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UCRL-51121

GRAY, A THREE-PHASE EQUATION OF STATE FOR METALS

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MS. date: September 3, 1971

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GRAY, A THREE-PHASE EQUATION OF STATE FOR METALS

Abstract

A three-phase equation of state for metals is developed, based on the following assumptions: (1) the entropy of melting is independent of pressure; (2) the temperature dependence of the specific heat in the liquid is a universal curve, scaled on the melting temperature; (3) the pressure dependence of the melting temperature is given by a modified Lindemann law; and (4) the liquid-vapor

region may be described by a hard-sphere model perturbed by a van der Waals attraction. The equation of state is laid out in a $P(V, E)$ form for use in numerical hydrodynamics calculations, and parameters are given for Be, Mg, Al, Ti, stainless steel, Ni, Monel, Cu, Nb, Ta, W, Au, Pb, Th, Mulberry, and U. Experimental evidence for the validity of the equation of state is presented.

I. Introduction

High-temperature and high-pressure equations of state are becoming increasingly useful and important in calculating the effects of rapid energy deposition in a variety of high-speed phenomena. Such phenomena include: the deposition of x-ray energy from the detonation of nuclear explosives; the deposition of electrons from high-energy electron-beam machines; exploding wire phenomena; and the explosive compression of magnetic flux.

All of these phenomena may be characterized by high energy densities, and take place over times of the order of a few nanoseconds to a few hundred nanoseconds. Thus, their experimental study is characterized by considerable

difficulty and sophistication, and there is a real need to be able to make reliable predictions of the results of such experiments. While there is a great deal that can be and has been done in the way of semiempirical modeling of these transient phenomena we are concerned here with a somewhat more fundamental approach to the problem, an approach based on obtaining good descriptions of the physics involved and applying high-speed computers to numerically solve the equations describing the physics.

The subject of this report is a three-phase equation of state for metals which can be used in the calculation of transient problems involving high energy densities.

II. Overview

It is convenient to think about the equation-of-state problem in three distinct regions. Material compressed adiabatically or by shock processes is relatively cool since most of the energy is stored elastically in the compression of the material. This equation-of-state region is well described by the ordinary Grüneisen equation of state up to a megabar or more, and has been thoroughly explored with the use of shock-wave techniques. Henceforth, familiarity with this field will be assumed; several recent reviews are available.^{1,2}

Temperatures encountered in such shock compression work seldom exceed a small fraction of an electron volt. The work reported here addresses the equation-of-state problem at higher temperatures in two distinct regions. The first of these is near normal density, but at high temperature and pressure. States in this region are reached when energy deposition takes place in times short compared to the hydrodynamic times in the system. The second region is at high temperature, but expanded volume. These states are reached as hydrodynamic rarefactions allow material to expand, lowering the pressure. These states are also reached directly when energy deposition processes are slow compared to the hydrodynamic times in the problem.

A. SOLID-LIQUID REGION

Material near normal density is described by a scaling-law equation of state (EOS) for metals developed by

Grover³ who assumes that: (1) entropy of melting is a constant, 2.3 cal/mole deg, independent of the material or the pressure under which melting takes place; and (2) the specific heat in the liquid decreases from its solid value of 6 cal/mole deg, by an amount $0.3 (T/T_M)$ cal/mole deg, where T_M is the melting temperature. The latter is taken as a function of volume by integrating a modified Lindemann law. The effect of the nondegeneracy of the conduction electrons at nonzero temperature is added in a free-electron approximation in which the electron gamma is two-thirds. The EOS is transformed smoothly to an ideal-gas thermal EOS at very high temperatures.

The scaling-law EOS also includes a Grüneisen description of the solid,¹ normalized to the experimental Hugoniot. The volume dependence of gamma in the solid is taken to be linear. Thus, the proper description of behavior on compression is included, along with a description of heating.

B. LIQUID-VAPOR REGION

Material in the liquid-vapor region is treated according to an EOS developed by Young and Alder.⁴ Their van der Waals model uses an analytic representation of the classical hard-sphere EOS with a van der Waals attractive term added. The two parameters in the theory can be evaluated from the cohesive energy and the density of the liquid near the melting point. Although the origin of this model lies in classical statistical mechanics, there is good evidence that it is a useful

approximation for metals, in spite of their nonclassical nature.

C. THE EQUATION OF STATE

The complete EOS is developed by analytically joining the Grover scaling law and the Young-Alder models at a volume in the range 1.3 to 1.5 times normal volume. This is accomplished by adding correction terms to the Young-Alder EOS employed on the low-density side of the join volume. These correction terms make the EOS continuous at the join volume by slightly modifying the Young-Alder EOS in that vicinity. They become insignificant at volumes well away from the join volume,

leaving the Young-Alder EOS unaffected. All of this is done in a thermodynamically consistent manner.

Since the EOS is analytic, it can fairly readily be developed for any metal. What is needed are the normal density, the Hugoniot, the melting temperature at zero pressure, and the cohesive energy. If data are available on the Grüneisen parameter or thermal expansion coefficient, or on liquid density near the melting point, they can also be included.

Extensions of the equation of state to nonmetals requires an identification of the molecular species in the vapor phase. While this EOS has been crudely extended to include this case, the work will not be discussed in this report.

III. Scaling-Law Equation of State

The scaling-law equation of state is described by the following equations:³

$$E_s(T, V) = E_0(V) + 3R'T + \frac{1}{2}G'T^2, \quad (1)$$

$$VP_s(T, V) = VP_0(V) + 3\gamma_s(V)R'T + \frac{1}{2}\gamma_e G'T^2. \quad (2)$$

• For $T \leq T_m(V) - \delta T(V)$:

$$E(T, V) = E_s(T, V), \quad (3)$$

$$P(T, V) = P_s(T, V). \quad (4)$$

• For $T_m(V) - \delta T(V) \leq T$

$$\leq T_m(V) + \delta T(V):$$

$$E(T, V) = E_s(T, V) + \nu[T - \nu\delta T(V)] \times (\Delta S' - \alpha'), \quad (5)$$

$$VP(T, V) = VP_s(T, V)$$

$$+ \lambda(V)\nu T_m(V)(\Delta S' - \alpha'). \quad (6)$$

• For $T_m(V) + \delta T(V) \leq T \leq T_G(V)$:

$$E(T, V) = E_s(T, V) + T_m(V) \times \left\{ \Delta S' - \frac{\alpha'}{2} \left(1 + \frac{T^2}{[T_m(V)]^2} \right) \right\}, \quad (7)$$

$$VP(T, V) = VP_s(T, V) + \lambda(V)T_m(V)$$

$$\times \left\{ \Delta S' - \frac{\alpha'}{2} \left(1 + \frac{T^2}{[T_m(V)]^2} \right) \right\}. \quad (8)$$

• For $T \geq T_G(V)$:

$$E(T, V) = E_G(V) + \frac{3}{2}R'T + \frac{1}{2}G'T^2, \quad (9)$$

$$VP(T, V) = VP_G(V) + \frac{3}{2} R'T \\ \times [2\gamma_s(V) - \lambda(V)] + \frac{\gamma_e G'T^2}{2V} \quad (10)$$

$$E_G(V) \equiv E_0(V) + T_m(V) \\ \times \left\{ \Delta S' + \frac{\alpha'}{2} \left[\left(\frac{3R'}{2\alpha'} \right)^2 - 1 \right] \right\}, \quad (11)$$

$$VP_G(V) \equiv VP_0(V) + \lambda(V) T_m(V) \\ \times \left\{ \Delta S' + \frac{\alpha'}{2} \left[\left(\frac{3R'}{2\alpha'} \right)^2 - 1 \right] \right\}. \quad (12)$$

In these expressions, E and P are the specific energy and pressure at a temperature and specific volume T and $V = \rho^{-1}$. $P_s(V)$ and $E_s(V)$ refer to quantities for the solid, described by a Grüneisen-type EOS, or to the extrapolation of the Grüneisen solid EOS to high temperatures. $P_0(V)$ and $E_0(V)$ refer to conditions at 0°K [$P_0(V) = -dE_0(V)/dV$]. $\gamma_s(V)$ is the volume-dependent Grüneisen gamma for the solid; the effective gamma for the liquid is temperature-, as well as volume-dependent.

The final terms in Eqs. (1) and (2) are the electronic contributions from the nondegeneracy of the conduction electrons at finite temperatures. G' is the electronic energy coefficient, given by

$$G' = \frac{\pi^2 N_e k R'}{2 E_f}, \quad (13)$$

where the Fermi energy E_f is given by

$$E_f = 26 \left(\frac{N_e}{AV_0} \right)^{2/3} \quad (14)$$

in eV, and N_e is the number of free electrons per atom. These equations represent a free electron gas, and N_e may be taken as the number of electrons

on the metal atom outside the closed shell. γ_e , the electronic gamma, is taken as 2/3, the free-electron value. The justification for the use of the free-electron approximation is given by Grover.³

At a particular specific volume, melting is assumed to start at a temperature $T_m(V) - \delta T(V)$, the solidus; and to be complete at a temperature $T_m(V) + \delta T(V)$, the liquidus. The slope of the phase line is given by $\lambda(V) = -d \ln T_m / d \ln V$. ν is a progress variable describing melting; $\Delta S'$ is the entropy of melting, a constant; and α' is a parameter describing the rate of decrease of the specific heat in the liquid, where

$$C_V'(T, V) = 3R' - \alpha' T / T_m(V). \quad (15)$$

$T_G(V) \equiv T_m(V) \cdot (3R'/2\alpha')$, is the temperature at which the hot liquid begins to behave like an ideal gas thermally. To see this, note that the Lindemann law requires $\lambda = 2\gamma - 2/3$. Thus, the thermal pressure in Eq. (10) is just $R'T$, the ideal gas value. Note that this is not strictly an ideal gas EOS, however, because of the volume-dependent pressure term $P_G(V)$ and the electronic term proportional to T^2 .

In this report, all specific quantities will be per gram. This differs from Grover's³ notation, where such quantities are written per gram-atom. Thus, if A is the atomic weight, we have $R = AR'$, $\alpha = A\alpha'$, $\Delta S = A\Delta S'$, and $g_e = AG'$, where g_e is the more conventional electronic energy coefficient, ΔS is Grover's constant entropy of melting ($= 2.3$ cal/g-atom deg), α is

Grover's specific heat coefficient (≈ 0.3 cal/g-atom deg), and R is the usual gas constant (≈ 2 cal/g-atom deg). (Note also, that Grover sometimes designates our variable λ as μ and δT as $\Delta T/2$. See Appendix A, Table A-1.)

A. GRÜNEISEN-LIKE REPRESENTATION

Our first task is to refer the equation of state to the Hugoniot and to write it in the form $P(V, E)$. As is usually done, we represent the Hugoniot with a linear shock-velocity—particle-velocity form,

$$U_s = C + S U_p, \quad (16)$$

$$P_H(V) = \frac{\rho_0 C^2 x}{(1 - Sx)^2}, \quad (17)$$

$$E_H(V) = \frac{1}{2} P_H(V) (V_0 - V) + E_{0H}, \quad (18)$$

where $x = (V_0 - V)/V_0$, a compression or volume variable, and E_{0H} is the energy at the foot of the Hugoniot. Now define $\Gamma(T, V)$ by the Grüneisen-like equation,

$$P(T, V) = P_0(V) + \frac{\Gamma(T, V)}{V} [E(T, V) - E_0(V)]. \quad (19)$$

If the experimental Hugoniot is in the solid, we may write

$$P_H(V) = P_0(V) + \frac{\gamma_s(V)}{V} [E_H(V) - E_0(V)] \quad (20)$$

and

$$P(T, V) = P_H(V) + \frac{\gamma_s(V)}{V} [E(T, V) - E_H(V)] + \frac{[\Gamma(T, V) - \gamma_s(V)]}{V} [E(T, V) - E_0(V)], \quad (21)$$

since $\Gamma(T = 0, V) = \gamma_s(V)$. Using Eq. (18) for $E_H(V)$ and rearranging terms yields

$$P(T, V) = P_H(V) \left[1 - \frac{\gamma_s(V)}{2V} (V_0 - V) \right] + \frac{\gamma_s(V)}{V} [E(T, V) - E_{0H}] + \frac{[\Gamma(T, V) - \gamma_s(V)]}{V} [E(T, V) - E_0(V)]. \quad (22)$$

