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THE MELTING OF SOLID AND POROUS ALUMINUM UNDER SHOCK COMPRESSION

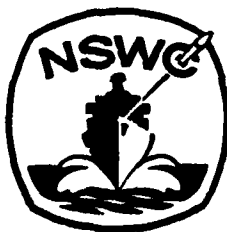
BY CLINTON T. RICHMOND

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The melting point of shock compressed aluminum is calculated according to the prediction of the Lindemann law and the Gruneisen equation of state. The position of this point on the Lindemann melting curve varies with two parameters - the initial state and the porosity of aluminum. Because the Hugoniot of aluminum depends upon these parameters, variation in either the initial state or the porosity implies a family of Hugoniots. Normally, a characteristic (complete)		

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equation of state is needed to determine these Hugoniot. But, in this work a family of Hugoniot is derived for each parameter by using the Gruneisen equation of state and a single experimental Hugoniot. Several melting points are calculated corresponding to various values of the parameter of a Hugoniot. These melting points, Hugoniot, and other thermal properties calculated from the theory are in excellent agreement with the data cited.

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CHAPTER 1
INTRODUCTION

Zel'Dovich¹ and Kormer² have pointed out the difficulties in attempting to measure temperatures in opaque solids. As a result, only limited data on temperatures at the melting state of a solid at ultra high pressures are available. However, a number of attempts have been made to calculate melting state temperatures by constructing the solid's equations-of-state. This approach was used by Urlin^{3,4} and Ivanov³ in attempts to calculate the melting points of the elements aluminum, copper, nickel, and lead at high, Hugoniot pressures. Except for some agreement on the pressures required for melting these elements, there is considerable difference between the melting temperatures. In the first treatment, Urlin uses the Lindemann law in conjunction with an equation of state to calculate the melting states of each metal. This particular procedure is supported by O'Keefe⁵ who has shown, in the case of copper, that the Lindemann law gives an accurate description of the experimentally determined melting states⁶ of a solid.

¹ Zel'Dovich, Ia. M.I.T. B. and Raiser, Ia. P., "Physical Phenomena that Occur When Bodies Compressed by Strong Shock Waves Expand in Vacuo," Soviet Physics, JETP, Vol. 35(8), No. 6, p. 980, June 1959.

² Kormer, S. B., Sinitsyn, M. V., Kirillov, G. A., and Urlin, V. D., "Experimental Determination of Temperature in Shock-Compressed NaCl and KCl and of Their Melting Curves at Pressures Up to 700 kbar," Soviet Physics JETP, Vol. 8, No. 4, p. 689, October 1963.

³ Urlin, V. D. and Ivanov, A. A., "Melting Under Shock-Wave Compression," Soviet Physics Doklady, Vol. 8, No. 4, p. 380, October 1963.

⁴ Urlin, V. D., "Melting at Ultra High Pressures in a Shock Wave," Soviet Physics JETP, Vol. 22, No. 2, p. 341, February 1966.

⁵ O'Keefe, David J., "Melting of Solids with a Linear $U_s - U_p$ Relationship," Applied Physics Letters, Vol. 21, No. 8, p. 360, 15 October 1972.

⁶ Mitra, N. R., Decker, D. L., and Vanfleet, H. B., "Melting Curves of Copper, Silver, Gold, and Platinum to 70 kbar," Physical Review, Vol. 161, No. 3, p. 613, 15 September 1967.

O'Keefe's technique⁷ minimizes the number of approximations needed in the equation of state. Thus, more reliability is provided to his predictions. On the other hand, the equation-of-state used by Urlin contain additional approximations, such as, constant specific heat capacity and the Dugdale-MacDonald formula⁸ for the Gruneisen parameter. Pastine⁹, White¹⁰, and Anderson have demonstrated the inadequacy of the Dugdale-MacDonald formula.

In this report, O'Keefe's procedure will be used to recalculate the melting point of aluminum on its Hugoniot by using a Gruneisen equation of state which does not contain any of the approximations already mentioned. Pastine¹¹, Forbes, and O'Keefe⁷ have shown that this equation-of-state gives an accurate description of the thermal properties of a metal. A more detailed description of this equation and how it is used to calculate the temperature on the Hugoniot as a function of pressure are discussed in Chapters 2 and 4.

A Hugoniot describes the behavior of a specific property of a material as it is compressed through various shock states. A Hugoniot for any flow or thermal property is derivable from the shock relations and a characteristic equation of state. It is clear from the shock relations that the initial state and the initial porosity are parameters of the Hugoniot. A family of Hugoniots can be generated by simply varying either parameter.

A characteristic equation of state is not used for porous aluminum. Instead, a Gruneisen equation of state is used to generate a family of Hugoniots from a single experimental Hugoniot. This procedure is described in Chapter 3.

⁷O'Keefe, David, J., "Accurate Pressure, Volume, Temperature Relations for Copper," Journal of Geophysical Research, Vol. 75, p. 1947, 1970.

⁸Dugdale, J. S. and MacDonald, D. K. C., "The Thermal Expansion of Solids," Physical Review, Vol. 89, No. 4, p. 832, February 1953.

⁹Pastine, D. John, "Formulation of the Gruneisen Parameter for Monatomic Cubic Crystals," The Physical Review, Vol. 138, No. 3A, p. A767, May 1965.

¹⁰White, G. K. and Anderson, O. L., "Gruneisen Parameter of Magnesium Oxide," Journal of Applied Physics, Vol. 37, No. 1, p. 430, January 1966.

¹¹Pastine, D. John and Forbes, J. W., "Accurate Relations Determining the Volume Dependence of the Quasiharmonic Gruneisen Parameter," Physical Review Letters, Vol. 21, No. 23, p. 1582, December 1968.

The Lindemann law is used to describe the melting states in both solid and porous aluminum. Therefore, the melting point of aluminum is in a shock state satisfying both the Lindemann law and the Hugoniot of aluminum. Since the Hugoniot is parametric, there is a "family" of melting points corresponding to a family of Hugoniots due to a specific parameter. These melting points and their Hugoniots are compared with data cited from other reports. Thermal properties-e.g., the zero-degree isotherm, the enthalpy at zero pressure, the temperatures and pressures on the various Hugoniots-are calculated and compared to the results of other investigators.

CHAPTER 2

EQUATION OF STATE FOR ALUMINUM

Temperatures on a Hugoniot cannot be determined without an equation of state unless they are measured experimentally. In this section, an equation of state for aluminum will be described.

In simple solids, such as aluminum, copper, lead, etc., the Gruneisen equation^{7,11} of state is accurate enough for calculating Hugoniot temperatures. The components of this equation are the zero-degree isotherm, $P_0(x)$, the Gruneisen function, $\Gamma(x)$, and the specific thermal energy, $E_T(x,T)$. The variables are x , the compression ratio, and T , the temperature. In this case, the compression ratio is defined as

$$x = V/V_0$$

where V is the specific volume. The density of the solid is $\rho = 1/V$. A zero subscript on variables denotes their values at zero absolute temperature and zero pressure.

The Gruneisen equation of state for the pressure-volume-temperature relationship is

$$P(x,T) = P_0(x) + \rho_0 \Gamma(x) E_T(x,T)/x \quad (1)$$

in which $P(x,T)$ is the pressure. The second term in this equation is referred to as the thermal pressure.

The specific thermal energy for the metals of interest can be described reasonably well by the Debye relation

$$E_T(x,T) = 3 N_0 k T D(\theta/T)/M. \quad (2)$$

The constants in this equation are N_0 , k , and M which are respectively Avogadro's number, the Boltzmann constant, and the atomic or molecular weight of the solid. In Equation (2), $D(\theta/T)$ is the Debye function, and θ is the Debye temperature (see Appendix A). In the limit, $T = 0$, $E_T(x,0) = 0$.

The specific internal energy of a material may be written as

$$E(x,T) = \phi(x) + E_T(x,T) \quad (3)$$

where $\phi(x)$ is associated with the zero-degree isotherm and is defined as

$$\phi(x) = E(x, 0) \quad (4)$$

The zero-degree isotherm is defined by

$$P_0(x) = -\rho_0 \frac{d\phi(x)}{dx} \quad (5)$$

and the Gruneisen function is defined by the relation

$$\rho_0 \Gamma(x) = x \left(\frac{\partial P}{\partial E} \right)_x \quad (6)$$

However, a function defined by

$$\psi(x, T_i) = \rho_0 \left[\phi(x_i) - \phi(x) + E_T(x_i, T_i) \right] \quad (7)$$

is found more convenient to work with in describing the zero-degree isotherm along a Hugoniot which takes the form

$$S = a + bu \quad (8)$$

Here, S is the shock velocity and u is the particle velocity. The subscript i on a variable is used to indicate the initial value of that variable. It is clear from Equation (5) that

$$P_0(x) = \left(\frac{\partial \psi}{\partial x} \right)_{T_i} \quad (9)$$

in terms of $\psi(x, T_i)$ as expressed by Equation (7). The function $\psi(x, T_i)$ and $\left(\frac{\partial \psi}{\partial x} \right)_{T_i}$ are calculated by solving the differential equation,

$$\left(\frac{\partial \psi}{\partial x} \right)_{T_i} + \Gamma(x) \psi / x = \rho_0 a^2 (x_i - x) \left[2x - \Gamma(x) (x_i - x) / 2x x_i - b(x_i - x)^2 \right] \quad (10)$$

which is valid on the shock Hugoniot. See Appendix B for a derivation of this equation. In this equation, $\rho_0 = 2.7334$ g/cc, the initial state parameters^{12,13} are $a = 5.4$ km/sec, $b = 1.351$, and $x_i = 0.0127$ at

¹² Simmons, Gene and Wang, Herbert, Single Crystal Elastic Constants Calculated Aggregate Properties: A Handbook, Cambridge, Mass., The M. I. T. Press, pp. 4-8, 1971.

