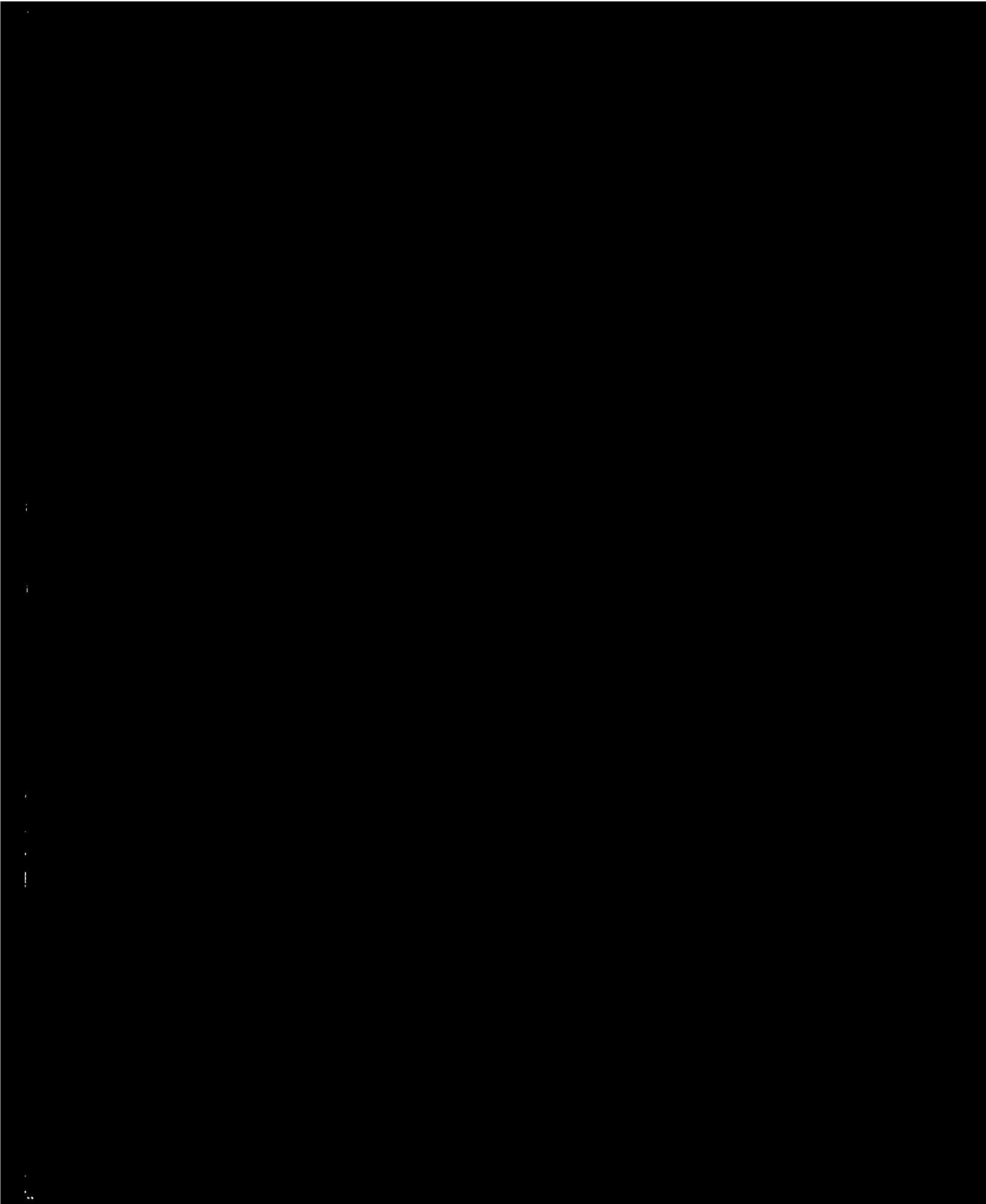


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THE DETERMINATION OF EQUATION OF STATE DATA
FROM MEASUREMENTS IN SHOCKS

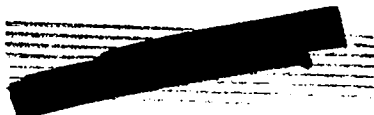
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UNCLASSIFIEDABSTRACT

This paper details the procedure for determining the constants in a reasonable empirical form of equation of state of solids from data on the isothermal compressibility at zero pressure, the coefficient of thermal expansion, and a single Hugoniot curve. The method is illustrated by application to aluminum. The exact equation relating the material velocity to the experimentally measured free surface velocity is worked out, since both material and shock velocities are needed to construct the Hugoniot curve.

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I. INTRODUCTION

A shock wave of pressure P , moving with the velocity s , into material at rest, and at zero pressure, compresses the material from the specific volume V_0 to a smaller specific volume V , by an amount $\Delta V = V - V_0 < 0$, and leaves the material behind the shock front moving with the material velocity u_s .

A measurement of the shock velocity, s , and the material velocity, u_s , uniquely determine P and V if V_0 is known, by the relations:

$$s^2 = V_0^2 P / (-\Delta V) \quad (I.1)$$

$$u_s^2 = (-\Delta V)P \quad (I.2)$$

so that:

$$(-\Delta V) = V_0 u_s / s \quad (I.3)$$

$$P = u_s s / V_0 \quad (I.4)$$

If the equation of state of the material is known, so that the internal energy E , of the material in which the shock front moves, is given as a function of P and V , then the Hugoniot Relation:

$$\Delta E = \frac{1}{2} P(-\Delta V) \quad (I.5)$$

which must hold between the internal energy increase, ΔE , in the shock, and P and $-\Delta V$, permits a unique evaluation of the value of $(-\Delta V)$ for any pressure P . Conversely measurement of u_s and s for various shock intensities, lead, through equations (3) and (4) to an evaluation of the Hugoniot Curve of related P and $-\Delta V$ values, for which the internal energy change ΔE , must be given by (5).

The shock velocity, s , may be measured with accuracies of the order of one per cent by the pin technique. The material velocity, u , is not readily measured directly. Instead, one measures what is called the "free surface velocity", u_{fs} , which is approximately twice the material velocity behind the shock, u_s :

$$u_{fs} \cong 2u_s \quad (I.6)$$

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Equation (I.7) can be rewritten in terms of quantities whose measurement is anticipated:

$$\frac{\partial P}{\partial V} = -\frac{1}{V^2} \frac{\partial P}{\partial S} = -\frac{C^2}{V^2}$$

or in I.7

$$U_r = -\int_0^P \frac{V}{C} dP$$

The free surface velocity, u_{fs} , is the material velocity acquired by matter at rest which has been subjected to a shock wave followed by a rarefaction wave to zero pressure, the rarefaction wave moving directly opposite to the direction of shock wave. This is observed experimentally by determining the velocity of a surface in contact with a region of zero pressure (actually air at atmosphere pressure) after a shock has reached it from the inside, travelling in a direction normal to the free surface.

The free surface velocity, u_{fs} , may be written as the sum of two approximately equal velocities, u_s and u_r , the former being the material velocity acquired in the shock, and the latter being that acquired in the (adiabatic) rarefaction wave reducing the pressure to zero. The latter velocity is given by the equation:

$$u_r = \int_0^P (-\partial V / \partial P)_s^{\frac{1}{2}} dP \quad \text{Result obtained by assumption of a centered rarefaction wave. (I.7)}$$

where $(-\partial V / \partial P)_s$ is the derivative taken at constant entropy, S .