Note that the first two terms on the right-hand side of Eq. (12) constitute a Grüneisen-like equation of state for a solid. The last term is a correction; i.e.,

$$P = P_1(V, E) + P_c(T, V). \quad (23)$$

For use in hydrodynamics calculations, we want $P(V, E)$ rather than $P(T, V)$, $E(T, V)$. Thus, P_1 is already in the form we want it; we must now calculate and transform P_c , the last term in Eq. (22). To accomplish this, we observe from Eq. (19) that $(\Gamma/V) (E - E_0)$ is just $(P - P_0)$. We then calculate P_c as $(P - P_0) - \gamma_s(E - E_0)/V$ from Eqs. (1)-(12). For $T \leq T_m - \delta T$,

$$P_c(T, V) = [\gamma_e - \gamma_s(V)] \frac{G' T^2}{2V}, \quad \equiv P_{cs}(T, V). \quad (24)$$

• For $T_m - \delta T \leq T \leq T_m + \delta T$,

$$P_c(T, V) = P_{cs}(T, V) + \frac{\nu(\Delta S' - \alpha')}{V} \times [T_m(V) \lambda(V) - (T - \nu \delta T) \gamma_s(V)]. \quad (25)$$

• For $T_m + \delta T \leq T \leq T_G$,

$$P_c(T, V) = P_{cs}(T, V) + \frac{T_m(V)}{V} \times \left\{ \Delta S' - \frac{\alpha'}{2} \left[1 + \left(\frac{T}{T_m(V)} \right)^2 \right] \right\} \times [\lambda(V) - \gamma_s(V)]. \quad (26)$$

• For $T \geq T_G$,

$$P_c(T, V) = P_{cs}(T, V) + \frac{T_m(V)}{V} \left\{ \Delta S' - \frac{\alpha'}{2} \left[1 - \left(\frac{3R'}{2\alpha'} \right)^2 + 2 \left(\frac{3R'}{2\alpha'} \right) \frac{T}{T_m(V)} \right] \right\} \times [\lambda(V) - \gamma_s(V)]. \quad (27)$$

This still gives $P_c(T, V)$ rather than $P_c(V, E)$. To take the last step, we note that Eqs. (1), (3), (5), (7), (9), and (11) give the energy $E(T, V)$ in terms of $E_0(V)$ and a quadratic function of the temperature T . Thus, each of these expressions can be inverted to give $T(V, E)$, and this value can then be substituted into the expression for P_c . A little inspection will identify which root is wanted (see Appendix A). Of course $E_0(V)$ must be known, and in the next section we develop and approximate expression for this quantity.

Note that in writing Eq. (20), we conveniently ignored the electronic contributions. At megabar pressures on the Hugoniot, these terms can make a correction of several percent in the temperature. However, Eq. (20) involves only the variables (P, V, E) , and their inter-relationship is changed by less than a percent over the range of interest. Thus, the simplification of omitting the electronic terms in Eq. (20) is justified. There is,

however, a problem at room temperature and normal density, where $P_1 = 0$ but P_c does not. The error is only a few bars, but comes as a little surprise to users who expect the pressure there to be zero. Thus, for essentially esthetic reasons, we add to the pressure [Eq. (23)] an additional correction $P_{cc} = -P_{cs}(T = T_R, V = V_0)$, where T_R is room temperature and V_0 is the normal specific volume.

B. COLD COMPRESSION ENERGY $E_0(V)$

By referencing the EOS to the experimental Hugoniot, we have eliminated the necessity of writing out an explicit expression for $P_0(V)$. However, the calculation of the temperature as a function of energy, which is needed for the calculation of the pressure contribution $P_c(V, T)$, requires a knowledge of $E_0(V)$, the energy on the cold compression curve, and we now develop an approximate expression for $E_0(V)$. Note that at low and modest temperatures, the thermal energy $E - E_0(V)$ will be the difference of comparable numbers, and hence only poorly known, if $E_0(V)$ is approximated. Similarly, the temperature will be poorly known. The resulting error in the total pressure, however, will be only a few percent since P_c is a correction term, much smaller than P_1 . At high temperatures, several times the melting temperature, P_c is an appreciable component of the total pressure. But under these conditions $E_0(V)$ is a small part of the total energy, and errors in $E_0(V)$ will have only a small effect on the calculated thermal energy, temperature, and correction term P_c .

We rewrite Eq. (20), assuming the Hugoniot to be in the solid:

$$\begin{aligned}
 P_0(V) - \frac{\gamma_s(V)}{V} E_0(V) \\
 = P_H(V) - \frac{\gamma_s(V)}{V} E_H(V) \\
 = \left[1 - \frac{\gamma_s(V)(V_0 - V)}{2V} \right] P_H(V) \\
 - \frac{\gamma_s(V)}{V} E_{0H}. \quad (28)
 \end{aligned}$$

We then define the right-hand side of Eq. (28) as $F'(V)$ and let $F(V) = F'(V) + \gamma_s(V) E_{0H}/V$. But

$$F'(V) = -\frac{dE_0(V)}{dV} - \frac{\gamma_s(V)}{V} E_0(V), \quad (29)$$

or

$$E_0(V) = E_1(V) \exp \left[- \int_{V_0}^V \frac{\gamma_s(V)}{V} dV \right]. \quad (30)$$

$$\begin{aligned}
 E_1(V) = - \int_{V_0}^V dV \\
 \times \left\{ F'(V) \exp \left[\int_{V_0}^V \frac{\gamma_s(V)}{V} dV \right] \right\} + E_{0k}, \quad (31)
 \end{aligned}$$

where

$$E_{0k} = E_1(V = V_0) = E_0(V = V_0). \quad (32)$$

At this point we must adopt a specific form for the volume dependence of gamma,

$$\gamma_s = \gamma_0 - a \frac{(V_0 - V)}{V_0} = \gamma_0 - ax, \quad (33)$$

where x is the compression variable, $(V_0 - V)/V_0$. Hence,

$$F = \left[1 - \frac{V_0}{2V} (\gamma_0 - ax)x \right] P_H, \quad (34)$$

$$= \left[1 - \left(\frac{\gamma_0}{2} + 1 \right) x + \frac{a}{2} x^2 \right] \frac{P_H}{(1-x)}, \quad (35)$$

and P_H is given by Eq. (17). But

$$\begin{aligned}
 \exp \left[\int_{V_0}^V \frac{\gamma_s}{V} dV \right] \\
 = \exp \left\{ \int_{V_0}^V \left[\frac{(\gamma_0 - a)}{V} + \frac{a}{V_0} \right] dV \right\} \\
 = \exp \left[(\gamma_0 - a) \ln \left(\frac{V}{V_0} \right) + \frac{a}{V_0} (V - V_0) \right] \\
 = (1-x)^{\gamma_0 - a} \exp(-ax). \quad (36)
 \end{aligned}$$

Thus

$$\begin{aligned}
 E_0 = (1-x)^{a-\gamma_0} [\exp(ax)] \\
 \times \{A(x) - B(x) + E_{0k}\}, \quad (37)
 \end{aligned}$$

where

$$\begin{aligned}
 A(x) = -E_{0H} \int_0^x dx \\
 \times \left[\frac{(\gamma_0 - ax)}{(1-x)} (1-x)^{\gamma_0 - a} \exp(-ax) \right] \quad (38)
 \end{aligned}$$

and

$$\begin{aligned}
 B(x) = -V_0 \int_0^x dx \\
 \times \left\{ \frac{\rho_0 C^2 x \left[1 - \left(\frac{\gamma_0}{2} + 1 \right) x + \frac{a}{2} x^2 \right]}{(1-Sx)^2 (1-x)} \right. \\
 \left. \times (1-x)^{\gamma_0 - a} \exp(-ax) \right\}. \quad (39)
 \end{aligned}$$

In evaluating $B(x)$, we make the following expansion:

$$\begin{aligned}
 (1-x)^{\gamma_0 - a - 1} \exp(-ax) \doteq 1 - (\gamma_0 - 1)x \\
 + \frac{1}{2} [(\gamma_0 - 1)(\gamma_0 - 2) + a] x^2. \quad (40)
 \end{aligned}$$

Carrying this expansion one term further indicates that Eq. (40) is probably good

to $\pm 10\%$ for x in the range of interest. This error will be reduced on integration. Further expansion yields

$$B(x) \doteq -V_0 \int_0^x dx \times \left\{ \frac{\rho_0 C^2 x \left[1 - \frac{3}{2} \gamma_0 x + (\gamma_0^2 - \gamma_0 + a) x^2 \right]}{(1 - Sx)^2} \right\} \quad (41)$$

$$\doteq \frac{C^2 x^2}{2(1 - Sx)} \left[1 - \left(\gamma_0 - \frac{S}{3} \right) x + \frac{1}{2} \left(\gamma_0^2 - \gamma_0 + a - S\gamma_0 + \frac{S^2}{3} \right) x^2 \right]. \quad (42)$$

Truncation of the expansion used in the numerator of Eq. (41) should be expected to lead to an error of no worse than $\pm 10\%$ after integration. This includes the error introduced by the truncation in Eq. (40). However, since the last term in Eq. (42) is only a 5% term, Eq. (42) is probably actually good to better than $\pm 10\%$.

Going back to Eq. (37), we expand

$$(1 - x)^{a - \gamma_0} \exp(ax) \doteq 1 + \gamma_0 x + \frac{1}{2} (\gamma_0^2 + \gamma_0 - a) x^2. \quad (43)$$

Hence, the contribution to E_0 from $B(x)$ is

$$\frac{C^2 x^2}{2(1 - Sx)} \left[1 + \frac{S}{3} x + \frac{S^2}{6} \left(1 - \frac{\gamma_0}{S} \right) x^2 \right]. \quad (44)$$

This is the principal term in E_0 .

The $A(x)$ and E_{0H} terms in Eq. (37) are correction terms and small. Using Eq. (40) and keeping only linear terms in x ,

$$A(x) + E_{0k} \doteq -E_{0H} \int_0^x dx \times \left\{ (\gamma_0 - ax) \left[1 - (\gamma_0 - 1)x \right] \right\} + E_{0k} \quad (45)$$

$$= -\gamma_0 E_{0H} \left[x - \frac{1}{2\gamma_0} (\gamma_0^2 - \gamma_0 + a) x^2 \right] + E_{0k}. \quad (46)$$

From Eq. (37), and using Eq. (43), we obtain the correction to E_0 from the $A(x)$ and E_{0k} terms as

$$\left[A(x) + E_{0k} \right] (1 + \gamma_0 x) \doteq E_{0k} + (E_{0k} - E_{0H}) \gamma_0 x. \quad (47)$$

We have kept only the linear term, since the whole expression is small compared to the term given by Eq. (44). Collecting Eq. (44) and (47), we finally have

$$E_0 = \frac{C^2 x^2}{2(1 - Sx)} \left[1 + \frac{S}{3} x + \frac{S^2}{6} \left(1 - \frac{\gamma_0}{S} \right) x^2 \right] + E_{00} (1 + \gamma_0 x) + E_{0H}, \quad (48)$$

where $E_{00} = E_{0k} - E_{0H}$. This formula is conservatively estimated to be correct to $\pm 10\%$ for compressions up to two-fold. Comparisons with the results of calculation based on the integration of the Dugdale-MacDonald equation¹ show deviations of the order $\pm 5\%$, consistent with this estimate.