¹³ Mitchell, A. C. and Shaner, J. W., Lawrence Livermore Laboratory, University of California, Livermore, California 94550 (Private Communication).

$T_i = 298^\circ\text{K}$ for aluminum. The computed boundary conditions are

$$\psi(x_i, T_i) = \rho_0 E_T(x_i, T_i) = 4.4918 \text{ kbars cc/g}, \quad (11)$$

$$P_0(x_i) = \left. \frac{\partial \psi}{\partial x_i} \right|_{T_i} = -\Gamma(x_i) \psi(x_i, T_i)/x_i = -9.96911 \text{ kbars}. \quad (12)$$

$E_T(x_i, T_i)$ is calculated from Equation (2) with an initial Debye temperature taken from Reference 14 and adjusted to the value $\theta_i = 386.059$ so that the condition

$$P(1,0) = P_0(1) = 0$$

is satisfied. This condition describes the uncompressed state of aluminum at $V = V_0$ and $T = 0^\circ\text{K}$. An explicit expression for the Gruneisen function, defined by Equation (6), has been derived by Pastine and Forbes.¹¹ The value of $\Gamma(x_i)$ in Equation (12) is calculated by using this expression. See Appendix C.

¹⁴Gschneidner, Jr., Karl A., "Physical Properties and Interrelationships of Metallic and Semi-Metallic Elements," Solid State Physics Advances in Research and Applications, New York, Academic Press, Vol. 16, p. 369, 1965.

CHAPTER 3 GENERATING A FAMILY OF HUGONIOTS

A strong shock wave can raise the temperature of a solid to the point of melting. This melting point is one of the shock states specified by a Hugoniot of the solid. Thus, a Hugoniot must be known before the melting point on it can be determined. In this section, a procedure will be described for calculating a family of Hugoniots from a single experimental Hugoniot, the Gruneisen equation of state, and the shock relation¹⁵ for the conservation of energy.

From an experimental Hugoniot of the type given by the shock velocity, particle velocity relation the pressure in Equation (8), can be calculated by eliminating $E(x, T)$, $\phi(x)$, and $E_T(x, T)$ from equations (1), (3), (7), and the Hugoniot relation

$$E - E_i = (x_i - x)(P + P_i)/2\rho_0 \quad (13)$$

for the conservation of energy across a shock front (see Appendix B). The result at $P_i = 0$ is

$$P(x, T_i) = \frac{P_0(x) + (x) \psi(x, T_i)/x}{1 - \Gamma(x)(x_i - x)/2x} \quad (14)$$

This form of the Hugoniot clearly indicates that the pressure is dependent upon the initial state of the material. All of the initial state parameters associated with Equation (14), i.e., a , b , x_i , $\phi(x_i)$, $E_t(x_i, T_i)$, etc. can be viewed as functions of the initial temperature, T_i . Therefore, Equation (14) represents a one-parameter family of Hugoniots, and each member of the family is distinguished by its initial temperature. Consequently, a different Hugoniot is obtained each time the initial temperature, T_i , changes to another initial temperature, T'_i . The resulting Hugoniot pressure, $P(x, T'_i)$, can readily be obtained from Equation (14) by evaluating $\psi(x, T'_i)$ and x_i .

¹⁵Landau, L. D. and Lipshitz, E. M., Fluid Mechanics, New York, Bergman Press, p. 319, 1975.

The compression ratio, x_i' , at a temperature of T_i' can be calculated from experimental information on the density of the material¹². The function, $\psi(x, T_i')$, may be evaluated by observing that for an initial temperature of T_i' , Equation (7) becomes

$$\psi(x, T_i') = \rho_0 [\phi(x_i') - \phi(x) + E_T(x_i', T_i')]. \quad (15)$$

If $x = x_i'$ in Equation (7), then its value is

$$\psi(x_i', T_i) = \rho_0 [\phi(x_i) - \phi(x_i') + E_T(x_i, T_i)] \quad (16)$$

Elimination of $\phi(x)$, $\phi(x_i)$, $\phi(x_i')$, and $E_T(x_i, T_i)$ from Equations (7), (15), and (16) leads immediately to

$$\psi(x, T_i') = \psi(x, T_i) - \psi(x_i', T_i) + \rho_0 E_T(x_i', T_i'). \quad (17)$$

Making use of the boundary conditions from Equations (11) and (12) for an initial temperature of T_i' , Equation (17) reduces to

$$\psi(x, T_i') = \psi(x, T_i) - \psi(x_i', T_i) - x_i' P_0(x_i') / \Gamma(x_i'). \quad (18)$$

Each term on the right of Equation (18) can be evaluated from the solution of Equation (10) which can be obtained from a single known Hugoniot. (The third term on the right side of Equation (17) could be calculated using Equation (2), but this is not needed.)

Since the new initial temperature, T_i' , is arbitrary, a family of Hugoniots, $P(x, T_i')$, in the form of Equation (14), can be calculated by using Equation (18), which is evaluated from data along a single Hugoniot.

CHAPTER 4

MELTING OF ALUMINUM ON A SHOCK HUGONIOT

A procedure is described in this section for calculating the melting temperature on any member of the family of Hugoniot for aluminum. The first step in this procedure is to eliminate x between Equations (1) and (14) to obtain the temperature which can be expressed in the form

$$T = f(P, T_i) \quad (19)$$

Without the single experimental Hugoniot of Equation (8), this result could not be achieved without a characteristic equation of state.¹⁶ For example, an equation of state in the form $E = E(x, P)$ is sufficient to produce a family of Hugoniot of the form $P = P(x, T_i)$ from Equation (13). However, without additional information, the temperatures on these Hugoniot cannot be calculated.

Next, apply the Lindemann law^{5,17} for melting in the form

$$T = T_s (\theta/\theta_s)^2 (x/x_s)^{2/3}. \quad (20)$$

Here the subscript s refer to the static values of T , θ , and x for melting at a pressure of $P = 0$. These values^{12,18} are $T_s = 932^\circ\text{K}$, $\theta_s = 324.085^\circ\text{K}$, and $x_s = 1.07106$ for aluminum. Elimination of x between Equations (1) and (20) leads to a melting law which can be expressed in the form

$$T = g(P). \quad (21)$$

¹⁶Callen, Herbert B., Thermodynamics, New York, John Wiley and Sons, Inc., p. 50, 1960.

¹⁷Lindemann, F. A., "The Calculation of the Natural Molecular Frequency," Physikalische Zeitschrift, Vol. 11, p. 609, July 1910.

¹⁸Hultgren, Ralph, Orr, Raymond L., Anderson, Phillip D., and Kelley, Kenneth A., Selected Values of Thermodynamic Properties of Metals and Alloys, Berkeley, California, John Wiley and Sons, Inc., pp. 33-37, 1963.

The simultaneous solution to Equations (19) and (21) is the melting point of aluminum on a family-member Hugoniot. The solution will be denoted by

$$T_m = T_m(T_i), P_m = P_m(T_i) \quad (22)$$

which shows that the melting state (T_m, P_m) is dependent upon the initial temperature, T_i .

CHAPTER 5
THE HUGONIOT FOR POROUS ALUMINUM

Let V' represent the specific volume of porous aluminum, V_h , the specific volume of the holes, and V , the specific volume of the solid portion of aluminum, then

$$V' = V + V_h.$$

Dividing all specific volumes by V_0 leads to

$$x' = x + x_h. \quad (23)$$

Porosity, M , is defined by the ratio

$$M = \frac{V'}{V} = x'/x.$$

The initial porosity is

$$M_i = x'_i/x_i. \quad (24)$$

Assuming that the Gruneisen equation of state and the conservation law apply to porous aluminum, it follows immediately that Equation (14) is the Hugoniot of porous aluminum with the quantities x , x_i , and T_i replaced by x' , x'_i , and T'_i . Except for the initial values, thermal quantities do not depend significantly upon the details^{19,20,21} of compaction behavior at high pressures. This means that the shock pressure is too high to experience any substantial resistance to collapse in the porous part of the solid. After collapse, $x_h = 0$, and Equation (14) reduces to

$$P(x, T'_i) = \frac{P_0(x) + \Gamma(x) \psi(x, T_i)/x}{1 - \Gamma(x) (M_i x_i - x)/2x}. \quad (25)$$

¹⁹Herrmann, W., "Constitutive Equation for the Dynamic Compaction of Ductile Porous Materials," Journal of Applied Physics, Vol. 40, No. 6, p. 2490, May 1969.