For weak shocks, in solid materials, $(-\partial V / \partial P)_s$ may be regarded as constant, so that:

$$u_r \cong P (-\partial V / \partial P)_{s, P=0}^{\frac{1}{2}} \quad (I.7')$$

Since, for weak shocks, the Hugoniot curve follows the adiabatic, $(-\Delta V) \cong P (-\partial V / \partial P)_{s, P=0}$, one has, from (2),

$$u_s \cong P (-\partial V / \partial P)_{s, P=0}^{\frac{1}{2}} \quad (I.2')$$

and equation (6) that $u_{fs} \cong u_r + u_s$ is approximately twice u_s follows. For strong shocks appreciable deviations from (6) occur.

The exact equation relating u_s and the free surface velocity, u_{fs} , may be written:

$$u_s = \frac{1}{2} u_{fs} [1 + g(P)] \quad (I.8)$$

where

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$$g(P) = \left\{ 1 - \frac{\int_0^P (-\partial v / \partial P)_s^{\frac{1}{2}} dP}{(-\Delta v / P)^{\frac{1}{2}} P} \right\} \left\{ 1 + \frac{\int_0^P (-\partial v / \partial P)_s^{\frac{1}{2}} dP}{(-\Delta v / P)^{\frac{1}{2}} P} \right\}^{-1} \quad (1.9)$$

$$= [1 - (u_r / u_s)] / [1 + u_r / u_s]$$

is a number which approaches zero for small pressures, and is presumably never large.

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II. EQUATION OF STATE ASSUMPTIONS.

A knowledge of the common "first derivatives", compressibility, β , coefficient of thermal expansion, α , and specific heat, c_p at room temperature and zero pressure, plus a measurement of a single Hugoniot curve is not sufficient to establish the complete equation of state of the material in the neighborhood of those pressures and volumes reached on the Hugoniot.

In principle, at least, a measurement of a family of Hugoniot curves, obtained by measuring the shock and material velocities in shocks produced in the same material, but at different initial densities, would establish a unique equation of state. However, it appears to be more practical, at least as an initial attempt, to assume a simple and reasonable analytical form for the equation of state, and to use the Hugoniot curve to determine the parameters of the equation.

The three quantities:

$$\alpha = (1/V)(\partial V/\partial T)_P \quad . \quad (II.1)$$

$$\beta = -(1/V)(\partial V/\partial P)_T \quad . \quad (II.2)$$

$$c_p = (\partial H/\partial T)_P \quad . \quad (II.3)$$

commonly known at room temperature and zero pressure, serve to fit three parameters in any assumed equation of state. These three quantities also determine the initial slope of the Hugoniot curve:

$$\lim_{P \rightarrow 0} \left[\frac{(-\Delta V)}{P} \right]_{\text{Hug}} = \left(\frac{-\partial V}{\partial P} \right)_{S, P=0} = V_0 \beta_{ad} \quad . \quad (II.4)$$

$$\beta_{ad} = \beta_{c_v}/c_p \quad . \quad (II.5)$$

$$c_p/c_v = 1 + (TV_0 \alpha^2 / \beta_{c_v}) \quad . \quad (II.6)$$

A measurement of $(-\Delta V)/P$ at a pressure sufficiently high to show a significant deviation from (4) would permit one to obtain a fourth parameter, say by writing:

$$\left[\frac{-\Delta V}{P} \right]_{\text{Hug}} = \left(-\frac{\partial V}{\partial P} \right)_{S, P=0} \left[1 - A(-\Delta V) - B(-\Delta V)^2 \right] \quad (II.6)$$

and determining A. Measurements of greater accuracy, and at higher pressures, may permit the determination of a fifth parameter by the use of an equation:

$$\left[\frac{-\Delta V}{P} \right]_{\text{Hug}} = \left(-\frac{\partial V}{\partial P} \right)_{S, P=0} \left[1 - A(-\Delta V) - B(-\Delta V)^2 \right]. \quad (II.7)$$

Very considerable refinement in accuracy, and extension of the pressure range over that now measured, would be required for the evaluation of a sixth parameter.

The question is then to find simple four and five parameter equations of state which satisfy our prejudices of reasonableness in analytical form and which can be readily handled.

From a theoretical point of view the equation of state may be regarded as determined if both the energy E, and entropy S, are given as functions of volume and temperature. However, the two derivatives with respect to temperature must bear the relationship:

$$\left(\frac{\partial S}{\partial T} \right)_V = c_V/T = (1/T) \left(\frac{\partial E}{\partial T} \right)_V. \quad (II.8)$$

No necessary relationship need exist between the volume derivatives.

A simple and convenient form to assume for the volume dependence of the internal energy at $T=0$ is

$$E(T=0) = AV + B(V-b)^{-(\gamma-1)} + C.$$

By introducing:

$$V^* = V - b \quad (II.9)$$

one may write this as:

$$E(T=0) = \pi V^* \left[1 + \frac{1}{\gamma-1} \left(\frac{V_{\infty}^*}{V^*} \right)^{\gamma} \right] - \frac{\gamma}{\gamma-1} \pi V_{\infty}^*.$$

so that

$$P(T=0) = - \frac{\partial E(T=0)}{\partial V} = \pi \left[1 - \left(\frac{V_{\infty}^*}{V^*} \right)^{\gamma} \right]$$

and V_{00}^* is seen to be the value of the specific volume at $P=0$, $T=0$, minus the parameter b .

At the entropy of the material at room temperature, $P=0$, most metals, at least, have the constant DuLong and Petit value for c_V . Except for extremely intense shocks, in which the temperature becomes so high that electronic degrees of freedom are excited, it is probably reasonable to assume that:

$$\left. \begin{aligned} c_V &= 3R \\ R &= (1.986/M) \text{ cal deg}^{-1} \end{aligned} \right\} \quad (\text{II.10})$$

with M the (average) gram atomic weight.

We, therefore, assume for $E(V,T)$ the form:

$$E = \pi V^* \left[1 + \frac{1}{\gamma-1} \left(\frac{V_{00}^*}{V^*} \right)^\gamma \right] + 3RT - \frac{\delta}{\gamma-1} \pi V_{00}^* \quad (\text{II.11})$$

The last term, $-(\delta/\gamma-1)\pi V_{00}^*$ is constant, and of no real significance, but merely fixes $E=0$ at $P=0$, $T=0$.

If the heat capacity per gram at constant volume, $c_V = (\partial E / \partial T)_V$, is assumed to have the constant value $3R$ one may write the entropy, S , as

$$S = 3R \ln(kT/h\nu)$$

where ν is some average frequency. In general ν increases with decreasing volume, but probably depends very little on the temperature. If one assumes that the volume dependence of ν can be adequately expressed as an inverse power of $V^* = V-b$, with the same parameter b as occurs in the energy expression, one may write:

$$S = 3R \ln (T/\theta) (V^*/V_{00}^*)^{\gamma+\Delta\gamma-1} \quad (\text{II.12})$$

In this expression θ , of dimensions of temperature, is merely introduced for the convenience of having all subsequent equations dimensionally correct, but plays no other role than that of fixing the absolute value of the entropy, which is chosen as zero at $V=V_{00}$, $T=0$.

Equation (11) for E has four independent parameters, which are

b , dimensions volume per gram

π , dimensions pressure

R , energy per degree, assumed given by (10)

γ , dimensionless.

Equation (12) for S introduces one more parameter:

$\Delta\gamma$, dimensionless,

besides the completely immaterial θ . Thus (11) and (12) constitute the two fundamental equations for a five parameter equation of state.

If for no good reason but that of convenience one chooses

$$\Delta\gamma = 0 \quad (\text{II.13})$$

one has a four parameter equation of state.

