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GRUNEISEN PARAMETER STUDY

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Lockheed Missiles and Space Company,
Incorporated
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INTRODUCTION

The problem of characterizing shock wave properties in solid materials necessitates a knowledge of the solid equation of states at high pressures.

The pressures attainable in strong shock waves can exceed considerably the pressures attainable by experimental, static techniques. Static pressures which have been attained experimentally are about in the hundred kilobar range, whereas dynamically, pressures of about five megabars have been attained. Thus, it has been necessary to use dynamic techniques to determine equations of state for use in shock wave calculations.

One common technique to obtain an equation of state at high pressure is to calibrate an assumed equation of state, i.e., the Mie-Grüneisen equation of state, in terms of a shock Hugoniot. The Mie-Grüneisen equation of state is

$$P - P_0 = \frac{\gamma}{V} (E - E_0)$$

where γ is the Grüneisen parameter. For the state of a material after shock passage, one can write

$$P_H - P_0 = \frac{\gamma}{V} (E_H - E_0)$$

Combining the above two equations and assuming that the Grüneisen parameter is a function of volume only gives

$$P - P_H = \frac{\gamma}{V} (E - E_H)$$

The above equation represents an equation of state for small excursions from the calibrating Hugoniot. Its validity depends on the assumptions that

the compression at P_H is the same as would be produced by a hydrostatic pressure of the same magnitude; the Hugoniot state after shock passage is an equilibrium state; and that the Grüneisen parameter does not vary with temperature but is a function of volume only.

Recently, shock work with foams and measurements of the sound velocity behind shock waves have raised the question as to whether γ is indeed independent of temperature.

Also a problem in calculating the shock properties of foamed and distended materials is how to formulate equations of state in the lower pressure regions. At lower pressures, the assumption of these materials attaining states of "true" thermodynamic equilibrium may no longer be tenable. (The term true is put in quotes because, as is discussed in Section 6B, the definitions of various equilibria are rather confused.)

In trying to evaluate the possible temperature dependency of γ , it was soon found that the topic of the Grüneisen parameter is treated in the literature in a limited, fragmentary way. Nowhere does there exist a systematic, overall treatment. Also, there appears to be a confusion about possible definitions of the Grüneisen parameter. Thus, the task objective, as presented in Experimental Memo PR961, set for the present study was:

"Contribute to better understanding of the Grüneisen parameter; its theoretical basis, experimental determination, and usage in present hydrodynamic response code."

The tasks set for this study were:

Task 1 - Compile systematic, overall treatment of theoretical aspects of the Grüneisen parameter (starting with original Grüneisen work, circa 1912). Include complete bibliography and pertinent excerpt from source documents.

Task 2 - Review all experimental techniques (past and present) used to derive experimental values of Grüneisen parameter. Compare data for selected materials (choose materials relatively insensitive to fabrication variables and anisotropic effects).

Suggest most useful approaches for typical spectrum of reentry vehicles materials, i.e., organic composites, epoxy adhesives and light metals. Include complete bibliography and pertinent excerpts from source documents. Describe experimental setups in detail.

Task 3 - Calculate Grüneisen parameter for aluminum, beryllium, tungsten, tantalum, tungsten carbide and silicon carbide as function of pressure to 30 kilobars and temperature up to melt. Do same for nylon phenolic and refracil phenolic to 50 kilobars pressure and temperatures of 500°F.

During the last three months of the study work was concentrated on the following task, as presented in the Task Memo TP7087:

"Continue the Grüneisen parameter study in the area of porous, foamed and distended materials. Review all techniques used for deriving the Grüneisen parameter for such materials and present any pertinent data. Make recommendations for the incorporation of this parameter into our present computer code."

The preceding tasks are covered in this report in the following manner. Fundamental thermodynamic and physical definitions are covered in Section 1. The theoretical bases of equations of state and the Mie-Grüneisen Equation of State are discussed in Sections 2 and 3. The experimental techniques of determining the various Grüneisen parameters for solid materials are reviewed in Section 4, and actual calculations of the various Grüneisen parameters for the materials of the study are presented in Section 5. The thermodynamics of foamed and distended materials are considered in Section 6.

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FINAL REPORT
GRÜNEISEN PARAMETER STUDY

October 1967

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FOREWORD

The study, performed at Lockheed's Huntsville Research & Engineering Center during the period 28 September 1966 to 27 October 1967, is in accordance with the task objectives and task statements presented in the Lockheed/Sunnyvale Experimental Memos PR961 and TP7087. Technical direction was furnished by Mr. D. Fenton (Dept. 81-23) and Mr. E. L. Esch (Dept. 31-73). Their support and encouragement are gratefully acknowledged.

Mr. Ivan Landis contributed significantly to the study by performing the mathematical analysis reported in Section 5C and conducting the study phase reported in Sections 5D and 5E. Mr. Ernest Raper performed the calculations presented in Section 5E.

SUMMARY

The theoretical basis of the Mie-Grüneisen equation of state was considered and systematized. The most important experimental techniques for determining the several Grüneisen parameters were reviewed. Several Grüneisen parameters for some of the materials of the study were calculated by methods presented in the literature and by an original method developed in the course of the study. Also, the problems involved in characterizing the states of foamed materials before and after irreversible changes were reviewed.

The most important facts drawn from the study of the theoretical basis of the Mie-Grüneisen equation of state are (a) the Mie-Grüneisen equation is necessarily valid if γ_2 , not γ_3 , in a certain temperature range is independent of temperature and (b) the Mie-Grüneisen equation is necessarily valid if γ_3 is temperature independent throughout the temperature range from 0°K upwards.

Although our calculations of γ_1 at low pressures for the metals of the study do not show much temperature variation from room temperature up, values of γ_3 at very low temperatures found in the literature for aluminum do vary considerably as apparently do the γ_2 values, which we have calculated by the method of Beecroft and Swenson and our own method. Thus, it would appear that the use of the Mie-Grüneisen equation of state for metals at low temperatures is not valid.

At moderate pressures our calculations of γ_2 for sodium and aluminum indicate that the variation of γ_2 with temperature is about the same as observed at low pressures with perhaps very unusual behavior in the very high pressure regions. However, time limitations did not permit a check of the sensitivity of the calculation to the approximations made, so the results cannot be considered conclusive.

The conclusions derived from a review of the thermodynamics of foamed and distended materials are that considerable confusion exists about basic definitions of various types of equilibrium and, therefore, about calculation of thermodynamic state functions for materials which have undergone changes involving hysteresis of one sort or another. However, a classical thermodynamic approach to "totally" irreversible processes promises to yield much information once the discussions of various authors are clarified and correlated. The preceding state of affairs is really pertinent to the calculations of a Grüneisen parameter in the low pressure region. The high pressure region where the foam is assumed completely crushed and annealed can be handled straightforwardly.

Time limitations did not permit the full exploration of the effects of material anisotropy, material rigidity, melting, or material porosity and inhomogeneity. Because the problems associated with the last two factors have not yet been resolved, Grüneisen parameters for the plastics of the study were not calculated.

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GLOSSARY

A	Gibb's free energy ($= H - TS$), also used as constant in various equations, see pp. 4-16, 5-2, 5-23, and 5-30
a_0	functions in Slater's formulation of hydrostatic data, see p. 4-1
a_1	
a_2	
a	functions in Bridgman's formulation of hydrostatic data, see p. 4-1
b	
B	isothermal bulk modulus $\left(-v \left(\frac{\partial P}{\partial v} \right)_T \right)$
B'	$\left(\frac{\partial B}{\partial P} \right)_T$
C	speed of sound, also used as constant, see p. 4-16
C_0	speed of sound at $T = 0^\circ K$, also used as constant, see p. 4-17
C_V, C_P	heat capacities
E	total internal energy
E_0	total internal energy at $T = 0^\circ K$
E_{00}	internal energy at $P = 0, T = 0^\circ K$
E_C	cohesive energy
E_S	static energy
E_T	thermal energy
E_V	vibrational energy
E_V^0	zero-degree vibrational energy

F	Helmholtz free energy ($= E - TS$)
F_T	thermal free energy
F_V	vibrational free energy
g	constant, see p. 6-2
H	enthalpy ($= E + PV$)
h	Plank's constant, also see p. 6-2
j	index of mode of oscillation
K	internal kinetic energy, also constant, see p. 5-23
K_V	vibrational kinetic energy
L	length
l	length
m	constants, see p. 4-4
n	
P	pressure (a pressure of 1 atm. is considered as essentially equal to zero)
P_0	pressure at $T = 0^\circ K$
P_A	pressure along an adiabat
P_H	pressure after shock passage
P_{0H}	pressure before shock passage
P_T	thermal pressure
P_S	static pressure
P_X	functions in equation representing experimental hydrostatic data, see p. 4-2
P_1	
P_2	
R	function, see p. 2-6

S	entropy, also constant, see p. 4-17
T	temperature
U	internal potential energy
U_V	vibrational potential energy
V	volume
V_{00}	volume at $P = 0$, $T = 0^\circ K$
V_{0T}	volume at $P = 0$, $T = T$
V_{P0}	volume at $P = P$, $T = 0^\circ K$
V_{PT}	volume at $P = P$, $T = T$
V_{0H}	volume before shock passage
V_H	volume after shock passage
V_f	volume of foam before shock passage
V'_f	volume of foam after shock passage
V_S	shock velocity
V_P	particle velocity
V_m	molar volume

Greek

α	coefficient of thermal expansion $\left(= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \right)$, also internal disorder parameter, see p. 6-16
β_T	isothermal compressibility $\left(= - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \right)$
β_S	isentropic compressibility $\left(= - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \right)$

γ_1	see p. 2-4
γ_2	see p. 2-5
γ_3	see p. 2-7
γ_G	see p. 3-2
γ_S	see p. 4-8
γ_a	see p. 6-4
γ_e	see p. 6-4
γ_{OH}	Grüneisen parameter in material before shock passage
θ	function, see p. 3-1, also Debye temperature
μ	$\rho/\rho_0 - 1$
ν	frequency
ρ	density
ρ_0	density of material before shock passage
σ	Poisson's ratio, also = ρ/ρ_0
τ	stress
ϕ	function, see p. 3-1

INTRODUCTION

The problem of characterizing shock wave properties in solid materials necessitates a knowledge of the solid equation of states at high pressures.