²⁰Pastine, D. John, "Theoretical Shock Properties of Porous Aluminum," Journal of Applied Physics, Vol. 41, No. 7, p. 3144, June 1970.

²¹O'Keeffe, David J., "Theoretical Determination of the Shock States of Porous Copper," Journal of Applied Physics, Vol. 42, No. 2, p. 888, February 1971.

The fact that $\psi(x, T'_i) = \psi(x, T_i)$ is a direct consequence of the theory¹⁹ that the initial energy of a solid does not change with its porosity. Thus, the Hugoniot of a porous material is related to that of a solid by the relation,

$$P(x, T'_i) = \frac{2x - \Gamma(x) (x_i - x)}{2x - \Gamma(x) (M_i x_i - x)} P(x, T_i). \quad (26)$$

In this relation, $P(x, T_i)$ is the Hugoniot of the solid defined by Equation (14). This relation shows that the pressure in a porous solid is greater than the pressure in a non-porous solid. The temperature corresponding to the porous pressure, $P(x, T'_i)$, is calculated from Equation (1). The shock velocity (S') and particle velocity (u') for a porous solid may be calculated from the shock relations in the form

$$S' = x'_i \sqrt{\frac{P(x, T'_i)}{\rho_0 (x'_i - x)}} \quad (27)$$

$$u' = \sqrt{(x'_i - x) P(x, T'_i) / \rho_0} \quad (28)$$

CHAPTER 6

DISCUSSION OF RESULTS

The results from certain components of the Gruneisen equation of state are discussed and compared in this section to the work of other investigators. Also the numerical results for the pressures and temperatures on several Hugoniot-family members are presented and the numerical values of the melting points on these Hugoniots are given.

The Gruneisen equation of state is a sum of two important terms: the zero-degree isotherm and the thermal pressure. (See Chapter 2)

The zero-degree isotherm, $P_0(x)$, defined by Equation (9), was evaluated from the numerical solution to Equation (10). The values $P_0(x)$ is tabulated in Table 1. A corresponding graph of $P_0(x)$ is compared to Pastine's²² calculation in Figure 1. Although Pastine used a different approach to compute $P_0(x)$ for aluminum, his results are quite close to the current results, especially at lower pressures.

Since $P_0(x)$ is connected to the function $\psi(x, T_i)$ through the differential Equation (10), there is an indirect way in which $P_0(x)$ can be compared to experimental data. Consider the thermal quantity, enthalpy, which is given

$$H = E + PV.$$

At a pressure of $P = 0$, the enthalpy,

$$H = E.$$

From Equations (3) and (7), it is obvious that

$$\Delta H = E(x'_i, T'_i) - E(x_i, T_i) = V_O \psi(x, T'_i) - V_O \psi(x, T_i)$$

²²Pastine, D. John and Carroll, M. J., "Equations of State for Sodium and Aluminum," Accurate Characterization of the High Pressure Environment, Gaithersburg, Maryland, USA, 14-18 October 1968, Washington, D. C., USA National Bureau of Standards, pp. 91-104, 1971.

TABLE 1 NUMERICAL EVALUATION OF THE ZERO ISOTHERM AND RELATED FUNCTIONS

X	$\Psi(X, T_i)$ (Kbars · cc/g)	$\Gamma(X)$	$P(X, T_i)$ (Kbars)	$P_0(X)$ (Kbars)
1.0127	4.49180	2.24759	0.0000	-9.96911
1.0000	4.56213	2.19871	10.2135	0.040132
0.9873	4.50132	2.15322	21.1497	10.7469
0.9746	4.30024	2.11113	32.8673	22.1960
0.9619	3.94920	2.07240	45.4304	34.4358
0.9492	3.43785	2.03702	58.9098	47.5181
0.9365	2.75518	2.00496	73.3834	61.4991
0.9238	1.88942	1.97618	88.9370	76.4384
0.9111	0.828037	1.95065	105.666	92.4003
0.8984	-0.442348	1.92830	123.674	109.453
0.8857	-1.93600	1.90915	143.079	127.669
0.8730	-3.66815	1.89281	164.010	147.124
0.8603	-5.65498	1.87947	186.610	167.899
0.8476	-7.91375	1.86886	211.042	190.078
0.8349	-10.4628	1.86082	237.484	213.748
0.8222	-13.3216	1.85513	266.138	238.999
0.8095	-16.5107	1.85155	297.231	265.923
0.7968	-20.0519	1.84979	331.017	294.612
0.7841	-23.9682	1.84954	367.784	325.161
0.7714	-28.2838	1.85045	407.858	357.664
0.7587	-33.0239	1.85215	451.610	392.214
0.7460	-38.2151	1.85422	499.461	428.901
0.7333	-43.8851	1.85626	551.892	467.814
0.7206	-50.0625	1.85784	609.457	509.040
0.7079	-56.7773	1.85854	672.790	552.661
0.6952	-64.0601	1.85795	742.625	598.758
0.6825	-71.9429	1.85567	819.813	647.411
0.6698	-80.4584	1.85136	905.345	698.697
0.6571	-89.6404	1.84471	1000.38	752.696
0.6444	-99.5238	1.83545	1106.28	809.492
0.6317	-110.144	1.82339	1224.65	869.174
0.6190	-121.539	1.80839	1357.40	931.842
0.6063	-133.745	1.79036	1506.81	997.611
0.5936	-146.804	1.76928	1675.61	1066.61
0.5809	-160.757	1.74521	1867.13	1139.01
0.5682	-175.646	1.71821	2085.39	1215.00
0.5555	-191.519	1.68844	2335.35	1294.80
0.5428	-208.423	1.65606	2623.15	1378.71
0.5301	-226.414	1.62127	2956.43	1467.06
0.5174	-245.546	1.58430	3344.87	1560.28
0.5047	-265.885	1.54538	3800.80	1658.89

X = V/V₀, THE COMPRESSION RATIO $\Psi(X, T_i)$ = ENERGY DENSITY OF EQ (7) $\Gamma(X)$ = GRÜNEISEN FUNCTION $P(X, T_i)$ = HUGONIOT PRESSURE $P_0(X)$ = ZERO ISOTHERM