C. MELTING TEMPERATURE $T_m(V)$

The melting temperature $T_m(V)$ is calculated from a modified Lindemann law. This melting law has been shown to reproduce recent melting correlations made by Kraut and Kennedy.³ We define $\lambda(V)$ and $\gamma_m(V)$ by the equation

$$-\frac{d \ln T_m(V)}{d \ln V} \equiv \lambda(V) \equiv 2\gamma_m(V) - \frac{2}{3}. \quad (49)$$

The Lindemann law equates the melting gamma $\gamma_m(V)$ with gamma for the solid

$\gamma_s(V)$. In analogy with Eq. (32), we write

$$\begin{aligned}\gamma_m &= \gamma_{0m} - a_m \left(\frac{V_0 - V}{V_0} \right) \\ &= \gamma_{0m} - a_m x.\end{aligned}\quad (50)$$

Hence,

$$T_m = T_{m0} \exp \left[- \int_{V_0}^V \frac{\lambda(V)}{V} dV \right] \quad (51)$$

$$\begin{aligned}T_m &= T_{m0} \exp \left\{ - \int_{V_0}^V dV \right. \\ &\quad \times \left[\frac{(2\gamma_{0m} - 2a_m - \frac{2}{3})}{V} + \frac{2a_m}{V_0} \right] \Big\} \\ &= T_{m0} \left(\frac{V_0}{V} \right)^{2\gamma_{0m} - 2a_m - \frac{2}{3}} \\ &\quad \times \exp \left[2a_m \left(\frac{V_0 - V}{V_0} \right) \right]\end{aligned}\quad (52)$$

$$\begin{aligned}T_m &= T_{m0} (1-x)^{-2(\gamma_{0m} - a_m - \frac{1}{3})} \\ &\quad \times \exp(2a_m x).\end{aligned}\quad (53)$$

Expansion of Eq. (53) in powers of x yields

$$\begin{aligned}T_m &\approx T_{m0} \left\{ 1 + \left(2\gamma_{0m} - \frac{2}{3} \right) x \right. \\ &\quad \left. + \left[\left(\gamma_{0m} - \frac{1}{3} \right) \left(2\gamma_{0m} + \frac{1}{3} \right) - a_m \right] x^2 \right\}.\end{aligned}\quad (54)$$

Of course, T_{m0} is just $T_m(V = V_0)$. Equation (54) was given by Grover.³

Equation (54) is reasonably well behaved on compression since the variable x is usually less than half. On expansion, however, x may be as negative as -1, and the predictions from Eq. (54) may be

unrealistic. For this reason, it is useful to derive an expression based on an expansion in the variable μ , where

$$\mu = (V_0 - V) / V = x / (1 - x),$$

and

$$x = \mu / (1 + \mu). \quad (55)$$

Substitution in Eq. (53) yields

$$\begin{aligned}T_m &= T_{m0} (1 + \mu)^{2(\gamma_{0m} - a_m - \frac{1}{3})} \\ &\quad \times \exp \left[\frac{2a_m \mu}{(1 + \mu)} \right].\end{aligned}\quad (56)$$

Expansion in powers of μ yields

$$\begin{aligned}T_m &= T_{m0} \left\{ 1 + \left(2\gamma_{0m} - \frac{2}{3} \right) \mu \right. \\ &\quad \left. + \left[\left(2\gamma_{0m} - \frac{5}{3} \right) \left(\gamma_{0m} - \frac{1}{3} \right) - a_m \right] \mu^2 \right\}.\end{aligned}\quad (57)$$

It is convenient to substitute for μ so that we will have an expression in x , our usual volume variable,

$$\begin{aligned}T_m &= \frac{T_{m0}}{(1-x)^2} \left\{ 1 + 2\left(\gamma_{0m} - \frac{4}{3} \right) x \right. \\ &\quad \left. + \left[\left(2\gamma_{0m} - \frac{5}{3} \right) \left(\gamma_{0m} - \frac{4}{3} \right) - a_m \right] x^2 \right\}.\end{aligned}\quad (58)$$

Equation (58) is more regularly behaved than Eq. (54) on expansion, as we should expect. It turns out to be reasonably well behaved on compression as well, so that it could be used for both compression and expansion. However, we choose to take T_m from Eq. (54) for compression ($x \geq 0$) and from Eq. (58) for expansion ($x \leq 0$).

D. TEMPERATURE CHANGE ON
MELTING AT CONSTANT
VOLUME $2\delta T(V)$

Grover³ has developed the following expression for the temperature change on melting at constant volume:

$$2\delta T(V) = \frac{[\lambda(V)T_m(V)]^2 \Delta S'}{[1 + \lambda(V)\kappa(V)T_m(V)]\beta_T(V)V}, \quad (59)$$

where κ is the thermal expansion coefficient ($= (\partial V/\partial T)_p/V$), and β_T is the isothermal bulk modulus. Since $2\delta T$ is typically only 10% to 20% of T_m , we can be rather casual in evaluating Eq. (59). λ is typically of the order 2.5, and κT_m is the thermal expansion to melting, typically 0.08. Thus, we may replace the square bracket in the denominator by a constant value 1.2. For our present purposes, we may replace $\beta_T(V)$ by $\beta_s(V)$, the adiabatic bulk modulus, but we must take into account the increase of $\beta_s(V)$ on compression. We make a first-order expansion

$$\begin{aligned} \beta_s(V) &\doteq \beta_s(V_0) - V_0 \left(\frac{d\beta_s}{dV} \right) \Big|_{V=V_0} \left(\frac{V_0 - V}{V_0} \right) \\ &\doteq \beta_s(V_0) + \left(\frac{d\beta_s}{dV} \right) \Big|_{V=V_0} \\ &\quad \times \beta_s(V_0) \left(\frac{V_0 - V}{V_0} \right). \end{aligned} \quad (60)$$

But noting the tangency between the Hugoniot and isentrope at $V = V_0$ and differentiating Eq. (17), we may write⁵

$$\frac{d\beta}{dP} = 4S - 1, \quad (61)$$

and $\beta_s(V_0) = V_0^{-1} C^2$. Hence we have

$$2\delta T = \frac{\left[2\gamma_m(x) - \frac{2}{3} \right]^2 [T_m(x)]^2 \Delta S'}{1.2 C^2 [1 + (4S - 1)x] (1 - x)}. \quad (62)$$

We use this expression for compression ($x \geq 0$), but omit the square bracket in the denominator on expansion ($x \leq 0$) because of the singularity. This may be justified in part by noting that the singularity is an artifact of the expansion of β_s and that it has no real physical significance.

E. EVALUATION OF PARAMETERS

Compression behavior is characterized by the Hugoniot parameters V_0 , C and S . Where the experimental Hugoniot is not linear, as for Al and Ti, C , and S were taken from a linear fit to the higher compression part of the Hugoniot. The rationale for this procedure is that C and S become important only at high compressions. At lower compressions, the interest is usually in the high-temperature states, and C and S are less important. Errors in calculated pressures arising from this procedure are seldom more than a few percent, in any case.

Thermal pressure in the solid is characterized by the variable $\gamma_s(V)$ in Eq. (2), the volume-dependent lattice gamma. To see this, recall that the contribution from electron thermal pressure, contained in the electronic gamma term, the γ_e term in Eq. (2), is much smaller than the lattice contribution.

Shock-wave gammas as functions of volume have been calculated from Hugoniot data on normal density samples and the integration of the Dugdale-MacDonald differential equation for

gamma.^{1,2} The details of this procedure have been outlined elsewhere.^{1,6} The results of these calculations, which are in numerical form, were then fitted with the linear relation given in Eq. (32), for volumes between $0.7 V_0$ and $1.0 V_0$. This results in $\gamma_0 = 2S - 1$, the usual Dugdale-MacDonald result, and $(\gamma_0 - a)$ generally ranging from 0.2 to 0.6, with a mean value around 0.4 for values of γ_0 around 1.8 to 2.0. The difference $(\gamma_0 - a)$ is somewhat larger where γ_0 is large and somewhat smaller where γ_0 is small. For very strong compressions, the limiting value of the lattice gamma should be near one-half,^{1,7} so the fits used have a surprisingly reasonable behavior on extrapolation to strong compressions, well beyond the range of the data used for the fits. In this discussion we have assumed, of course, that the shock-wave gamma is essentially the lattice gamma. This is, in fact, a good approximation over the range of the experimental Hugoniot for engineering metals.

One may also obtain values of gamma from thermal expansion data, with the use of the usual relation

$$(\gamma_0)_{th}^{\ell} = \kappa V_0 / \chi C_V^{\ell}. \quad (63)$$

In Eq. (63) κ is the volume coefficient of thermal expansion, χ the compressibility ($= \beta^{-1}$), and C_V^{ℓ} the lattice component of the specific heat, all evaluated at normal temperature and density. The total specific heat C_V includes a small contribution from the finite temperature nondegeneracy of the conduction electrons, and is used in calculating $(\gamma_0)_{th}$. We use only the lattice component here, since

we are treating the electrons explicitly. We term $(\gamma_0)_{th}$ and $(\gamma_0)_{th}^{\ell}$ "thermodynamic gammas." Such gammas are tabulated in the literature.⁸

While these thermodynamic values for γ_0 are usually comparable to the shock-wave values $2S - 1$, they tend to be somewhat larger in several cases. If thermodynamic values of gamma are to be used in the equation of state, we must also obtain a value for a . This can be done by scaling the value of a from the shock-wave analysis by the ratio of the thermodynamic γ_0 to the shock-wave γ_0 . This results in values of $(\gamma_0 - a)$ of the order 0.5, consistent with the expected limiting behavior of gamma at high compressions.

The decision as to which of these gammas to use in the equation of state needs further experimental evidence to decide it. From the comparisons with experimental data presented in the following section, it will be shown that the best value for the lattice gamma is obtained from the tabulated⁸ values of the thermodynamic lattice gamma, this value being taken as the value of the parameter γ_0 . The parameter a is then evaluated as outlined above.

We must also evaluate the melting gamma, characterizing the volume dependence of the melting temperature, as parameterized by γ_{0m} and a_m in Eq. (50). Comparisons with experimental data,³ unfortunately to only modest compressions, indicate that the assumption that $\gamma_{0m} = \gamma_0$ and $a_m = a$ is a reasonable approximation. This is, of course, the Lindemann law. In the absence of detailed data to challenge the

Lindemann approximation, we use it to evaluate γ_{0m} and a_m .

The equation of state is written so that the melting gamma may be different from the lattice gamma ($\gamma_{0m} \neq \gamma_0$, $a_m \neq a$), but we have not thoroughly tested this option. Thus, users of the equation of state should exercise caution if they do not set the melting and lattice gammas equal.

The evaluation of the melting temperature parameter T_{m0} requires a bit of effort. The normal melting temperature T_{mN} is defined by the relations

$$T_{mN} = T_m(V = V_m) - \delta T(V = V_m),$$

$$P(V = V_m, T = T_{mN}) = 0, \quad (64)$$

where V_m is the specific volume at which melting begins at zero pressure. These equations, together with Eq. (58) and the modified Eq. (62), provide two implicit equations in the two unknowns T_{m0} and V_m . They are most easily solved by an iterative scheme, as outlined in Appendix C. T_{m0} ranges from 15% to 45% larger than T_{mN} , the average being around 30%.

Appendix B gives GRAY equation-of-state parameters for a number of metals, developed in the manner outlined above. For metals not given there, the following procedure may be used:

- Evaluate V_0 , C and S from Hugoniot data. If no Hugoniot data are available, set C^2/V_0 equal to the bulk modulus and $S = 1.4$.
- Set γ_0 equal to the thermodynamic lattice value, the thermodynamic value, or $2S - 1$, in order of preference. Set $a = \gamma_0 - 0.5$.

- Fit γ_{0m} and a_m to melting line data, or set $\gamma_{0m} = \gamma_0$, $a_m = a$.
- Calculate T_{m0} from the normal melting temperature T_{mN} , according to the procedure in Appendix C, or set $T_{m0} = 1.30 T_{mN}$.
- The entropy of melting, ΔS , may be taken as the experimental value or as the standard value 2.3 cal/mole deg. Where there are appreciable deviations of the liquid specific heat from the assumed universal curve, the standard value of ΔS is probably the best one to use in the equation of state.

F. COMPARISON WITH EXPERIMENTAL DATA

The most useful data available for testing the scaling-law EOS are Hugoniot data taken on porous samples under strong shock compression. The shock compression of such samples results in states of very high internal energy. The resulting high temperatures produce a large thermal pressure so that the Hugoniot from the porous state lies at far higher pressures than does the Hugoniot from normal density.^{1,9} This can readily be seen by noting that the Rankine-Hugoniot relation for the conservation of energy is

$$E - E_i = \frac{1}{2} P (V_i - V), \quad (65)$$

where the subscript i denotes the initial conditions of the material before shock compression. (The subscript 0 will denote conditions at zero pressure and normal density.)

For samples with initial distentions of the order two-fold, the final volumes under shock compression will be near the normal uncompressed volume for the

undistended material. Since the temperatures are very high, however, the material will be in the liquid state, and such data are ideally suited to testing the scaling-law liquid EOS.

However, for such a test to be significant, the thermal component of the pressure must be a significant portion of the total pressure on the porous Hugoniot. Otherwise, experimental uncertainties (which become particularly severe with porous materials) obscure the results. This can be easily seen when it is noted that information about the thermal pressure is obtained by subtracting values of the pressure and energy on the normal Hugoniot from the corresponding values on the porous Hugoniot, at the same specific volume.

For this reason, only porous Hugoniot points representing thermal pressures greater than a half megabar or so will be reviewed here. Such work is either Russian or British. A great deal of work has been done at Los Alamos and elsewhere on lower pressure porous Hugoniots, but these low-pressure results do not provide good tests of liquid equation-of-state models. Almost all reasonable models will predict their results satisfactorily.

As we have noted, because of the high thermal pressures reached on the porous Hugoniots, materials are not compressed much beyond normal density. Most of the experimental points we will use in this comparison represent states of density within 20% of normal density, though a few points represent compressions of as much as 35% from normal density. For this reason, the volume dependence of the effective gamma does not have a large effect on the comparison.