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Section 1

ELEMENTARY PHYSICS AND THERMODYNAMICS OF SOLIDS

The total internal energy of any isolated system is made up of a kinetic part and a potential part.

$$E = K + U \quad (1)$$

The potential energy of a solid has its origin in the attractive and repulsive forces between the atoms, molecules, or ions. In an ideal gas it is assumed that the forces between the molecules are so small that the average potential energy is negligible compared to the average kinetic energy. In a solid, on the other hand, the potential energy plays a very important role.

The internal energy of a solid is often represented as (Fumi and Tosi, 1962)

$$E(V, T) = E_S(V) + E_V(V, T) \quad (2)$$

where $E_S(V)$ represents purely volume-dependent static energy of the solid, or lattice energy, and $E_V(V, T)$ represents the vibrational energy. The term E_S can be further defined as the potential energy if the amplitude of the thermal vibrations were all zero. Fletcher (1957) points out that in general E_S is not a function of volume only. However, it is a fair approximation where electronic effects are negligible. Thus, we will not concern ourselves further with the possible temperature dependence of E_S .

Another equivalent way of representing the energy is

$$E(V, T) = E_0(V) + E_T(V, T) \quad (3)$$

where $E_0(V)$ is the energy of the solid at absolute zero, and $E_T(V, T)$ represents the thermal energy.

At zero degrees absolute, the term $E_T(V, T)$ becomes zero, but $E_V(V, T)$ does not. The term $E_V(V, T)$, at absolute zero, is designated as the zero-point vibrational energy. Thus, the relation between E_0 and E_S can be written

$$E_0(V) = E_S(V) + E_V^0(V) \quad (4)$$

where E_V^0 is a function of volume only and represents the zero-point vibrational energy. In statistical mechanics E_V^0 is given as (Slater, 1939, p. 216)

$$E_V^0 = \sum_{j=1}^{3N} \frac{1}{2}(h\nu_j) \quad (5)$$

where ν_j is the frequency of the j mode of oscillation.

In materials where the interatomic forces and the atomic masses are great, the zero-point energy is small and can usually be neglected. However, in a substance like helium, the zero-point energy is very significant. (Zemansky, 1957, p. 378)

The general variation of E_0 as a function of volume is shown in Figure 1-1.

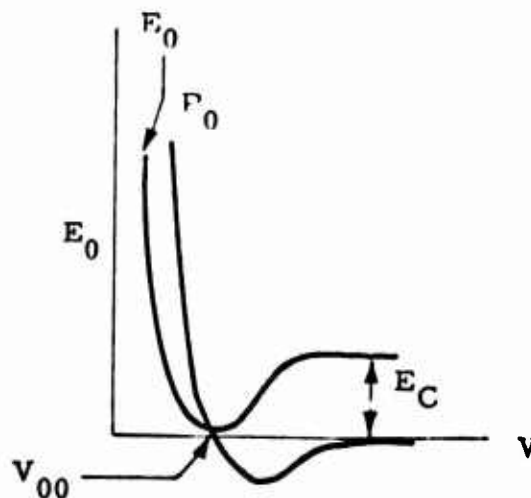


Figure 1-1 - Energy and Pressure as a Function of Volume at Zero Degrees Absolute (after Zel'dovich, Ya. B, and Yu. P. Rayzer, 1965, p. 843)

As Figure 1-1 shows, E_0 is a minimum at V_{00} , the volume at zero degrees absolute and zero pressure. (NOTE: The energy at this point E_{00} is arbitrarily assigned the value of zero). The pressure, P_0 , at absolute zero is sometimes called the elastic pressure and is given by:

$$P_0 = - \frac{dE_0}{dV} \quad (6)$$

The term E_0 for volumes not too far removed from V_{00} , can be expanded to (Mott and Jones, 1958, p. 16)

$$E_0(V) = (E_0)_{V_{00}} + \left(\frac{dE_0}{dV} \right)_{V_{00}} (V - V_{00}) + \frac{1}{2} \left(\frac{d^2E_0}{dV^2} \right)_{V_{00}} (V - V_{00})^2 + \dots \quad (7)$$

The second term on the right vanishes because dE_0/dV at V_{00} is zero.

The term E_S can be similarly expanded, but the volume at which dE_S/dV is zero is slightly different from V_{00} (Huang, 1951, p. 205). In this case the volume should be the static equilibrium volume. This distinction appears to be generally ignored or confused in the literature.

Using the first or vibrational formulation the energies can be further broken down to

$$E(V, T) = K_V(V, T) + U_V(V, T) + E_S(V) \quad (8)$$

The terms K_V and U_V represent the kinetic and potential parts of the vibrational energy. In statistical mechanics equation 8 is written (Slater, 1959, p. 217)

$$E = E_S(V) + \sum_{j=1}^{3N} n_j h \nu_j \quad (9)$$

where n_j represents the quantum number of the j vibration mode. The term $\sum_{j=1}^{3N} n_j h \nu_j$ includes K_V and U_V , that is, the vibrational contributions to the internal energy.

A frequently made approximation is (Fumi and Tosi, 1962)

$$E = E_S(V) + E_V(T) \quad (10)$$

and

$$E = E_0(V) + E_T(T) \quad (11)$$

This division of total internal energy in a volume-dependent term and a temperature-dependent term is called Hildebrand's approximation.

In this report the contribution of electrons to the internal energy will be largely ignored. It should be mentioned, however, that for metals at low temperatures, electron heat capacities predominate over the lattice heat capacities (Gopal, 1966, p. 62).

For a solid the Helmholtz free energy function (Fumi and Tosi, 1962)

$$F = E - TS$$

may be written

$$F = E_0 + E_T - TS$$

and F_T , the thermal free energy, defined as

$$F_T = E_T - TS \quad (12)$$

Thus, the pressure at any given temperature becomes

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{-dE_0}{dV} - \left(\frac{\partial F_T}{\partial V} \right)_T$$

or

$$P(V, T) = P_0(V) + P_T(V, T) \quad (13)$$

where P_T may be defined as the thermal pressure which becomes zero at absolute zero. Equation 12 may be written in terms of vibrational energies, i.e.,

$$F = E_S + E_V - TS$$

$$F = E_S + F_V$$

and

$$P = - \frac{dE_S}{dV} - \left(\frac{\partial F_V}{\partial V} \right)_T$$

or

$$P = - \frac{dE_S}{dV} + P_V(V, T) \quad (14)$$

where P_V may be defined as vibrational pressure. P_V does not become zero at absolute zero. The term $-dE_S/dV$, which it would seem reasonable to designate as some sort of pressure, does not appear to have a name in the literature. We will call it the static pressure.

A few more of the features of the zero degree isotherm should be pointed out: The term E_C in Figure 1-1 represents the energy that would be required, at absolute zero, to separate the atoms of the solid to infinity. It is called cohesive energy and is approximately equal to the heat of evaporation at absolute zero, (Zel'dovich and Rayzer, 1965, p. 843). It should be noted

that the term cohesive energy also is used in the literature for E_0 . In this report, however, cohesive energy will be reserved for E_C .

The cohesive energy can be given by

$$\int_{V_{00}}^{\infty} P_0 dV = -E_C$$

The fundamental equation of thermodynamics which is applicable to any reversible process, or irreversible process providing that the states considered are equilibrium states, is

$$dE = TdS - PdV \quad (15)$$

At zero degrees absolute T , dS and TdS are equal to zero, so that

$$dE = -PdV \quad (16)$$

and

$$(\partial P / \partial V)_S = (\partial P / \partial V)_T \quad (17)$$

Hence, the zero degree isotherm is also an adiabat for which $dS = 0$.

The compressibility at zero pressure and ordinary temperatures is approximately equal to the compressibility at zero pressure and absolute zero (Zel'dovich and Rayzer, 1965, p. 845), i.e.,

$$-\frac{1}{V_{00}} \left(\frac{\partial V}{\partial P} \right)_{T=0} \approx -\frac{1}{V_{0T}} \left(\frac{\partial V}{\partial P} \right)_{T=T}$$

Thus, the speed of sound, considered as a purely thermodynamic quantity,

$$C = V \left(\frac{\partial P}{\partial V} \right)_S^{\frac{1}{2}}$$

is determined by the slope of the PV zero degree isotherm.

The purpose of the preceding discussion is to bring together in one place the various definitions and formulations of thermodynamic terms pertaining to solids found scattered in the literature as an aid for quick reference.

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Section 2

THERMODYNAMICS OF EQUATION OF STATE

A thermodynamic state is specified in terms of the independent variables of the system. The number of independent variables necessary to specify the state, however, must be decided by the experimenter (Reiss, p. 5, 1965). For example, usually only two state variables are necessary to specify the state of a solid, but if the surface area becomes appreciable, as in a powder, another state variable is needed.