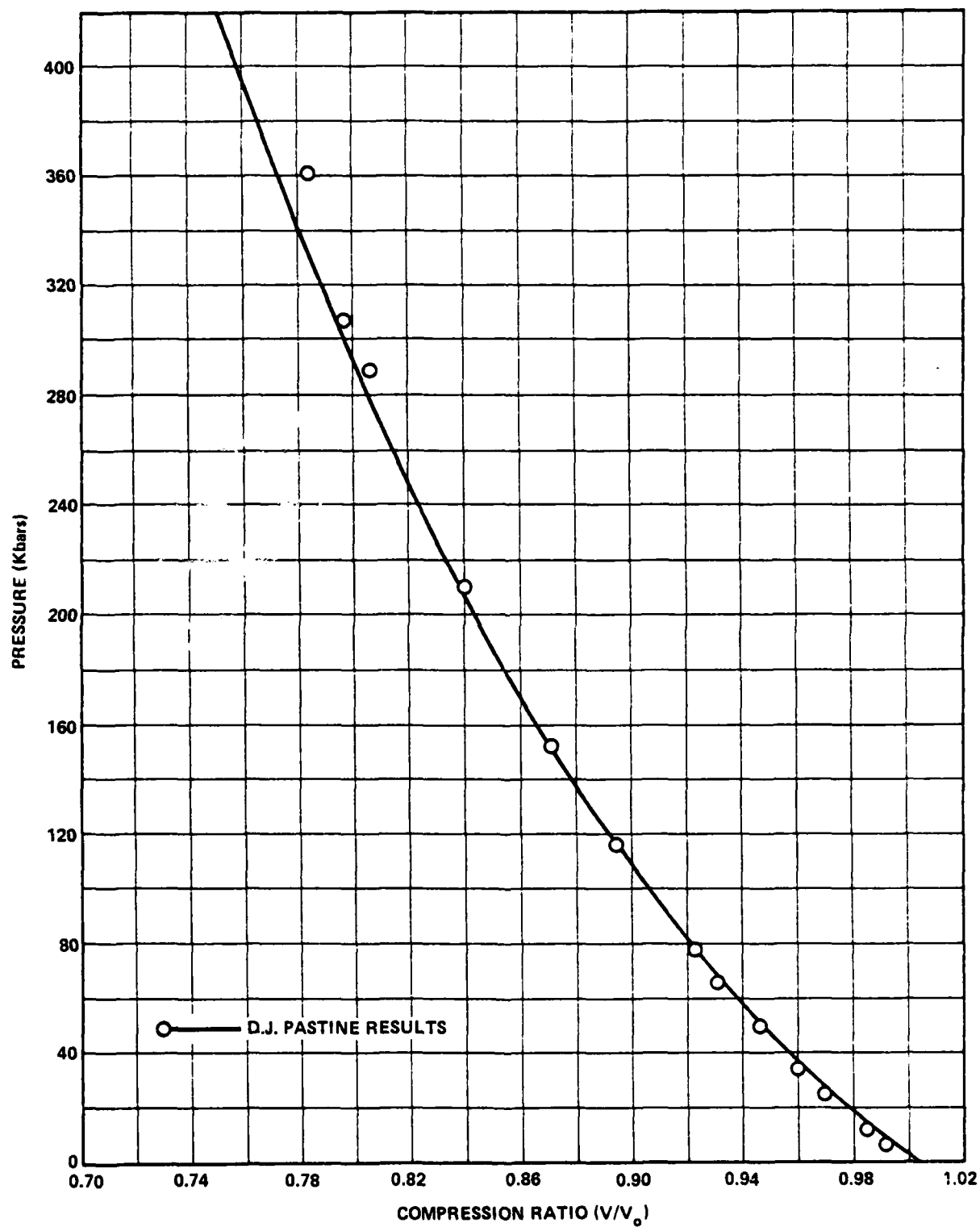


FIGURE 1 ZERO DEGREE ISOTHERM FOR ALUMINUM

Using Equation (18), the change in enthalpy reduces to

$$H = -V_0 \psi(x'_i, T_i) - V'_i P_0(x'_i) / \Gamma(x'_i) \quad (29)$$

which was readily evaluated numerically and listed in Table 2. The graph of these calculations in Figure 2 is in good agreement* with the experimental data¹⁸ plotted in Figure 2.

A list of values from the Gruneisen function, $\Gamma(x)$ is also included in Table 1. The Gruneisen function is a factor used to calculate the thermal pressure. A listing of thermal pressure on three Hugoniot of the same family for initial temperatures of $T_i = 278^\circ\text{K}$, 298°K , and 318°K , is in each of the Tables 3, 4, and 5.

The pressures and temperatures on these same three Hugoniot were calculated using the procedure of Section 4 as represented by Equation (19). These results are also listed in Tables 3, 4, and 5. The experimental Hugoniot at $T_i = 298^\circ\text{K}$ is in Figure 3 and is compared with data from the other two Hugoniot at $T_i = 278^\circ\text{K}$ and 318°K .

A list of temperatures and pressures calculated from the Lindemann law in the form of Equation (21) is in Table 6. This list is used to graph the melting states of aluminum in Figure 3. The intersections of this curve from Table 6 with the three Hugoniot are the melting points of aluminum for three of its initial states. These three points are listed in Table 7 along with other parameters dependent upon the initial temperature. Since these three points and all other similar melting points must fall on the Lindemann melting curve, this curve gives the melting point of aluminum as a function of initial temperature. Equation (22) is the parametric representation of this melting curve.

The results in Table 7 for the melting point of aluminum may be compared with the calculations of Urlin.^{3,4} He calculated the melting point to be (1.15 Mbars, 4000°K) or (1 Mbar, 3000°K), the results of two different procedures. Evidence of melting in aluminum at about 1 Mbar of shock pressure has been indicated also by experiments of Isbell and Sakharov.^{23,24}

²³ Isbell, W. M. Shipman, F. H., and Jones, A. H., "Hugoniot Equation of State of Eleven Materials to Five Megabars," General Motors Materials and Structures, Laboratory Report MSL-68-13.

²⁴ Sakharov, A. D., Zaidel, R. M., Mineev, V. N., and Oleinik, A. G., "Experimental Investigation of the Stability of Shock Waves and the Mechanical Properties of Substances at High Pressures and Temperatures," Soviet Physics-Doklady, Vol. 9, No. 12, p. 1091, June 1965.

*This agreement is quite good even though ΔH is calculated beyond the range defined by Equation (29). Equation (29) defines ΔH only within the range of $x'_i \leq x_i$, i.e., within the limiting range of the Hugoniot ($x \leq x_i$).

TABLE 2 ENTHALPY AS A FUNCTION OF TEMPERATURE AT P = 0

T (°K)	X	ΔH (CAL/MOL)	ΔH_{exp} (CAL/MOL)
300.000	1.01270	-2.01053E-11	0
399.888	1.02114	683.58	610
500.047	1.02976	1352.56	1240
600.424	1.03853	2005.82	1890
700.042	1.04739	2636.62	2580
799.803	1.05642	3250.37	3290
899.659	1.06561	3846.33	4040
999.560	1.07496	4423.84	4280

T = ABSOLUTE TEMPERATURE

X = V/V₀, THE COMPRESSION RATIO ΔH = THE CALCULATED CHANGE IN ENTHALPY ΔH_{exp} = THE EXPERIMENTAL CHANGE IN ENTHALPY (REFERENCE 18)