There exists a theoretical argument for assuming the frequencies proportional to $(\partial^2 E / \partial V^2)^{\frac{1}{2}}$ or, from (11),

$$\nu \sim (v_{00}^* / v^*)^{(\gamma+1)/2}$$

$$\gamma + \Delta\gamma \sim 1 = \frac{1}{2}(\gamma+1)$$

or,

$$\Delta\gamma = \frac{3}{2} - \frac{1}{2}\gamma = \frac{1}{2}(3-\gamma) \quad (\text{II.13}')$$

Since numerical values of about three seem to fit for γ this equation would lead to small values of $\Delta\gamma$. The theoretical argument for assuming the frequency square to be proportional to $\partial^2 E / \partial V^2$ is sufficiently weak to make it appear inadvisable to sacrifice the real convenience of the assumption (II.13) that $\Delta\gamma = 0$ and replace it by (II.13'). However, either (13) or (13') might be used to eliminate $\Delta\gamma$ in order to have a four parameter equation of state.

Equations (11) and (12), with or without the assumption of (13) that $\Delta\gamma = 0$ have been referred to as four and five parameter equations respectively. Actually equation (II.10) fixes one of the parameters, namely R , in a trivial way from the

atomic weight. Insofar as α_V differs significantly from the value of equation (10) the assumption of a constant value for α_V will be erroneous. The three (or four) remaining parameters, π , b , γ (and $\Delta\gamma$ if 13 is not used) must be determined from experimental values of the quantities: β_0 , the isothermal compressibility at $P=0$; α_0 , the coefficient of thermal expansion; and A (or A and B) of equation (7) (or of equation 7').

In order to accomplish this it is necessary to use the equations (II.11) and (II.12) to express these measurable quantities, α_0 , β_0 , A, and B. The rather tedious mathematics are accomplished in sections III, IV, and V. The useful equations are summarized in section VI for $\Delta\gamma = 0$, and in VII for $\Delta\gamma \neq 0$. An application to some available data for Al is given in section VIII.

III. MANIPULATION OF THE FUNDAMENTAL EQUATIONS.

All extensive quantities, E, energy; S, entropy, and V, volume, are per unit mass. Introduce

$$V_{00} = \text{volume (per unit mass) at } T=0 \text{ and } P=0,$$

$$V_0(T) = \text{volume (per unit mass) at } T \text{ and } P=0,$$

$$V_0(S) = \text{volume (per unit mass) at } S \text{ and } P=0,$$

$$V^* = V - b,$$

$$V_0^*(T) = V_0(T) - b,$$

$$V_0^*(S) = V_0(S) - b,$$

$$v_{0T} = V_0^*(T) / V_{00}^*,$$

$$v_{0S} = V_0^*(S) / V_{00}^*,$$

$$v_T = V^* / V_0^*(T),$$

$$v_S = V^* / V_0^*(S),$$

$$v = V^* / V_{00}^*$$

so that

$$V^* / V_{00}^* = v_T v_{0T} = v_S v_{0S} = v. \quad (\text{III.1})$$

Use, also,

$$\epsilon = \pi V_{00}^* \quad (\text{III.2})$$

and introduce two functions, one of the entropy alone and one of the temperature alone,

$$g = g(S) = 3R(\gamma + \Delta\gamma - 1) \theta e^{S/3R} v_{0S}^{-(\gamma + \Delta\gamma)} \epsilon^{-1} \quad (\text{III.3})$$

$$f = f(T) = 3R(\gamma + \Delta\gamma - 1) T v_{0T}^{-1} \epsilon^{-1} \quad (\text{III.4})$$

Equation (II.12) is:

$$S = 3R \ln (T/\theta) v^{\gamma + \Delta\gamma - 1} \quad (\text{III.5})$$

$$T = \theta v^{-(\gamma + \Delta\gamma - 1)} e^{S/3R} \quad (\text{III.6})$$

Substitute (1) for v^*/v_{00}^* and (6) for T in (II.11) for E, to obtain

$$E = \epsilon \left[v + \frac{1}{\gamma-1} v^{-(\gamma-1)} + \frac{v_{0s}^{\gamma+\Delta\gamma}}{\gamma+\Delta\gamma-1} \epsilon v^{-(\gamma+\Delta\gamma-1)} - \frac{\gamma}{\gamma-1} \right] \quad (III.7)$$

Since,

$$\begin{aligned} \partial/\partial v &= (v_{00}^*)^{-1} \partial/\partial v, \\ &= (v_{00}^* v_{0s})^{-1} \partial/\partial v_s \end{aligned} \quad (III.8)$$

differentiation of (7) at constant entropy, and hence at constant g leads to:

$$\begin{aligned} P &= (-\partial E/\partial v)_s = \pi \left[v^{-\gamma} + \epsilon v_{0s}^{-(\gamma+\Delta\gamma)} v^{-(\gamma+\Delta\gamma)} - 1 \right] \\ &= \pi \left[(v_{0s} v_s)^{-\gamma} + \epsilon v_s^{-(\gamma+\Delta\gamma)} - 1 \right] \quad (III.9) \end{aligned}$$

At zero pressure $v_s \equiv 1$ so that

$$v_{0s}^{-\gamma} = 1 - g. \quad (III.10)$$

Use this, in (9), to write

$$P = \pi \left[v_s^{-\gamma} + g (v_s^{-(\gamma+\Delta\gamma)} - v_s^{-\gamma}) - 1 \right] \quad (III.11)$$

Since from (1) $v_{0s} v_s = v_{0T} v_T$ comparison of (3), (4) and (6) shows that

$$f v_T^{-1} = \epsilon v_s^{-(\gamma+\Delta\gamma)}, \quad (III.12)$$

so that (9) may be written:

$$\begin{aligned} P &= \pi \left[v^{-\gamma} + f v_{0T} v^{-1} - 1 \right] \\ &= \pi \left[(v_T v_{0T})^{-\gamma} + f v_T^{-1} - 1 \right] \quad (III.13) \end{aligned}$$

and since $v_T \equiv 1$ at zero pressure,

$$v_{0T}^{-\gamma} = 1 - f \quad (III.14)$$

and,

$$P = \pi \left[v_T^{-\delta} + f(v_T^{-1} - v_T^{-\delta}) - 1 \right]. \quad (\text{III.14})$$

For any given volume, since $(v_{OT} v_T)^{-\delta} = (v_{OS} v_S)^{-\delta} = v_T^{-\delta} (1-f) = v_S^{-\delta} (1-g)$

we have:

$$v_T^{-\delta} (1-f) = v_S^{-\delta} (1-g) \quad (\text{III.15})$$

In general,

$$(\partial f / \partial V)_T = 0, \quad (\partial g / \partial V)_S = 0,$$

that is, f is a function of T alone and g one of S alone. Use (3) and (10) or (4) and (13), to find:

$$df/d \ln T = f \left[1 - d \ln v_O / d \ln T \right],$$

$$dg/dS = g \left[(1/3R) - (\gamma + \Delta\gamma) d \ln v_O / dS \right],$$

$$d \ln v_O / d \ln T = \left[(1/\gamma) f / (1-f) \right] d \ln f / d \ln T,$$

$$d \ln v_O / dS = \left[(1/\gamma) g / (1-g) \right] d \ln g / dS,$$

so that:

$$df/dT = (f/T)(1-f) / \left[1 - \frac{\gamma-1}{\gamma} f \right], \quad (\text{III.16})$$

$$dg/dS = (g/3R)(1-g) / \left[1 + \frac{\Delta\gamma}{\gamma} g \right]. \quad (\text{III.17})$$

Now differentiate (11) with respect to V , using (8), to obtain:

$$\begin{aligned} (-\partial P / \partial V)_S &= 1/V\beta_{ad} = \frac{\pi\gamma}{V^*} \left\{ v_S^{-\delta} g \left[\frac{\gamma + \Delta\gamma}{\gamma} v_S^{-1} - v_S^{-\delta} \right] \right\} \\ &= \frac{\pi\gamma}{V^*} \left\{ v_T^{-\delta} + f \left[\frac{\gamma + \Delta\gamma}{\gamma} v_T^{-1} - v_T^{-\delta} \right] \right\}, \quad (\text{III.18}) \end{aligned}$$

where, in the last expression, use has been made of (12) and (15).