A system is completely defined thermodynamically if the entropy is known as a function of the extensive parameters. For a closed system in which the amount of single-phase matter remains constant and which can be specified as a function of two extensive parameters, the entropy can be written as

$$S = S(E, V) \quad (1)$$

Equation 1 may be written in the alternate form,

$$E = E(S, V) \quad (2)$$

The differential form of Equation (2) determines changes of state:

$$dE = (\partial E / \partial S)_V dS + (\partial E / \partial V)_S dV \quad (3)$$

The partial derivatives in the above equation have the following meanings:

$$(\partial E / \partial S)_V = T \quad \text{and} \quad (\partial E / \partial V)_S = -P$$

The above partials were derived from

$$dE = TdS - PdV \quad (4)$$

which is called the fundamental equation. Equivalent expressions of Equation (4) are:

$$dH = VdP + TdS \quad (5)$$

$$dF = -PdV - SdT \quad (6)$$

$$dA = VdP - SdT \quad (7)$$

Because Equations (1) and (2) contain all the information necessary to completely define a system thermodynamically, they are called fundamental relationships or complete equations of state. Other complete equations of state, corresponding to Equations (5) through (7) are

$$H = H(S, P)$$

$$F = F(V, T)$$

$$A = A(P, T)$$

As is evident in the above discussion, knowledge or specification of two independent variables, S and V , or E and V , depending on whether Equations (1) or (2) are used, completely defines the system, providing, of course, that E or S , the dependent variables, are known as a function of E and V or S and V . The quantities S and E , however, are not measurable experimentally. Variables that can be measured experimentally are P , V , and T . Because P and T are functions of S and V , specification of any two of the variables P , V , or T also completely determines the thermodynamic state of the system.

Experimentally, the functional relationships that are usually determined are:

$$P = P(V, T)$$

and

$$E = E(V, T)$$

Neither one of the above two equations, however, supply all the information necessary to completely define the system thermodynamically. To do so, both equations must be used. In other words, although specification of V and T completely determine the system, more than one equation is necessary to obtain

all the thermodynamic information about it.

Because thermal, $P = P(V, T)$, and caloric, $E = E(V, T)$, equations of state do not supply by themselves all the necessary information, they are called incomplete.

The preceeding discussion of equations of states is based on similar discussions in Anderson, Doran, and Fabrenbruch, 1965, pp. 3-5, and Callen, 1960, p. 25 and pp. 33-34.

The following discussion concerns itself with the derivation of some incomplete equations of state.

An equation of state may be derived from the free energy because

$$P(V, T) = -(\partial F / \partial V)_T \quad (8)$$

Using the vibrational form of free energy, Equation (8) becomes

$$-P = \frac{dE_S(V)}{dV} + \left(\frac{\partial F_V}{\partial V} \right)_T \quad (9)$$

Performing the following manipulations on the term $\left(\frac{\partial F_V}{\partial V} \right)_T$, it can be easily shown that Equation (9) reduces to an equation similar to the Mie-Grüneisen equation of state.

The manipulations of $\left(\frac{\partial F_V}{\partial V} \right)_T$ are:

$$\begin{aligned}
\left(\frac{\partial F_V}{\partial V}\right)_T &= T \left(\frac{\partial (F_V/T)}{\partial V}\right)_T \\
&= -T \frac{\left(\frac{\partial (F_V/T)}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_{F_V} \frac{F_V}{T}} \\
&= -T \left(\frac{\partial T}{\partial V}\right)_{F_V} \cdot \frac{V}{T} \cdot \frac{T}{V} \left(\frac{\partial (F_V/T)}{\partial T}\right)_V \\
&= \gamma_1 \frac{T^2}{V} \left(\frac{\partial (F_V/T)}{\partial T}\right)_V
\end{aligned}$$

$$P + \frac{dE_S(V)}{dV} = \frac{\gamma_1}{V} E_V \quad (10)$$

The thermal formulation of free energy leads to

$$P + \frac{dE_0(V)}{dV} = \frac{\gamma_2}{V} E_T \quad (11)$$

or

$$P - P_0(V) = \frac{\gamma_2}{V} E_T$$

The terms γ_1 and γ_2 are generalized Grüneisen parameters equal to (Fumi and Tosi, 1962)

$$\gamma_1 = -\frac{V}{T} \left(\frac{\partial T}{\partial V}\right)_{F_V/T} = \frac{V}{T} \frac{\left(\frac{\partial (F_V/T)}{\partial V}\right)_T}{\left(\frac{\partial (F_V/T)}{\partial T}\right)_V} \quad (12)$$

and

$$\gamma_2 = -\frac{V}{T} \left(\frac{\partial T}{\partial V} \right)_{F_T/T} = \frac{V}{T} \frac{\left(\frac{\partial \left(\frac{F_T}{T} \right)}{\partial V} \right)_T}{\left(\frac{\partial \left(\frac{F_T}{T} \right)}{\partial T} \right)_V} \quad (13)$$

Let us now see what sort of an equation results from manipulation of the following equation:

$$\left(\frac{\partial E}{\partial V} \right)_S = -P(S, V) \quad (14)$$

The manipulations are:

$$\begin{aligned} \frac{dE_0}{dV} + \left(\frac{\partial E_T}{\partial V} \right)_S &= -P \\ P - P_0 &= -\left(\frac{\partial E_T}{\partial V} \right)_S \\ P - P_0 &= -\left(\frac{\partial E_T}{\partial T} \right)_S \left(\frac{\partial V}{\partial T} \right)_S \\ P - P_0 &= \frac{\gamma_3}{V} T \left(\frac{\partial E_T}{\partial T} \right)_S \end{aligned} \quad (15)$$

where

$$\gamma_3 = -\frac{V}{T} \left(\frac{\partial T}{\partial V} \right)_S = \frac{V}{T} \frac{\left(\frac{\partial S}{\partial V} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_V}$$

The term $\left(\frac{\partial E_T}{\partial T}\right)_S$ can be expanded further to

$$\left(\frac{\partial E_T}{\partial T}\right)_S = \left(\frac{\partial E_T}{\partial T}\right)_V - \left(\frac{\partial E_T}{\partial V}\right)_T \frac{V}{\gamma_3 T}$$

So Equation (15) becomes (Fowles, 1964, p. 51)

$$P - P_0(V) = \frac{\gamma_3}{V} T \left(\frac{\partial E_T}{\partial T}\right)_V - \left(\frac{\partial E_T}{\partial V}\right)_T \quad (16)$$

Other equivalent ways of writing Equation (16) are:

$$P - P_0 = \frac{\gamma_3}{V} [E - E_0] + X(V, T) \quad (17)$$

where

$$X(V, 0) \equiv 0, \quad \left(\frac{\partial X}{\partial T}\right)_V = -\left(\frac{E - E_0}{V}\right) \left(\frac{\partial \gamma_3}{\partial T}\right)_V$$

and

$$P = \frac{\gamma_3}{V} E + R(V, T) \quad (18)$$

where

$$R(V, 0) = -\frac{dE_0}{dV} - \frac{\gamma_3(V, 0)}{V}$$

and

$$\left(\frac{\partial R}{\partial T}\right)_V = -\frac{E}{V} \left(\frac{\partial \gamma_3}{\partial T}\right)_V$$

Equations (16), (17), and (18) are general Mie-Grüneisen equations of state. In these general Mie-Grüneisen equations γ_3 is a function of two state variables, usually given as V and T .

It can also be expressed in the following ways: (Anderson, Doran, and Fabrenbruch, 1965, p. 6)

$$\gamma_3(X, Y) = v \left(\frac{\partial P}{\partial E} \right)_V = v \frac{(\partial P / \partial T)_V}{(\partial E / \partial T)_V} = \frac{v(\partial S / \partial V)_T}{T(\partial S / \partial T)_V} = \frac{v\alpha}{\beta_T C_V}$$

The terms X and Y in the above expression stand for the variables γ_3 is a function of. For example,

$$\gamma_3(E, V) = v \left(\frac{\partial P}{\partial E} \right)_V$$

To sum up the discussion concerning the derivation of incomplete equations of state, Equations (10) and (11) which involve γ_1 and γ_2 are equations of isotherms while Equations (16), (17) and (18) which involve γ_3 are equations of isentropes.

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Section 3

A. THE MIE-GRÜNEISEN EQUATION OF STATE AND THE GRÜNEISEN CONSTANT

The assumption that γ_3 is a function of volume only restricts the fundamental dependencies of T , S , and E , and makes possible the derivation of a useful equation of state. The following discussion should make obvious these points.

If γ_3 is a function of volume only, then integration of $\gamma_3 = -\frac{V}{T} \left(\frac{\partial T}{\partial V} \right)_S$ yields

$$\int \frac{dT}{T} = - \int \gamma_3 \frac{dV}{V} + \ln \phi(S)$$

$$\ln T = - \int \gamma_3 \frac{dV}{V} + \ln \phi(S)$$

$$\frac{T}{\phi(S)} = \theta_0 e^{-\int \gamma_3 \frac{dV}{V}} = \theta(V)$$

$$T(S, V) = \phi(S) \theta(V)$$

or

$$S = S\left(\frac{T}{\theta(V)}\right)$$

The form of E is obtained by integration of

$$T = \left(\frac{\partial E}{\partial S} \right)_V = \phi(S) \theta(V)$$

or

$$E - E_0(V) = \theta(V) \int_0^S \phi(S) dS \quad (1)$$

Now

$$-\left(\frac{\partial E}{\partial V}\right)_S = P$$

so differentiation of Equation (1) leads to

$$P + \frac{dE_0}{dV} = -\frac{d\theta(V)}{dV} \int_0^S \phi(S) dS$$

or

$$P - P_0(V) = \frac{\gamma_G(V)}{V} \theta(V) \int_0^S \phi(S) dS \quad (2)$$

where γ_G is Grüneisen's constant and is defined by

$$\gamma_G(V) = -\frac{d \ln \theta(V)}{d \ln V} \quad (3)$$

Equation (2) finally can be reduced to

$$P - P_0(V) = \frac{\gamma_G(V)}{V} (E - E_0(V)) \quad (4)$$

or

$$P - P_0(V) = \frac{\gamma_G(V)}{V} E_T \quad (5)$$

Utilizing the vibrational formulation of energy,

$$E = E_S(V) + E_V(V, T)$$

leads to

$$P + \frac{dE_S}{dV} = \frac{\gamma_G(V)}{V} (E - E_S) \quad (6)$$

$$P + \frac{dE_S}{dV} = \frac{\gamma_G(V)}{V} E_V \quad (7)$$

Equations (4) and (5) or (6) and (7) are the Mie-Grüneisen equations of state.

