{\partial V}\right)_{S,1}\right] = -T\left(\frac{dp}{dT}\right)^2 - \left[\left(\frac{\partial p}{\partial V}\right)_{T,1} - \frac{T}{c_{V,1}}\left(\frac{\partial p}{\partial T}\right)^2_{V,1}\right]\left[c_{V,1} - T\left(\frac{\partial p}{\partial V}\right)_{T,1}\left(\frac{dV_1}{dT}\right)^2\right] \tag{85a}$$

$$= -c_{V,1}\left(\frac{\partial p}{\partial V}\right)_{T,1} + T\left[\left(\frac{\partial p}{\partial T}\right)^2_{V,1} - \left(\frac{dp}{dT}\right)^2\right] + T\left(\frac{\partial p}{\partial V}\right)^2_{T,1}\left(\frac{dV_1}{dT}\right)^2 - \frac{T^2}{c_{V,1}}\left(\frac{\partial p}{\partial V}\right)_{T,1}\left(\frac{\partial p}{\partial T}\right)^2_{V,1}\left(\frac{dV_1}{dT}\right)^2 .$$

The quantity in the square bracket can be transformed, using Eq. (84e):

$$\left(\frac{\partial p}{\partial T}\right)^2_{V,1} - \left(\frac{dp}{dT}\right)^2 = -\left(\frac{\partial p}{\partial V}\right)_{T,1}\frac{dV_1}{dT}\times\left\{2\left(\frac{\partial p}{\partial T}\right)_{V,1} + \left(\frac{\partial p}{\partial V}\right)_{T,1}\frac{dV_1}{dT}\right\} . \tag{85b}$$

The second term in Eq. (85b) cancels the next to the last term in Eq. (85a). The remaining terms in Eqs. (85a) and (85b) give a full square, and we obtain

$$\left(\frac{\partial p}{\partial V}\right)_{SM} - \left(\frac{\partial p}{\partial V}\right)_{S,1} = - \left(\frac{\partial p}{\partial V}\right)_{T,1} \frac{c_{V,1}}{c_{VM}} \left[1 + \frac{T}{c_{V,1}} \left(\frac{\partial p}{\partial T}\right)_{V,1} \frac{dV_1}{dT}\right]^2 . \qquad (86)$$

Since $(\partial p/\partial V)_T$ is always negative, and $c_{V,1}$ and c_{VM} always positive, the right-hand side of Eq. (86) is always positive; therefore

$$\left(\frac{\partial p}{\partial V}\right)_{SM} > \left(\frac{\partial p}{\partial V}\right)_{S,1} . \qquad (86a)$$

We have derived the result [Eq. (86a)] without any assumption regarding the relative magnitudes of V_1 and V_2, or S_1 and S_2. The result will therefore be valid for both boundaries of the two-phase region.

We find therefore:

At the boundary between a two-phase region (in the p,V-diagram) and a single-phase region the adiabatic compression modulus, $-(\partial p/\partial V)_S$, will always be greater for the single phase than for the mixture of the two phases.

We are interested in the sign of the second derivation, $(\partial^2 p/\partial V^2)_S$, or, more correctly, in the sign of the discontinuity of $(\partial p/\partial V)_S$ when we follow the adiabatic in the direction of increasing volume V. This sign will depend on the direction in which the adiabatic crosses the boundary between the two-phase and one-phase regions: If adiabatic expansion will lead to the phase transition, then $(\partial p/\partial V)_S$ will increase discontinuously as the adiabatic enters the two-phase region. Then $(\partial^2 p/\partial V^2)_S$ is positive (infinite) at the boundary, and postulate (I) remains true. If, however, adiabatic compression leads from the pure phase to the mixture of two phases, $(\partial p/\partial V)_S$ will decrease discontinuously at the boundary if we proceed in the direction of increasing volume. Then $(\partial^2 p/\partial V^2)_S$ is negative at the boundary, and *condition (I) is violated*.

The transition between a condensed phase and the vapor has generally the property that adiabatic expansion leads to the phase transition, both if we start from the condensed phase and if we start from the vapor. The former is rather obvious since adiabatic expansion of a liquid or solid at low pressure is almost identical with isothermal expansion, and will therefore ultimately lead to evaporation. The other part of the statement is a well-known experimental fact: adiabatic expansion of nearly saturated vapor leads to condensation (principle of cloud chamber). Therefore, *condition (I) is generally satisfied for evaporation and condensation*.

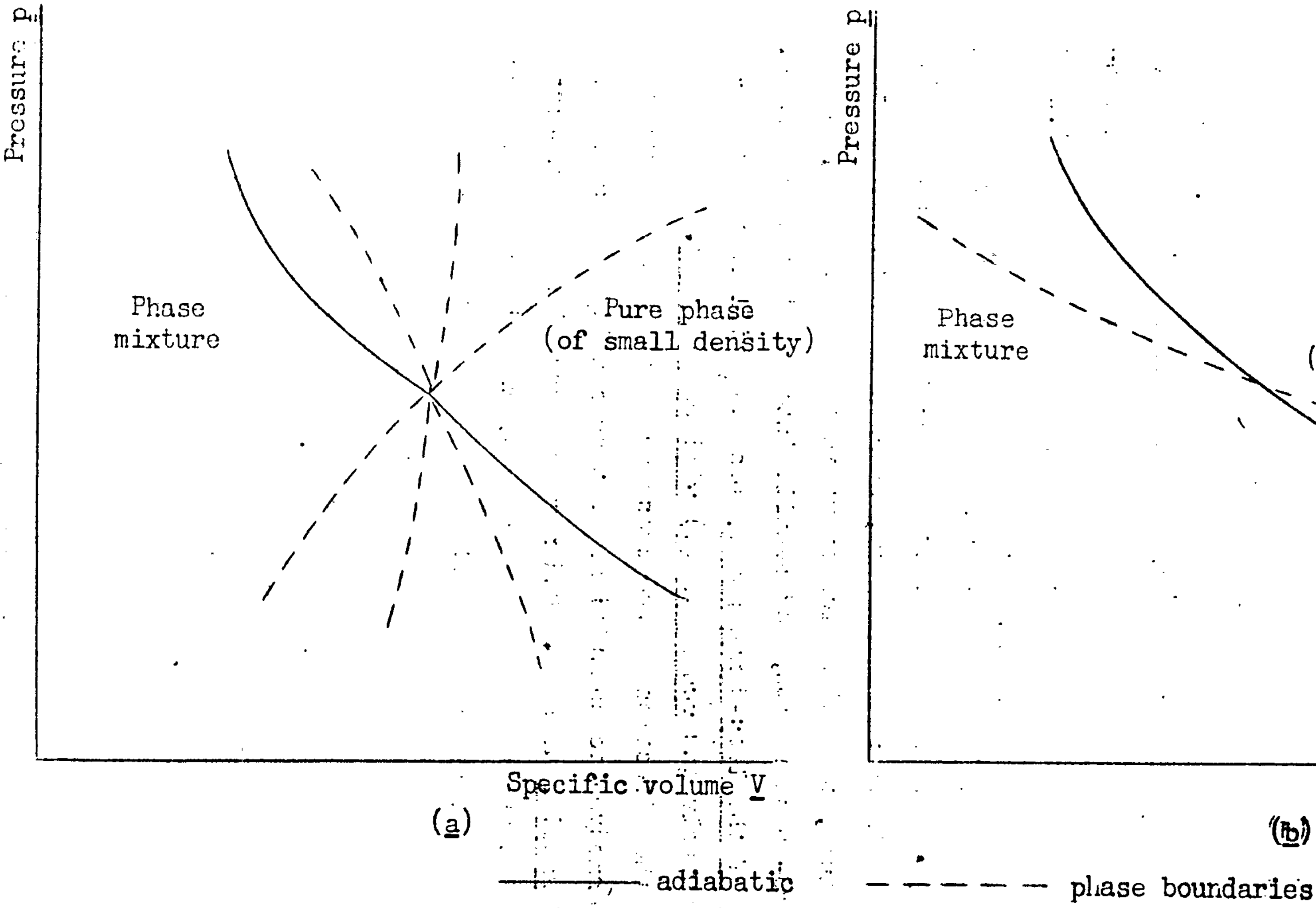
On the other hand, for transitions between two condensed phases -- liquid and solid, or two solid modifications -- the adiabatics usually run similar to the isothermals; that is, proceeding in the direction of increasing volume, the adiabatics start in the denser phase, then pass into the two-phase region, and finally into the less dense phase. *At the boundary of the less-dense phase*, $(\partial p/\partial V)_S$ will therefore decrease discontinuously and *condition (I) will be violated*.