Similarly, differentiate (14) with respect to V , obtaining:

$$\begin{aligned}
 (-\partial P/\partial v)_T &= 1/\beta = \frac{\pi \gamma}{V^*} \left\{ v_T^{-\gamma} + F \left[\frac{1}{\delta} v_T^{-1} - v_T^{-\delta} \right] \right\} \\
 &= \frac{\pi \gamma}{V^*} \left\{ v_T^{-\gamma} + g \left[\frac{1}{\delta} v_s^{-(\gamma+\Delta\gamma)} - v_s^{-\delta} \right] \right\}.
 \end{aligned} \tag{III.19}$$

The ratio of these, from (II.5) gives

$$\begin{aligned}
 c_p/c_v &= 1 + \frac{\gamma+\Delta\gamma-1}{\gamma} g v_s^{-\Delta\gamma} \left\{ 1 + \frac{1}{\delta} g \left[v_s^{-\Delta\gamma} - \delta \right] \right\}^{-1} \\
 &= 1 + \frac{\gamma+\Delta\gamma-1}{\gamma} f v_T^{-(\gamma-1)} \left\{ 1 + \frac{1}{\delta} f \left[v_T^{\delta-1} - \delta \right] \right\}^{-1}.
 \end{aligned} \tag{III.20}$$

Differentiation of (9*) with respect to T, using (4) gives:

$$(\partial P/\partial T)_v = \alpha/\beta = \frac{3R(\gamma+\Delta\gamma-1)}{V^*} = \pi f / T v_T \tag{III.21}$$

The energy E may be expressed as a function of P and v. From (9)

$$E v_{os}^{\gamma+\Delta\gamma} = (P/\pi) v^{\gamma+\Delta\gamma} - v^{\Delta\gamma} + v^{\gamma+\Delta\gamma}, \tag{III.22}$$

and if this is used in (7)

$$E = \frac{\epsilon}{\gamma+\Delta\gamma-1} \left\{ \left[(\gamma+\Delta\gamma) + \frac{P}{\pi} \right] v + \frac{\Delta\gamma}{\delta-1} v^{-(\delta-1)} - \frac{\gamma(\gamma+\Delta\gamma-1)}{\gamma-1} \right\}. \tag{III.23}$$

If (22) is used with (3) one finds

$$S = 3R \ln \frac{\epsilon}{3R(\gamma+\Delta\gamma-1)\theta} \left\{ \frac{P}{\pi} v^{\gamma+\Delta\gamma} - v^{\Delta\gamma} + v^{\gamma+\Delta\gamma} \right\}. \tag{III.24}$$

From (9*)

$$f v_{oT} = (P/\pi) v - v^{-(\gamma-1)} + v, \tag{III.25}$$

which, with (4) gives

$$T = \frac{\epsilon}{3R(\gamma+\Delta\gamma-1)} \left\{ \frac{P}{\pi} v - v^{-(\gamma-1)} + v \right\}. \tag{III.26}$$

These equations express the corresponding functions in terms of P and v.

One may introduce, instead of v, either $v_T = V^*/V_o^*(T)$ and $f(T)$ or

$v_s = V^*/V_o^*(s)$ and $g(s)$, using (1) and (13) or (10). One obtains:

$$E = \frac{\pi v_o^*(g)}{\gamma + \Delta\gamma - 1} \left\{ \left[\gamma + \Delta\gamma + \frac{P}{\pi} \right] v_s + \frac{\Delta\gamma}{\gamma - 1} (1-g) v_s^{-(\gamma-1)} \right\} - \frac{\gamma \epsilon}{\gamma - 1}$$

$$= \frac{\pi v_o^*(T)}{\gamma + \Delta\gamma - 1} \left\{ \left[\gamma + \Delta\gamma + \frac{P}{\pi} \right] v_T + \frac{\Delta\gamma}{\gamma - 1} (1-f) v_T^{-(\gamma-1)} \right\} - \frac{\gamma \epsilon}{\gamma - 1} \quad . \quad (\text{III.27})$$

$$S = S_o + 3R \ln(1/g_o) \left\{ \left[1 + \frac{P}{\pi} \right] v_s^{\gamma + \Delta\gamma} - (1-g) v_s^{\Delta\gamma} \right\} \quad . \quad (\text{III.28})$$

$$T = (T_o/f_o) v \left\{ \left[1 + \frac{P}{\pi} \right] - (1-f_o) v_T^{-\gamma} \right\} \quad . \quad (\text{III.29})$$

IV. THE HUGONIOT CURVE.

Start at the initial pressure, P_0 , to be zero, $P_0 = 0$, so that the free volume is V_0^* , at temperature T_0 , entropy S_0 . The relation (I.5) determines that Hugoniot curve:

$$\Delta E = \frac{1}{2} P V_0^* (-\Delta V) = \frac{1}{2} P V_0^* x, \quad (IV.1)$$

$$-x = \Delta V = V_{\text{final}} - 1 = \frac{V^* - V_0^*}{V_0^*}. \quad (IV.2)$$

From (III.27),

$$\Delta E = \frac{P V_0^*}{\gamma + \Delta\gamma - 1} (1-x) - \frac{\pi V_0^*}{\gamma + \Delta\gamma - 1} (\gamma + \Delta\gamma)x + \frac{\pi V_0^* \Delta\gamma}{(\gamma + \Delta\gamma - 1)(\gamma - 1)} (1-f_0) \left[(1-x)^{-(\gamma-1)} - 1 \right]$$

which, if equated to (1) gives

$$P = \gamma \pi \left[1 + \frac{\Delta\gamma}{\gamma} f_0 \right] x \left[1 - (\gamma + \Delta\gamma + 1)x \right]^{-1} \left\{ 1 - \frac{\Delta\gamma}{\gamma(\gamma-1)} \frac{1-f_0}{1 + \frac{\Delta\gamma}{\gamma} f_0} \left[(1-x)^{-\gamma-1} - 1 - (\gamma-1)x \right] x^{-1} \right\}$$

$$\left[-\Delta V / P \right]_{\text{Hug}} = \left(-\partial V / \partial P \right)_{s, P=0} x F(-\Delta V / V_0^*) \quad (IV.3)$$

with

$$F(x) = \frac{1 - \frac{1}{2}(\gamma + \Delta\gamma + 1)x}{1 - \frac{\Delta\gamma}{\gamma(\gamma-1)} \frac{1-f_0}{1 + \frac{\Delta\gamma}{\gamma} f_0} \left[(1-x)^{-\gamma-1} - 1 - (\gamma-1)x \right] x^{-1}} \quad (IV.4)$$