The preceding discussion was taken mainly from Anderson, Doran, and Fabrenbruch, 1965, pp. 5-6, and Fowles, 1964, pp. 49-53.

The preceding derivation of the Mie-Grüneisen equation is not the original derivation of Grüneisen. Originally, Grüneisen derived Equation (7) from force-field theory (Partington, 1957, p. 346). Various other derivations from Debye's theory and from entropy have also been presented. It would not be worthwhile, for the purposes of this report, to go into the details of these derivations. However, a point of definition of γ_G which appears in these derivations is important.

In statistical mechanics the isothermal equation of state may be represented as (Slater, 1939, p. 217)

$$P - P_0 = \frac{1}{V} \sum_j \gamma_j \frac{h \nu_j}{e^{\frac{h \nu_j}{RT}} - 1}$$

where ν_j represents the vibrational frequency of the j normal mode and

$$\gamma_j = - \left(\frac{\partial \ln \nu_j}{\partial \ln V} \right)_T$$

Grüneisen assumed that all of the γ_j were equal to each other and to a constant γ (Slater, 1939, p. 219). Under this assumption

$$\gamma_2 = - \left(\frac{\partial \ln \nu_j}{\partial \ln V} \right)_T = - \frac{d \ln \nu_j}{d \ln V} = \gamma_3 = \gamma_G$$

According to the Debye theory, the limiting frequency $\nu_{\max}$ defines the frequency spectrum. The frequencies of all the oscillations change in the same ratio as the change in $\nu_{\max}$. (Slater, 1939, p. 238)

Thus

$$\gamma = - \frac{d \ln \nu_{\max}}{d \ln V}$$

In practical applications of the Mie-Grüneisen equation, the Grüneisen parameter γ_3 has been used rather indiscriminately. Fumi and Tosi, 1962, have noted the conditions under which its use is valid. The following is a discussion, taken from their paper, of the use of γ_3 in equations of state.

Because γ_3 is usually the easiest to determine experimentally, it has often been substituted for γ_1 and γ_2 . Such a substitution, however, is valid only if γ_1 or γ_2 do not change with temperature, as seen from the following equations which relate γ_3 with γ_1 and γ_2 :

$$\gamma_3 - \gamma_1 = \frac{E_V}{C_V} \left(\frac{\partial \gamma_1}{\partial T} \right)_V \quad (8)$$

$$\gamma_3 - \gamma_2 = \frac{E_T}{C_V} \left(\frac{\partial \gamma_2}{\partial T} \right)_V \quad (9)$$

It does not follow that because γ_3 does not change with temperature that γ_1 and γ_2 also do not. It can be shown, however, that if, in a temperature range from 0°K upwards,

$$S = S\left(\frac{T}{\theta(V)}\right)$$

as would be the case if γ_3 were a function of volume only, then $\gamma_3 = \gamma_2$ in the same temperature range. This equality also applies if, from 0°K upwards,

$$C_V(V, T) = C_V\left(\frac{T}{\theta(V)}\right)$$

and the entropy at 0°K is a constant.

In other words, to summarize the preceding discussion, if γ_1 or γ_2 are functions of volume only, then

$$\gamma_1 = \gamma_3 = \gamma_G$$

or

$$\gamma_2 = \gamma_3 = \gamma_G$$

Because γ_3 is a function of volume only in a certain range of temperature does not mean, however, that Equations (4) and (5) or (6) and (7) are necessarily valid. Equations (4) and (5) are valid if γ_3 is a function of volume only in the temperature range from zero degrees absolute upwards, or if

$$C_V(V, T) = C_V\left(\frac{T}{\theta(V)}\right) \quad (0^\circ\text{K upwards})$$

in the same temperature range and the entropy at zero degrees absolute is constant.

If the energy can be expressed according to Hildebrand's approximation:

$$E = E_0(V) + E_T(T)$$

or

$$E = E_S(V) + E_V(T)$$

then the relationship between the various γ s are

$$E_V \gamma_1(V, T) = T C_V \gamma_3(V, T) \quad (10)$$

and

$$E_T \gamma_2(V, T) = T C_V \gamma_3(V, T) \quad (11)$$

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Section 4

EXPERIMENTAL DETERMINATION OF GRÜNEISEN PARAMETERS

A. UNDER HYDROSTATIC CONDITIONS

a. Form of Experimental Data

Before discussing the experimental determination of the various γ 's, it will be well to review the form in which experimental data is presented.

Experimental, hydrostatic data are usually presented in one of two ways. In Slater's notation (Slater, 1939, p. 200)

$$V = V_{00}(1 + a_0(T) - a_1(T)P + a_2(T)P^2 + \dots) \quad (1)$$

Thus, at zero pressure

$$\alpha = (1/V_{0T})(\partial V/\partial T)_{P=0} = (1/1+a_0) da_0/dT \approx da_0/dT \quad (2)$$

and

$$\beta_T = -(1/V_{0T})(\partial V/\partial P)_{T, P=0} = a_1/1+a_0 \approx a_1 \quad (3)$$

Bridgman, on the other hand, presents his data in the form

$$-\frac{V - V_{0T}}{V_{0T}} = aP - bP^2 \quad (4)$$

When V_{0T} is the volume at zero pressure and temperature T . Thus,

$$\beta_T = -(1/V_{0T})(\partial V/\partial P)_{T, P=0} = a \quad (5)$$

To convert Bridgman's data to Staler's notation (Overton, 1962, p. 118):

$$V_{0T} = V_{00}(1 + a_0)$$

$$a = a_1/1 + a_0$$

$$b = a_2/1 + a_0$$

Equation (1) can be rewritten in the following form

$$P = P_0(T) + P_1(T) \left[(V_{00} - V)/V_{00} \right] + P_2(T) \left[(V_{00} - V)/V_{00} \right]^2 \dots \quad (6)$$

where $P_0(T)$ becomes zero at absolute zero*. In terms of Equation (6) the heat capacity at constant volume is (see Slater, 1939, p. 204)

$$C_V = C_V^0 - V_{00}T \left[d^2 P_X / dT^2 \left[(V_{00} - V)/V_{00} \right] + 1/2 d^2 P_1 / dT^2 \left[(V_{00} - V)/V_{00} \right]^2 + 1/3 d^2 P_2 / dT^2 \left[(V_{00} - V)/V_{00} \right]^3 \dots \right] \quad (7)$$

where C_V^0 is the heat capacity at volume V_{00} .

b. Grüneisen Parameter γ_3

As mentioned previously, the Grüneisen parameter, γ_3 , is usually determined experimentally from the relationship

$$\gamma_3(V, T) = \alpha V / \beta_T C_V \quad (8)$$

* This $P_0(T)$ is not the same as $P_0(V)$ used previously. The latter represents the elastic pressure on the zero-degree isotherm while the former is the pressure required to reduce the volume to V_{00} . To avoid confusion $P_0(T)$ will be called $P_X(T)$ in this paper.

or alternatively

$$\gamma_3(V, T) = \alpha V / \beta_S C_P \quad (9)$$

where β_S is the adiabatic compressibility

$$\beta_S = -(1/V)(\partial V / \partial P)_S, \quad \beta_S C_P = \beta_T C_V$$

Like any other state variable, the Grüneisen parameter is a function of two independent variables. If one independent variable is set, then the parameter becomes a function of the other. Because the independent variables most convenient to work with are pressure and temperature, Equation (8) could just as well be written in terms of P and T. Such an equation can be written

$$\gamma_3(P, T) = \frac{\alpha(P, T) V(P, T)}{\beta(P, T) C_V(P, T)} \quad (10)$$

If P is set at zero, Equation (10) becomes a function of temperature alone. Equation (10) thus gives us the temperature dependency of γ_3 along an isobar. Because the volume expansion of a solid at zero pressure is relatively slight - aluminum increases its volume by only some 5% from 20°C to 600°C - Equation (10) is only slightly volume-dependent.

In principle, the volume dependency of γ_3 could be checked by holding temperature constant and letting volume or pressure vary. This procedure would require thermal expansion, heat capacity, and compressibility data at various pressures. Unfortunately, such data is not generally available.

Barron, Leadbetter, and Morrison, 1964, p. 75, have made a rough estimate of the volume dependency of γ_3 from Equation (8) for NaCl and KCl. Their thermodynamic equation, derived from Equation (8), for this dependency is

$$\left(\frac{\partial \ln \gamma_3}{\partial \ln V} \right)_T = \frac{1}{\beta_T} \left\{ \frac{1}{\alpha V} \left[\frac{\partial (\beta_T V)}{\partial T} \right]_P + \frac{T}{C_P} \left[\frac{\partial (V \alpha)}{\partial T} \right]_P - \frac{1}{\beta_S} \left(\frac{\partial \beta_S}{\partial P} \right)_T \right\} \quad (11)$$

At $T \sim 300^\circ\text{K}$ they found (pressure presumably zero)

$$\left(\frac{\partial \ln \gamma_3}{\partial \ln V}\right)_T \sim 0.3 \text{ (NaCl)}$$

$$\sim 1.9 \text{ (KCl)}$$

It is pointed out, however, that the accuracy of the above results may be in error by $\pm 100\%$, or more, for NaCl and $\pm 50\%$ for KCl.