Generally, the direction of the crossing of the boundary can be deduced from thermodynamic quantities. Let us consider the boundary of the phase of *smaller* density. Under which conditions is postulate (I) still satisfied at this boundary; that is, when do the adiabatics go with increasing volume from the dilute phase into the two-phase region? The condition for this is (see Fig. 4)

$$\left(\frac{\partial V}{\partial p}\right)_{S,1} > \frac{dV_1}{dp}, \tag{87}$$

the total derivative referring, as usual, to the equation of the phase boundary. We have

$$\left(\frac{\partial V}{\partial p}\right)_{S,1} = \left(\frac{\partial V}{\partial p}\right)_{T,1} + \left(\frac{\partial V}{\partial T}\right)_{p,1} \left(\frac{\partial T}{\partial p}\right)_{S,1}, \tag{87a}$$



(a)

(b)

Fig. 4. Crossing of phase boundary by adiabatic. To the right of the dotted li
phase (small density); to the left is the phase mixture.

- (a) The adiabatic goes with increasing volume from the mixture to the pure phas
turning the diagram through 90° it can be seen that the slope $-\partial V/\partial p$ is grea
the adiabatic than for the phase boundaries.
- (b) The adiabatic goes with increasing volume from the pure phase to the mixtur
slope $-\partial V/\partial p$ is smaller for the adiabatic than for the phase boundary.

$$\frac{dV_1}{dp} = \left(\frac{\partial V}{\partial p}\right)_{T,1} + \left(\frac{\partial V}{\partial T}\right)_{p,1} \frac{dT}{dp} . \tag{87b}$$

If the expansion coefficient of the dilute phase, $(\partial V/\partial T)_{p,1}$ is positive — and we do not know any exception from this — Eq. (87) is equivalent to

$$\left(\frac{\partial T}{\partial p}\right)_{S,1} > \frac{dT}{dp} ; \tag{88}$$

that is, the temperature must rise more rapidly for adiabatic compression than for compression along the phase boundary. For dT/dp we have the Clapeyron equation (82b), whereas

$$\left(\frac{\partial T}{\partial p}\right)_{S,1} = - \frac{(\partial S/\partial p)_{T,1}}{(\partial S/\partial T)_{p,1}} = \frac{T}{c_{p,1}} \left(\frac{\partial V}{\partial T}\right)_{p,1} , \tag{88a}$$

using a well-known thermodynamic relation. Then Eq. (88) becomes

$$T\left(\frac{\partial V}{\partial T}\right)_{p,1} > c_{p,1} \frac{\Delta V}{\Delta S} , \tag{89}$$

which is the desired condition.

If phase 1 obeys the ideal gas equation, we have

$$T \left(\frac{\partial V}{\partial T}\right)_{p,1} = V \approx \Delta V , \tag{89a}$$

so that Eq. (89) reduces to

$$\Delta S > c_{p,1} . \tag{89b}$$

This is ordinarily fulfilled with a wide margin; for example, for water at 100°C, $\Delta S = 6.05$ joule/gm-deg (Dorsey,[7] p. 616), while $c_p \approx 2$ joule/gm-deg (Dorsey,[7] p. 101). For solids and liquids, on the other hand, $(\partial V/\partial T)_p$ is usually quite small and Eq. (89) will, in general, not be fulfilled. For example, for the transition from water to ice VI we have at 30°C (data from Dorsey[7/])

$$p = 10{,}250 \text{ atm}, \qquad \text{[Dorsey, p. 467]}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = 3.3 \times 10^{-4} \text{ cm}^3/\text{gm-deg}, \qquad \text{[Dorsey, p. 216]}$$

$$c_V = 4.072(1 - 0.210) = 3.22 \text{ joule/gm-deg}$$
$$\text{at } 40^\circ \text{ and } 10{,}250 \text{ atm}, \qquad \text{[Dorsey, p. 261]}$$

$$\approx 3.1 \text{ joule/gm-deg at } 30^\circ.$$

$$c_p - c_V = - T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)^2,$$

$$- \frac{\partial p}{\partial V} = 1.0 \times 10^5 \text{ bar-gm/cm}^3. \qquad \text{[Dorsey, p. 216]}$$

Therefore

$$c_p - c_V = 3.3 \text{ bar-cm}^3/\text{gm-deg} = 0.33 \text{ joule/gm-deg},$$

$$c_p = 3.4 \text{ joule/gm-deg},$$

$$\Delta S = 1.09 \text{ joule/gm-deg}, \qquad \text{[Dorsey, p. 617]}$$

$$\Delta V = 0.0663 \text{ cm}^3/\text{gm}. \qquad \text{[Dorsey, p. 613]}$$

Inserting these values into Eq. (89) we get

$$T \frac{\partial V}{\partial T} = 0.100 \text{ cm}^2/\text{gm},$$

$$c_p \frac{\Delta V}{\Delta S} = \frac{3.4 \times 0.0663}{1.09} = 0.21 \text{ cm}^3/\text{gm}.$$

Condition (I) is therefore not fulfilled at the boundary between water and water + ice VI.

On the boundary of the denser phase, the condition for the validity of condition (I) is reversed, as can easily be seen. We have then instead of Eq. (89)

$$T\left(\frac{\partial V}{\partial T}\right)_{p,\text{dense}} < c_{p,\text{dense}}\frac{\Delta V}{\Delta S}\,. \qquad (90)$$

For evaporation, this is practically always fulfilled, because ΔV is almost equal to the volume of the vapor and therefore very large compared with the volume of the liquid or solid, which in turn is large compared with $T\partial V/\partial T$. On the other hand, for transitions between condensed phases Eq. (90) is not always valid; in particular, if $\Delta V/\Delta S$ happens to be small or negative for a transformation, so that Eq. (89) is fulfilled, Eq. (90) will in general not be fulfilled. This is the case, for example, for the transition from ice I to water for which $\Delta V/\Delta S$ is negative: then condition (I) breaks down at the boundary of the denser phase, that is, of the water.