The function $F(x)$ may be developed as a power series in $(-\Delta V) = x V_0^*$, as in equation II 7'. One writes.:

$$\left[-\Delta V / P \right]_{\text{Hug}} = \left(-\partial V / \partial P \right)_{s, P=0} \left[1 - A(-\Delta V) - B(-\Delta V)^2 \dots \right] \quad (IV.5)$$

$$V_0^* A = \frac{1}{2} \left\{ (\gamma + 1) + \left[\Delta\gamma f_0 \left[1 + \frac{\Delta\gamma}{\gamma} \right] / \left[1 + \frac{\Delta\gamma}{\gamma} f_0 \right] \right] \right\}$$

$$\left(V_0^* \right)^2 B = \frac{1}{12} \Delta\gamma \frac{1-f_0}{1 + \frac{\Delta\gamma}{\gamma} f_0} \left\{ 5(\gamma + 1) + 5\Delta\gamma f_0 \frac{1 + \frac{\Delta\gamma}{\gamma}}{1 + \frac{\Delta\gamma}{\gamma} f_0} \right\}$$

$$\left(-\partial V / \partial P \right)_{s, P=0} = \left(V_0^* / \gamma \pi \right) \left(1 + \frac{\Delta\gamma}{\gamma} f_0 \right)$$

$$f_0 = 3RT(\gamma + \Delta\gamma - 1) / \pi v_0^*$$

If $\Delta\gamma = 0$ it is seen that $B \equiv C$ in the development IV.5, as would be all higher terms of the development. For this case:

$$\left(\frac{-\Delta V}{P}\right)_{\text{Hug}} = \left(\frac{-\partial V}{\partial P}\right)_{s, P=0} \left[1 - \frac{1}{2}(\gamma+1) \frac{(-\Delta V)}{v_0^*} \right], \quad (\Delta\gamma=0), \quad (\text{IV.6})$$

which can be solved explicitly for $(-\Delta V)$:

$$\left(\frac{-\Delta V}{P}\right)_{\text{Hug}} = \left(\frac{-\partial V}{\partial P}\right)_{s, P=0} \left\{ 1 + \frac{1}{2}(\gamma+1) \left(\frac{-\partial V}{\partial P}\right)_{s, P=0} \frac{P}{v_0^*} \right\}^{-1}, \quad (\text{IV.7})$$

$$\left(\frac{P}{-\Delta V}\right)_{\text{Hug}} = \left(-\partial P / \partial V\right)_{s, P=0} + \frac{1}{2}(\gamma+1)P/v_0^*,$$

$$\left(-\partial V / \partial P\right)_{s, P=0} = (v_0^* / \gamma \pi), \quad (\Delta\gamma=0).$$

V. THE RAREFACTION WAVE. ($\Delta\gamma=0$).

In order to calculate the relatively small deviation, $g(P)$ of equation (I.9), by which the free surface velocity u_{fs} differs from twice the material velocity, u_s , we limit ourselves to the case $\Delta\gamma=0$.

In this case (III.11) gives us

$$P + \pi = \pi v_s^{-\gamma} \quad (V.1)$$

$$v^*/v_o^* = v_s = \left[1 + (P/\pi) \right]^{-1/\gamma} \quad (V.1')$$

whereas from (III.13)

$$(-\partial P/\partial V)_s = (\gamma\pi/v_o^*) v_s^{-(\gamma+1)} \quad (V.2)$$

Combining these two equations one finds

$$\left. \begin{aligned} (-\partial P/\partial V)_s &= (\gamma\pi/v_o^*) \left[1 + (P/\pi) \right]^{(\gamma+1)/\gamma} \\ (-\partial P/\partial V)_s^{\frac{1}{2}} &= (\gamma\pi/v_o^*)^{\frac{1}{2}} \left[1 + (P/\pi) \right]^{(\gamma+1)/2\gamma} \end{aligned} \right\} \quad (V.3)$$

Integrate (3) from $P=0$ to P , and obtain:

$$\begin{aligned} u_r &= \int_0^P (-\partial V/\partial P)_s^{\frac{1}{2}} dP \\ &= (\pi v_o^*/\gamma)^{\frac{1}{2}} \int_0^{P/\pi} (1+x)^{-(\gamma+1)/2} dx \\ &= \frac{2\gamma}{\gamma-1} (\pi v_o^*/\gamma)^{\frac{1}{2}} \left\{ \left[1 + (P/\pi) \right]^{(\gamma-1)/2\gamma} - 1 \right\} \quad (V.4) \end{aligned}$$

However, V_o^* in this equation is the free volume, $V=b$, at zero pressure but at the entropy after the shock, and not identical to that before the shock.

From IV.7 we have, in the shock

$$\begin{aligned} (-\Delta V/V_o^*) &= (1/\gamma)(P/\pi) \left[1 + \frac{\gamma+1}{2\gamma} (P/\pi) \right]^{-1} \quad (V.5) \\ &= (V_o^*-V^*)/V_o^* = -(V^*/V_o^*)+1 \end{aligned}$$

$$v^*/v_o^* = \left[1 + \frac{\gamma-1}{2\gamma} \frac{P}{\pi} \right] / \left[1 + \frac{\gamma+1}{2\gamma} \frac{P}{\pi} \right] \quad (V.6)$$

which latter gives the ratio of free volume after shock to that before.

Let V_0^* be V_0 -b before shock, and V_{or}^* the free volume at zero pressure after the shock, that is the free volume to which the material returns after the rarefaction wave. Using (6) and (1') one has:

$$V_{or}^* = V_0^* \left[1 + (P/\pi) \right]^{1/\delta} \left[1 + \frac{\gamma-1}{2\gamma} \frac{P}{\pi} \right] \left[1 + \frac{\gamma+1}{2\gamma} \frac{P}{\pi} \right]^{-1} \quad (V.7)$$

Rewriting (4) and replacing the V_0^* occurring in that equation by (7):

$$u_T = \frac{2\gamma}{\gamma-1} (\pi V_0^* / \delta)^{\frac{1}{2}} \frac{\left[1 + \frac{P}{\pi} \right]^{\frac{1}{2\delta}} \left[1 + \frac{\gamma-1}{2\gamma} \frac{P}{\pi} \right]^{\frac{1}{2}} \left[\left(1 + \frac{P}{\pi} \right)^{\frac{\gamma-1}{2\gamma}} - 1 \right]}{\left[1 + \frac{\gamma+1}{2\gamma} \frac{P}{\pi} \right]^{\frac{1}{2}}} \quad (V.8)$$

From (IV.7) we have, for u_s

$$u_s = P(-\Delta V/P)^{\frac{1}{2}}_{Hug} = (P/\pi) (\pi V_0^* / \delta)^{\frac{1}{2}} \left\{ 1 + \frac{\gamma+1}{2\gamma} \frac{P}{\pi} \right\}^{-\frac{1}{2}} \quad (V.9)$$

Combine this with (V.8) to obtain:

$$u_T/u_s = \frac{2\gamma}{\gamma-1} - \left\{ \left[1 + \frac{P}{\pi} \right]^{\frac{1}{2\delta}} - \left[1 + \frac{P}{\pi} \right]^{\frac{1}{2\delta}} \right\} \left\{ 1 + \frac{\gamma-1}{2\gamma} \frac{P}{\pi} \right\}^{\frac{1}{2}} \quad (V.10)$$

This may be developed as a power series in P/π and one obtains:

$$u_T/u_s = 1 + \frac{3\delta^2 - 2\gamma - 5}{96\delta^2} (P/\pi)^2 + \dots \quad (V.10')$$

VI. EQUATION SUMMARY. ($\Delta\gamma=0$).

We summarize the equations first with the assumption $\Delta\gamma = 0$. One then has four constants, of which the first, R, is trivial:

$$R = 1.986/M \text{ cal deg}^{-1} \text{ ,}$$

(M = atomic weight),

b volume per gram,

π pressure,

γ dimensionless.

From these we form one useful combination:

$$f = 3R(\gamma-1)T/\pi(V_0-b), \quad (\text{VI.1})$$

with

$$V_0 = \text{volume per gram at } T, P_0=0. \quad (\text{VI.2})$$

Then with

$$\beta_0 = \text{isothermal compressibility} = (-1/V)(\partial V/\partial P)_{T, P_0=0}$$

$$\beta_0 = \left[1 - (b/V_0)\right] \left[1/\gamma\pi\right] \left[1 - \frac{\gamma-1}{\gamma}f\right]^{-1}, \quad (\text{VI.3})$$

from (III.19),

$$\alpha_0 = \text{coefficient of thermal expansion} = (1/V)(\partial V/\partial T)_{P_0=0}$$

$$\alpha_0/\beta_0 = 3R(\gamma-1)/V_0-b = \pi f/T, \quad (\text{VI.4})$$

from (III.21)

$$c_v = 3R$$

$$c_p/c_v = 1 + (TV\alpha_0^2/\beta_0c_v)$$

$$= 1 + \frac{\gamma-1}{\gamma}f \left[1 - \frac{\gamma-1}{\gamma}f\right]^{-1} \quad (P_0=0), \quad (\text{VI.5})$$

from (III.20).