Making various approximations and interpolations of experimental data, Ku (1967) used Equation (10) to calculate γ_3 values at different temperatures and pressures for a number of different plastics. His results are given in Tables 4-1 through 4-4.

c. Determination of Grüneisen Parameter from Thermal Expansion and Heat Capacity Data

Although heat capacity and thermal expansion data at zero pressure are readily available for most elements and compounds, compressibility data over extensive temperature ranges is very limited. Thus, Equation (10) cannot be used in most cases to test the temperature dependence of γ_3 . Another equation, however, was derived by Grüneisen which does not require compressibility data over an extended temperature range. The derivation of this equation is based on the expansion of the term $V dE_S/dV$ in the Mie-Grüneisen equation. At zero pressure (Partington, 1962, p. 351)

$$-V \frac{dE_S}{dV} = \gamma_G E_V$$

and after expansion of $V dE_S/dV$ in powers of $(V - V_{00})$

$$\frac{V_{0T} - V_{00}}{\beta_{00}} \left[1 - \frac{1+(n+m)/3}{2} \cdot \frac{V_{0T} - V_{00}}{V_{00}} + \dots \right] = \gamma_G E_V \quad (12)$$

Table 4-1
GRÜNEISEN PARAMETER γ_3 OF SOME COMMON PLASTICS (Ku, 1967)

Plastics	Grüneisen Parameter	Pressure atm	Temp °C
Polyethylene - low density	1.213	10,000	20
Polyethylene - high density	0.812	2,000	20
Teflon	0.941	10,000	20
Nylon	0.796	1	20
Kel-F	0.305	10,000	20
PMMA	0.285	1,000	21.1
Polyester (Sectron 5003) ^o	1.04	10,000	20
Polystyrene	1.44	1	—
	0.995	1,910	29
Polypropylene	1.80	618	23
Cellulose acetate Butyrate	0.595	1,910	181
Ethyl Cellulose	0.480	1,910	196
Polyvinyl Chloride - Pure	0.646	1,000	0
	0.865	1,000	20
- 10% Plasticizer	0.819	1,000	0
	0.866	1,000	20
- 20% Plasticizer	1.32	1,000	0
	0.910	1,000	20
- 30% Plasticizer	1.16	1,000	0
	0.913	1,000	20

Table 4-2
GRÜNEISEN PARAMETER γ_3 OF TEFLON (Ku, 1967)

Pressure, atm	Temperature °C			
	20	40	60	80
1	.935	.768	.374	.290
1,000	.651	.698	.411	.355
2,000	.591	.611	.469	.417
3,000	.547	.577	.505	.459
4,000	.568	.520	.538	.505
5,000	.598	.557	.561	.533
6,000	.615	.576	.577	.556
7,000	.656	.627	.611	.581
8,000	.724	.680	.645	.611
9,000	.819	.774	.720	.657
10,000	.941	.866	.808	.741

Table 4-3
GRÜNEISEN PARAMETER γ_3 OF POLYETHYLENE (Ku, 1967)

Pressure, atm	Temperature °C			
	20	40	60	80
1	1.177	.815	.539	.918
1,000	1.990	1.431	1.041	1.585
2,000	1.664	1.164	.885	1.147
3,000	1.657	1.172	.927	1.047
4,000	1.654	1.226	.977	1.172
5,000	1.559	1.198	.959	1.074
6,000	1.597	1.254	1.015	1.271
7,000	1.398	1.121	.920	1.330
8,000	1.332	1.088	.896	1.269
9,000	1.216	1.019	.840	1.393
10,000	1.213	1.026	.846	.776

Table 4-4
GRÜNEISEN PARAMETER γ_j OF KEL-F (Ku, 1967)

Pressure, atm	Temperature °C			
	20	40	60	80
1	.857	.693	.730	.604
1,000	.710	.620	.588	.545
2,000	.645	.594	.554	.535
3,000	.623	.586	.534	.510
4,000	.617	.579	.500	.515
5,000	.614	.580	.538	.502
6,000	.599	.557	.507	.482
7,000	.565	.516	.473	.447
8,000	.502	.455	.416	.398
9,000	.416	.374	.346	.324
10,000	.305	.271	.251	.235

where n and m are constants associated with the repulsive and attractive forces. Equation (12), after some simplifying assumptions, can be written (Grüneisen, 1926, p. 46)

$$\frac{V_{0T} - V_{00}}{V_{00}} = \frac{E_V}{Q_0 - (\gamma_G + \frac{2}{3}) E_V} \quad (13)$$

$$\text{where } Q_0 = \frac{V_{00}}{\gamma_G \beta_{00}}$$

Differentiation of Equation (13) with respect to temperature, assuming

$$\left(\frac{\alpha E_V}{\alpha T}\right)_P \approx \left(\frac{\alpha E_V}{\alpha T}\right)_V, \text{ gives}$$

$$\frac{1}{V_{00}} \left(\frac{\alpha V}{\alpha T}\right)_{P=0} = \frac{C_V}{Q_0 \left[1 - (\gamma_G + \frac{2}{3}) \frac{E_V}{Q_0}\right]^2} \quad (14)$$

As pointed out by Hume-Rothery, 1945, p. 210, the term $(\gamma_G + \frac{2}{3}) \frac{E_V}{Q_0}$ becomes increasingly important at high temperatures.

To a first approximation Equation (14) can be written

$$\gamma_G = \frac{V_{00} \alpha}{\beta_{00} C_V} \quad (15)$$

The assumed temperature independence of γ_G can thus be tested by using α and C_V values at various temperatures and zero pressure.

d. Slater and Dugdale-MacDonald Relations

Because the volume dependencies of γ_G and γ_2 are of great interest, and the data for their calculation from thermodynamic equations are in short supply, great use has been made of the Slater relationship (Slater, 1939, p. 239):

$$\gamma_S(V) = -2/3 - 1/2 V (\partial^2 P / \partial V^2)_T / (\partial P / \partial V)_T \quad (16)$$

This equation was derived by assuming that

$$\gamma_S(V) = -d \ln \nu_{\max} / d \ln V$$

where $\nu_{\max}$ is Debye's limiting frequency. It is also assumed that the Poisson ratio is independent of volume.

The Grüneisen parameter determined by Equation (16) is labeled γ_S because, as Collins, 1962, p. 323, points out, γ_S can be identified with γ_G obtained from thermal expansion only if Poisson's ratio is independent of volume. Usually this is not the case.

At absolute zero and zero pressure, the volume is V_{00} and Equation (16) takes the form

$$\gamma_S = -\frac{2}{3} + \frac{P_2^0}{P_1^0} \quad (17)$$

where P_1^0 and P_2^0 represents the temperature dependent parameters at $T = 0^\circ\text{K}$. Because to a good approximation P_1^0 and P_2^0 can be taken as equal to P_1 and P_2 at room temperature (Kachhava and Saxena, 1965, p. 986) and thermal volume expansion is assumed negligible (Slater, 1940, p. 745), Slater's relation can be written

$$\gamma_S = -\frac{2}{3} + \frac{P_2}{P_1} \quad (18)$$

or, in Bridgman's notation

$$\gamma_S = \frac{b}{a} - \frac{2}{3} \quad (19)$$

for room temperature and zero pressure.

Gillvarry, 1957, p. 1258, using a generalized isothermal equation of state, showed that even though γ_S is temperature dependent, this dependency is not manifest at zero pressure. At zero pressure γ_S is strictly constant at any temperature. Thus, Slater's relation apparently cannot be used to test the temperature dependency of γ_S at zero pressure.

If the preceding assumptions are granted, Equation (16) can be used to determine the volume dependence of γ_S . In Bridgman's notation, Equation (16) becomes

$$\gamma_S(V) = -\frac{2}{3} + \frac{b}{a^2} \left[\frac{V/V_{00}}{1 + 2 \frac{b}{a^2} (1 - V/V_{00})} \right] \quad (20)$$

To the best of our knowledge the above equation has not appeared as such in the literature nor has a critical evaluation of its validity.

There appears in the literature another equation for Slater's relation. This is

$$\gamma_S(V) = -\frac{2}{3} - \frac{V}{2} \frac{\left(\frac{\partial^2 P}{\partial V^2} \right)_S}{\left(\frac{\partial P}{\partial V} \right)_S} \quad (21)$$

Although no discussion has been found in the literature about the conditions under which Equations (16) or (21) should be used, some pertinent points have been found:

Slater's derivation of Equation (16) is based on the relationship (Slater, 1939, p. 238)

$$v_{\max} = \left(\frac{9}{4\pi} \frac{N}{V} \frac{1}{\frac{1}{v_l^3} + \frac{2}{v_t^3}} \right)^{1/3} \quad (22)$$

where v_l and v_t are the velocities of the longitudinal and transverse waves. The wave velocities are related to compressibility by the following equations.

$$v_l = \sqrt{\frac{3(1-\sigma)}{\beta\rho(1-\sigma)}} \quad \text{and} \quad v_t = \sqrt{\frac{3(1-2\sigma)}{2\beta\rho(1+\sigma)}}$$

where σ is Poisson's ratio.

Dugdale and MacDonald, 1953, p. 834, state that the propagation of a sound wave (presumably under zero applied pressure) at low temperatures will be isothermal, while at higher temperatures, including room temperature, the process will be practically adiabatic. Gilvarry, 1956, p. 333, on the other hand, points out that at low pressure the adiabatic or isothermal compressibilities are for practical purposes, identical.

It is apparent that more study of this matter is required to resolve the confusion. Of course, at zero degrees absolute, no ambiguity exists because, at $T = 0^{\circ}\text{K}$,

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T$$

Dugdale and MacDonald (1953) objected to Slater's relation because they claimed that the effect of finite strain was neglected. They proposed the following relationship instead

$$\gamma = -\frac{V}{2} \frac{\partial^2(PV^{2/3})/\partial V^2}{\partial(PV^{2/3})/\partial V} - \frac{1}{3} \quad (23)$$

Their reasoning was shown to be in error by Gilvarry (1956) and Barron (1957). However, Equation (23) has shown good agreement for zero pressure tests (Rice, McQueen, and Walsh, 1958, p. 44). Generally, there is no firm basis for preferring Equation (23) over Equation (16) (Doran, 1960, p. 29).

e. Grüneisen Parameter γ_2

If a means is available for obtaining $P_T(V, T)$, then $\gamma_2(V, T)$ can be determined from

$$P_T = \frac{\gamma_2(V, T)}{V} E_T$$

The term P_T can be easily obtained if the P - V zero degree isotherm and P - V isotherms are available. From such data, P_T is obtained by

$P_T = P - P_0$. Unfortunately, compressibility data is in short supply, so some other expedient for obtaining P_T is desirable.