With possibly a few exceptions, we can therefore state: Condition (I) will break down for transitions between two condensed phases at one of the two boundaries between pure phase and mixture. Condition (I) will remain valid for evaporation and condensation.

14. Consequences of the breakdown of condition (I) at phase boundaries

If we compress a liquid adiabatically, we finally come to the phase boundary with the solid. As we have shown in the last section, the derivative $(\partial^2 p/\partial V^2)_S$ will in general be negative (infinite) at one of the boundaries between pure phase and phase mixture. For water, this occurs at the boundary between liquid water and the mixture of water and ice VI. Therefore, if the phase transition is not forbidden by its long relaxation time, all proofs given in Part II will break down.

It is easy to show that the negative discontinuity of $(\partial p/\partial V)_S$ will actually have serious consequences for the theory of shock waves. Consider an initial state V_1, S_1 close to the phase boundary, but still on the side of liquid water. Then we may neglect the change of $(\partial p/\partial V)_S$ from V_1, S_1 to the phase boundary; moreover, the shock curve will cross the phase boundary at an entropy S_C very close to S_1, and at a certain volume $V_C < V_1$. For the state V_C, S_C, we have very nearly

$$\frac{\Delta p}{\Delta V} = \frac{p_C - p_1}{V_C - V_1} = \left(\frac{\partial p}{\partial V}\right)_{SL}, \tag{91}$$

where the subscript L refers to the liquid. If we then go a small distance into the two-phase region, we have from Eq. (31)

$$\left(\frac{dS}{dV}\right)_M = \frac{\Delta p - \Delta V(\partial p/\partial V)_{SM}}{2T_2 + \Delta V(\partial p/\partial S)_{VM}}, \tag{91a}$$

where the index M refers to the mixture. Neglecting ΔV in the denominator and inserting Eq. (91), we find

$$\left(\frac{dS}{dV}\right)_M = \frac{\Delta p}{2T_2}\left(1 - \frac{(\partial p/\partial V)_{SM}}{(\partial p/\partial V)_{SL}}\right). \tag{92}$$

Now we know from Eq. (86a) that

$$\frac{(\partial p/\partial V)_{SM}}{(\partial p/\partial V)_{SL}} < 1 \tag{92a}$$

since $(\partial p/\partial V)_S$ is negative. Therefore Eq. (92) is positive; that is, the entropy will decrease with further compression, in contrast to our theorems in Secs. 3, 4, and 7. Since we have assumed that S_C is very close to S_1, the entropy will soon fall below S_C. Therefore the compressional shock waves will become unstable.

The solution of this difficulty seems to be that there will be two shock waves proceeding in the same direction. In the space between the two shock waves the state of the material is given by V_C, S_C; that is, the state lies just on the phase boundary. Behind the second shock wave the material is a mixture of liquid and solid. (There may, of course, be some question whether such a mixture can occur behind a shock wave.) The second shock wave moves approximately with the velocity of sound characteristic of the mixture and will therefore remain behind the first wave which moves nearly with the velocity of sound of the pure liquid. This result is in striking contrast to that found in Sec. 10 for a material obeying condition (I): we proved that for such a material there can always be only one shock wave starting from a given point in a given direction.

As the difference between the specific volumes in front of the first wave (V_1) and behind the second one (V_2) increases, the velocity u' of the second wave will increase, following the ordinary laws[10] developed in Part II, with the state V_C, S_C playing the role of "initial state." The velocity u of the first shock wave remains constant. Ultimately, u' will become equal to u. Suppose this happens for $V_2 = V_D$, $p_2 = p_D$; then V_D, p_D are given by

$$V_C^2\, u'^2 = \frac{p_D - p_C}{V_C - V_D} = \frac{p_C - p_1}{V_1 - V_C} = V_C^2\, u^2 \qquad (93)$$

(u' and u are velocities relative to the material between the shock waves). If the volume V_2 is decreased below V_D, we shall again get one shock wave, with state 1 in front of and state 2 behind the shock front. The state p_D, V_D satisfying Eq. (93) may occur either in the two-phase region or may lie already in the pure dense phase (in our case, ice VI).

For the two separate shock waves, the stability considerations of Part II will all be valid, because in the liquid and in the mix-

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[10] We have not proved that condition (I) is fulfilled in the two-phase region, but we believe this to be true.

ture separately condition (I) is fulfilled. Likewise, the proofs of stability will hold for the single wave occurring at pressures greater than p_D; in this case, the theorems may be proved by starting from state D and continuing along the shock curve to higher pressures and entropies.

Thus far we have considered an initial state V_1, S_1 very close to the phase boundary. On the other hand, the shock curve may cross a phase boundary at a density and entropy far above those of the initial state. Then it may easily happen that the single shock wave will remain stable even if the state behind the shock wave lies beyond the phase boundary. If u_{C2} is the shock-wave velocity at the point C at which the shock curve belonging to state 1 crosses the phase boundary, then the condition for the single shock wave to remain stable is that u_{C2} be smaller than the sound velocity in the phase mixture; that is,

$$\frac{p_C - p_1}{V_1 - V_C} < \left|\left(\frac{\partial p}{\partial V}\right)_{SM}\right| \qquad (94)$$

[see also Eqs. (31c) and (31d)]. Equation (94) may be fulfilled for large shock waves because their velocity, with respect to the medium C behind the wave, is known to be considerably smaller (Sec. 9) than the sound velocity in that medium; that is [see Eqs. (6) and (10)],

$$\frac{p_C - p_1}{V_1 - V_C} \ll \left|\left(\frac{\partial p}{\partial V}\right)_{SL}\right| . \qquad (94a)$$

Whether or not Eq.(94) is true for a given initial state and a given phase boundary must be investigated in each particular case. If the initial state is water at 1 atm and the phase boundary to ice VI is crossed at 30°C, we have (see p. 62) p = 10,250; further (Dorsey,[7] p. 467) $V_C = 0.8055$, $V_1 = 1.00$, $p_1 = 0$; therefore

$$\frac{p_C - p_1}{V_1 - V_C} = 52{,}600 \text{ atm-cm}^3/\text{gm} = 53{,}400 \text{ bar-cm}^3/\text{gm}. \qquad (94b)$$

The data for the calculation of $(\partial p/\partial V)_{SM}$ are mostly given on page 62 of this report; we have [See Eqs. (82a), (82b), (84e), and (85)]

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = 164 \text{ bar/deg},$$

$$\frac{dV_1}{dT} = 1.2 \times 10^{-3} \text{ cm}^3\text{/gm-deg}, \qquad \text{[Dorsey, p. 467]}$$

$$c_{V,1} = 31 \text{ bar-cm}^3\text{/gm-deg}, \qquad \text{[This report, p. 62]}$$

$$c_{VM} = 31 + 303 \times (1.2 \times 10^{-3})^2 \times 10^5$$

$$= 75 \text{ bar-cm}^3\text{/gm-deg.} \qquad \text{[This report, pp. 57, 62]}$$

$$-\left(\frac{\partial p}{\partial V}\right)_{SM} = \frac{303}{75} \times 164^2 = 108{,}000 \text{ bar-cm}^3\text{/gm.} \quad \text{[This report, Eq. (82a)]} \tag{94c}$$

This is greater than Eq. (94b) so that Eq. (94) is fulfilled. Therefore, even if the transformation of water to ice VI could take place in shock waves, the theorems of Part II would remain valid. (This holds if the initial state is at 1 atm pressure; if we started from a high pressure, let us say 8,000 atm, we should obtain two shock waves as described above.)