The Grüneisen gamma, which is normally assumed independent of temperature, could be evaluated as

$$\gamma_{sw} = V(P_{H_2} - P_{H_1}) / (E_{H_2} - E_{H_1}) \quad (66)$$

in terms of differences in pressure and energy between two Hugoniots, provided both Hugoniots were in the solid range. For liquids, however, the effective gamma defined by Eq. (66) is not independent of the temperature (and hence, of the pressure or energy), and is not a very useful parameter. We shall work mainly with a thermal pressure ($P - P_H$) and a thermal energy ($E - E_H$) directly, where the subscript H now denotes states on the normal Hugoniot. We must realize, of course, that P_H and E_H contain a thermal, as well as a cold-compression component, and we discuss here only the thermal component above the normal Hugoniot.

As was pointed out in the previous section, several methods of evaluating gamma give somewhat different values since they all use various theoretical models to extract gamma from different kinds of experimental data. The "shock-wave" gamma defined by Eq. (66) is one such gamma. Another that can be evaluated from ordinary shock-wave data is the Dugdale-MacDonald gamma. The procedure for calculating this gamma, described in the previous section, yields a volume-dependent gamma characterized by the parameters γ_0 and a [cf. Eq. (32)].

For purposes of comparison, we also consider "thermodynamic" and "acoustic" gammas. The former⁸ is derived from ordinary thermodynamic data with the use

Table 1. Values of the parameter gamma, γ_0 .

	Dugdale-MacDonald shock-wave values		Thermodynamic values ⁸		Acoustic values ¹³
	$(\gamma_0)_{DM}$	$(a)_{DM}$	$(\gamma_0)_{th}^{\ell}$	$(\gamma_0)_{th}$	$(\gamma_0)_{ac}$
U	2.10	1.51	2.07	1.82	
W	1.47	1.23	1.78	1.76	
Cu	1.98	1.44	1.97	1.96	1.98
Ni	1.89	1.41	2.00	1.83	
Pb	2.08	1.35	2.84	2.74	
Al	1.68	1.33	2.18	2.14	2.64

of Eq. (63), as discussed in the previous section. The acoustic gamma¹⁰⁻¹³ $(\gamma_0)_{ac}$ is evaluated from data on the volume dependence of acoustic velocities, measured in static high-pressure apparatus using ultrasonic techniques.

Table 1 lists values of γ_0 and a , evaluated in various ways for six metals for which there are shock-wave data on porous samples suitable to test the theory.

Porous Hugoniot data were used to generate the quantities

$$(\Delta P)_{exp} = (P - P_H)_{exp} \quad (67)$$

and

$$(\Delta E)_{exp} = (E - E_H)_{exp} \quad (68)$$

Here P and E represent a porous Hugoniot point at volume V [see Eq. (65)] and P_H and E_H represent a point on the normal Hugoniot at the same volume. Data were taken from the Russian literature for Cu,¹⁴ Ni,¹⁴ Pb,¹⁴ W,¹⁵ and Al,¹⁴ and from Skidmore and Morris for U.¹⁶

To make comparisons with model equations of state, the experimental V, E points from the porous Hugoniot work were used to calculate P from the models.

If a model describes experimental reality, the ratio $R = (P - P_H)/(P - P_H)_{exp}$ should be 1. Figures 1 through 6 show this ratio for several models as a function of the thermal pressure $(P - P_H)_{exp}$.

The EOS models used to calculate values of P were the scaling-law model, described in previous sections of this report, and a simple Grüneisen model, taken as the $P_1(V, E)$ term in Eq. (23). In the Grüneisen model, γ_0 and a were taken as their Dugdale-MacDonald values

Fig. 1. Ratio of thermal pressure calculated from the equation-of-state models to the experimental value vs thermal pressure for uranium.

Fig. 2. Ratio of thermal pressure calculated from the equation-of-state models to the experimental value vs thermal pressure for tungsten.

Fig. 5. Ratio of thermal pressure calculated from the equation-of-state models to the experimental value vs thermal pressure for lead.

Fig. 3. Ratio of thermal pressure calculated from the equation-of-state models to the experimental value vs thermal pressure for copper.

Fig. 6. Ratio of thermal pressure calculated from the equation-of-state models to the experimental value vs thermal pressure for aluminum.

Fig. 4. Ratio of thermal pressure calculated from the equation-of-state models to the experimental value vs thermal pressure for nickel.

given in Table 1. The same values were also used in the scaling-law model. In addition, the scaling-law model was used to calculate P with several other values of γ_0 given in Table 1. In these cases, values of a were scaled from the Dugdale-MacDonald values by the ratio of the corresponding values of γ_0 , as outlined in the previous section.

In comparing the Grüneisen results with the scaling-law results, it is clear that the Grüneisen model yields results systematically high. This is particularly evident in Table 2 where the mean value

Table 2. Ratio $R = (P - P_H)/(P - P_{H\text{exp}})$.

	Grüneisen		Scaling law	
	$(\gamma_0)_{\text{DM}}$	$(\gamma_0)_{\text{th}}^{\ell}$	$(\gamma_0)_{\text{DM}}$	$(\gamma_0)_{\text{th}}^{\ell}$
U	1.60		0.97	
W	0.97	1.17	0.75	0.85
Cu	1.94		1.02	
Ni	1.54	1.63	0.82	0.88
Pb	1.92		1.00	
Al	1.28	1.66	0.81	0.99
Average	1.54	1.65	0.90	0.95

of R is tabulated. As can be seen from the table, the use of the Dugdale-MacDonald gamma in a Grüneisen model gives thermal pressures 54% too high on the average, whereas the same gamma in the scaling law gives pressures some 10% too low on the average. These comparisons are for thermal pressures in the range 1-5 Mbar.

Turning to a more detailed examination of the results of the comparison, we find that for U, Cu, and Pb the correlation of experiments with the scaling-law results is excellent, and seems to be a clear expression of the superiority of the scaling law as a high-temperature model. Note also, that for U and Cu, the values of $(\gamma_0)_{\text{th}}^{\ell}$ and $(\gamma_0)_{\text{DM}}$ are very close, so the picture is quite self-consistent.

For Al, the scaling law with $\gamma_0 = (\gamma_0)_{\text{DM}}$ yields thermal pressures significantly too low. However, for Al, there is some uncertainty as to the appropriate $U_s - U_p$ fit to describe the Hugoniot. For the fit used, $(\gamma_0)_{\text{DM}} = 2S - 1$ is significantly lower than the thermodynamic or acoustic values of gamma. Accordingly, γ_0 was increased to $(\gamma_0)_{\text{th}}^{\ell}$. This increased the mean value

of R to a completely satisfactory value. (It is not clear why the acoustic gamma is still higher.)

Nickel and tungsten present more difficult problems. Increasing the value of γ_0 from $(\gamma_0)_{\text{DM}}$ to the thermodynamic value improves the agreement with experiment, but the mean values of R for all points are still low. A further increase in γ_0 so that the mean value of R is one can be made, but the values of γ_0 appear somewhat high.

The agreement between the scaling-law model results and experiments extends to thermal pressures of several megabars for U, Cu, and Pb. For these metals, the ratio R appears to be independent of thermal pressure and energy. For Ni and W, however, there seems to be a difference between the high- and low-pressure results. The low-pressure points are reasonably calculated with either $\gamma_0 = (\gamma_0)_{\text{DM}}$ or $\gamma_0 = (\gamma_0)_{\text{th}}^{\ell}$, though the latter appears to be somewhat better. It is interesting to note that the high-pressure points that are in the hot-liquid region are rather insensitive to variations in γ_0 . This is consistent with the idea that the material is approaching a high-temperature fluid whose properties are relatively independent of the properties of the parent solid. The scaling-law treatment of the high-pressure, high-temperature region of the liquid is based on an extrapolation of lower temperature specific heat data. Thus, probably, the relatively low thermal pressures predicted by the scaling-law EOS model at high thermal energies for these metals is most likely due to a poor model in this region, rather than a poor estimate of gamma.

Since the electronic thermal pressure goes at T^2 , it seemed possible that the poor results of the scaling law at high temperatures might be from a poor treatment of this effect. The values of the electronic energy coefficient g_e are rather uncertain for U, Cu, Ni, and W because of uncertainties arising from the contributions of d-electrons to the conduction band. For Cu, Ni, and W, the value of g_e was changed by a factor of two, corresponding to a factor of eight in the number of effectively free electrons. The calculated thermal pressures varied by only 2% to 3%. To a considerable extent, this is because the model assumes the electron gamma to be equal to two-thirds, the free-electron value. At high temperatures, the scaling-law lattice gamma also approaches two-thirds, and the number of free electrons is then unimportant. However, at lower temperatures, where band structures are well-defined, the electron gammas may differ widely from two-thirds. In reality, electronic effects may be more significant than the model predicts. Some of the disagreement between the scaling-law model results and experiment may be due to an improper treatment of such electronic effects.

Summarizing, we note that comparisons between the Grüneisen and scaling-law EOS models and porous Hugoniot results show the following:

- For U and Cu, the porous Hugoniot data to several Mbar are well reproduced by the scaling-law EOS and not by the Grüneisen EOS. Dugdale-MacDonald shock-wave values and thermodynamic values of γ_0 are comparable.

- The scaling-law EOS also reproduces the porous Hugoniot data for Al, Ni, and W up to 1 Mbar or so. Best results are obtained by setting γ_0 equal to the thermodynamic gamma, rather than the Dugdale-MacDonald gamma. At thermal pressures of several megabars, the scaling law underestimates the thermal pressure for Ni and W.

These comparisons clearly demonstrate the inadequacy of the simple Grüneisen EOS in treating states in the liquid region. The scaling-law EOS appears to be valid up to temperatures of several times the melting temperature, at least as a (P, V, E) relation. At temperatures of ten or more times the melting temperature the scaling law gives good results for some metals, but only fair results for others. The difficulty is probably due either to an unreliable extrapolation of lower-temperature specific heat data inherent in the model or to an incorrect estimate of the effective electron gamma and possibly of the number of effectively free electrons.

It should also be observed that the lower thermal pressures predicted by the scaling law as compared to the Grüneisen model and the agreement of the scaling law with experiment have important implications as to the form of the true EOS. Grover³ notes the existence of the identity

$$\left[\frac{\partial(\gamma C_V)}{\partial \ln T} \right]_V = \left[\frac{\partial C_V}{\partial \ln V} \right]_T, \quad (69)$$

which shows the connection between the temperature dependence of gamma and the volume and temperature dependence of the specific heat. From the porous

Hugoniot data near normal density, we see that gamma must have a negative temperature dependence in the liquid, and from Eq. (69) this implies that C_V must be either temperature- or volume-dependent, or both. In the scaling-law model, $\gamma(\partial C_V / \partial \ln T)_V \sim -\gamma\alpha$ contributes a positive term to $(\partial\gamma / \partial \ln T)_V$, but this term is overwhelmed by the negative contribution from $(\partial C_V / \partial \ln V)_T \sim -\lambda\alpha$.

It has been tempting to construct an equation of state which ignores the melting transition and which makes C_V volume-dependent only. Equation (69) shows that such an EOS can, indeed, produce the appropriate temperature-dependent gamma in the liquid, but at the expense of making C_V also strongly volume-dependent in the normal solid. This seems unphysical, and suggests the importance of including the melting transition explicitly.

IV. Modified van der Waals Equation of State

The Young-Alder EOS⁴ may be written in the form

$$P = \frac{R'T}{V} \frac{(1 + z + z^2 - z^3)}{(1 - z)^3} - \frac{a'_Y}{V^2} \quad (70)$$

$$E = \frac{3}{2} R'T - \frac{a'_Y}{V}. \quad (71)$$

As before we write the EOS per gram, rather than per gram-atom as Young and Alder do. Thus, if A is the atomic weight, we have $R' = R/A$ and $a'_Y = a_Y/A^2$, where a_Y is the Young-Alder-van der Waals coefficient a . The variable z is a scaled density, $z = V_b/V$, where

$$V_b = \pi N_0 \sigma^3 / 6 A. \quad (72)$$

The first term on the right-hand side of Eq. (70) represents the repulsive interaction of hard spheres, and σ is the hard-sphere diameter. N_0 is Avogadro's number. Young and Alder present evidence that for metals $V_b = 0.45 V_L$, where V_L is the specific volume of the liquid near the melting point.

The second term on the right-hand side of Eq. (70) represents the classical van der Waals mean-field attraction. Alder and Young present arguments to suggest that one can evaluate a'_Y as $V_0 E_{coh}$, where E_{coh} is the cohesive energy or energy of sublimation (per gram).

In the classical van der Waals equation, the repulsive term is written $R'T/(V-b)$, where the parameter b is one-third the volume at the liquid-vapor critical point. Since the latter volume is usually four to five times the normal volume of the solid, the classical EOS has a singularity at a density less than normal density. On the other hand, the parameter V_b is roughly one-half of normal volume, so the singularity in the Young-Alder EOS does not come until a density of twice normal density.