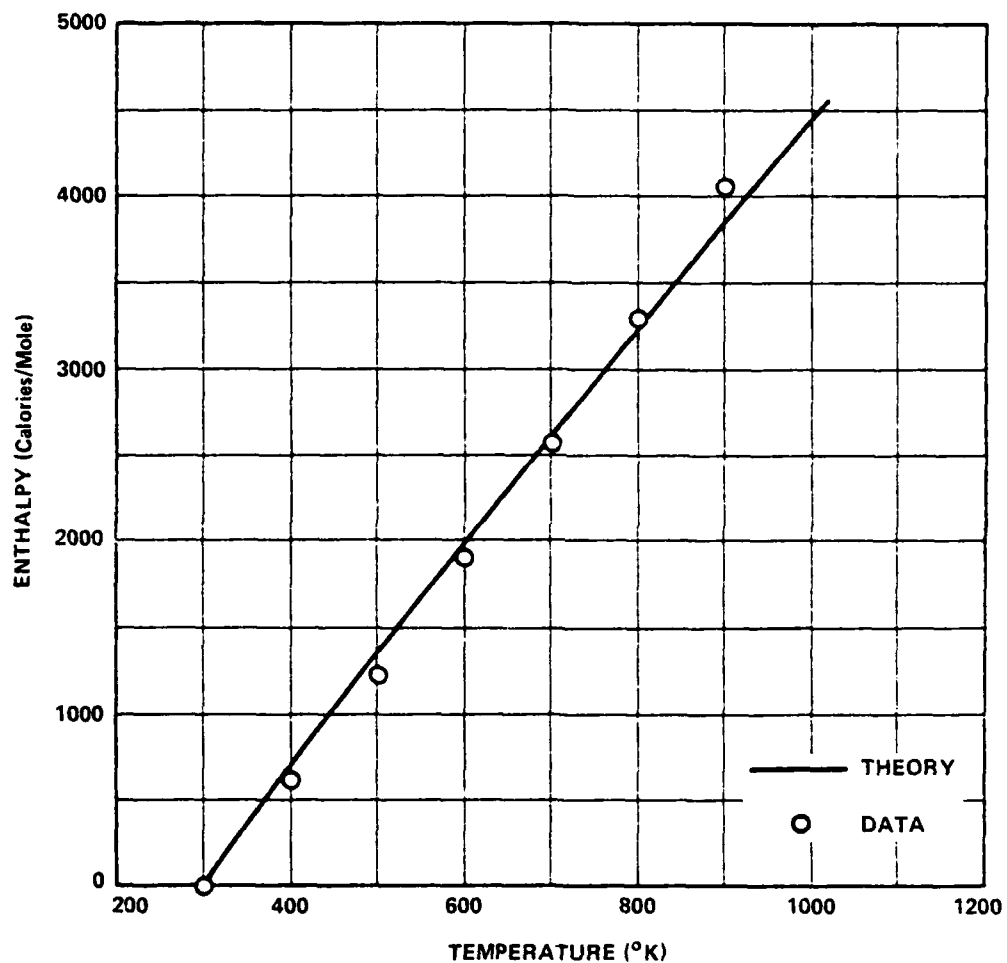


FIGURE 2 CHANGE OF ENTHALPY WITH ABSOLUTE TEMPERATURE AT P = 0

TABLE 3 HUGONIOT PRESSURES AND TEMPERATURES FOR $T_i = 278^\circ \text{K}$

X	$T(X, T_i)$ ($^\circ \text{K}$)	$P(X, T_i)$ (Kbars)	$U(X, T_i)$ (KM/SEC)	$P_T(X, T_i)$ (Kbars)
1.0127	279.102	-0.971025	6.65703E-3	8.99838
1.0000	287.402	9.22374	6.21659E-2	9.18602
0.9873	296.191	20.1388	0.133397	9.40273
0.9746	304.980	31.8325	0.207166	9.62504
0.9619	314.746	44.3688	0.283609	9.90286
0.9492	326.465	57.8178	0.362876	10.2856
0.9365	340.137	72.2571	0.445125	10.7745
0.9238	355.762	87.7719	0.530528	11.3722
0.9111	371.387	104.457	0.619270	11.9847
0.8984	394.824	122.415	0.711552	13.0066
0.8857	418.262	141.764	0.807588	14.0547
0.8730	449.512	162.631	0.907612	15.5331
0.8603	484.668	185.159	1.01188	17.2583
0.8476	523.730	209.509	1.12067	19.2438
0.8349	578.418	235.857	1.23427	22.1336
0.8222	640.918	264.405	1.35302	25.5511
0.8095	711.230	295.376	1.47727	29.5273
0.7968	789.355	329.024	1.60742	34.0945
0.7841	898.73	365.632	1.74390	40.6472
0.7714	1015.92	405.525	1.88717	47.9136
0.7587	1156.54	449.069	2.03776	56.8744
0.7460	1328.42	496.680	2.19624	68.1040
0.7333	1515.92	548.836	2.36326	80.7322
0.7206	1750.29	606.082	2.53951	96.827
0.7079	2031.54	669.046	2.72580	116.552
0.6952	2344.04	738.453	2.92299	139.006
0.6825	2750.29	815.143	3.13207	168.533
0.6698	3187.79	900.094	3.35417	201.055
0.6571	3719.04	994.448	3.59052	241.006
0.6444	4350.00	1099.55	3.84255	288.999
0.6317	5100.00	1216.97	4.11186	345.586
0.6190	6006.25	1348.60	4.40031	416.641
0.6063	7068.75	1496.68	4.71001	499.307
0.5936	8318.75	1663.89	5.04339	596.975
0.5809	9818.75	1853.50	5.40328	714.382
0.5682	11631.3	2069.45	5.79297	856.274
0.5555	13756.3	2316.60	6.21632	1022.55
0.5428	16318.8	2600.95	6.67790	1222.57
0.5301	19443.8	2929.98	7.18311	1465.62
0.5174	23193.8	3313.14	7.73847	1756.00
0.5047	27693.8	3762.44	8.35182	2102.59

X = V/V_0 , THE COMPRESSION RATIO $T(X, T_i)$ = HUGONIOT TEMPERATURE $P(X, T_i)$ = HUGONIOT PRESSURE $U(X, T_i)$ = HUGONIOT PARTICLE SPEED $P_T(X, T_i)$ = THERMAL PRESSURE ON HUGONIOT

TABLE 4 HUGONIOT PRESSURES AND TEMPERATURES FOR $T_i = 298^\circ \text{K}$

X	$T(X, T_i)$ ($^\circ \text{K}$)	$P(X, T_i)$ (Kbars)	$U(X, T_i)$ (KM/SEC)	$P_T(X, T_i)$ (Kbars)
1.0127	298.000	0.0000	0.00000	9.96911
1.0000	306.789	10.2135	6.88871E-2	10.1727
0.9873	316.067	21.1497	0.14019	10.4065
0.9746	325.832	32.8673	0.214039	10.6713
0.9619	336.574	45.4304	0.290572	10.9931
0.9492	348.293	58.9098	0.369938	11.3730
0.9365	361.965	73.3834	0.452298	11.8616
0.9238	377.590	88.9370	0.537824	12.4613
0.9111	397.121	105.666	0.626703	13.2736
0.8984	420.559	123.674	0.719135	14.3048
0.8857	443.996	143.079	0.815339	15.3636
0.8730	475.246	164.010	0.915548	16.8570
0.8603	514.309	186.610	1.02002	18.8038
0.8476	553.371	211.042	1.12903	20.8116
0.8349	608.059	237.484	1.24289	23.7289
0.8222	670.559	266.138	1.36191	27.1758
0.8095	740.871	297.231	1.48647	31.1831
0.7968	834.621	331.017	1.61696	36.6742
0.7841	928.371	367.784	1.75381	42.3716
0.7714	1053.37	407.858	1.89750	50.1388
0.7587	1194.00	451.610	2.04855	59.1469
0.7460	1365.87	499.461	2.20755	70.4250
0.7333	1562.50	551.892	2.37514	83.6794
0.7206	1812.50	609.457	2.55203	100.844
0.7079	2093.75	672.790	2.73902	120.650
0.6952	2406.25	742.625	2.93701	143.183
0.6825	2812.50	819.813	3.14698	172.788
0.6698	3265.63	905.345	3.37007	206.472
0.6571	3812.50	1000.38	3.60755	247.618
0.6444	4468.75	1106.28	3.86084	297.528
0.6317	5218.75	1224.65	4.13158	355.233
0.6190	6125.00	1357.40	4.42165	425.397
0.6063	7187.5	1506.81	4.73319	508.160
0.5936	8500.0	1675.61	5.06867	610.616
0.5809	10000.0	1867.13	5.43096	728.134
0.5682	11812.5	2085.39	5.82342	870.118
0.5555	14000.0	2335.35	6.24997	1041.27
0.5428	16625.0	2623.15	6.71525	1246.17
0.5301	19750.0	2956.43	7.22480	1489.29
0.5174	23562.5	3344.87	7.78525	1784.53
0.5047	28187.5	3800.80	8.40462	2140.79

X = V/V_0 , THE COMPRESSION RATIO $T(X, T_i)$ = HUGONIOT TEMPERATURE $P(X, T_i)$ = HUGONIOT PRESSURE $U(X, T_i)$ = HUGONIOT PARTICLE SPEED $P_T(X, T_i)$ = THERMAL PRESSURE ON HUGONIOT

TABLE 5 HUGONIOT PRESSURES AND TEMPERATURES FOR $T_i = 318^\circ \text{K}$

X	$T(X, T_i)$ ($^\circ \text{K}$)	$P(X, T_i)$ (Kbars)	$U(X, T_i)$ (KM/SEC)	$P_T(X, T_i)$ (Kbars)
1.0127	316.650	0.968041	6.64679E-3	10.9369
1.0000	325.928	11.2003	7.55983E-2	11.1568
0.9873	335.693	22.1577	0.146974	11.4077
0.9746	346.436	33.8992	0.220903	11.7158
0.9619	358.154	46.4893	0.297526	12.0821
0.9492	369.873	59.9991	0.376992	12.4587
0.9365	385.498	74.5071	0.459463	13.0449
0.9238	401.123	90.0995	0.545113	13.6459
0.9111	420.654	106.872	0.634128	14.4628
0.8984	444.092	124.930	0.726712	15.5015
0.8857	471.436	144.391	0.823083	16.7698
0.8730	502.686	165.386	0.923478	18.2780
0.8603	541.748	188.059	1.02816	20.2430
0.8476	588.623	212.573	1.13739	22.6868
0.8349	635.498	239.109	1.25150	25.2117
0.8222	697.998	267.870	1.37080	28.6847
0.8095	776.123	299.084	1.49567	33.1579
0.7968	869.873	333.009	1.62650	38.6886
0.7841	963.623	369.936	1.76373	44.4258
0.7714	1088.62	410.192	1.90783	52.2359
0.7587	1244.87	454.153	2.05935	62.2374
0.7460	1416.75	502.245	2.21887	73.5805
0.7333	1619.87	554.954	2.38703	87.3119
0.7206	1854.25	612.839	2.56456	103.542
0.7079	2135.50	676.543	2.75227	123.402
0.6952	2479.25	746.809	2.95105	148.087
0.6825	2885.50	824.499	3.16192	177.782
0.6698	3354.25	910.618	3.38694	212.642
0.6571	3885.50	1006.34	3.62462	252.782
0.6444	4556.25	1113.05	3.87918	303.813
0.6317	5337.50	1232.37	4.15137	363.881
0.6190	6243.75	1366.25	4.44307	434.152
0.6063	7337.5	1517.01	4.75647	519.341
0.5936	8650.0	1687.43	5.09407	621.906
0.5809	10181.3	1880.88	5.45880	741.886
0.5682	12025.0	2101.50	5.85406	886.349
0.5555	14212.5	2354.32	6.28385	1057.58
0.5428	16900.0	2645.62	6.75290	1267.37
0.5301	20087.5	2983.24	7.26686	1515.36
0.5174	23962.5	3377.08	7.83248	1815.48
0.5047	28712.5	3839.80	8.45799	2181.41

X = V/V_0 , THE COMPRESSION RATIO $T(X, T_i)$ = HUGONIOT TEMPERATURE $P(X, T_i)$ = HUGONIOT PRESSURE $U(X, T_i)$ = HUGONIOT PARTICLE SPEED $P_T(X, T_i)$ = THERMAL PRESSURE ON HUGONIOT