We thus get the following picture. If the initial state V_1, p_1 lies fairly close to a phase boundary, there will be a region of "final" pressures p_2 between p_C and p_D [see Eq. (93)], for which two shock waves exist behind one another. In this whole region, the velocity of the first wave remains constant, equal to that for $p_2 = p_C$. For greater final pressure ($p_2 > p_D$) there will be a single shock wave whose velocity increases with increasing p_2. If we now move the initial state farther away from the phase boundary, the region from p_C to p_D will become smaller and will finally disappear.

This result may be applicable to extremely large shock waves in solids. As we have pointed out,[4] a solid under compression and extremely high temperature may not go over smoothly into the quasi-gaseous state; in other words, there may be no critical point for a solid. However, the phase transition, if any, will occur at such a high pressure that the single shock wave will almost certainly remain stable.

The double shock wave will never occur for *gases*, for we have shown in Sec. 13 that a vapor just on the verge of condensation will be removed from the phase boundary by adiabatic compression. Therefore a gas under any amount of adiabatic compression will always remain a gas, and this will be *a fortiori* true under shock compression, which leads to an even higher temperature. Therefore, for gases, whether ideal or not, the results of Part II are valid.

We shall now turn to rarefaction waves. Consider as initial state V_1, S_1, a state on the high-density side of a phase boundary at which condition (I) breaks down, so that adiabatic expansion leads from V_1, S_1 across the boundary. (This can occur only when the initial state is a mixture of two condensed phases.) If we follow the shock curve to larger volumes, we can see from an argument exactly similar to Eqs. (91) to (92a), that the entropy will first decrease to the phase boundary and then increase. We thus obtain the possibility of stable *rarefaction waves of finite amplitude*. In fact, if we tried to work with infinitesimal rarefaction waves, those corresponding to the change from the initial state to the phase boundary would travel with the sound velocity of the mixture, while those corresponding to the further expansion of the pure phase would travel with the greater sound velocity of the pure phase, which leads to a contradiction. Thus we not only can but actually must have a rarefaction shock wave.

With increasing expansion, we shall come to a point V_E, p_E at which the velocity of sound in the pure phase has dropped to a value equal to that of the rarefaction shock wave. For any expansion beyond this point, we shall get a rarefaction shock wave in which the substance expands to the volume V_E, followed by a train of infinitesimal waves of further rarefaction.

As the initial state V_1, p_1 is removed from the phase boundary, the point V_E, p_E will move also; we have not investigated in which direction. If the initial state is in the pure dense phase, there must still be a rarefaction shock wave since the rarefaction still cannot be accomplished by infinitesimal waves, because the sound velocity in the pure dilute phase is greater than in the phase mixture. It does not seem obvious which part of the rarefaction is accomplished by a shock wave and which part by infinitesimal waves. It seems reasonably certain that there will be infinitesimal waves in which the material is expanded down to the boundary of the dense phase; then possibly a shock wave will follow which carries the material over the mixed region and into the dilute phase, and this may be followed by another train of infinitesimal waves. But it may also be that the shock wave "starts" with a state in the region of mixed phases. In any case, these rarefaction shock waves can start only from initial states of very high pressure and can occur at all only if the phase transformation is rapid enough to take place in the shock wave.

The strange phenomenon of rarefaction shock waves will not occur for gases, nor for liquids or solids initially at atmospheric or other low pressures. By adiabatic expansion we obtain in each case a mixture of gas and condensed phase, and we have shown in Sec. 13 that condition (I) is valid for the transition into this mixed phase, both from the condensed and from the gaseous state.

15. Condition (II): $V(\partial p/\partial E)_V \geq -2$

Condition (II) is automatically fulfilled for all substances with a positive expansion coefficient; these include gases as well as practically all liquids and solids. We need only investigate the case of negative expansion coefficient, of which water is the most notable example.

(a) Liquid water. — The greatest negative expansion coefficient is reached for 0°C and 1 atm pressure. (At lower temperatures water is stable only under higher pressures, for which the expansion coefficient becomes positive.) The value of $\partial p/\partial T$ for 0°C was given in Eq. (79d) and is -0.62 bar/deg. With $c_V = 42$ bar-cm^3/gm-deg, and $V = 1$ cm^3/gm, we get

$$V\left(\frac{\partial p}{\partial E}\right)_V = -\frac{0.62}{42} = -0.015\ , \qquad (95)$$

as compared with the limit of −2 set by condition (II).

(b) *Ice at extremely low temperatures.* — A relatively large negative expansion coefficient was found by Jakob and Erk for ice at extremely low temperatures (Dorsey,[7] p. 473). At −250°C, the *linear* expansion coefficient is -6.1×10^{-6}. If we assume the cubic expansion coefficient to be three times as large, we have

$$\beta = \frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_p = -18.3 \times 10^{-6} , \qquad (95a)$$

where V_o [= 1.09] is the specific volume at 0°C. The compressibility has not been measured at these low temperatures. Near the melting point, the experimental results differ widely (Dorsey,[7] p. 471). Bridgman finds $\gamma \, [= -(1/V_o)(\partial V/\partial p)_T]$ to decrease from 33×10^{-6} at 0°C to 19×10^{-6} at −10° and 18×10^{-6} at −15°, while Richards and Speyers find γ as low as 12×10^{-6} at −7°. If we assume the last-mentioned figure for −250°C, we get

$$\frac{\partial p}{\partial T} = -\frac{18.3 \times 10^{-6}}{12 \times 10^{-6}} = -1.5 \text{ bar/deg.} \qquad (95b)$$

The specific heat, according to Pollitzer (see Dorsey,[7] p. 479) is 1.28 bar-cm^3/gm-deg; therefore

$$V \frac{\partial p}{\partial E} = -1.07 \cdot \frac{1.5}{1.28} = -1.25 , \qquad (95c)$$

which is of the same order of magnitude, but smaller in absolute value, than the value permitted by condition (II).