Beecroft and Swenson (1961) found that if the isothermal compressibility of a substance is linear with volume and independent of temperature, the determination of P_T is greatly facilitated. The following will briefly review the approach of Beecroft and Swenson.

If the compressibility is a function of volume alone and independent of temperature, then P_T becomes a function of temperature alone. This becomes obvious if one integrates the expression for compressibility, i.e.,

$$\begin{aligned} -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T &= f(V) \\ \int dP &= - \int f(V) \frac{dV}{V} + g(T) \\ P &= P_0(V) + P_T(T) \end{aligned} \quad (24)$$

Thus, if the compressibility is a function of volume alone, $P_0(V)$ and $P_T(T)$ can be evaluated,

Furthermore, if P_T is a function of temperature alone then

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\beta} = \frac{dP_T}{dT}$$

so that α/β is a function of temperature alone. Thus α/β found at $P = 0$ can be considered as a constant for a given temperature.

The expression for E_T is found by integrating

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

or

$$\left(\frac{\partial E}{\partial V} \right)_T = T \frac{\alpha}{\beta} - P$$

Thus,

$$\int_{E(V_{0T}, T)}^{E(V_{PT}, T)} E = T \frac{\alpha}{\beta} \int_{V_{0T}}^{V_{PT}} dV - \int_{V_{0T}}^{V_{PT}} P dV \quad (25)$$

and

$$\int_{E_{00}}^{E_0} E = - \int_{V_{00}}^{V_{P0}} P dV \quad (26)$$

Subtracting Equations (25) and (26) gives

$$E_T = E(V, T) - E_0(V) = E(V_{0T}, T) - E_{00} + T \frac{\alpha}{\beta} (V_{PT} - V_{0T})$$

$$- \int_{V_{0T}}^{V_{PT}} P dV + \int_{V_{00}}^{V_{P0}} P dV \quad (27)$$

The terms

$$E(V_{0T}, T) - E_{00}$$

can be replaced by H at P=0 and T. This follows from

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

at P=0

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_P = C_P$$

and

$$H(P=0, T) = E(P=0, T) = \int_0^T C_P dT$$

The term E_{00} is arbitrarily set equal to zero. The last two integrals of Equation (27) can be evaluated from experimental, compressibility data.

Beecroft and Swenson found for sodium, that the compressibility could be assumed, to a first approximation, as independent of temperature and a linear function of volume. Their experimental data is shown in Figure 4-1.

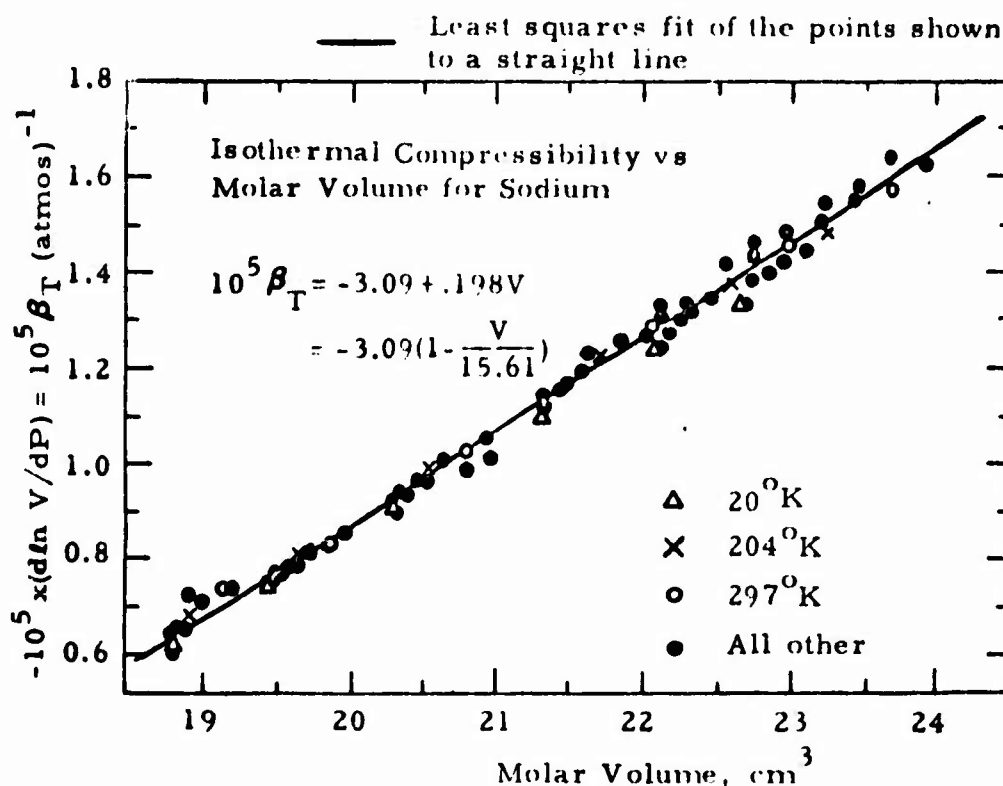


Figure 4-1 - The Isothermal Compressibility of Sodium as a Function of Molar Volume

From this data and heat capacity data at zero pressure the temperature and volume dependence of γ_2 was calculated. The results are shown in Figure 4-2.

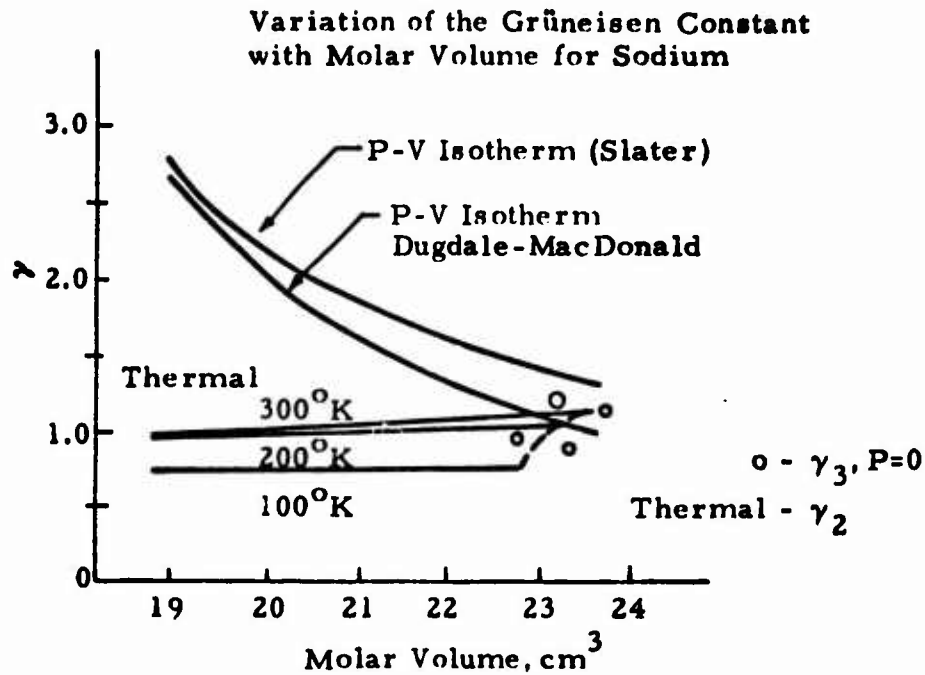


Figure 4-2 - The Volume Variation of the Grüneisen Constant as Given by Various Definitions

B. UNDER DYNAMIC CONDITIONS

a. Method of Rice, Walsh, and McQueen

In the shock wave determination of the Grüneisen constant, the form of the Mie-Grüneisen equation of state usually assumed is the thermal formulation

$$P - P_0 = (\gamma_G/V)(E - E_0) \quad (28)$$

Equation (28) combined with the shock Hugoniot,

$$E_H - E_{0H} = (P_H/2)(V_{0H} - V) \quad (29)$$

where E_{0H} and V_{0H} are conditions ahead of the advancing shock and P_H the pressure behind the shock, gives

$$\gamma_G = V(P_H - P_0) / \left[(P_H/2)(V_{0H} - V) + E_{0H} - E_0 \right] \quad (30)$$

where $E_0 = - \int_{V_{00}}^V P_0 dV$ (E_{00} the energy at zero degrees absolute and zero pressure is arbitrarily assumed zero). The term E_{0H} is found by integrating the Debye specific heat curve from zero degrees absolute to the temperature at the initial shock conditions.

It is further assumed that

$$\gamma_G = - 1/2 \left[(d(P_0 V^{2/3})/dV^2)(d(P_0 V^{2/3})/dV) \right] - 1/3 \quad (31)$$

This latter equation is the Dugdale-MacDonald modification of Slater's formula assumed to be valid along the zero degree isotherm. Thus,

$$\begin{aligned} & - V/2 \left[(d(P_0 V^{2/3})/dV^2)/(dP_0 V^{2/3}/dV) \right] - 1/3 \\ & = V(P_H - P_0) / \left[(P_H/2)(V_{0H} - V) + E_{0H} - E_0 \right] \end{aligned} \quad (32)$$

Knowing the initial conditions of specific volume, compressibility at zero degrees absolute and zero pressure, and specific internal energy E_{0H} (relative to E_{00}), Equation (32) can be integrated. The result is the zero degree isotherm. From this zero degree isotherm, γ_G is evaluated using Equation (31).

The preceding discussion was taken mainly from Rice, McQueen, and Walsh, 1958, and Deal, 1962.