The adiabatic compressibility at zero pressure, β_{ado} is

$$\rho_0 = \dots$$

$$= \left[1 - (b/V_0) \right] / \gamma \pi \quad (\text{VI.7})$$

from (III.18)

The Hugoniot Curve, starting from zero pressure, is; from (IV.6)

$$(-\Delta V) = (V_0 - b) \frac{P}{\gamma \pi} \left[1 + \frac{\gamma+1}{2} \left(\frac{P}{\gamma \pi} \right) \right]^{-1} \quad (\text{VI.8})$$

$$P = (-\Delta V) \frac{\gamma \pi}{V_0 - b} \left[1 - \frac{1}{2}(\gamma+1) \frac{(-\Delta V)}{V_0 - b} \right]^{-1}$$

The ratio of the free surface velocity, u_{fs} , to the material velocity, u_s , behind the shock, is given by the equations:

$$u_s = \frac{1}{2} u_{fs} \left[1 + \varepsilon(P) \right]$$

$$\varepsilon(P) = \left[1 - (u_r/u_s) \right] / \left[1 + (u_r/u_s) \right]$$

$$u_r/u_s = \frac{2\gamma}{\gamma-1} \frac{\pi}{P} \left\{ \left[1 + \frac{P}{\pi} \right]^{\frac{1}{2}} - \left[1 + \frac{P}{\pi} \right]^{\frac{1}{2\gamma}} \right\} \left\{ 1 + \frac{\gamma-1}{2\gamma} \frac{P}{\pi} \right\}^{\frac{1}{2}}$$

$$\approx 1 + \frac{3\gamma^2 - 2\gamma - 5}{96\gamma^2} (P/\pi)^2 + \dots \quad (\text{VI.9})$$

from (I.9) and (V.10) and (V.10').

To solve for the parameters from the experimental data one may proceed as follows.

Use

V_0 = specific volume at $T, P=0$,

c_p = specific heat at $T, P=0$,

$\alpha_0 = (1/V)(\partial V/\partial T)_P$ at $T, P=0$,

$\beta_0 = -(1/V)(\partial V/\partial P)_T$ at $T, P=0$.

form:

$$\beta_{\text{ado}} = \beta_0 \left[1 - \frac{TV_0 \alpha_0^2}{\beta_0 c_p} \right] = \beta_0 c_v / c_p \quad (\text{VI.10})$$

$$G = \frac{V_0 \alpha_0}{\beta_0 c_p} \left[\frac{1}{1 - \frac{TV_0 \alpha_0^2}{\beta_0 c_p}} \right] = \frac{V_0 \alpha_0}{\beta_0 c_v} \quad (\text{VI.11})$$

Use

$$u_s \cong \frac{1}{2} u_{fs} \quad (\text{VI.12})$$

$$P = \rho u_s V_0 \quad (\text{VI.13})$$

$$(-\Delta V) = V_0 u_s / s \quad (\text{VI.14})$$

from the data on shocks. From this determine A in the equation

$$(1/V_0 \beta_{\text{ado}}) \left[(-\Delta V)/P \right]_{\text{Hug}} = 1 - A(-\Delta V) \quad (\text{VI.15})$$

Then use, from (4) and (5),

$$G = V_0 \alpha_0 / \beta_0 c_v = \frac{\gamma - 1}{[1 - (b/V_0)]} \quad (\text{VI.16})$$

from (7)

$$(1/\beta_{\text{ado}}) = \frac{\gamma \pi}{[1 - (b/V_0)]} \quad (\text{VI.17})$$

and from (8)

$$AV_0 = \frac{\frac{1}{2}(\gamma + 1)}{[1 - (b/V_0)]} \quad (\text{VI.18})$$

Solving these equations:

$$1/[1 - (b/V_0)] = AV_0 - \frac{1}{2}G \quad (\text{VI.19})$$

$$b = V_0 \left\{ 1 - \frac{1}{AV_0 - \frac{1}{2}G} \right\} \quad (\text{VI.20})$$

$$\gamma = \left[AV_0 + \frac{1}{2}G \right] / \left[AV_0 - \frac{1}{2}G \right] \quad (\text{VI.21})$$

$$\pi = (1/\beta_{\text{ado}}) / [AV_0 + \frac{1}{2}G] \quad (\text{VI.22})$$

$$\begin{aligned} f &= \left[\gamma / (\gamma - 1) \right] \left[1 - (c_w / c_p) \right] \\ &= \frac{\gamma}{\gamma - 1} \left[TV_0 \alpha^2 / \beta_0 c_p \right] \quad (\text{VI.23}) \end{aligned}$$

Use the results to compute u_r/u_s and $g(P)$, equation (VI.9), $u_s^{(2)} = u_s^{(0)} [1 + g(P)]$.

From (VI.13) and (VI.14) it is seen that $P/(-\Delta V)$ remain unchanged by the correction, but $(-\Delta V)$ is increased:

$$(-\Delta V)^{(1)} = (-\Delta V)^{(0)} [1 + g(P)].$$

VII. EQUATION SUMMARY ($\Delta\gamma f_0$).

There are now five constants, of which, again, R is trivial. These are:

$$R = (1.986/M) \text{ cal deg}^{-1}, M = \text{atomic weight}$$

$$b = \text{volume per gram,}$$

$$T = \text{pressure,}$$

$$\gamma = \text{dimensionless,}$$

$$\Delta\gamma = \text{dimensionless.}$$

The combination

$$f = 3R(\gamma + \Delta\gamma - 1)T/\pi(V_0 - b), \quad (\text{VII.1})$$

occurs frequently, with

$$V_0 = \text{volume per gram at } T, P=0. \quad (\text{VIII.2})$$

Then from (III.19), (III.21) and (III.20):

$$\beta_0 = \text{isothermal compressibility} = (-1/V)(\partial V/\partial P)_{T, P=0}$$

$$\beta_0 = \left[1 - (b/V_0) \right] \left[1/\gamma\pi \right] \left[1 - \frac{\gamma-1}{\gamma} f \right]^{-1}, \quad (\text{VII.3})$$

$$\alpha_0 = \text{coefficient of thermal expansion,} = (1/V)(\partial V/\partial T)_P$$

$$\alpha_0/\beta_0 = 3R(\gamma + \Delta\gamma - 1)/V_0 - b = \pi f/T, \quad (\text{VII.4})$$

$$c_v = 3R, \quad (\text{VII.5})$$

$$c_p/c_v = 1 + (TV_0\alpha^2/\beta c_v).$$

$$= 1 + \frac{\gamma + \Delta\gamma - 1}{\gamma} f \left[1 - \frac{\gamma-1}{\gamma} f \right]^{-1}, \quad (\text{VII.e})$$

$$\beta_{\text{ado}} = (-1/V)(\partial V/\partial P)_{s, P=0}$$

$$= \left[1 - (b/V_0) \right] \left[1/\gamma\pi \right] \left[1 + \frac{\Delta\gamma}{\gamma} f \right]^{-1}. \quad (\text{VII.7})$$