(c) *Melting ice.* — The largest contraction with increasing energy is found for melting ice I. From the Clapeyron equation we have

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} , \qquad (96)$$

where p is the melting pressure at temperature T. The entropy change from ice I to water is (Dorsey,[7] p. 617)

$$\Delta S = 12.2 \text{ bar-cm}^3/\text{gm-deg at } 0^\circ\text{C},$$

$$= 9.55 \text{ bar-cm}^3/\text{gm-deg at } -20^\circ\text{C}.$$

The change of volume is

$$\Delta V = -0.0900 \text{ cm}^3/\text{gm at } 0^\circ\text{C},$$

$$= -0.1313 \text{ cm}^3/\text{gm at } -20^\circ\text{C}.$$

Accordingly,

$$\left.\begin{aligned} \frac{dp}{dT} &= -136 \text{ bar/deg at } 0^\circ\text{C}, \\ &= -73 \text{ bar/deg at } -20^\circ\text{C}. \end{aligned}\right\} \qquad (96a)$$

These values are very much greater than $\partial p/\partial T$ for water at 0°C, which we found to be −0.62 bar/deg [Eq. (84d)]. In fact, if the specific heat c_V of the mixture of water and ice were between the specific heats of water (42 bar-cm^3/deg) and of ice (20 bar-cm^3/deg), condition (II) would be violated by a large amount.

Actually, we know from Eq. (85) that c_V for the mixture is larger than for the pure phases. It can easily be shown that c_{VM} is smallest when the mixture contains mostly ice; first, because the c_V of pure ice is smaller than that of pure water and, second, because the volume change dV_1/dT, is also smaller. We have

$$c_{V\,\text{ice}} = 21.15 \text{ bar-cm}^3/\text{deg at } 0^\circ\text{C},$$

$$= 19.59 \text{ bar-cm}^3/\text{deg at } -20^\circ\text{C};$$

$$dV_1/dT \approx 3.5 \times 10^{-3} \text{ cm}^3/\text{gm-deg at } 0^\circ\text{C},$$

$$\approx 0.8 \times 10^{-3} \text{ cm}^3/\text{gm-deg at } -20^\circ\text{C};$$

$$- -\partial p/\partial V \approx 4 \times 10^4 \text{ bar-gm/cm}^3 \text{ at } 0^\circ\text{C},$$

$$\approx 10.5 \times 10^4 \text{ bar-gm/cm}^3 \text{ at } -20^\circ\text{C}.$$

Therefore from Eq. (85),

$$c_{VM} \approx 21.15 + 273 \times 4 \times 10^4 \times (3.5 \times 10^{-3})^2 \approx 156 \text{ bar-cm}^3/\text{deg at } 0^\circ\text{C}, \quad (96b)$$

$$= 19.59 + 253 \times 10.5 \times 10^4 \times (0.8 \times 10^{-3})^2 = 36.5 \text{ bar-cm}^3/\text{deg at } -20^\circ\text{C}. \quad (96c)$$

Therefore

$$V\left(\frac{\partial p}{\partial E}\right)_V = \frac{V}{c_{VM}}\left(\frac{dp}{dT}\right)_V = -\frac{1.09 \times 136}{156} \approx -0.95 \text{ at } 0^\circ\text{C}, \qquad (96d)$$

and

$$V\left(\frac{\partial p}{\partial E}\right)_V = -\frac{1.06 \times 73}{36.5} = -2.12 \text{ at } -20^\circ\text{C}. \qquad (96e)$$

The last-mentioned value is just slightly below the limit set by condition (II), the difference being within the probable error of measurement of dV_1/dT. It seems therefore that melting ice forms an exception to condition (II), but that this condition is fulfilled for pure water as well as for pure ice, and probably for most other substances.

16. Condition (III): $(\partial p/\partial V)_E < 0$

Condition (III) is obviously fulfilled for ideal gases because for these gases constant energy is equivalent to constant temperature, and the isothermal value of $\partial p/\partial V$ must always be negative.

The condition is fulfilled *a fortiori* for practically all substances for which the internal energy increases with isothermal expansion. We have

$$\left(\frac{\partial p}{\partial V}\right)_E = \left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial p}{\partial T}\right)_V \frac{(\partial E/\partial V)_T}{c_V}. \qquad (97)$$

If $(\partial p/\partial T)_V > 0$, which is true for almost all substances (except water below 4°C), the last term is negative for positive $(\partial E/\partial V)_T$. Therefore

$$\left(\frac{\partial p}{\partial V}\right)_E < \left(\frac{\partial p}{\partial V}\right)_T < 0 \tag{97a}$$

if

$$\left(\frac{\partial E}{\partial V}\right)_T > 0 . \tag{97b}$$

A great many substances fulfill the condition $(\partial E/\partial V)_T > 0$. Some of the most important are the following.

(a) Dissociating gases. — The dissociation increases with the volume at constant temperature, and the dissociation increases the internal energy. This case is the most important of all because condition (III) is required (Sec. 8) to prove that the energy has no extremum in the part of the shock curve beyond the minimum of the volume V_2, that is, at very high temperatures at which dissociation progresses rapidly.

(b) Any fairly dilute, imperfect gas. -- The attractive forces (Van der Waals' forces) must be taken into account while the repulsive forces are unimportant. Since the attractive forces decrease with increasing volume, the energy must increase with V. An example is provided by a gas obeying Van der Waals' equation, namely

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT . \tag{98}$$

From the thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{98a}$$

we find

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2} > 0 . \tag{98b}$$

(c) Most solids and liquids at ordinary temperatures. — From measurements such as those of Gibson and Loeffler,[5,6] $\partial E/\partial V$ turns out to be positive for practically all liquids at ordinary temperatures. The only notable exception is water below 4°C [see Sec. 16(c)]. The argument given in the literature for the "normal" behavior is the same as that given in Sec. 16(b) for gases, namely that the most important volume-dependent contribution to E arises from attractive forces, which give a positive $\partial E/\partial V$. This argument may be expected to hold for solids as well as for liquids.

Other substances still fulfill condition (III) although $(\partial E/\partial V)_T$ is negative. Examples follow.

(d) Water below 4°C. — The $(\partial p/\partial T)_V$ at zero pressure is negative so that Eq. (98a) yields a negative $(\partial E/\partial V)_T$. However, since at the same time $\partial p/\partial T$ is negative, the last term of Eq. (97) remains negative. It is true that there is a region of pressures for which $\partial E/\partial V$ is still negative while $\partial p/\partial T$ is already positive [because of the term $-p$ in Eq. (98a)], but in this region the last term in Eq. (97) is entirely negligible compared with the first, namely about 1 part in 10,000.