Rice, et al, 1958, p. 57, present their calculations of γ_G in the form

$$\gamma_G(V) = \gamma_{0H} + A\mu + B\mu^2 + C\mu^3 \quad (33)$$

where $\mu = \rho/\rho_{0H} - 1$, A, B, and C are constants, and γ_{0H} is the value of γ_G at zero

pressure. The values of γ_{0H} were chosen to correspond to those obtained, at zero pressure, from the equation

$$\gamma = \frac{V\alpha}{\beta C_V} \quad (34)$$

To check the consistency of the preceding method, the Dugdale-MacDonald γ is found at zero pressure from the relationship

$$\gamma = 2S - 1 \quad (35)$$

where S is the constant in the linear relationship between shock velocity and particle velocity, i.e.,

$$V_S = C_0 + SV_P$$

Equation (35) represents the Dugdale-MacDonald parameter at zero pressure as derived entirely from shock data. The derivation of Equation (35), which is not discussed here, is straightforward (see Deal, 1962, p. 206). The parameter determined from Equation (35) may now be compared to that determined by Equation (34). Such a comparison shows that the two γ 's agree fairly well for many elements (McQueen, 1964, p. 68).

b. $(\partial E/\partial P)_V$ Assumed Constant

If the assumption is made that $(\partial E/\partial P)_V$ is independent of pressure and volume in the vicinity of the Hugoniot, and γ_3 is a function of volume only, then γ_G can be determined from the equation (Deal, 1962, p. 206, and McQueen and Marsh, 1960, p. 1267):

$$\gamma_G(V) = V / \left(\frac{\partial E}{\partial P} \right)_V \quad (36)$$

The term $\left(\frac{\partial E}{\partial P}\right)_V$ is determined from zero pressure, thermodynamic data by

$$\left(\frac{\partial E}{\partial P}\right)_V = \frac{\left(\frac{\partial E}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_V} = \frac{C_V \beta_T}{\alpha}$$

Deal, 1962, p. 206, states that the above procedure is justified because it reproduces well equations of state obtained by more complex procedures. A comparison of the results obtained by this method with other methods, however, has not been found.

c. γ_G from Speed of Sound Measurements behind Shock Waves

An adiabatic equation of state may be written in terms of the Hugoniot, just as an isotherm was in Section 4 B.a. Consider Figure 4-3.

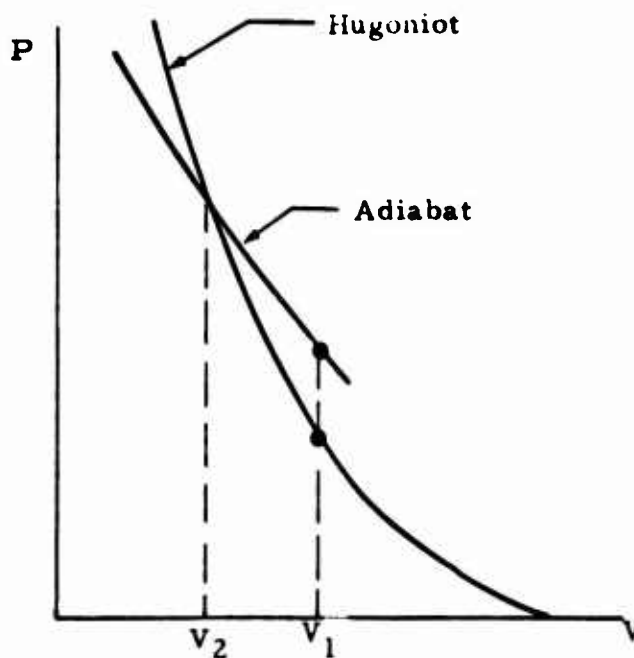


Figure 4-3 - P vs V Curve to Illustrate Relationship Between Sound Speed Behind a Shock Wave and Intersection Between Adiabats and Hugoniots

At volume V_1 the pressure on the Hugoniot can be given by

$$P_H - P_0 = \frac{\gamma_G}{V_1} (E_H - E_0)$$

while that on the isentropic by

$$P_A - P_0 = \frac{\gamma_G}{V_1} (E_A - E_0)$$

Thus,

$$P_A - P_H = \frac{\gamma_G}{V_1} (E_A - E_H)$$

Or, generally

$$P_A - P_H = \frac{\gamma_G}{V} (E_A - E_H)$$

Differentiation of the above equation gives (Deal, 1962, p. 205)

$$P_A = -\frac{dE_H}{dV} + (P_H - P_A) \frac{d}{dV} \left[\frac{V}{\gamma} \right] + \frac{V}{\gamma} \left[\frac{dP_H}{dV} - \frac{dP_A}{dV} \right] \quad (37)$$

At volume V_2 where the Hugoniot and adiabat intersect, Equation (37) becomes

$$P_H = P_A = -\frac{dE_H}{dV} + \frac{V}{\gamma} \left[\frac{dP_H}{dV} - \frac{dP_A}{dV} \right]$$

or

$$\gamma = \frac{\left[\frac{dP_H}{dV} - \frac{dP_A}{dV} \right] V}{P_H + \frac{dE_H}{dV}} \quad (38)$$

To find $\frac{dE_H}{dV}$, the equation of the Hugoniot is differentiated, i.e.,

$$E_H - E_{0H} = \frac{P_H}{2} (V_{0H} - V)$$

$$\frac{dE_H}{dV} = \frac{1}{2} \frac{dP_H}{dV} (V_{0H} - V) + \frac{P_H}{2}$$

So that Equation (38) becomes, at volume V_2 (McQueen, 1964, p. 70)

$$\gamma_G(V) = \frac{\left[\frac{dP_H}{dV} - \frac{dP_A}{dV} \right] 2V}{P_H + \frac{dP_H}{dV} (V_{0H} - V)} \quad (39)$$

The speed of sound, it may be recalled, is given by

$$C^2 = -V^2 \left(\frac{\partial P}{\partial V} \right)_S$$

Thus, if the speeds of sound along a Hugoniot can be measured and the slopes of the Hugoniot as functions of volume known, $\gamma_G(V)$ can be calculated with the aid of Equation (39).

The preceding discussion, taken from McQueen, 1964, p. 70, and Deal, 1962, p. 205 represents the general basis of the method. The actual determination of γ from sound speeds behind shock waves, however, (Al'tshuler, Kormer, Brazhnik, Vladimirov, Speranskaya, and Funtikov, 1960; see also, Anderson, 1965) was approached in a slightly different manner apparently, because Hugoniot slopes obtained from dynamic measurements are inaccurate. In the experimental paper (Al'tshuler et al, 1960), it is reasoned that since

$$P_H = P_0 + P_T$$

and

$$\left(\frac{\partial P_T}{\partial V} \right)_S > 0$$

then

$$\left(\frac{\partial P_H}{\partial V} \right)_S > \left(\frac{\partial P_0}{\partial V} \right)_S$$

or

$$C_H^2 > C_0^2$$

where C_H is the isentropic sound speed along the Hugoniot and C_0 the sound speed at absolute zero. The sound speed C_0 may be written

$$C_0^2(\sigma) = \frac{1}{\rho_0} \frac{dP_0}{d\sigma} \quad (40)$$

where ρ_0 is the density of the initial Hugoniot state and $\sigma = \rho/\rho_0$. If expression (40) is integrated using C_H^2 instead of C_0^2 , i.e.,

$$P_0(\sigma) < \int_{\sigma_{00}}^{\sigma} \rho_0 C_H^2 d\sigma = I(\sigma) - I(\sigma_{00}) = I(\sigma, \sigma_{00})$$

where $\sigma_{00} = \rho/\rho_{00}$, ρ_{00} being the density at $T = 0^\circ\text{K}$ and $P = 0$, then the function $I(\sigma, \sigma_{00})$ provides an upper limit to the zero degree isotherm.

The Grüneisen parameter is then determined by using a Mie-Grüneisen equation for P_H which includes electronic contributions. For P_0 , $I(\sigma, \sigma_{00})$ is substituted.

The Grüneisen parameters obtained in this manner are 20 to 25% lower than those obtained by the method of Rice, Walsh and McQueen in which the electronic contributions are taken into account.

d. Other Methods

Other methods of determining the Grüneisen parameter which are mentioned in the literature include varying the initial E_{0H} state before shocking by heating or by the method of reflected shocks. However, very little work appears to have been done in this area. These methods have not been investigated thoroughly.

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Section 5
CALCULATIONS OF VARIOUS GRÜNEISEN PARAMETERS FOR
MATERIALS OF STUDY*

A. GRÜNEISEN'S PARAMETER γ_3 FROM HYDROSTATIC DATA AT
ZERO PRESSURE

a. Calculations

As discussed in Section 4A.b., the relationship

$$\gamma_3(V, T) = \frac{\alpha V}{\beta_T C_V} = \frac{\alpha V}{\beta_S C_P}$$

is usually used to test the constancy, at zero pressure, of γ_3 with temperature (the slight volume dependency of γ_3 because of thermal expansion is usually ignored).

To use the above formula, thermal expansion, compressibility, and heat capacity data at various temperatures are required. Although thermal expansion and heat capacity data at zero pressure are readily available, compressibility data is scarce. For the materials of this study, compressibility data over an extended temperature range was found only for aluminum. For the other materials, with the exception of the plastics, enough data was found to enable calculations of γ_3 at room temperature.

Because the plastics of the study are composite materials that have varying compositions and porosities, they presented special problems which, unfortunately, have not yet been resolved.

*In this section the references are numbered.

The results of the calculations of γ_3 from hydrostatic data at zero pressure are presented in Table 5-1.

b. Discussion of Results

Because of the approximations made in the calculations and uncertainties in some of the experimental data, it is hard to state with certainty the errors associated with the calculated values. Gschneider (Reference 12, p. 416) states that most of the Grüneisen parameter data agree with each other only to about 10%.

What would be desirable to increase the precision of the above γ_3 calculations are more precise coefficients of thermal volume expansion.

Some of the other uncertainties which influence the accuracy of the above calculation are:

1. The data on thermal expansions and heat capacities of metals have been evaluated for accuracy. In Reference 8 the data of various investigators is reduced to curves through "most probable values." No such evaluation exists, as far as we know, for compressibility data. The data available on compressibility is limited and as yet has not been critically evaluated in a comprehensive way. A brief discussion of the errors involved in compressibility data is given by Gschneider (Reference 12, pp. 298-305).
2. Although accurate data exist on heat capacities at constant pressure of metals over a wide temperature range, uncertainties creep in when this data is converted to heat capacity at constant volume.