TABLE 6 MELTING TEMPERATURE AND PRESSURE AS A FUNCTION OF COMPRESSION RATIO

X	T (°K)	P (Kbars)	$\Gamma(X)$
1.07106	932.000	1.33014E-3	2.51666
1.06523	954.399	4.19652	2.48642
1.05939	977.142	8.51557	2.45693
1.05356	1000.24	12.9622	2.42819
1.04772	1023.68	17.5403	2.40019
1.04188	1047.49	22.2539	2.37293
1.03605	1071.67	27.1072	2.34640
1.03021	1096.22	32.1048	2.32061
1.02437	1121.15	37.2512	2.29554
1.01854	1146.48	42.5514	2.27120
1.0127	1172.20	48.0102	2.24759
1.0000	1229.60	60.4414	2.19871
0.9873	1289.03	73.7065	2.15322
0.9746	1350.63	87.8692	2.11113
0.9619	1414.54	102.999	2.07240
0.9492	1480.92	119.172	2.03702
0.9365	1549.96	136.472	2.00496
0.9238	1621.88	154.987	1.97618
0.9111	1696.93	174.816	1.95065
0.8984	1775.38	196.064	1.92830
0.8857	1857.56	218.844	1.90905
0.8730	1943.81	243.278	1.89281
0.8603	2034.54	269.493	1.87947
0.8476	2130.20	297.629	1.86886
0.8349	2231.27	327.828	1.86082
0.8222	2338.31	360.242	1.85513
0.8095	2451.92	395.030	1.85155
0.7968	2572.78	432.353	1.84979
0.7841	2701.59	472.379	1.84954
0.7714	2839.16	515.277	1.85045
0.7587	2986.32	561.220	1.85215
0.7460	3144.00	610.377	1.85422
0.7333	3313.18	662.919	1.85626
0.7206	3494.88	719.013	1.85784
0.7079	3690.20	778.821	1.85854
0.6952	3900.28	842.500	1.85795
0.6825	4126.32	910.204	1.85567
0.6698	4369.54	982.078	1.85136
0.6571	4631.19	1058.26	1.84471
0.6444	4912.55	1138.90	1.83545
0.6317	5214.90	1224.13	1.82339
0.6190	5539.50	1314.08	1.80839
0.6063	5887.63	1408.89	1.79036
0.5936	6260.49	1508.73	1.76928
0.5809	6659.28	1613.75	1.74521
0.5682	7086.08	1724.15	1.71821
0.5555	7538.96	1840.14	1.68844
0.5428	8021.83	1961.98	1.65606
0.5301	8534.54	2089.97	1.62127
0.5174	9077.79	2224.48	1.58430
0.5047	9652.14	2365.98	1.54538

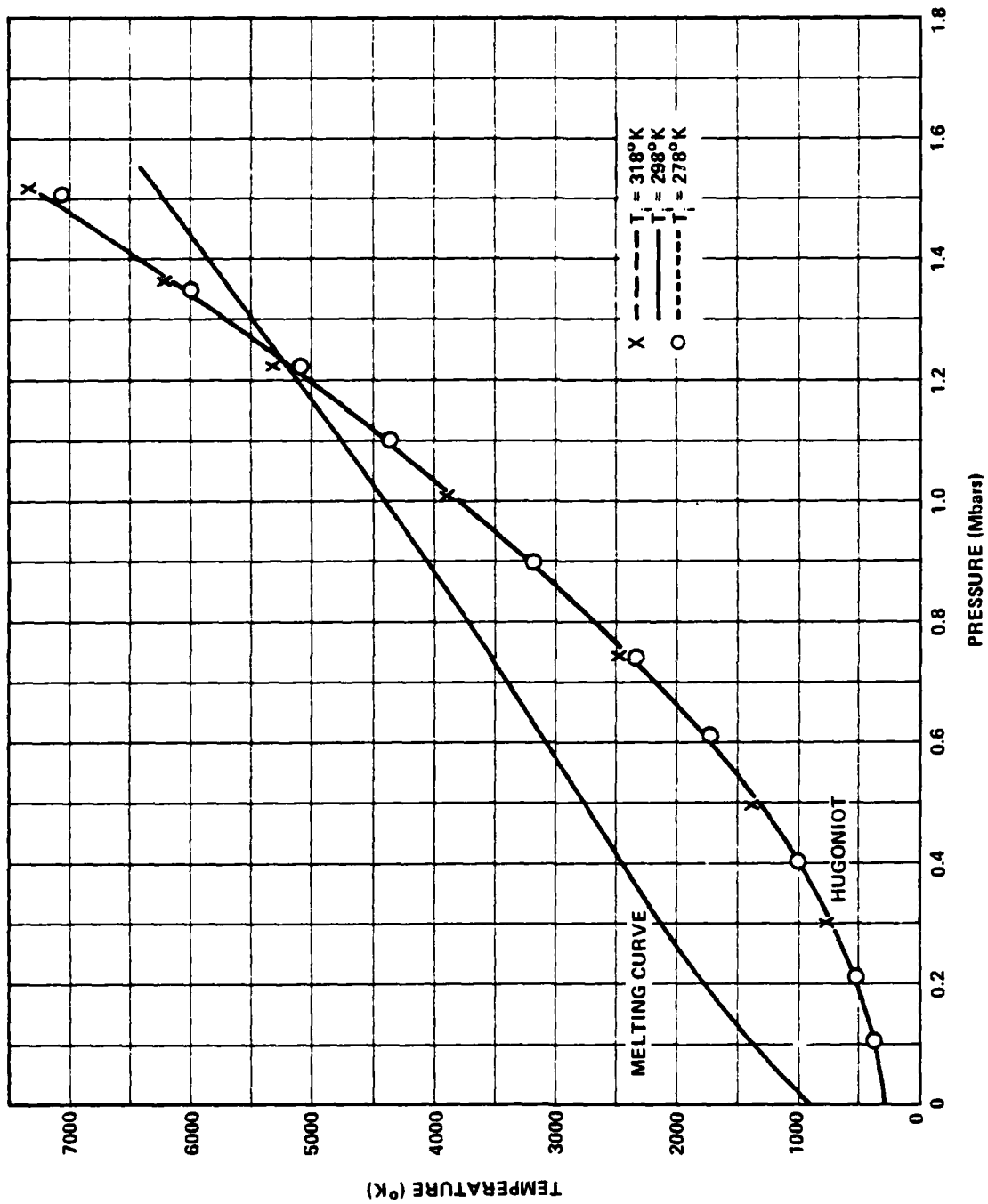


FIGURE 3 THE MELTING POINT OF ALUMINUM AS THE INTERSECTION OF LINDEMANN'S MELTING CURVE AND THE HUGONIOT (SHIFTS IN HUGONIOT DUE TO INITIAL TEMPERATURE DIFFERENCES IS ALSO SHOWN)

TABLE 7
MELTING POINT DEPENDENT ON INITIAL STATE OF Al

T_i	P_m	T_m	$a(T_i)$	$b(T_i)$	x_i
(°K)	(Mbars)	(°K)	(mm/μsec)		
278	1.24	5268	4.40647	1.3486	1.01145
298	1.223	5218	5.4	1.351	1.0127
318	1.204	5147	5.39349	1.35338	1.01395

Once the Hugoniot is established, a similar procedure is used to calculate the melting point of porous aluminum at porosities of $M_i = 1.4$ and 1.7 . To accomplish this, the Gruneisen relation is used to express the Hugoniot, Equation (25), of a porous solid into the form of Equation (19).

The intersection of these Hugoniots with the melting curve is in Figure 4. These points show that the melting point of aluminum decreases as its porosity increases. At $M_i = 1.7$, Figure 4 shows that the melting point is about 66 kbars and 1260°K. This result is in excellent agreement with the experimental estimate of 66 kbars 1220°K reported by Asay and Hayes.²⁵ They calculated a value of 75 kbars and 1340°K as their best theoretical result for this point. This indicates that the theoretical result from Figure 4 is more accurate than their result.

The straight-line appearance of the Hugoniot graphs in Figure 4 indicate that the slope of these graphs may be constant. Plots of the slope, $\frac{dT}{dP}$, as a function of pressure are in Figure 5. These plots show that the slope of the Hugoniot, $\frac{dT}{dP}$, does vary with the pressure, but is not much different from the initial value,

$$\frac{dT}{dP} \bigg|_{P=0} = \frac{x'_i - x_i}{2\rho_0 C_{vi}} + \Gamma_i T_i x_i - \Gamma_i (x'_i - x_i)/2 / \rho_0 a^2.$$

(Note that C_{vi} is the initial specific heat at constant volume, $\Gamma_i = \Gamma(x_i)$, and $x'_i = M_i x_i$.)

The theoretical Hugoniots of porous aluminum are calculated from Equations (27) and (28). Figure 6 shows that these Hugoniots are in good agreement with reported data.^{25,26} Pastine²⁰ has also calculated the results shown in Figure 6, but he used first principles to derive the Gruneisen equation of state.

The specific values of $M_i = 1.4$ and 1.7 above no porosity of $M_i = 1$ were chosen because these values clearly show the dramatic change that porosity can produce in the melting point of a simple solid. Figure 4 clearly shows the large changes in the melting point of aluminum as the porosity of aluminum takes on the values of

²⁵ Asay, J. R. and Hayes, D. B., "Shock-Compression and Release Behavior Near Melt States in Aluminum," Journal of Applied Physics, Vol. 46, No. 11, p. 4789, November 1975.