(e) Solids at low temperature. — The last term in Eq. (97) may be expected to be large and positive — that is, unfavorable for relation (III) — if c_V is small, $\partial p/\partial T$ positive, and p large [see Eq. (98a)]. All these conditions are fulfilled for solids at low temperature. The value of c_V is given by Eq. (77), namely

$$c_V = a(T/\theta)^3, \tag{77}$$

and goes to zero for zero temperature. Fortunately, $\partial p/\partial T$ also goes to zero; we have from Eqs. (77c) and (77)

$$\frac{\partial p}{\partial T} = \frac{\partial S}{\partial V} = \frac{1}{3}\,\frac{\partial c_V}{\partial V} = -\frac{1}{3}\,c_V\,\frac{\partial \log \theta}{\partial V}\,. \tag{99}$$

This expression is positive because the Debye temperature decreases with increasing volume. Since θ is proportional to the frequency of the vibrations of the crystal lattice, therefore approximately

$$\Theta = bV^{-1/3}a \,, \tag{99a}$$

where b is a constant depending on the crystal structure but not on V, while a is the velocity of sound, namely

$$a^2 = -V^2(\partial p/\partial V)_T \,. \tag{99b}$$

Therefore

$$\frac{\partial \log \Theta}{\partial V} = \frac{2}{3V} + \frac{(\partial^2 p/\partial V^2)_T}{(\partial p/\partial V)_T} \,. \tag{99c}$$

Inserting Eqs. (99), (98a), and (99c) into Eq. (97) and neglecting $T(\partial p/\partial T)$ against p we obtain

$$\left(\frac{\partial p}{\partial V}\right)_E = \left(\frac{\partial p}{\partial V}\right)_T \left[1 - \frac{1}{3}\,\frac{p(\partial^2 p/\partial V^2)_T}{(\partial p/\partial V)^2_T}\right] - \frac{2}{9}\,\frac{p}{V} \,. \tag{100}$$

The last term is certainly negative (and small). In order that condition (III) be fulfilled, it is therefore sufficient that the bracket be positive. This is almost certainly the case because solids very nearly obey the Tait equation. Choosing $V_o = V_T$, Eq. (79) becomes

$$p = B\left[e^{(V_o - V)/\kappa} - 1\right] , \tag{100a}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -(B/\kappa)e^{(V_o - V)/\kappa} \,, \tag{100b}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = (B/\kappa^2)e^{(V_o - V)/\kappa} \,. \tag{100c}$$

Therefore

$$p\,\frac{\partial^2 p}{\partial V^2} < \left(\frac{\partial p}{\partial V}\right)^2 \tag{100d}$$

and the expression in the square bracket in Eq. (100) is positive.

(f). Phase transitions. — This is the only case for which we have found condition (III) not always satisfied. In the two-phase region, p depends on T only, that is, $(\partial p/\partial V)_T = 0$. The specific heat, c_V, is always positive. Therefore condition (III), Eq. (97), reduces to

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial E}{\partial V}\right)_T > 0 \,. \tag{101}$$

Using Eq. (98a), the Clapeyron equation (82b), and (84c), this gives

$$\frac{\Delta S}{\Delta V}\left(T\,\frac{\Delta S}{\Delta V} - p\right) = \frac{\Delta E \Delta S}{\Delta V^2} > 0 \,, \tag{101a}$$

or simply

$$\Delta E \Delta S > 0 \,. \tag{102}$$

The condition is therefore that the energy and the entropy should change in the same direction. This is fulfilled for practically all phase transitions, but there are a few exceptions, such as the transformations ice I to ice II, or ice III to ice V (Dorsey,[7] p. 617).

Summarizing, we find that condition (III), like the other two conditions, seems to be satisfied for practically all homogeneous (one-phase) systems but to break down for a few phase transformations. The condition seems to be more generally fulfilled than condition (I).

17. Discussion of a hypothetical case: A material which satisfies conditions (I) and (II) but not (III)

We have shown in Sec. 16 that probably all materials satisfying condition (I) will also satisfy (III). However, since no general proof could be given, it may still be worthwhile to discuss the consequences of a violation of condition (III) in a material which satisfies (I) and (II).

Condition (III) was used in Sec. 8 to show that the energy increases monotonically with the entropy. Condition (III) is only a sufficient, not a necessary, condition for this; in order that the energy have a maximum, $(\partial p/\partial V)_E$ must not only be positive but also must satisfy Eq. (43). If Eq. (43) is fulfilled for some point on the shock curve, the energy must have a maximum at this point, must then decrease, have a <u>minimum</u>, and finally increase again with <u>S</u> at extremely high temperatures. Of course, <u>E</u> may have several maxima and minima.

As we have shown in connection with Eq. (47), the <u>pressure</u> will increase with the entropy at least as long as the energy does. Only if E_2 decreases sufficiently rapidly with increasing entropy and increasing V_2, will

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

reach a maximum and then decrease. To find the condition for a maximum of p_2, we proceed in a manner similar to that used in Eq. (42), only considering <u>p</u> and <u>V</u> as independent variables. Then we have

$$\left(\frac{\partial E}{\partial p}\right)_V dp + \left(\frac{\partial E}{\partial V}\right)_p dV = -\frac{1}{2}(p_2 + p_1)dV + \frac{1}{2}(V_1 - V_2)dp \ . \tag{103}$$

In order that dp/dV = 0, we must have

$$\left(\frac{\partial E}{\partial V}\right)_p = -\frac{1}{2}(p_2 + p_1) \ . \tag{103a}$$

The left-hand side can be transformed, using the thermodynamic relations given by Eqs.(11) and (12),

$$\left(\frac{\partial E}{\partial V}\right)_p = \left(\frac{\partial E}{\partial V}\right)_S + \left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_p = -p_2 - T_2 \frac{(\partial p/\partial V)_S}{(\partial p/\partial S)_V} \tag{103b}$$

so that condition (103a) reduces to

$$\Delta p\left(\frac{\partial p}{\partial E}\right) = -2\left(\frac{\partial p}{\partial V}\right) \ . \tag{104}$$

There is no general thermodynamical or statistical reason why Eq. (104) should not be fulfilled for some substance. If it is fulfilled, p_2 will have a maximum. If this is the case, the extrema of the various variables of state must follow each other, in the order of increasing entropy, like this: first a minimum of the volume, then a maximum of the energy, then a maximum of the pressure, followed by a minimum of the pressure, a minimum of the energy, and finally a maximum of the volume.

We shall now investigate the consequences of the maxima and minima of energy and pressure for the stability of shock waves. We have shown in Sec. 11 that a shock wave cannot split into two waves going in opposite directions if, for all values $p_2 < p_4$, we have

$$(p_4 - p_1)(V_1 - V_4) > (p_2 - p_1)(V_1 - V_2) \qquad (105)$$

[reverse of Eq. (62)]. We showed in Sec. 11 that condition (105) is certainly fulfilled if the energy increases monotonically with increasing pressure and entropy. We showed further that a maximum of the energy on the shock curve is a necessary but not a sufficient condition for a splitting of shock waves.

However, it can easily be seen that a maximum of the pressure on the shock curve is a sufficient (not necessary) condition for instability of shock waves. If a shock wave with "initial" state 1 and "final" state 4 is to split, Eq. (57) must be fulfilled. To show that this is possible, we compare the expressions

$$\delta = u_{C,4} - u_{C,3} \qquad (106)$$

and

$$D = (u_{0,1} - u_{0,4}) - (u_{A,1} - u_{A,2}) \, . \qquad (106a)$$

The first of these is very easy to calculate if the pressures p_4 and

$p_3 = p_2$ differ only slightly, for then wave C is a small shock wave and can be treated as almost adiabatic (see Sec. 3); we have [see Eqs. (58), (10)]

$$\delta = u_{C,4} - u_{C,3} = \frac{V_4 - V_3}{V_4} u_{C,4} \approx \frac{1}{V_4}\left(\frac{\partial V}{\partial p}\right)_S (p_4 - p_3) a_4 = \frac{V_4}{a_4}(p_2 - p_4). \quad (107)$$

This is always negative if $p_4 > p_2$.