Thus, in addition to representing an increased sophistication over the classical EOS (and presumably hence a better representation of reality) the Young-Alder form has the advantage of being useable at much higher densities than is the classical form. This is a great advantage in

joining it to a high-density EOS such as the Grover scaling law or the Grüneisen form.

A. COMPARISON WITH EXPERIMENTAL DATA

To test the validity of the Young-Alder EOS against experimental data in the region of application, we would need data at temperatures up to 1 or 2 eV at all densities less than normal density. This would involve pressures of 10 to 20 kbar near the liquid-vapor critical density, and much higher at higher densities.

Unfortunately, static high-temperature data extend to only a quarter eV or so and are at rather modest pressures. Young and Alder review these data and make appropriate comparisons in their paper, so we need only summarize their arguments here.

The most sensitive test of any liquid-vapor EOS model is in its predictions of conditions at the liquid-vapor critical point. This is because the critical parameters are extremely sensitive to the detailed shape of the EOS surface. Variations of only a few percent in the pressure calculated by a model, for example, may produce changes in critical parameters of several tens of percent, under certain circumstances.

Only for Hg and Cs have critical parameters actually been measured. For Rb, measurements have extended almost to the critical point. For other metals, they may be inferred from the extrapolation of experimental data. Table 3, taken from Young and Alder's paper, compares critical parameters calculated from their model and inferred from experimental

data. The former are obtained from the relations:

$$v_c = 2.417 \times 10^{24} \sigma^3, \quad (73)$$

$$P_c = 0.2596 a_Y/v_c^2, \quad (74)$$

$$T_c = 0.7232 a_Y/Rv_c, \quad (75)$$

$$Z_c = P_c v_c/RT_c. \quad (76)$$

Here v_c is per gram-atom.

Table 3 shows that the model does a good job of predicting the critical temperature. Critical pressures are predicted somewhat high, and critical volumes somewhat low. The calculated values are always good within a factor of two, however, and the quality of the estimated "experimental data" is often little better than this. Note that the critical compressibility Z_c is a constant in the model, whereas it is estimated to vary from 0.2 to 0.4 for real metals. The addition of a third parameter to the model would allow Z_c to be variable, but Young and Alder argue that the experimental data are not reliable enough to warrant such a treatment for metals.

The van der Waals model provides semi-quantitative agreement with experimental data on metals near the critical point. At present, it appears to be at least as accurate as other theories in predicting behavior in the critical region. Substantial improvement will require extensive new experimental data in regimes where experiments are exceedingly difficult.

It should, of course, also be remarked that the Young-Alder model goes over to an ideal gas at sufficiently expanded volumes, as it should. Thus, the limiting behavior is correct, and the main

Table 3. Comparison of critical constants of metals computed from the van der Waals model and estimated from experimental thermodynamic data.⁴

	v_c (cm ³ /mole)		T_c (k°K)		P_c (kbar)	
	Model	Expt.	Model	Expt.	Model	Expt.
Li	47	66	3.8	3.2	2.42	0.69
Na	85	116	2.64	2.57	0.92	0.35
Mg	53	59	3.4	3.8	1.93	1.75
Al	—	—	7.2	8.6	—	—
K	165	209	2.18	2.22	0.40	0.16
Ca	101	134	4.0	4.6	—	—
Fe	28	42	9.3	6.8	—	—
Ni	26	40	9.6	6.0	—	—
Cu	27	61	7.6	8.9	—	—
Zn	33	30	3.2	3.4	—	—
Ga	40	75	7.0	7.6	—	—
Ge	—	—	9.8	8.4	—	—
Rb	200	247	2.06	2.09	0.31	0.16
Mo	—	—	14.6	17.0	—	—
Ag	40	58	6.4	7.5	4.8	5.1
Cd	48	41	2.62	2.97	—	—
In	56	83	5.8	6.7	3.1	2.4
Sn	58	100	7.3	8.0	3.7	2.0
Sb	—	—	6.4	5.1	—	—
Cs	249	299	1.94	2.05	0.23	0.12
Ba	143	193	4.2	4.7	—	—
Ta	—	—	17.3	22.0	—	—
W	—	—	18.5	23.0	—	—
Re	—	—	17.3	20.5	—	—
Pt	—	—	12.5	14.6	—	—
Au	—	—	8.3	9.5	—	—
Hg	50	35	1.56	1.75	0.92	1.52
Tl	62	86	4.4	4.8	—	—
Pb	67	94	4.7	5.4	2.08	0.86
Bi	72	80	5.4	4.6	—	—
U	—	—	13.0	12.5	—	—

problems will be in predicting critical behavior correctly—the problem we have been discussing above.

B. JOIN TO SCALING-LAW EQUATION OF STATE

The scaling-law EOS can be extrapolated to as much as a 50% expansion while remaining a reasonably good representation of physical reality. To see this, note that V_0 is not a unique specific volume where discontinuous behavior should be expected. Rather, it simply represents the minimum of some continuous energy curve. Thus, given an EOS valid at V_0 and on compression, we may extend it analytically into the expanded volume region with considerable confidence as to its reliability for modest extensions. The limit of 50% expansion is based on a detailed study of the analytic expansions used in the scaling-law EOS.

In the modified van der Waals EOS, the repulsive interaction is treated in a hard-sphere approximation, so the EOS should not be expected to be valid where details of this interaction are important. Thus, the model should not be taken to volumes as low as V_0 . It is a little hard to see how far the van der Waals model can be extended toward V_0 , but it seems reasonable to expect that in the range $1.25 V_0$ to $1.50 V_0$ both the scaling law and van der Waals models should be valid, and it should be relatively easy to join them in that region.

Examination of isotherms and isentropes calculated from the two models reveals curves for the two models having very similar shapes and slopes in the range $1.25 V_0$ — $1.35 V_0$. In many cases, isotherms are very nearly coincident.

There would appear to be reason for greater confidence in the validity of the scaling-law model than the van der Waals model in this region of overlapping validity. For this reason, we modify the van der Waals EOS by the addition of terms to it in order to force a continuous join to the scaling-law EOS at some specific volume V_J . These terms are selected to leave the general shape of the van der Waals EOS unchanged and to die off smoothly as the volume increases from V_J .

At V_J , we write the scaling-law EOS in the form

$$P = P^{(1)} + P^{(2)}T + P^{(3)}T^2 \quad (77)$$

$$E = E^{(1)} + E^{(2)}T + E^{(3)}T^2 \quad (78)$$

where $P^{(1)}$, $P^{(2)}$, $P^{(3)}$, $E^{(1)}$, $E^{(2)}$, $E^{(3)}$, are all constants (functions of V_J). We now write the pressure in the van der Waals region as

$$P = \frac{R'T}{V} \frac{(1 + z + z^2 - z^3)}{(1 - z)^3} - \frac{a_Y'}{V^2} + F_p(V) (C_1 + C_2T + C_3T^2), \quad (79)$$

where $F_p(V) = 1$ at $V = V_J$ and falls off smoothly as V increases. If $z_J = V_b/V_J$, inspection reveals

$$C_1 = P^{(1)} + \frac{a_Y'}{V_J^2} \quad (80)$$

$$C_2 = P^{(2)} - \frac{R'}{V_J} \frac{(1 + z_J + z_J^2 - z_J^3)}{(1 - z_J)^3} \quad (81)$$

$$C_3 = P^{(3)} \quad (82)$$

Now near V_J , the singularity in the first term on the right-hand side of (70) dominates the behavior of the EOS.

Hence, if the general shape of the EOS is to be preserved in the join process, we want $F_p(V)$ to have a $(1 - z)^3$ denominator. On the other hand, the last term on the right-hand side of (70) falls off as $1/V^2$ at large volumes. If we want the effects of the join to fall off faster, we must take $F_p(V) \sim 1/V^3$. Hence, we take

$$F_p = \left[\frac{z}{z_J} \frac{(\theta - z_J)}{(\theta - z)} \right]^3. \quad (83)$$

The parameter θ will allow us to change the shape of the EOS in the join region if desirable; otherwise it can be taken equal to one.

Now thermodynamic consistency requires that

$$\left(\frac{\partial E}{\partial V} \right)_T = -P + T \left(\frac{\partial P}{\partial T} \right)_V. \quad (84)$$

Hence we must add to (71) a term

$$F_e(V) (C_1 - C_3 T^2), \quad (85)$$

where

$$\begin{aligned} F_e &= - \int_{V_J}^V F_p(V) dV \\ &= V_b \int_{z_J}^z F_p(z) \frac{dz}{z^2} \\ &= \frac{V_b (\theta - z_J)^3}{2 z_J^3} \left[\frac{(2z - 2 + \theta)}{(1 - z)^2} \right. \\ &\quad \left. - \frac{(2z_J - 2 + \theta)}{(1 - z_J)^2} \right]. \quad (86) \end{aligned}$$

In addition, we may add to (71) any expression independent of V , so the total energy expression becomes

$$E = \frac{3}{2} R' T - \frac{a_Y}{V} + F_e (C_1 - C_3 T^2) + (D_1 + D_2 T + D_3 T^2). \quad (87)$$

Inspection reveals that

$$D_1 = E^{(1)} + \frac{a_Y}{V_J} \quad (88)$$

$$D_2 = E^{(2)} - \frac{3}{2} R' \quad (89)$$

$$D_3 = E^{(3)}. \quad (90)$$

We now have the problem of evaluating the coefficients $P^{(n)}$ and $E^{(n)}$. In doing this we must note that for most of the temperatures of interest the scaling-law EOS will be in the hot liquid region, but that at low temperatures it could be in the liquid or perhaps the two-phase region. The coefficients $P^{(n)}$ and $E^{(n)}$ will take on different values in each of these regions. Thus, it would appear that we would have to define various expanded-volume regions, where the coefficients C_n and D_n would take on different values.

This problem can be circumvented by noting that we are never interested in negative pressures, once the material is outside the solid range. Furthermore, as material expands at zero pressure, it must, of course, be heated and eventually enter the hot liquid region at an expansion generally between 30% and 40%. The solution to our problem is, then, to take the volume where this takes place as V_J . Thus, for positive pressures at this specific volume, the scaling-law EOS

will always be in the hot liquid region, and we may use hot liquid values of $P^{(n)}$ and $E^{(n)}$ in calculating C_n and D_n . The use of these same values of C_n and D_n for negative pressures will result in a discontinuity in the EOS at V_J , since the scaling-law EOS will be in the liquid or two-phase region. To prevent this from being a problem, a spall routine must be used to prevent anything but the solid from supporting a negative pressure.

The $E^{(n)}$ coefficients may now simply be evaluated as the coefficients of various powers of T in Eq. (9), evaluated at $V = V_J$. The $P^{(n)}$ coefficients may be obtained by identifying coefficients of various powers of T in the equation for P that results from Eq. (23) when $P_1(V, E)$ is evaluated from the first two terms in Eq. (22) with E evaluated from Eq. (78), and $P_c(T, V)$ is evaluated from Eq. (27). (See Appendix A for results.)

It should be noted that the join could not have been performed in the manner outlined above without the Young-Alder modification to the van der Waals EOS. If we had had to join the classical van der Waals model to the scaling-law model, we would have found no region of overlapping validity. We would have had to make the join by constructing an interpolation function between the highest density at which the van der Waals model is valid and the lowest density at which the scaling-law model is valid. Attempts to carry out such a program revealed that this is a region of rapidly changing slope and curvature in the EOS, and that the construction of a satisfactorily smooth interpolation is exceedingly complex, though possible. Thus, it is easy to see why simplified EOS models, such as the

modified ideal gas used in the PUFF EOS, have been resorted to in the past.

C. EVALUATION OF FINAL PARAMETERS

As we have indicated previously, V_b may be evaluated as $0.45 V_L$, where V_L is the specific volume of the liquid metal just above melting. It turns out that the resulting values of V_b are $0.50 V_0$ on the average; typical deviations being no more than 10%. Thus, if data are available, we may take $V_b = 0.45 V_L$; otherwise $V_b = 0.50 V_0$.

If the Young-Alder model is extended to V_0 , the cohesive energy, the energy difference between the zero temperature states at $\rho = 0$ and $\rho = \rho_0$ is just $E_{coh} = a_Y^1/V_0$ (per gram), as we mentioned before. Thus, a_Y^1 can be adjusted to make E_{coh} equal an experimental value. For the joined, three-phase EOS, however, the cohesive energy is given by

$$E_{coh} = -E_{0H} - E_{00} + D_1 + C_1 F_e(z = 0). \quad (91)$$

Since C_1 and D_1 depend on a_Y^1 , a_Y^1 may be adjusted to again make E_{coh} equal to the experimental value. This results in a significant increase in a_Y^1 —55% on the average but ranging from 10% to 100% for various metals. Appendix C outlines a simple method for evaluating a_Y^1 from E_{coh} .