The Hugoniot curve, starting from zero pressure, is, from (IV.3), (IV.4) and (IV.5)

$$\left[-\Delta V/P \right]_{\text{Hug}} = \frac{V_0 - b}{\gamma\pi} \frac{1}{\left[1 + \frac{\Delta\gamma}{\gamma} f \right]} P \left[-\Delta V/(V_0 - b) \right] \quad (\text{VII.8})$$

with,

$$F(x) = \frac{1 - \frac{1}{2}(\gamma + \Delta\gamma + 1)x}{1 - \frac{\Delta\gamma}{\gamma(\gamma-1)} \frac{1-f_0}{1 + \frac{\Delta\gamma}{\gamma} f_0} \left[(1-x)^{-\gamma-1} - 1 - (\gamma-1)x \right] x^{-1}} \quad (\text{VII.9})$$

or if

$$\left[-\Delta V/P \right]_{\text{Hug}} = (-\partial V/\partial P)_{s, P=0} \left[1 - A(-\Delta V) - B(-\Delta V)^2 \dots \right] \quad (\text{VII.10})$$

$$A = \frac{1}{2(V_0 - b)} \left\{ (\gamma+1) + \Delta\gamma f_0 \left[1 + \frac{\Delta\gamma}{\gamma} \right] / \left[1 + \frac{\Delta\gamma}{\gamma} f_0 \right] \right\} \quad (\text{VII.10}^a)$$

$$B = \frac{1}{12(V_0 - b)^2} \Delta\gamma \frac{1-f_0}{1 + \frac{\Delta\gamma}{\gamma} f_0} \left\{ 5[\gamma+1] + 3\Delta\gamma f_0 \frac{1 + \frac{\Delta\gamma}{\gamma}}{1 + \frac{\Delta\gamma}{\gamma} f_0} \right\} \quad (\text{VII.10}^b)$$

To determine the parameters from experimental data one may proceed first as in section VI under the assumption that $\Delta\gamma = 0$. That is, use:

V_0 = specific volume at $T, P=0$,

c_p = specific heat at $T, P=0$,

$\alpha_0 = (1/V)(\partial V/\partial T)_P$ at $T, P=0$,

$\beta_0 = (-1/V)(\partial V/\partial P)_T$ at $T, P=0$,

as experimental quantities, and compute:

$$\beta_{\text{ado}} = \beta_0 \left[1 - (TV_0 \alpha_0^2 / \beta_0 c_p) \right]$$

$$G = \left[V_0 \alpha_0 / \beta_0 c_p \right] / \left[1 - (TV_0 \alpha_0^2 / \beta_0 c_p) \right]$$

$$u_s^{(0)} \approx \frac{1}{2} u_{fs}$$

$$p^{(0)} = s u_s^{(0)} / V_0$$

$$(-\Delta V)^{(0)} = V_0 u_s^{(0)} / s$$

Determine $A^{(0)}$, and $A^{(1)}$ and $B^{(1)}$ by fitting

$$(1/V_0 \beta_{ado}) \left[(-\Delta V/P) \right]_{Hug} = 1 - A^{(0)} (-\Delta V^{(0)})$$

$$(1/V_0 \beta_{ado}) \left[(-\Delta V/P) \right]_{Hug} = 1 - A^{(1)} (-\Delta V^{(1)}) - B^{(1)} (-\Delta V^{(1)})^2$$

Actually the determination of $A^{(1)}$, $B^{(1)}$ should not be undertaken at this stage, but must wait on the computation of $\Delta V^{(1)}$, which can only be completed after the step of equation (VII.16).

From $A^{(0)}$, G , β_{ado} compute

$$\left[1 - (b^{(0)}/V_0) \right] = 1 / \left[A^{(0)} V_0 - \frac{1}{2}G \right] \tag{VII.11}$$

$$b^{(0)}/V_0 = \left[A^{(0)} V_0 - \frac{1}{2}G - 1 \right] / \left[A^{(0)} V_0 - \frac{1}{2}G \right]$$
(VII.12)

$$\gamma^{(0)} = \left[A^{(0)} V_0 + \frac{1}{2}G \right] / \left[A^{(0)} V_0 - \frac{1}{2}G \right]$$
(VII.13)

$$\pi^{(0)} = 1/\beta_{ado} \left[A^{(0)} V_0 + \frac{1}{2}G \right]$$
(VII.14)

$$r^{(0)} = \left[\gamma^{(0)} / (\gamma^{(0)} - 1) \right] \left[TV_0 \alpha_0^2 / \beta_0 c_p \right]$$
(VII.15)

With $\bar{\pi} = \pi^{(0)}$ and $\bar{\gamma} = \gamma^{(0)}$ compute:

$$u_r/u_s = \frac{2\bar{\gamma}}{\bar{\gamma}-1} \frac{\bar{\pi}}{P} \left\{ \left[1 + \frac{P}{\bar{\pi}} \right]^{\frac{1}{2}} - \left[1 + \frac{P}{\bar{\pi}} \right]^{\frac{1}{2\bar{\gamma}}} \right\} \left\{ 1 + \frac{\bar{\gamma}-1}{2\bar{\gamma}} \frac{P}{\bar{\pi}} \right\}^{\frac{1}{2}}$$
(VII.16)

$$\cong 1 + \frac{2\bar{\gamma}^2 - 2\bar{\gamma} - 5}{96\bar{\gamma}^2} (P/\bar{\pi})^2 + \dots$$
(VII.16')

$$\epsilon(P) = \left[1 - (u_r/u_s) \right] / \left[1 + (u_r/u_s) \right]$$
(VII.16'')

and

$$(-\Delta V)^{(1)} = (-\Delta V)^{(0)} \left[1 + \epsilon(P) \right]$$
(VII.16''')

With the corrected values of $(-\Delta V)^{(1)}$, (noting that $P/(-\Delta V)$ does not change when u_s is altered by equations (1C)) one now computes $A^{(1)}$ and $B^{(1)}$ of the expansion for $\left[-\Delta V/P \right]_{Hug} / V_0 \beta_{ado}$.

Then, (from VII.10'') compute consecutively:

$$\Delta \gamma^{(0)} = V_0^2 B^{(1)} \left[1 - (b^{(0)}/V_0) \right]^2 \left[12/5(\gamma^{(0)} + 1) \right] \sqrt{1 - f_0^{(0)}} \quad (VII.17)$$

$$\Delta \gamma^{(1)} = \Delta \gamma^{(0)} \left[1 + (\Delta \gamma^{(0)}/\gamma^{(0)}) f_0^{(0)} \right] / \left[1 + \frac{3 \Delta \gamma^{(0)}}{5(\gamma^{(0)} + 1)} f_0^{(0)} \frac{1 + \frac{\Delta \gamma^{(0)}}{\gamma^{(0)}}}{1 + \frac{\Delta \gamma^{(0)}}{\gamma^{(0)}} f_0^{(0)}} \right] \quad (VII.17')$$

With $A^{(1)}$, $B^{(1)}$ and $\Delta \gamma^{(1)}$ form

$$G' = c - \Delta \gamma^{(1)} / \left[1 - (b^{(0)}/V_0) \right] \quad (VII.18)$$

$$A'V_0 = A^{(1)}V_0 - \frac{\frac{1}{2} \Delta \gamma^{(1)} f_0^{(0)} \left[1 + (\Delta \gamma^{(1)}/\gamma^{(0)}) \right]}{\left[1 - (b^{(0)}/V_0) \right] \left[1 + (\Delta \gamma^{(1)}/\gamma^{(0)}) f_0^{(0)} \right]} \quad (VII.19)$$

$$\beta' = \beta_{ado} \left[1 + (\Delta \gamma^{(1)}/\gamma^{(0)}) f_0^{(0)} \right] \quad (VII.20)$$

With these recompute:

$$1 - (b^{(1)}/V_0) = 1 / \left[A'V_0 - \frac{1}{2} G' \right] \quad (VII.21)$$

$$b^{(1)}/V_0 = \left[A'V_0 - \frac{1}{2} G' - 1 \right] / \left[A'V_0 - \frac{1}{2} G' \right] \quad (VII.22)$$

$$\gamma^{(1)} = \left[A'V_0 + \frac{1}{2} G' \right] / \left[A'V_0 - \frac{1}{2} G' \right] \quad (VII.23)$$

$$\pi^{(1)} = 1 / \left\{ \beta' \left[A'V_0 + \frac{1}{2} G' \right] \right\} \quad (VII.24)$$

$$f_0^{(1)} = \left[1 + \frac{\Delta \gamma^{(1)}}{\gamma^{(1)}} f_0^{(0)} \right] \left[\frac{\gamma^{(1)}}{\gamma^{(1)} + \Delta \gamma^{(1)} - 1} \right] \left[\frac{TV_0 \alpha_0^2 / \beta_0 c_F}{\gamma^{(1)} + \Delta \gamma^{(1)} - 1} \right] \quad (VII.25)$$

These first order parameters will usually be sufficiently close to those obtained after infinite repetition. If necessary, one may return to (17) at this stage and repeat.