On the other hand, we have from Eqs. (61), (61a):

$$D = \sqrt{(p_4 - p_1)(V_1 - V_4)} - \sqrt{(p_2 - p_1)(V_1 - V_2)}\,. \quad (108)$$

If condition (105) is fulfilled, D will be positive and therefore

$$D > \delta\,. \quad (108a)$$

On the other hand, if p_4 and p_2 are near the maximum of p, we have $p_4 - p_1 \approx p_2 - p_1$, so that

$$D \approx -\frac{1}{2}(V_4 - V_2)\sqrt{\frac{p_4 - p_1}{V_1 - V_4}}\,. \quad (108b)$$

This is negative (because, just before the maximum of p, V increases with increasing p) and $|D|$ can be made as large as we wish in comparison with $|\delta|$ [Eq. (107)]. Therefore, near the pressure maximum, we have

$$D < \delta\,. \quad (108c)$$

Therefore there must be a certain intermediate value of p_4 (between the energy maximum and the pressure maximum) for which $D = \delta$, so that Eq. (57) is fulfilled. Shock waves in which the pressure behind the wave lies within a certain range, close to the pressure maximum, can split into two waves going in opposite directions, as described in the beginning of Sec. 11.

Let us investigate the way in which the split occurs, as a function of p_4. We shall assume that the pressure does not vary much over the region in which a split may occur. Then Eq. (107) for $\underline{\delta}$ will be sufficiently accurate, while $\underline{D}$ can be obtained by expanding Eq. (108):

$$D = \frac{(V_2 - V_4)(p_4 - p_1) - (p_2 - p_4)(V_1 - V_4)}{2(u_{0,1} - u_{0,4})} . \qquad (109)$$

Condition (57) requires $\delta = D$; that is,

$$p_2 - p_4 = \frac{p_4 - p_1}{V_1 - V_4 + 2V_4(u_{0,1} - u_{0,4})/a_4} (V_2 - V_1) = c(V_2 - V_1), \qquad (109a)$$

where $\underline{c}$ is a constant, depending very slightly on the state $\underline{4}$. Graphically, we can interpret Eq. (109a) as follows (see Fig. 5). On the one hand, we draw the shock curve which gives p_2 as a (complicated) function of V_2. On the other hand, we consider the straight line Eq. (109a) whose slope, $\underline{c}$, can be calculated from known quantities. The intersections of the two curves will give the possible solutions p_2, V_2 for given p_4, V_4 (see Fig. 5). If $\underline{p}$ has a maximum and a minimum, then for states p_4 near these extrema, there will be three intersections of the straight line with the p(V) curve, including the intersection of p_4, V_4; for values of p_4 far from the extrema, there will be only one intersection. In the latter case, shock waves corresponding to p_4, V_4 cannot split.

It is easy to see that three intersections may occur without $\underline{p}$ having a maximum and minimum if only at some point of the shock curve

$$dp/dV < c , \qquad (109b)$$

where dp/dV is taken along the shock curve, and $\underline{c}$ is the quantity defined in Eq. (109a).

If there are three intersections, a split is possible as far as the kinematics of the shock waves is concerned. Now, for thermo-

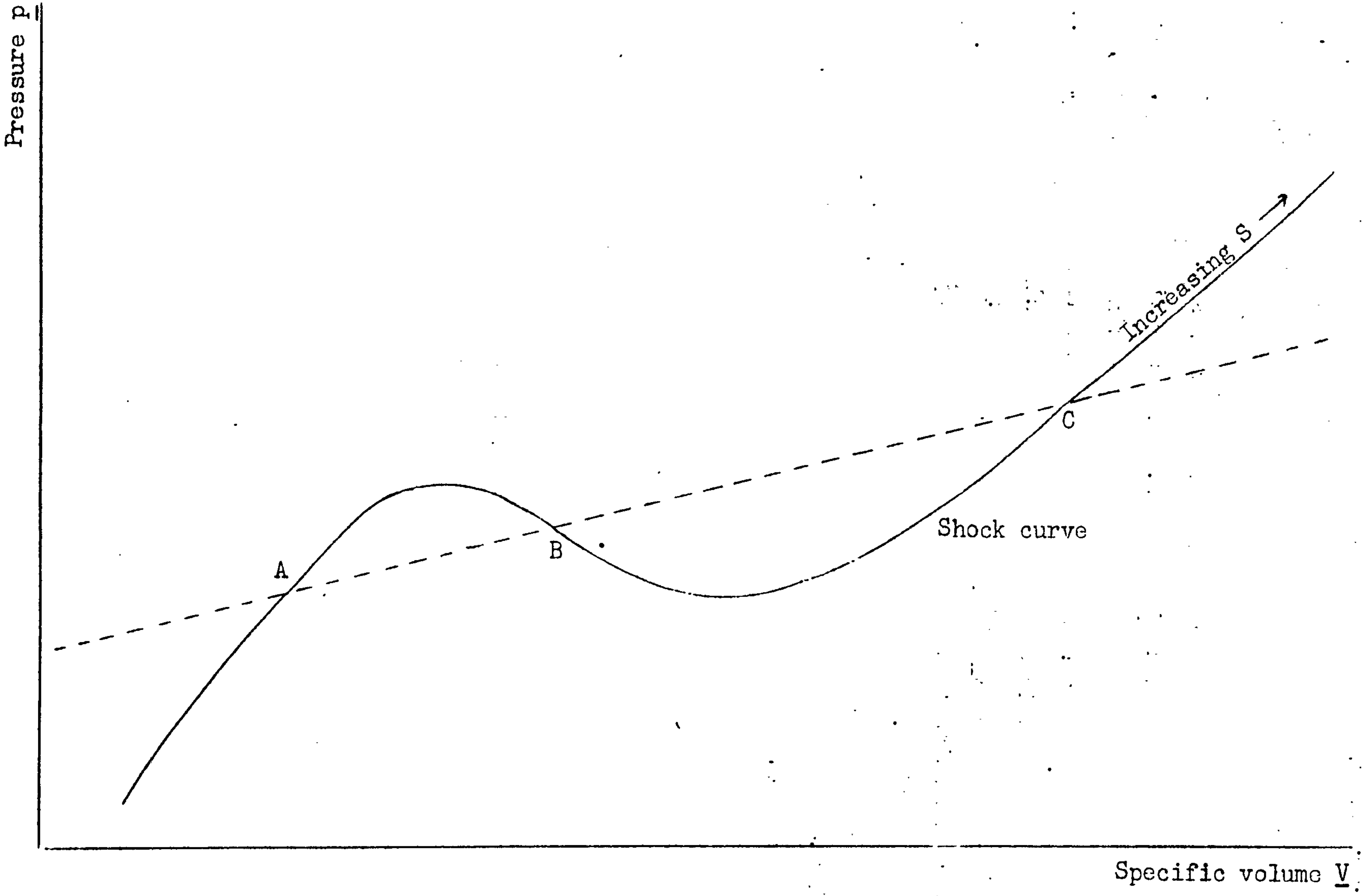

Fig. 5. Splitting of shock waves. ———, the shock curve in a p,V-diagram; the curve has a maximum and a minimum. ------, the straight line $p - p_4 = c(V - V_4)$ defined by Eq. (109a). The intersections *A* and *B* represent unstable shock waves; *C*, a stable shock wave.