As mentioned previously, we take the join volume as the volume where the metal changes from the liquid to the hot liquid region at zero pressure, i.e.,

$$P = P(T = T_G, V = V_J) = 0. \quad (92)$$

Appendix C contains a simple routine for calculating V_J from Eq. (92).

The parameter θ is normally taken equal to 1. If θ is taken as some other value slightly different from 1, the slope of the EOS on the low-density side of V_J can be modified. Since we have not forced continuity of slopes across V_J , we can take advantage of this feature where slope discontinuities appear

excessive. The effect is most easily seen in examining the change in sound velocity at V_J . Generally this change is less than 25%, and appears to cause no particular problems in hydrodynamic calculations. If the change was significantly larger, θ was taken as some value other than 1 in order to bring the change in sound velocity within this limit.

V. Yield and Spall Behavior

Previous sections of this report have concerned themselves with a thermodynamic equation of state, and this has been the principal emphasis of this work. It should be remarked, however, that if one is going to calculate the hydrodynamic behavior of a real material, some sort of mechanical constitutive relation must be added to this equation of state. Most usually, this takes the form of a simple elastic-plastic theory, where the yield behavior is characterized by a von Mises yield strength Y_0 . More sophisticated rate-dependent yield models may also be employed, of course.

With the GRAY model, however, we have available an estimated material temperature T and an estimated temperature where melting begins $T_m(V) - \delta T(V)$. Thus, it seems logical to set Y_0 equal to zero if the ratio $r = T/[T_m(V) - \delta T(V)] > 1$, since this represents material in the two-phase or liquid region. This should also be done for material where $V \geq V_J$, since this material would be in the liquid-vapor region. In the

solid region, where $r < 1$, the yield strength may be made a function of r to reproduce the temperature dependence of the yield strength. The discussion of the proper form of this temperature dependence is beyond the scope of this report, however.

If rarefaction processes and the blow-off of hot materials are to be properly calculated, a proper spall routine is also essential. As with Y_0 , it seems reasonable to set spall strengths equal to zero if $r \geq 1$ or $V \geq V_J$. Aside from getting the physics right, this procedure is also essential because of the discontinuous behavior of the equation of state for negative pressures at V_J . For $r < 1$, we are dealing with solid spall, as contrasted with the splash-off and blow-off occurring for $r \geq 1$. In the case of solid spall there are many criteria to choose from, and again a detailed discussion would be beyond the scope of this report. It should be remarked, however, that if desired, the solid spall criterion could be made a function of temperature.

VI. Equation-of-State Results

The complete GRAY equation of state is given in Appendix A in the form $P = P(V, E)$. Appendix B gives equation-of-state parameters for 16 metals: Be, Mg, Al, Ti, stainless steel, Ni, Monel, Cu, Nb, Ta, W, Au, Pb, Th, Mulberry, and U. To demonstrate the character of the EOS graphically, Figs. 7-18 were prepared, showing isentropes and isotherms for Be, Al, Cu, and U.

Isotherm temperatures were 2, 1, 0.5, 0.2, 0.1 eV and room temperature.

Isentropes were calculated by the integration of the equation

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_S &= \left(\frac{\partial P}{\partial V}\right)_E + \left(\frac{\partial P}{\partial E}\right)_V \left(\frac{\partial E}{\partial V}\right)_S \\ &= \left(\frac{\partial P}{\partial V}\right)_E - P \left(\frac{\partial P}{\partial E}\right)_V, \quad (93) \end{aligned}$$

Fig. 7. Pressure on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V_0/V$, for beryllium.

Fig. 8. Pressure on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V_0/V$, for aluminum

the solution of which is

$$P(V) - P(V_0) = \exp \left[- \int_{V_0}^V \left(\frac{\partial P}{\partial E} \right)_V dV_1 \right] \times \int_{V_0}^V \left(\frac{\partial P}{\partial V} \right)_E \exp \left[\int_{V_0}^{V_1} \left(\frac{\partial P}{\partial E} \right)_V dV_2 \right] dV_1, \quad (94)$$

$$E(V) - E(V_0) = - \int_{V_0}^V P dV_1. \quad (95)$$

These integrations must be carried out simultaneously, since E , from Eq. (95), is needed to evaluate $(\partial P/\partial V)_E$ and $(\partial P/\partial E)_V$ in Eq. (94).

Isotherms were calculated by using Eqs. (1), (3), (5), (7), (9), and (87) to calculate $E(T, V)$. The resulting (V, E) points were then used in the $P(V, E)$ EOS to complete the calculation.

Points that may be noted are the melting transition, clearly visible on the isotherms, the reduced effect of

Fig. 9. Pressure on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V_0/V$, for copper.

melting on isentropes, and the quality of the join between the high- and low-density models and the modest discontinuity in

the slope of the EOS there. The liquid-vapor critical region is at too low a pressure to show up on these logarithmic plots.

Fig. 10. Pressure on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V_0/V$, for uranium.

Fig. 11. Energy on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V_0/V$, for beryllium.

Fig. 12. Energy on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V_0/V$, for aluminum.

Fig. 13. Energy on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V/V_0$, for copper.

Fig. 14. Energy on isentropes, isotherms and the Hugoniot vs η , where $\eta = \rho/\rho_0 = V/V_0$, for uranium.

Fig. 15. Sound velocity on isentropes from Fig. 7 vs η , where $\eta = \rho/\rho_0 = V_0/V$, for beryllium.

Fig. 16. Sound velocity on isentropes from Fig. 8 vs η , where $\eta = \rho/\rho_0 = V_0/V$, for aluminum.

Fig. 17. Sound velocity on isentropes from Fig. 9 vs η , where $\eta = \rho/\rho_0 = V_0/V$, for copper.

Fig. 18. Sound velocity on isentropes from Fig. 10 vs η , where $\eta = \rho/\rho_0 = V_0/V$, for uranium.

VII. Accuracy of the Equation of State

The assessment of the accuracy of the GRAY equation of state is at best an

educated guess, since we have no way of really knowing a true EOS. (If we did,

there would be no point in playing with the approximations in GRAY.) On the other hand, the work of constructing GRAY has provided considerable insight into some of the limits on what a reasonable EOS might do. While these are admittedly subjective, in part, they are presented here to give potential users of GRAY some idea of how much confidence they should place in their results.

Looking first at the high-density regime, described by the scaling-law EOS, we may note that our normalization to ordinary experimental Hugoniot data assures us that the EOS will reliably treat shock-wave or other compression. The limit of applicability is probably around 2-1/2-fold compression because of the singularity in the representation of the Hugoniot we have employed. The much greater uncertainties are in the thermal EOS. In the solid, this is controlled primarily by the parameter γ_0 . On the other hand, proceeding to high temperatures in the liquid, we find that λ and α become increasingly important, as noted in the discussion following Eq. (69). For the solid γ_0 is probably good to $\pm 5\%$, on the average, though occasionally uncertainties of 10% are encountered. In the liquid, uncertainties in λ and α can probably be accounted for by assigning γ_{0m} an uncertainty $\pm 20\%$. If one wishes to maintain $\gamma_0 = \gamma_{0m}$, roughly the same effect in the liquid can be obtained by assigning them collectively an uncertainty of $\pm 10\%$.

The uncertainty in γ_0 and γ_{0m} (or λ and α) reflects itself in an uncertainty of the order $\pm 10\%$ in calculated thermal pressures. This will show up directly in peak pressures associated with rapid

energy deposition. This assignment of an uncertainty of $\pm 10\%$ in the thermal pressure is also entirely consistent with the comparison between predictions of the model EOS and porous Hugoniot data, as given in Table 2. Such a comparison further indicates that where there is good-quality porous Hugoniot data, γ_0 and/or γ_{0m} could be adjusted to reproduce these data. The result would probably be a reduction in the uncertainty in the EOS to perhaps $\pm 5\%$.

Turning to the lower densities, described by the Young-Alder model and its join to the scaling-law model, we find much larger uncertainties. While there are significant uncertainties introduced by the use of the relatively simple Young-Alder form and by its modification produced by the join procedure, these are overwhelmed by the uncertainties arising from the method of estimating the parameter a_Y (or a_Y'). Our procedure of adjusting a_Y so that the EOS will reproduce the cohesive energy correctly is difficult to justify, since it is not clear that our EOS form should get the cohesive energy right. (Recall that the cohesive energy involves the EOS in two very different regimes, described by two models, and joined by a rather ad hoc join procedure.) In view of this problem, it would appear that we should ascribe an uncertainty of at least $\pm 30\%$ to a_Y . This uncertainty will then dominate the low-density EOS, and will be reflected in calculations of the velocity or momentum of material blowing off a rapidly heated surface.

This uncertainty in the EOS is supported by comparisons with predicted critical temperatures (Table 3), and

cannot be significantly reduced without further recourse to experimental data. Transient, quasistatic heating experiments offer the possibility of extending usual thermodynamic measurements to higher temperatures and pressures, and such data would be quite valuable.

For the present EOS, however, outside the solid regime, an uncertainty of $\pm 10\%$ should be attributed to γ_0 and γ_{0m} , and an uncertainty of $\pm 30\%$ should be attributed to a_Y (or a'_Y). These numbers are appropriate for use in sensitivity analyses; there is no need to vary other parameters.

It should also be remarked that uncertainties in the EOS increase at high temperatures. At temperatures above 2 eV or so, electronic contributions become important in the EOS. At still higher temperatures, the electronic EOS is

properly described by the Thomas-Fermi model, and this model is not included in the present EOS. Thus, the high-temperature limiting behavior of the model is incorrect. Additionally, at lower temperatures there may be electronic phase transitions, even in the liquid. While the effects of such transitions may not be large, they are not included in the present model. Furthermore, as discussed in section III-F, above about ten times the melting temperature, the thermodynamics of the liquid may not be very accurate. Thus, from all of these considerations, it appears that the GRAY EOS should not be used for accurate calculations above 2 eV or so, though the EOS is well behaved and can be used with somewhat reduced reliability to temperatures over 5 eV.

VIII. Problems with the Form of the Equation of State and Potential Improvements

In the previous section we have discussed problems associated with the evaluation of equation-of-state parameters, the uncertainties in the equation of state caused by these problems, and possible methods of improving the situation. For the most part, these problems are considerably more important than any problems arising from the form assumed for the EOS. However, should new data make it possible to do a better job of evaluating EOS parameters, it may be necessary to clean up the form of the EOS. To accomplish this, several problems must be recognized. In no case is there real evidence that im-

provements designed to solve these problems will have a significant effect on practical calculations employing the EOS, but we cannot be sure that this is the case.

Many of the problems are associated with the rather crude nature of the join performed between the scaling-law EOS and the modified van der Waals EOS. At the join volume V_J , the slope of the EOS is discontinuous, though the discontinuity is not large in most cases. A more sophisticated join procedure should preserve slopes at V_J . A second, minor point that could be fixed in an improved join is the discontinuity in the EOS at V_J .

for negative pressures. (Continuity is preserved at positive pressures.)

A third and more subtle problem resulting from the join is the T^2 term in the energy in the van der Waals region. At very low densities, the EOS should go over to an ideal gas at high temperatures. The T^2 behavior is an artifact of the join. In practice, however, this problem is not serious since in most calculations, when material reaches these densities, it will have cooled adiabatically on rarefaction, and temperatures high enough to make the T^2 term important are not actually encountered. It would still be desirable to eliminate the T^2 term at very expanded volumes, and this should probably be done in a better join routine.

The present EOS treats the liquid-vapor region below the critical temperature with a series of isotherms showing van der Waals loops. One should really

put in the proper phase boundaries and perform a Gibbs construction, so that the pressure would be constant on an isotherm in the two-phase region. One might suspect that such loops would give rise to imaginary sound speeds. This is actually not the case, however, since isentropes are steep enough that their slopes are always positive in the P - ρ plane.

The final problem calling for attention is the temperature calculated on compression. Because of the approximations in the representation of $E_0(V)$, the thermal energy $E - E_0(V)$ is poorly calculated when E is comparable to $E_0(V)$. This also means that the temperature is poorly calculated for this case. We have shown earlier that the effect on the calculated pressure is small, since the temperature appears only in a correction term. However, an improvement in the approximation for $E_0(V)$ would still appear useful.

Acknowledgments

I am grateful to Richard Grover and David Young for their continued advice and technical assistance, and to Edwin

Collins for programming the EOS. Portions of this work were supported by Defense Nuclear Agency.