²⁶ Anderson, G. D., Doran, D. G., and Fahrenbruch, A. L., Equation of State of Solids: Aluminum and Teflon, Stanford Research Institute, Menlo Park, California, 1965, Technical Report No. AFWL-TR-65-147.

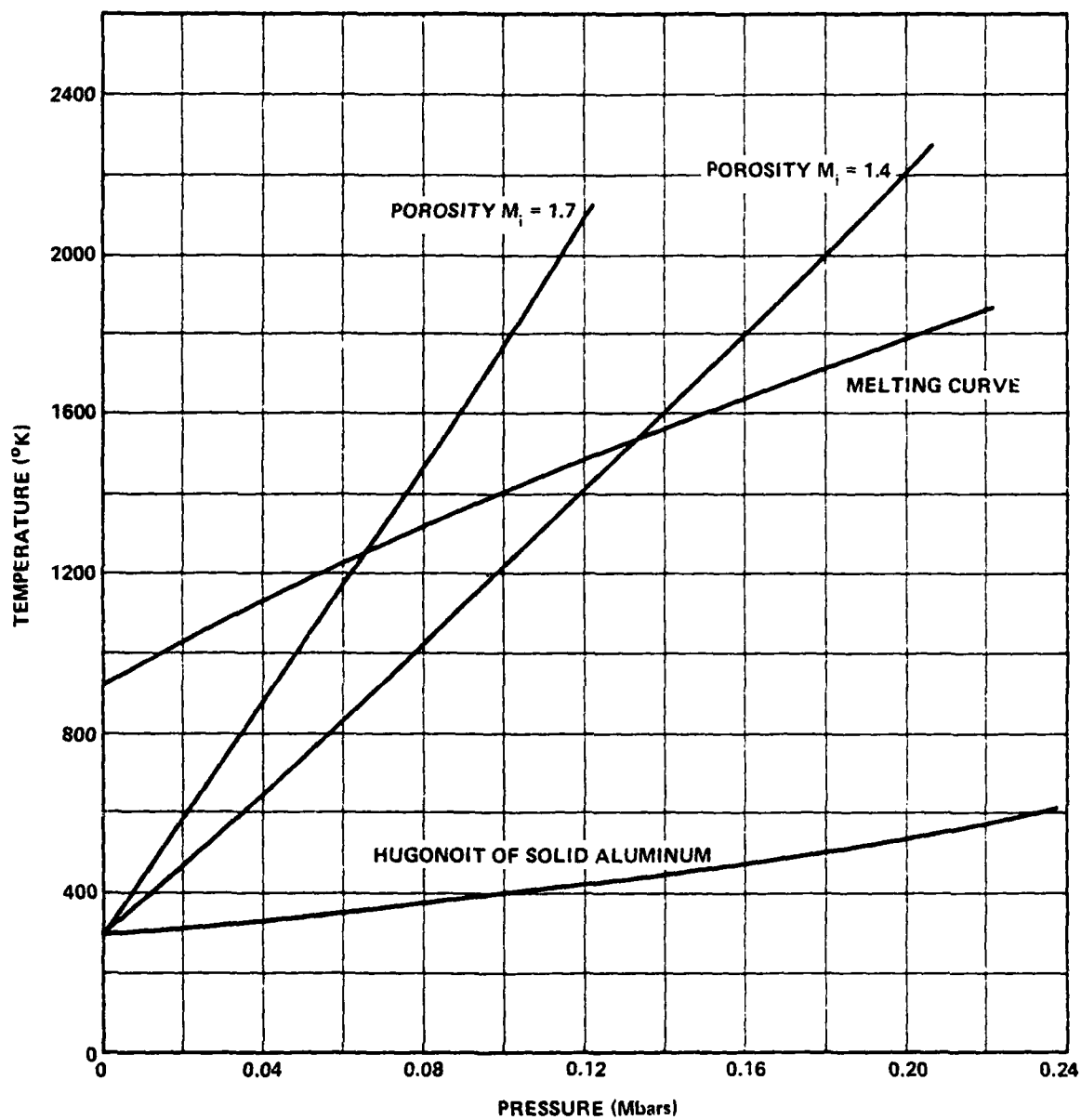


FIGURE 4 EFFECT OF POROSITY ON THE MELTING POINT OF ALUMINUM

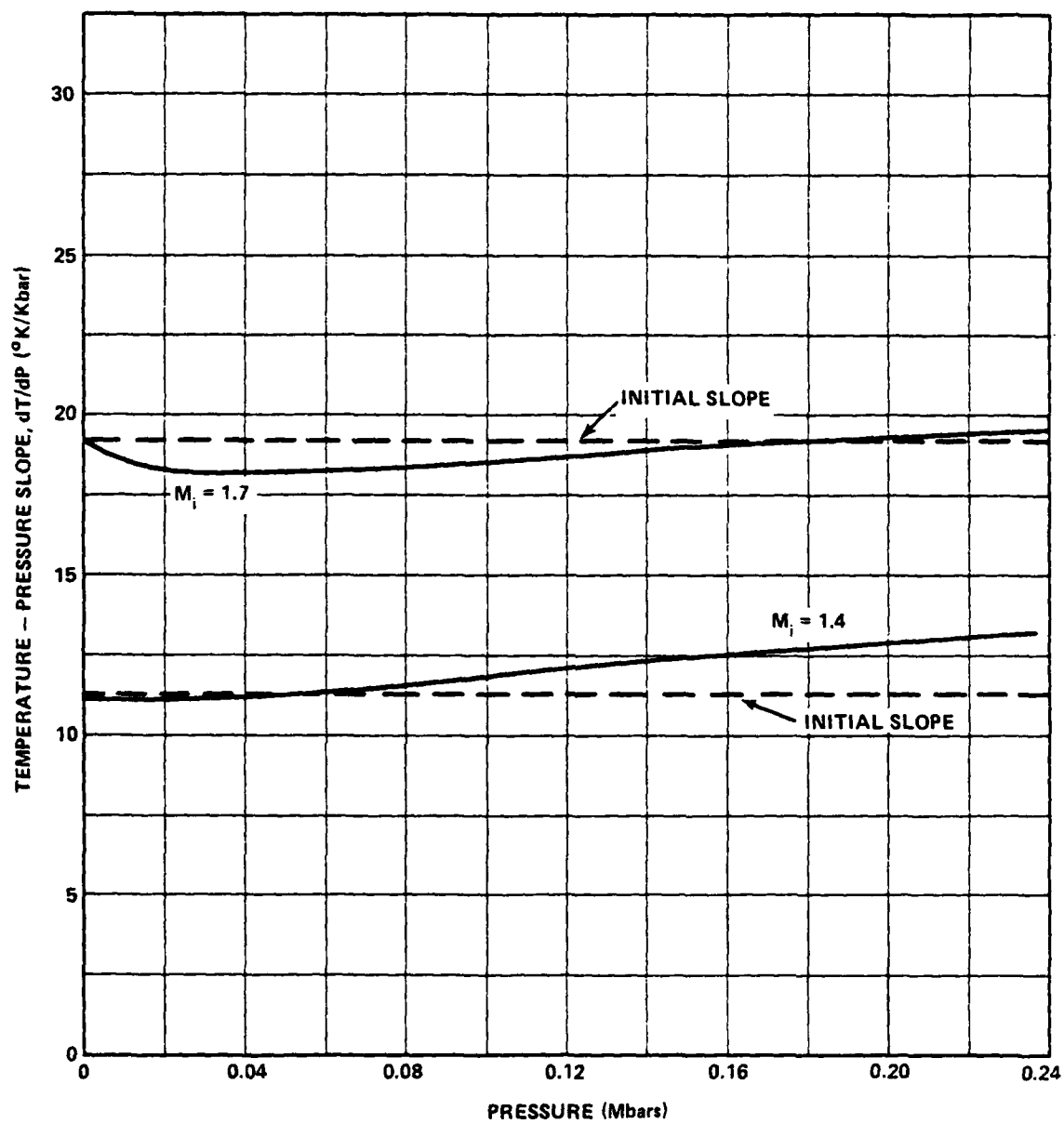


FIGURE 5 CHANGE IN TEMPERATURE - PRESSURE SLOPE WITH PRESSURE ON THE HUGONIOT OF POROUS ALUMINUM

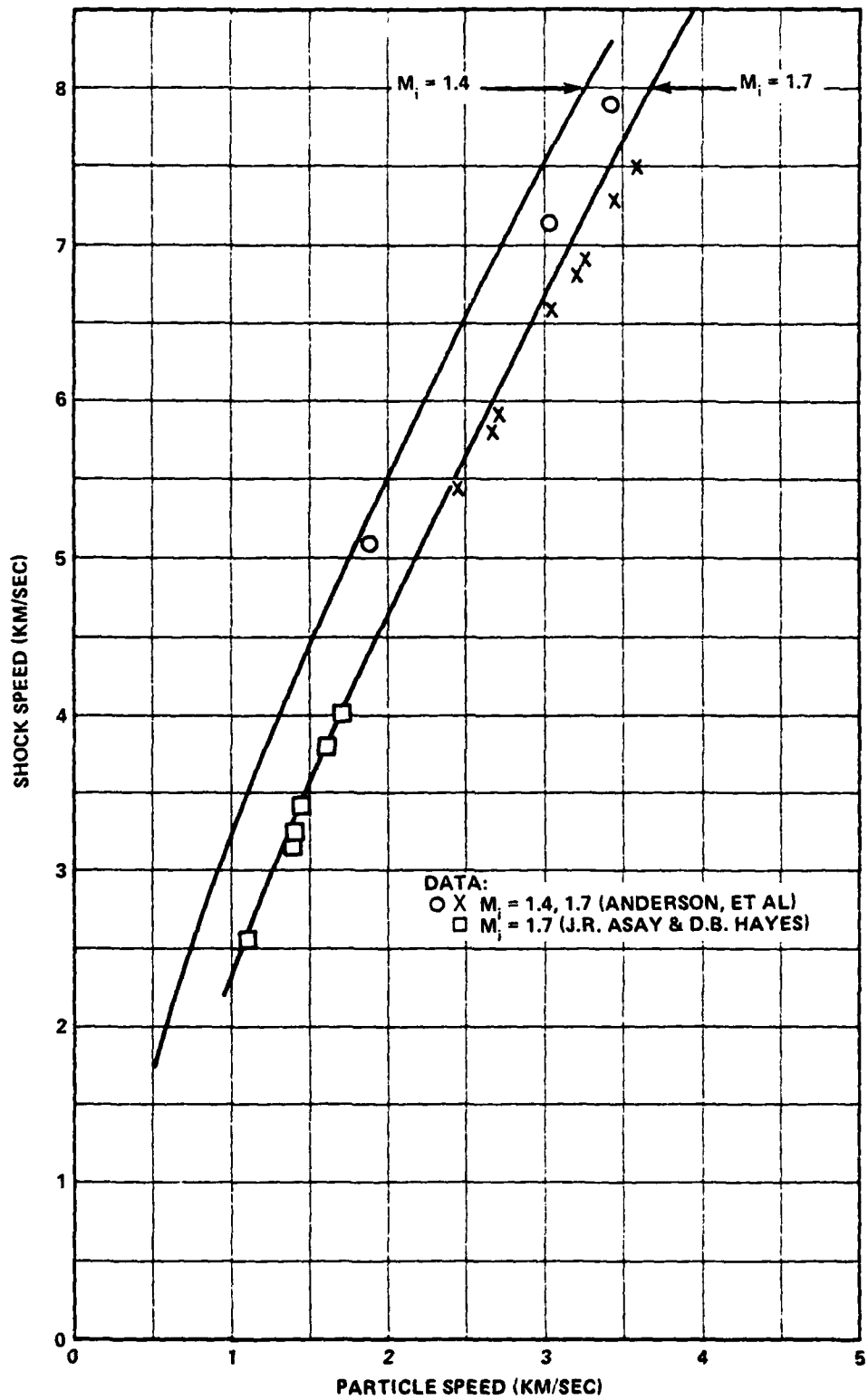


FIGURE 6 SHOCK SPEED VERSUS PARTICLE SPEED FOR POROUS ALUMINUM

$M_i = 1, 1.4, \text{ and } 1.7$. In addition, these specific values for M_i were chosen because data and other calculations have been reported on these same values of μ_i so that the current results can be compared to these previous works.

There was concern with whether small changes in the initial state of aluminum would change significantly the melting point of aluminum. As can be seen from Table 7 and Figure 3 that small changes in the initial state of aluminum from $T_i = 298^\circ\text{K}$ to $T_i = 318^\circ\text{K}$ or $T_i = 278^\circ\text{K}$ do not produce any great change in the melting point.

CHAPTER 7

SUMMARY

The dependence of a Hugoniot on the initial state of aluminum is represented by a one-parameter family of pressure-volume Hugoniots. The initial temperature is used as the parameter of the family. Instead of a characteristic equation of state for aluminum, the Gruneisen equation of state is used to generate a family of Hugoniots from a single experimental Hugoniot. In the absence of available experimental temperatures, the P-V-T form of the Gruneisen equation of state is used to calculate temperatures on these Hugoniots.

The Lindemann law of melting is used to calculate the melting point of aluminum on three Hugoniots. The pressures producing melting were calculated and are in good agreement with the results of other investigators. However, the corresponding melting temperatures differed appreciable from values reported by others. This difference is attributed to differences in the more exact form of the Gruneisen equation of state chosen for these calculations as compared to the equations used by other investigators. For this reason, the current results should be an improvement over previous calculations.

Using the theory of compaction, a one-parameter family of Hugoniots has been derived for porous aluminum with porosity as the family parameter. The melting points and the Hugoniots of porous aluminum are in good agreement with reported data.

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APPENDIX A
DEBYE FUNCTION

In terms of the Gruneisen function, the Debye temperature^{A-1} is

$$\theta(x) = \theta(x_i) \exp \left[\int_x^{x_i} \frac{\Gamma(z)}{z} dz \right] .$$