dynamic reasons, the split will occur in such a way that the entropy at the instant immediately after the split is as large as possible. This requires obviously the selection of the highest of the three intersections: for then the entropy of state 2 is greater than for either of the other two intersections, and, moreover, state 2 propagates most rapidly into medium 1 (see Sec. 9). In addition, state 3, having the highest pressure compatible with the kinematic conditions, will also have a higher entropy than 4, and will spread into 4. Therefore, if there should be a shock wave corresponding to one of the lower intersections (A and B) in Fig. 5, it would split into one shock wave corresponding to the highest intersection (C) and another small shock wave going in the opposite direction. The shock wave would thus increase in amplitude rather than decrease by its "split." The newly established shock wave of higher entropy change and velocity would then be stable.

IV. CONCLUSION

18. Relation to the theory of Duhem

The theory of shock waves in a medium with a general equation of state has been discussed previously by Duhem.[11] The principal difference between his treatment and the present one is that he did not make any assumptions about the equation of state, while we have made several -- namely, the conditions (I), (II), (III), and the facts about the equation of state at high temperatures (Sec. 5). Duhem was therefore not able to come to such general conclusions as we did.

Duhem did recognize the importance of condition (I). He possessed the main results of Sec. 3 of this paper, namely that small but finite compressional waves correspond to an increase of entropy if $\partial^2 p/\partial V^2 > 0$, while finite rarefaction waves would be stable if $\partial^2 p/\partial V^2 < 0$ (pp. 177-178 of his paper). He also found that for $\partial^2 p/\partial V^2 > 0$, the velocity of small compression waves, with respect to the less dense material, is greater than the velocity of sound; while relative to the denser material, the shock wave moves more slowly than sound [Eq. (15) of this paper, p. 178 of Duhem's paper]. However, he could claim the validity of his statements only for a rather restricted range of densities behind the shock wave, without being able to state the conditions of validity in physical terms.

Moreover, Duhem found already that the entropy change for small shock waves is proportional to a higher power of the density change than the first [his Eq. (19)], but he did not find the third-power law [Eq. (13) of our paper]. Generally speaking, his paper contains part of the results of our Sec. 3, but none of the later sections. In particular, he did not discuss the stability problems (Secs. 10 and 11) and he could not obtain the general results of Secs. 4, 7, and 9.

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[11] P. Duhem, Zeits. für Physik. Chemie 69, 169 (1909). I am indebted to Professor J. Von Neumann for drawing my attention to this paper.

19. Summary

We have shown in this paper:

(1) General theorems can be derived about shock waves in any substance whose equation of state satisfies the three conditions:

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

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

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

(2) The three conditions are satisfied for all single-phase systems which we have investigated (Secs. 12, 15, 16), namely, ideal gases with constant or variable specific heat, gases obeying Van der Waals' equation, dissociating gases, liquids and solids at normal temperatures, and solids at extremely low temperatures. Condition (I) is violated for most phase changes (Sec. 13). Phase changes can, however, be excluded from consideration because they require too long a time to occur in shock waves (Sec. 1).

(3) If condition (I) is satisfied for a substance, then all compressive waves of small but finite amplitude are connected with an increase of entropy (Sec. 3).

(4) The increase of entropy for small volume change ΔV is proportional to ΔV^3 [Eq. (13)].

(5) If, in addition to condition (I), also condition (II) is fulfilled — that is, $V(\partial p/\partial E)_V > -2$ everywhere — then all compressive waves of whatever amplitude are connected with an increase of entropy and are therefore thermodynamically stable (Sec. 4). Rarefaction waves of finite amplitude are unstable and dissolve into trains of infinitesimal waves.

(6) If condition (I) is not satisfied, as at the boundary of phases, rarefaction waves of finite amplitude may be stable (Sec. 14) provided the phase transition can occur, and compression waves may, under certain circumstances, consist of two shock waves of different velocities, one traveling behind the other.

(7) If conditions (I) and (II) are satisfied, and if the state of the material in front of the shock wave is given (V_1, S_1), there is one and only one solution for any value of the entropy S_2 behind the shock wave, between S_1 and infinity (Sec. 7). If the state of the material behind the shock wave is given (V_2, S_2), there is one and only one solution for any value of the entropy S_1 in front of the shock wave, from S_B to S_1 where S_B is either zero or corresponds to a phase boundary (Sec. 7).

(8) With increasing entropy of the material behind the shock wave the specific volume V_2 decreases to a minimum, $V_{2\ min}$, which is ordinarily reached at temperatures of the order of 10,000°. For still higher temperatures, V_2 increases again to $\frac{1}{4} V_1$ (Secs. 5,8). For some substances V_2 may have several minima and maxima, possibly including some at lower temperatures.

If the state behind the shock wave is given (V_2, S_2), then the specific volume V_1 of the material in front of the wave increases monotonically with decreasing entropy S_1 (Sec. 8).

(9) If condition (III) as well as conditions (I) and (II) is satisfied, the specific energy E_2 and the pressure p_2 of the material behind the shock wave increase monotonically with the entropy S_2 for given V_1, S_1. If the state behind the shock wave, V_2, S_2, is given, the specific energy in front, E_1, decreases monotonically with S_1 even if condition (III) is not fulfilled. No similar theorem holds for the pressure p_1 in front. In any case, the energy and pressure behind a shock wave are higher than the same quantities in front of the wave (Sec. 8).

(10) If conditions (I) and (II) are fulfilled, the velocity of any shock wave with respect to the material in front of it is always greater than the velocity of sound in that material. For a given

state in front of the shock wave, V_1, S_1, there is one and only one possible shock wave for every shock-wave velocity u_1 greater than the velocity of sound, a_1. Increasing shock-wave velocity u_1 corresponds to increasing entropy behind the shock wave, S_2 (Sec. 9).

(11) The velocity u_2 of the shock wave relative to the material behind it is always less than the sound velocity a_2 in that material. If the state behind the wave is given, there is one and only one possible shock wave for every velocity u_2 between a_2 and a certain minimum velocity u_{2B}. If the velocity is u_{2B}, the state of the material in front of the wave either lies on a phase boundary or has zero absolute temperature. Decreasing velocity u_2 corresponds to decreasing entropy in front of the shock wave, S_1 (Sec. 9).

(12) In a material satisfying conditions (I) and (II), a shock wave will overtake any waves, of infinitesimal or finite amplitude, which precede it, and will be overtaken by any wave following it.

(13) If conditions (I) and (II) are satisfied, no shock wave can start from the same point at the same time and in the same direction as any other wave, whether of infinitesimal or of finite amplitude (Sec. 10). No shock wave can split into any number of waves going in the same direction.

(14) In a material fulfilling also condition (III), no one-dimensional shock wave can split in any way whatsoever (Sec. 11).