Appendix A

The Equation-of-State

The complete GRAY three-phase equation of state is given by the following expressions:

1. INPUT PARAMETERS

- (A-1) $V_0 = 1/\rho_0$ —Normal volume of solid— cm^3/g .
- (A-2) C, S —Hugoniot parameters— $U_s = C + S U_p$ — $\text{cm}/\mu\text{sec}$. (16)
- (A-3) γ_0, a —Lattice gamma— $\gamma(V) = \gamma_0 - ax$. (33)
- (A-4) γ_{0m}, a_m —Melting gamma— $\gamma_m(V) = \gamma_{0m} - a_m x$ —normally equal to lattice gamma. (50)
- (A-5) γ_e —Electronic gamma—normally = $2/3$.
- (A-6) g_e —Electronic energy coefficient— $\text{Mbar cm}^3/\text{mole deg}^2$.
- (A-7) T_{m0} —Melting temperature parameter—deg.
- (A-8) ΔS —Entropy of melting—normally = $9.637 \times 10^{-5} \text{ Mbar cm}^3/\text{mole deg}$.
- (A-9) E_{0H} —Energy at $V = V_0, T = 300^\circ\text{K}, P = 0$ — $\text{Mbar cm}^3/\text{g}$ —normally = 0.
- (A-10) A —Atomic weight— g/mole .
- (A-11) V_J —Volume where equations of state are joined— cm^3/g .
- (A-12) V_b —Excluded volume for vapor phase— cm^3/g .
- (A-13) a_Y —Coefficient of attractive potential for vapor— $\text{Mbar (cm}^3/\text{mole)}^2$.
- (A-14) θ —Join parameter—normally = 1.

2. PARAMETERS CALCULATED AND USED IN CODE

- (A-15) $G' = g_e/A$ — $\text{Mbar cm}^3/\text{g deg}^2$.
- (A-16) $\Delta S' = \Delta S/A$ — $\text{Mbar cm}^3/\text{g deg}$.
- (A-17) $\alpha' = \alpha/A$ — $\text{Mbar cm}^3/\text{g deg}$, α = temperature coefficient of specific heat = $1.3 \times 10^{-5} \text{ Mbar cm}^3/\text{mole deg}$.
- (A-18) $R' = R/A$ — $\text{Mbar cm}^3/\text{g deg}$, R = gas constant = $8.134 \times 10^{-5} \text{ Mbar cm}^3/\text{mole deg}$.
- (A-19) $M = T_G/T_{m0} = 3R/2\alpha$, a constant = 9.38.
- (A-20) $P_{cc} = (300)^2 G'(\gamma_0 - \gamma_e)/2V_0$ — Mbar .
- (A-21) $E_{00} = -300(3R + 150 g_e)/(A)$ — $\text{Mbar cm}^3/\text{g}$ ($= E_{0K} - E_{0H}$, where E_{0K} is energy at $V = V_0, T = 0$)
- (A-22) $a'_Y = a_Y/(A)^2$ — $\text{Mbar (cm}^3/\text{g)}^2$.
- (A-23) $x_J = x(V = V_J)$.
- (A-24) $z_J = z(V = V_J)$.
- (A-25) $E_{0J} = E_0 (x = x_J)$.
- (A-26) $T_{mJ} = T_m (x = x_J)$.
- (A-27) $\lambda_J = \lambda (x = x_J)$.

$$(A-28) \quad D_1 = E_{0J} + T_{mJ} \left[\Delta S' - \frac{1}{2} \alpha' (1 - M^2) \right] + a_Y' / V_0 (1 - x_J) - \text{Mbar cm}^3 / \text{g}.$$

$$(A-29) \quad D_2 = \frac{3}{2} R' - M \alpha' - \text{Mbar cm}^3 / \text{g deg}.$$

$$(A-30) \quad D_3 = \frac{1}{2} G' - \text{Mbar cm}^3 / \text{g deg}^2.$$

$$(A-31) \quad P_{1J} = P_1 (x = x_J, E = D_1 - a_Y' / V_J) - \text{Mbar}.$$

$$(A-32) \quad C_1 = P_{1J} - \frac{T_{mJ} (\lambda_J + \gamma_0 - a x_J) \left[\Delta S' - \frac{1}{2} \alpha' (1 - M^2) \right]}{V_0 (1 - x_J)} + \frac{a_Y'}{V_0^2 (1 - x_J)^2} - \text{Mbar}.$$

$$(A-33) \quad C_2 = \frac{(\gamma_0 - a x_J)}{V_0 (1 - x_J)} (D_2 + \frac{3}{2} R') + \frac{\alpha' M (\lambda_J + \gamma_0 - a x_J)}{V_0 (1 - x_J)} - \frac{R'}{V_0 (1 - x_J)} \left[\frac{1 + z_J + z_J^2 - z_J^3}{(1 - z_J)^3} \right] - \text{Mbar/deg}.$$

$$(A-34) \quad C_3 = \frac{\gamma_e G'}{2 V_0 (1 - x_J)} - \text{Mbar/deg}^2.$$

3. VARIABLES

$$(A-35) \quad V - \text{specific volume} - \text{cm}^3 / \text{g}$$

$$V = \frac{V_0}{1 + \mu} = V_0 (1 - x).$$

$$(A-36) \quad \mu - \text{usual hydrodynamic compression variable.}$$

$$\mu = \frac{V_0 - V}{V} = \frac{x}{1 - x}.$$

$$(A-37) \quad x - \text{compression variable}$$

$$x = \frac{V_0 - V}{V_0} = \frac{\mu}{1 + \mu}.$$

$$(A-38) \quad z = V_b / V = V_b / V_0 (1 - x).$$

$$(A-39) \quad \epsilon = \text{usual hydrodynamic energy variable} - \text{Mbar cm}^3 / (\text{cm}^3)_0.$$

$$(A-40) \quad E = \text{Energy} = V_0 \epsilon - \text{Mbar cm}^3 / \text{g}.$$

$$(A-41) \quad T = \text{Temperature} - \text{deg (may be output if desired)}.$$

$$(A-42) \quad E_0(x) = \text{Energy on cold compression} - \text{Mbar cm}^3 / \text{g}$$

$$= \frac{C^2 x^2}{2(1 - Sx)} \left[1 + \frac{Sx}{3} + \frac{S^2}{6} \left(1 - \frac{\gamma_0}{S} \right) x^2 \right] + E_{00} (1 + \gamma_0 x) + E_{0H}. \quad (48)$$

$$(A-43) \quad T_m(x) = \text{"Melting Temperature"} - \text{deg}.$$

$$= \frac{T_{m0}}{(1 - x)^2} \left\{ 1 + 2 \left(\gamma_{0m} - \frac{4}{3} \right) x + \left[\left(2\gamma_{0m} - \frac{5}{3} \right) \left(\gamma_{0m} - \frac{4}{3} \right) - a_m \right] x^2 \right\}, \quad x \leq 0, \quad (58)$$

$$\text{or} = T_{m0} \left\{ 1 + \left(2\gamma_{0m} - \frac{2}{3} \right) x + \left[\left(\gamma_{0m} - \frac{1}{3} \right) \left(2\gamma_{0m} + \frac{1}{3} \right) - a_m \right] x^2 \right\}, \quad x \geq 0. \quad (54)$$

- (A-44) $T_G(x)$ = Temperature where C_v in liquid drops to $\frac{3}{2} R$ —deg
 $= M T_m(x)$, $M = 9.38$.
- (A-45) $\lambda(x) = (d \ln T_m / d \ln V) = -2\gamma_m(x) + \frac{2}{3} = \left(-2\gamma_{0m} + \frac{2}{3}\right) + 2a_m x$. (49), (50)
- (A-46) $2\delta T(x)$ = Temperature change on melting at constant V —deg

$$= \frac{\Delta S' \cdot D^2 \cdot T_m^2}{(1.2) C^2 (1-x) f(x)}$$
, (62)
- (A-47) $f(x) = [1 + (4S - 1)x]$, $x \geq 0$; $f(x) = 1$, $x \leq 0$.
- (A-48) $E_{m1}(x)$ = Energy on solidus
 $= E_0 + 3R'(T_m - \delta T) + \frac{1}{2} G'(T_m - \delta T)^2 - \text{Mbar cm}^3/\text{g}$.
- (A-49) $E_{m2}(x)$ = Energy on liquidus
 $= E_0 + 3R'(T_m + \delta T) + \frac{1}{2} G'(T_m + \delta T)^2$
 $+ T_m \left\{ \Delta S' - \frac{1}{2} \alpha' \left[1 + \frac{(T_m + \delta T)^2}{T_m^2} \right] \right\} - \text{Mbar cm}^3/\text{g}$.
- (A-50) $E_{GG}(x)$ = Energy above which C_v is constant
 $= E_0 + 3R' T_G + \frac{1}{2} G' T_G^2 + T_m \left[\Delta S' - \frac{1}{2} \alpha' (1 + M^2) \right] - \text{Mbar cm}^3/\text{g}$.
- (A-51) $\nu(x, E)$ = Progress variable for transformation in melt region
 $= (E - E_{m1}) / (E_{m2} - E_{m1})$.
- (A-52) P = Total pressure—Mbar, normal output.
- (A-53) $P_1(x, E)$ = Linear Grüneisen pressure

$$= \frac{C^2 x}{V_0 (1-x)(1-Sx)^2} \left[1 - \left(1 + \frac{\gamma_0}{2}\right) x + \frac{a}{2} x^2 \right]$$

 $+ \frac{(\gamma_0 - ax)}{V_0 (1-x)} (E - E_{0H}) - \text{Mbar}$. (22), (23)
- (A-54) P_c = Correction pressure—Mbar.

4. PRELIMINARY CALCULATIONS

Enter with usual hydrodynamic variables (μ, ϵ) .

Calculate $E(\epsilon)$, $x(\mu)$.

Branch, if $x < x_J$, go to liquid-vapor EOS, 6.

Otherwise calculate $E_0(x)$, $T_m(x)$, $T_G(x)$, $\lambda(x)$, $\delta T(x)$,

$E_{m1}(x)$, $E_{m2}(x)$, $E_{GG}(x)$, $P_1(x, E)$.

5. SOLID-LIQUID CALCULATION

Branch:

- (A-55) $E \leq E_{m1}$ — Solid.
- (A-56) $E_{m1} < E < E_{m2}$ — Melt (two-phase).
- (A-57) $E_{m2} \leq E \leq E_{GG}$ — Liquid.
- (A-58) $E_{GG} < E$ — Hot liquid.

Solid:

- (A-59) $T = \frac{1}{G'} \left\{ -3R' + \left[(3R')^2 + 2G' (E - E_0) \right]^{1/2} \right\}. \quad (1), (3)$
- (A-60) $P_c = \frac{1}{2 V_0 (1-x)} (\gamma_e - \gamma_0 + ax) G' T^2. \quad (24)$
- (A-61) $P = P_1 + P_c + P_{cc}.$

Melt:

- (A-62) $\nu = (E - E_{m1}) / (E_{m2} - E_{m1}).$
- (A-63) $T = \frac{1}{G'} \left(-[3R' + \nu(\Delta S' - \alpha')] + \left\{ [3R' + \nu(\Delta S' - \alpha')]^2 + 2G' [E - E_0 + \nu^2 \delta T (\Delta S' - \alpha')] \right\}^{1/2} \right). \quad (1), (5)$
- (A-64) $P_c = \frac{1}{V_0 (1-x)} \left\{ \frac{1}{2} (\gamma_e - \gamma_0 + ax) G' T^2 - \nu(\Delta S' - \alpha') [\lambda T_m + (T - \nu \delta T)(\gamma_0 - ax)] \right\}. \quad (24), (25)$
- (A-61) $P = P_1 + P_c + P_{cc}.$

Liquid:

- (A-65) $T = \frac{1}{\left(G' - \frac{\alpha'}{T_m}\right)} \left(-3R' + \left\{ (3R')^2 + 2 \left(G' - \frac{\alpha'}{T_m}\right) \times \left[E - E_0 - T_m \left(\Delta S' - \frac{1}{2} \alpha' \right) \right] \right\}^{1/2} \right). \quad (1), (7)$
- (A-66) $P_c = \frac{1}{V_0 (1-x)} \left\{ \frac{1}{2} (\gamma_e - \gamma_0 + ax) G' T^2 - T_m \left[\Delta S' - \frac{1}{2} \alpha' \times \left(1 + \frac{T^2}{T_m^2} \right) \right] (\lambda + \gamma_0 - ax) \right\}. \quad (24), (26)$
- (A-61) $P = P_1 + P_c + P_{cc}.$

Hot Liquid:

- (A-67) $T = \frac{1}{G'} \left[- (3R' - M\alpha') + \left\{ (3R' - M\alpha')^2 + 2G' \left\{ E - E_0 - T_m \left[\Delta S' - \frac{1}{2} \alpha' (1 - M^2) \right] \right\} \right\}^{1/2} \right]. \quad (9), (11)$

$$(A-68) \quad P_c = \frac{1}{V_0(1-x)} \left(\frac{1}{2} (\gamma_e - \gamma_0 + ax) G'T^2 - T_m \left\{ \Delta S' - \frac{1}{2} \alpha' \right. \right. \\ \left. \left. \times \left[1 - M^2 + 2M(T/T_m) \right] \right\} (\lambda + \gamma_0 - ax) \right). \quad (24), (27)$$

$$(A-61) \quad P = P_1 + P_c + P_{cc}.$$

6. LIQUID-VAPOR CALCULATION

Calculate $z(x)$.

$$(A-69) \quad F_e = \frac{V_b}{2} \left[\frac{(\theta - z_J)^3 (2z - 2 + \theta)}{z_J^3 (\theta - z)^2} - \frac{(\theta - z_J)(2z_J - 2 + \theta)}{z_J^3} \right]. \quad (86)$$

$$(A-70) \quad T = \left\{ (3R' + 2D_2) - \left[(3R' + 2D_2)^2 - 16 \left(E + \frac{a_Y'}{V_b} z - C_1 F_e - D_1 \right) \right. \right. \\ \left. \left. \times (C_3 F_e - D_3) \right]^{1/2} \right\} / 4(C_3 F_e - D_3). \quad (87)$$

$$(A-71) \quad F_p = \left[\frac{z(\theta - z_J)}{z_J(\theta - z)} \right]^3. \quad (83)$$

$$(A-72) \quad P = \left(\frac{R'T}{V_b} \right) \frac{z(1 + z + z^2 - z^3)}{(1 - z)^3} - \left(\frac{a_Y'}{V_b^2} \right) z^2 + F_p (C_1 + C_2 T + C_3 T^2). \quad (79)$$

Several preliminary versions of the GRAY or three-phase equation of state have had limited circulation, most recently in an LLL internal report.¹⁷ The notation used has changed from time to time, and Table A-1 lists changes in notation. The present equation of state is otherwise identical to Ref. 17 (with the formula for ΔT corrected). It differs from some earlier versions with regard to formulas or values for the following quantities: $A_t (= 1)$, $P_a (= a_Y' = a_Y/A^2)$, ΔT_J (omitted), C_3 (simplified), F_e (corrected), T_m (altered), and $\Delta T (= 2\delta T, \text{ altered})$.

Table A-1. Notation.

This report	Ref. 3	Ref. 4	Ref. 17	Early reports
A			AW	AW
a_Y		a	a_Y	
a'_Y			a'_Y	P_a
$\Delta S'$	$\Delta S/A$		D'_S	D'_S
R'	R/A	R/A	R'	R'
α'	α/A		A'	A'
G'	g_e/A		G'	G'
λ	(μ)		D	D
λ_J			D_J	D_J
T_G	T_G		$T_{\max}$	$T_{\max}$
δT	$(\Delta T/2)$		$\Delta T/2$	$\Delta T/2$
E_{GG}			$E_{\max}$	$E_{\max}$

Appendix B.

Equation-of-State Parameters

As outlined in Appendix A or in Ref. 17, the GRAY equation of state appears to have 17 independent input parameters. This is to allow the EOS to accommodate a rather large body of experimental thermodynamic data, should it be available on a particular metal. In various sections of this report, we outline methods of evaluating these parameters from the data, or of otherwise estimating values for them. In this appendix we summarize these procedures in one place for the convenience of the reader who may wish to develop parameters for some metal not listed in Table B-1, and we outline a simplified parameterization for use with limited data.

A fairly decent EOS can be developed with only five pieces of input data: (1) the normal density or specific volume, $V_0 = \rho_0^{-1}$; (2) the bulk modulus β , or intercept of the $U_s - U_p$ Hugoniot plot, $\beta = \rho_0 C^2$; (3) the normal melting temperature, T_{mN} ; (4) the atomic weight, A ; and (5) the cohesive energy or energy of sublimation, E_{coh} . It is difficult to imagine a three-phase EOS that would demand less input than this. For alloys, atomic-weighted mean values of these quantities may be used.

If there are Hugoniot data available,^{2,18} S (and C) can be evaluated from Eq. (16); otherwise S may be taken as 1.4. Various methods of getting values of γ_0 and a are outlined in section III-E, as are procedures for getting values of the melting parameters γ_{0m} , a_m , ΔS , and T_{m0} . Usually γ_0 is taken as the thermodynamic lattice value, $a = \gamma_0 - 0.5$, $\gamma_{0m} = \gamma_0$, $a = a_m$, and $S = 9.637 \times 10^{-5}$ Mbar-cm³/mole-deg (2.3 cal/mole-deg). T_{m0} is evaluated from T_{mN} or may be taken as $1.30 T_{mN}$. All of these procedures are summarized at the end of section III-E.

γ_e should normally be taken as two-thirds. Similarly, g_e (or G') should be evaluated from Eqs. (13) and (14). For this purpose, the effective number of free electrons per metal atom may be taken as the number of electrons outside a closed atomic shell (generally the column number of the metal in the usual periodic table). All of this is, of course, a free-electron model. Where there is strong evidence of important non-free-electron behavior at densities and temperatures of interest, different values may be given to γ_e and g_e , but this should be done only under unusual conditions and based on a complete familiarity with electronic equations of state.^{1,9}

E_{0H} is simply a reference energy, and may be given any value convenient for the problem at hand. Usually, $E_{0H} = 0$.

Methods of getting values of the van der Waals and join parameters V_J , V_b , a_Y , and θ are given in section IV-C. Generally, V_b is evaluated as $0.50 V_0$ or from liquid density data, V_J and θ are determined by conditions at the join point, and a_Y is determined from the cohesive energy.

Table B-1 lists GRAY EOS parameter values for 16 engineering metals. These values are identical to those given in Ref. 17. Appendix C outlines details of the calculation of T_{m0} , V_J , and a_Y (or a_Y').

Table B-1. Equation-of-state parameters.

Material	V_0 (cm ³ /g)	C (cm/ μ sec)	S	γ_0	a	$\frac{g_e \times 10^9}{\left(\frac{\text{Mbar} \cdot \text{cm}^3}{\text{Mole} \cdot \text{deg}^2}\right)}$	$T_{m0} \times 10^{-3}$ (deg)	AW (g/mole)	V_J/V_0	V_b/V_0	a_Y Mbar- (cm ³ /mole) ²
Be	0.540	0.800	1.124	1.16	1.0	4.8	1.82	9.01	1.55	0.49	24
Mg ^a	.562	.452	1.242	1.63	1.3	9.7	1.15	24.31	1.41	.50	41
Al ^b	.359	.533	1.338	2.18	1.7	8.7	1.22	26.98	1.32	.53	47
Ti ^c	.221	.470	1.146	1.3	1.1	10.1	2.26	47.90	1.43	.58	68
Stainless ^d	.1265	.457	1.490	2.0	1.5	9.6	2.38	55.38	1.40	.51	44
Ni	.1124	.465	1.445	2.00	1.5	10.1	2.33	58.71	1.38	.51	41
Monel ^e	.1135	.419	1.54	1.99	1.5	10.4	2.27	59.84	1.42	.50	38
Cu	.1118	.394	1.489	1.97	1.5	4.9	1.79	63.54	1.37	.50	35
Nb	.1167	.444	1.207	1.74	1.4	11.2	3.53	92.91	1.39	.51	116
Ta	.0602	.341	1.200	1.82	1.4	11.2	4.34	180.95	1.40	.50	121
W	.0518	.403	1.237	1.78	1.4	10.9	4.52	183.85	1.34	.50	102
Au	.0518	.308	1.560	3.09	2.5	6.2	1.97	196.97	1.30	.50	78
Pb	.0882	.201	1.54	2.84	2.3	14.7	.76	207.2	1.24	.48	49
Th	.0855	.213	1.278	1.41	1.2	15.5	2.39	232.0	1.47	.46	186
Mulberry ^f	.0602	.250	1.50	2.00	1.5	13.6	1.42	223.5	1.27	.42	108
U	0.0524	0.254	1.549	2.07	1.5	13.0	1.71	238.1	1.29	0.48	96

NOTE: $\gamma_{0m} = \gamma_0$ $a_m = a$ $\gamma_e = 2/3$ $\Delta S = 9.637 \times 10^5$ Mbar cc/mole deg
(= 2.3 cal/mole deg) $E_{0H} = 0$ $\theta = 1.0$, except $\theta = 1.1$ for Mg and Au^aMg - Alloy AZ31B, 96% Mg, 3% Al, 1% Zn.^bAl - Alloy 2024, 93.5% Al, 4.5% Cu, 1.5% Mg, 0.5% Mn.^cTi - Good representation at high pressure and/or high temperature. Solid below 0.2 Mbar only a fair representation because phase transition is ignored.^dStainless - Alloy 304, 72% Fe, 19% Cr, 9% Ni.^eMonel - Alloy 400, 66% Ni, 31.5% Cu, 1.5% Fe, 1% Mg.^fMulberry - Alloy, 90% U, 7.5% Nb, 2.5% Zr.

Appendix C.

Evaluation of Parameters T_{m0} , V_J , and $a_Y (a_Y')$

The evaluation of T_{m0} and V_J first requires a procedure for exploring the $P = 0$ isobar at volumes expanded from V_0 . This is most easily done by rewriting Eq. (22) in the form

$$P = P_a(V) + P_b(V) \cdot (E - E_{0H}) + P_c(T, V), \quad (C-1)$$

where $P_a(V)$, $P_b(V) \cdot (E - E_{0H})$ and $P_c(T, V)$ are the first, second, and third terms on the right-hand side of Eq. (22), respectively. Obviously,

$$P_1(V, E) = P_a(V) + P_b(V) \cdot (E - E_{0H}) \quad (C-2)$$

[cf. Eq. (23).] Using Eqs. (24), (25), (26), and (27), we have $P_c(T, V)$, and solving for T in Eqs. (1), (3), (5), (7), (9), and (11), we can get $P_c(V, E)$. This procedure is laid out in detail in Appendix A. We must now set $P = 0$ in Eq. (C-1) and solve for $E(V)$. With a computer, this is most easily done by successive approximation, noting that the P_c term is small compared to the P_a and P_b terms. We simply write

$$E_{(n)}(V) = - \frac{P_a(V) + P_c[V, E_{(n-1)}(V)]}{P_b(V)}, \quad (C-3)$$

where $E_{(n)}(V)$ is the n th trial value of $E(V)$. This procedure is found to converge well for the real EOS. The starting approximation can be taken as $E_{(0)}(V) = -P_a(V)/P_b(V)$.

From the above procedure, we get $E(V)$ at $P = 0$. We may then take this (V, E) pair, enter the EOS, and determine what state region the material is in. As detailed in Appendix A, this simply involves comparing the energy E with the quantities $E_{m1}(V)$, $E_{m2}(V)$, and $E_{GG}(V)$.

To calculate T_{m0} from T_{mN} , we carry out the procedure above, starting out by approximating T_{m0} as $1.30 T_{mN}$, and carry out the foregoing procedure for various volumes until we find a melt volume V_m , where $E(V_m) = E_{m1}(V_m)$. If T_{m0} were correct, we would find $T_{mN} = T_m(V_m) - \delta T(V_m)$, [Eq. (64)]. If this is not the case, we get a new approximation to T_{m0} as

$$T_{m0 \text{ new}} = \frac{T_{m0 \text{ old}} \cdot T_{mN}}{T_m(V_m) - \delta T(V_m)}. \quad (C-4)$$

This process is then repeated, and successive approximations to T_{m0} are found to converge to the desired value.

The calculation of V_J proceeds similarly. In this case, we search for a volume V_J such that at $P = 0$, $E(V_J) = E_{GG}(V_J)$. This is equivalent to Eq. (92).

The evaluation of a_Y' from the cohesive energy proceeds from Eq. (91), where we must recall that C_1 and D_1 are functions of a_Y' . a_Y' could be adjusted by trial and error so that Eq. (91) would yield the correct experimental value of E_{coh} . However, from Eqs. (80) and (88), we have

$$a_Y' = \frac{[E_{coh} + E_{00} + E_{0H} - E^{(1)} - P^{(1)} F_e(z=0)] V_J^2}{[V_J + F_e(z=0)]} \quad (C-5)$$

$P^{(1)}$ and $E^{(1)}$ may be most easily identified by comparing Eqs. (80) and (88) with the expressions for C_1 and D_1 given in Appendix A.

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