Correspondingly, the Debye function^{A-2} is defined by the integral relation

$$D(y) = \frac{3}{y^3} \int_0^y \frac{z^3 dz}{e^z - 1}$$

for $y = \theta/T$.

^{A-1}O'Keeffe, David J., "Melting of Solids with a Linear $U_S - U_P$ Relationship," Applied Physics Letters, Vol. 21, No. 8, p. 360, 15 October 1972.

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APPENDIX B

SHOCK RELATIONS AND THE HUGONIOT

The shock relations^{B-1} for the conservation of mass, momentum, and energy across the shock front are

$$x_i (S - u) = xS \quad (B1)$$

$$x_i (P - P_i) = \rho_o Su \quad (B2)$$

$$\frac{(S - u)^2}{2} + P/\rho + E = \frac{S^2}{2} + P_i/\rho_i + E_i. \quad (B3)$$

Elimination of S and u among the Equations (8), (B1), and (B2) leads to a Hugoniot of the form

$$P(x, T_i) = \frac{\rho_o a^2 (x_i - x)}{[x_i - b(x_i - x)]^2}, \quad (x \leq x_i). \quad (B4)$$

Elimination of S and u among Equations (B1), (B2), and (B3) leads to the conservation of energy Equation (13). Comparing Equations (14) to (B4) and making use of Equation (9) lead to the differential Equation (10).

^{B-1}Landau, L. D. and Lipshitz, E. M., Fluid Mechanics, New York, Bergman Press, p. 319, 1975.

APPENDIX C
GRUNEISEN FUNCTION

The Pastine-Forbes^{C-1} expression for the Gruneisen function is

$$\Gamma(x) = \frac{2x\eta \left[2bx - \delta(x_i - b\eta) \right] + 2x^2(x_i - b\eta) + 4x\eta^2 v}{2\eta^3 v + \eta^2 \left[2bx - s(x_i - b\eta) \right] + \eta(x + x_i)(x_i - b\eta) + 2(x_i - b\eta)^3 C_p / \alpha a^2}$$

In this equation, $\eta = x_i - x$. The unidentified parameters in this equation are C_p , the specific heat capacity at constant pressure; α , the volume coefficient of thermal expansion; and the others are defined by the relations^{C-2}

$$\delta = 1 - \frac{1}{\alpha} \left[\frac{\partial}{\partial T_i} \log a^2 \right]_{P_i=0}$$

$$v = \frac{1}{\alpha} \left(\frac{\partial b}{\partial T_i} \right)_{P_i=0}$$

^{C-1}Pastine, D. John and Forbes, J. W., "Accurate Relations Determining the Volume Dependence of the Quasiharmonic Gruneisen Parameter," Physical Review Letters, Vol. 21, No. 23, p. 1582, December 1968.

^{C-2}O'Keeffe, David, J., "Accurate Pressure, Volume, Temperature Relations for Copper," Journal of Geophysical Research, Vol. 75, p. 1947, 1970.

The values^{C-3,C-4,C-5} of the new parameters in the Gruneisen function are $\alpha = 69.6 \times 10^{-6}/^{\circ}\text{K}$, $C_D = 5.82 \text{ cal/mole } ^{\circ}\text{K} = .90298 \text{ J/g}^{\circ}\text{K}$, $\delta = 2.95135$, and $\nu = 1.9407$ for aluminum at $T_i = 298^{\circ}\text{K}$.

- C-3 Simmons, Gene and Wang, Herbert, *Single Crystal Elastic Constants Calculated Aggregate Properties: A Handbook*, Cambridge, Mass., The M. I. T. Press, pp. 4-8, 1971.
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