In general one will find that

$$\gamma^{(1)} + \Delta \gamma^{(1)} \cong \gamma^{(0)}$$

that is $\gamma^{(1)}$ differs from $\gamma^{(0)}$ by about the value of $\Delta \gamma$.

VIII. APPLICATION TO ALUMINUM.

Some data on Aluminum have been supplied by Mr. Elechar. The values of u_s had already been corrected by another equation of state than that to be determined here. The data are tabulated in Table 1.

From International Critical Tables we take:

$$V_0 = 1/2.699 = 0.371 \text{ cc/gm}, t=20^\circ\text{C},$$

$$c_p = 0.214 \text{ cal/gm}, \text{ " " " },$$

$$\alpha_0 = 76.5 \times 10^{-6} \text{ deg}^{-1}, \text{ " " " },$$

$$\beta_0 = 1.34 \times 10^{-6} \text{ atm}^{-1}, \text{ " " " },$$

$$1/\beta_{\text{ado}} = 0.800 \times 10^6 \text{ bars}, \tag{VIII.1}$$

$$V_0 \alpha_0 / \beta_0 c_p = C = 2.540, \tag{VIII.2}$$

$$TV_0 \alpha^2 / \beta c_p = 0.0539. \tag{VIII.3}$$

TABLE VIII.1

SHOCK DATA FOR AL.

No.	P kilobars	$-\Delta V/V_0$	$TV_0/(-\Delta V)$ $\times 10^{-6}$	$\frac{[-\Delta V/P]_{\text{thug}}}{V_0 \beta_{\text{ado}}}$
1	109.6	0.1035	1.060	0.7547
2	117.7	0.1035	1.035	0.7369
3	125.0	0.1165	1.073	0.7451
4	136.2	0.1230	1.108	0.7215
5	219.4	0.1635	1.342	0.5959
6	271.6	0.1845	1.472	0.5432
7	298.0	0.1965	1.517	0.5274
8	314.3	0.2045	1.537	0.5203
9	306.6	0.2060	1.489	0.5370
10	316.2	0.2090	1.512	0.5291
11	332.3	0.2180	1.525	0.5243

Least squares analysis of the data in table 1 gives:

$$\left[\left[-\Delta V/P \right]_{\text{Hug}} / V_0 \beta_{\text{ado}} \right] = 1 - 2.3209(-\Delta V/V_0)$$

or $= 1 - 2.496(-\Delta V/V_0) + 0.93(-\Delta V/V_0)^2$

so that we use either

$$A^{(0)} V_0 = 2.3209 \quad (\text{VIII.4})$$

or

$$A^{(1)} V_0 = 2.496 \quad (\text{VIII.5})$$

$$B^{(1)} V_0^2 = -0.93$$

Use (1), (2), (3) and (4) in equations (VI.19) to (VI.23) inclusive to find:

$$\left[1 - (b^{(0)}/V_0) \right] = 0.952$$

$$b^{(0)}/V_0 = 0.048$$

$$\pi^{(0)} = 0.223 \times 10^6 \text{ bars}$$

$$\gamma^{(0)} = 3.418, \quad \gamma^2 = 11.683$$

$$f^{(0)} = 0.0762$$

From this, using the approximate expression (VI.16') for u_T/u_S ,

$$\begin{aligned} u_T/u_S &= 1 + \frac{3\gamma^2 - 2\gamma - 5}{96\gamma^2 \pi^2} p^2 \\ &= 1 + \frac{23.113}{55.710} (P \times 10^{-6} \text{ bars})^2 \\ &= 1 + \underline{0.416} (P \times 10^{-6} \text{ bars})^2 \end{aligned}$$

Since the highest pressure gives $(P \times 10^{-6} \text{ bars})^2 = 0.110$ the largest correction to $(-\Delta V)$ should be

0.46% 7.6%

which we shall neglect. It was in anticipation of this that $A^{(1)}$ and $B^{(1)}$ could be computed before this stage.

We proceed with these values of $b^{(0)}$, $\pi^{(0)}$, and $\gamma^{(0)}$ to calculate $\Delta\gamma^{(0)}$ from equation (VII.17) and $\Delta\gamma^{(1)}$ from (VII.17'), using BV_0^2 of equation (VIII.5).

One finds:

$$\begin{aligned}\Delta\gamma^{(0)} &= (V_0^2 B^{(1)}) [1 - b^{(0)}/V_0] [12/5(\gamma^{(0)} + 1)] / [1 - f^{(0)}] \\ &= -0.4954,\end{aligned}$$

$$\Delta\gamma^{(1)} = -0.4954(0.989/0.995) = -0.4924$$

$$\approx -0.5.$$

The certainty of BV_0^2 from the experimental data is low enough that there may be some doubt if even the one significant figure is really significant.

Now use $A^{(1)}V_0$ of (VIII.5) instead of $A^{(0)}V_0$ from (VIII.4), and proceed with the equations (VII.18) to (VII.20) to find

$$\begin{aligned}G' &= G + [0.5/(0.952)] = 2.540 + 0.525 \\ &= 3.065\end{aligned}$$

$$\frac{1}{2}G' = 1.532.$$

$$\begin{aligned}A'V_0 &= A^{(1)}V_0 + \frac{0.25(0.0762)(0.8951)}{(0.952)(0.995)} \\ &= 2.496 + 0.017 = 2.513.\end{aligned}$$

$$\beta' = (0.125 \times 10^{-6})(0.989) = 0.124 \times 10^{-6} \text{ bars.}$$

Use these in VII.21 to VII.24 to find

$$b^{(1)}/V_0 = -0.019$$

$$\gamma^{(1)} = 4.090$$

$$\pi^{(1)} = 0.200 \times 10^6 \text{ bars}$$

$$\Delta\gamma^{(1)} = -0.5$$

$$f^{(1)} = 0.0841$$

A calculation to a higher order gives consecutively:

$$\Delta\gamma^{(2)} = -0.4920 \quad [\text{instead of } -0.4924]$$

$$\cong -0.5 .$$

$$G' = 3.031, \frac{1}{2}G' = 1.516 .$$

$$A'V_0 = 2.514 .$$

$$b^{(2)}/V_0 = -0.002 .$$

$$\gamma^{(2)} = 4.038 .$$

$$\pi^{(2)} = 0.200 \times 10^6 \text{ bars} .$$

$$\Delta\gamma^{(2)} = -0.5 .$$

$$f^{(2)} = 0.0848 .$$

The fact that b changes, in consecutive calculations by a large fraction is, of course, unimportant, since only the quantity

$$1-b/V_0 = 0.952 \text{ in zeroth order}$$

$$= 1.019 \text{ in first order}$$

$$= 1.002 \text{ in second order}$$

is of importance.

1. 2. 3. 4. 5. 6. 7. 8. 9. 10.

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