The Nernst-Lindemann relationship below is used for the conversion

$$C_p - C_v = A T C_p^2$$

For copper, A varies only by about 8% over a 1200°K temperature range (Reference 25, p. 264); its variation for other materials would need to be looked into in further detail.

Table 5-1
TEMPERATURE DEPENDENCE OF GRÜNEISEN PARAMETER γ_3 AT ZERO PRESSURE
FOR VARIOUS MATERIALS OF STUDY

Material	Temp. °K	(a) C_V cal(gm. atom °K) ⁻¹	(b) β_T (mb) ⁻¹	(c) $\alpha \times 10^{+5}$ (°K) ⁻¹	V (d) cm ³ gm. atom ⁻¹	(e) γ_3 Calculated	Literature Values	
							Temp. °K	Ref.
Aluminum	273	5.496	1.212	7.01	9.985	2.51	0	17
	293	5.606	1.327	7.01	9.999	2.25	50	
	296	5.603	1.378	7.01	10.000	2.17	100	
	298	5.602	1.381	7.01	10.000	2.16	150	
	303	5.623	1.365	7.48	10.000	2.33	200	
	373	5.837	1.272	7.48	10.050	2.41	250	
	436	5.997	1.438	8.47	10.090	2.36	300	
	573	6.252	1.452	8.47	10.190	2.27	350	
	708	6.385	1.601	9.92	10.350	2.40	400	
	773	6.491	1.680	9.92	10.390	2.26	Rm.	
Beryllium	303	3.884	0.795	3.35	4.846	1.26	298	12
Tungsten	298	5.89	0.320	1.12	9.53	1.35	298	12
Tantalum	298	6.02	0.497	1.80	10.90	1.70	298	12
Tungsten Carbide	296	9.869 (C_P)	0.3035(β_S)	1.35	12.50	1.35		
Silicon Carbide	Room	6.418 (C_P)	0.4344(β_S)	1.20	12.46	1.25		

Table 5-1 (Continued)

NOTES:

(a) C_V data calculated by the formula

$$C_P - C_V = A T C_P^2$$

The source of C_P data and the A values used are:

Material	C_P Source	A Values (gm.atom/cal)
Al	Ref. 8, p. 39	2.23×10^{-5} (Ref. 7)
Be	Ref. 20, p. 39	1.34×10^{-5} (Calculated)
W	Ref. 20, p. 337	2.45×10^{-6} (Calculated)
Ta	Ref. 20, p. 313	4.61×10^{-6} (Calculated)
WC	Ref. 20, p. 83	1.84×10^{-6} (Calculated)
SiC	Ref. 20, p. 73	2.33×10^{-6} (Calculated)

(b) Compressibility values were obtained from the following sources

Al	Ref. 5, p. 107
Be	Ref. 5, p. 107
W	Ref. 5, p. 111
Ta	Ref. 5, p. 111
WC	Ref. 4, p. 548
SiC	Ref. 21, p. 342

Table 5-1 (Continued)

- (c) To obtain the coefficients of thermal expansion, it was necessary to convert data given as % volume increase and % linear thermal expansion from 20°C (293°K). The coefficients presented above are rough approximations calculated by means of the formula

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P \approx \frac{2(\% \Delta_2 - \% \Delta_1)}{(200 + \% \Delta_2 + \% \Delta_1) \Delta T}$$

where the % Δ terms refer to the percent volume increase at a given temperature. For example, the percent volume increase for aluminum from 293.18 K to 373.18 K is 0.562. Thus α in this range is calculated by

$$\alpha \approx \frac{2 \times 0.562}{(200 + 0.562) 80} = 7.01 \times 10^{-5} / ^\circ \text{K}$$

Where the data is in the form of linear expansion, the above formula, using % Δ to represent percent linear expansion, gives the coefficient of linear expansion. This is then multiplied by three to obtain the coefficient of volume expansion.

The sources and forms of the thermal expansion data are

Material	Source	Form
Al	Ref. 5, p. 78	% vol. exp.
Be	Ref. 5, p. 78	% vol. exp.
W	Ref. 23, p. 880	% linear exp.
Ta	Ref. 8, p. 619	% linear exp.
WC	Ref. 10, p. 143	% linear exp.
SiC	Ref. 9, p. 933	% linear exp.

Table 5-1 (Concluded)

(d) The volumes were calculated from the densities found in the following sources.

Material	Density gm/cm ³	Temp. °K	Source
Al	2.69802	298	Ref. 16, p. 285
Be	1.848	293	Ref. 22, p. 695
W	19.3	293	Ref. 22, p. 695
Ta	16.6	293	Ref. 22, p. 695
WC	12.50 (V_m)	296	Ref. 4, p. 548
SiC	3.21	293	Ref. 21, p. 342

(e) In the units given for the thermodynamic quantities, the calculation of $qV/\beta_T C_V$ needs to be divided by the conversion factor 4.185×10^{-5} to make γ_3 dimensionless.

(f) The parentheses mean that the values presumably are uncertain.

3. Possible errors arising from crystal anisotropy were not investigated. It is assumed that the data used to calculate γ_3 are representative of isotropic polycrystalline material.

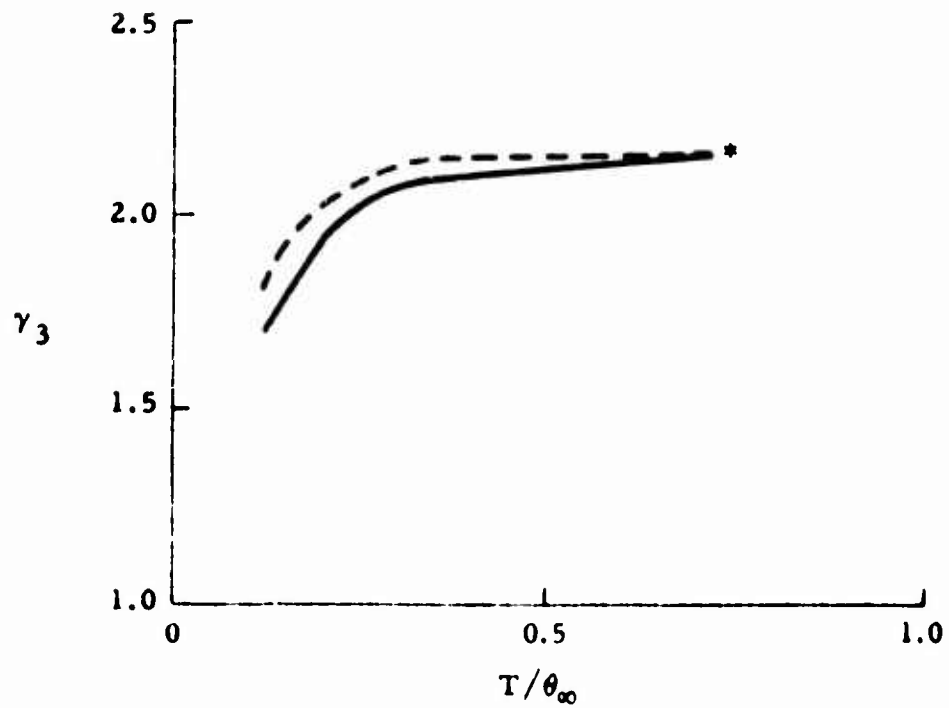
From Table 5-1, it can be seen that γ_3 for aluminum shows no consistent variation with temperature from room temperature to 773°K.

Although the present aluminum values of γ are higher than those given by Moelwyn-Hughes (Reference 17), very little variation of γ with temperature is indicated in both sets of values. The reason for our γ values being higher than those of Moelwyn-Hughes lies in different values of the thermodynamic functions. However, our value at 293°K, 2.25, compares well with the value, 2.17, given by Grüneisen in his paper "The State of a Solid Body" (Reference 11).

Discussion of the temperature variation of γ found in the literature indicates that the variation is greatest at temperatures below the Debye temperature. Bijl and Pullan present the figure (Figure 5-1) on the following page for the γ variation at low temperatures (Reference 3).

In contrast to the results of Bijl and Pullan, the experimental results of Figins, James, and Riley (Reference 6) indicate that γ_3 increases at very low temperatures. Apparently, the variation of γ_3 with temperature is still an open question.

Alder (Reference 1) makes the statement that γ_3 might be expected to decrease from about two to its classical perfect-gas value of 2/3, if the temperature is raised holding the density constant. On the other hand, C_V and, hence, γ might be nearly independent of temperature.



- calculated with constant volume and compressibility
- corrected for variation of volume
- * experimental value given by Grüneisen
- θ_∞ 389°K for aluminum

Figure 5-1 - Variation of Grüneisen Parameter at Low Temperatures for Aluminum (Reference 3)

The calculated γ_3 values for the rest of the metals, with the exception of tungsten, agree fairly well with those given in the literature. For tungsten, our lower γ_3 value undoubtedly arises from our value of α which is lower than that usually found in the literature. Our α value was calculated from very recent data. However, the accuracy of this data needs to be evaluated.

B. γ_G FROM THERMAL EXPANSION DATA AT ZERO PRESSURE

a. Calculations

As discussed in Section 4. A.c., the constancy of γ_G with temperature may be tested by the relationship

$$\gamma_G = \frac{V_{00} \alpha}{\beta_{00} C_V}$$

In this study the calculation of γ_G by the above formula was accomplished by calculating the ratio V_{00}/β_{00} at room temperature using the values of γ_3 , C_V , and α from Table 5-1. Whether this procedure is strictly valid needs further investigation. The values of α and C_V at temperatures other than room were calculated in the same manner as in Table 5-1. The results of these calculations are presented in Table 5-2.

b. Discussion of Results

The accuracy of the preceding results suffer, as did the results of the calculation of γ_3 , from a lack of knowledge of precise values of coefficients of thermal expansion. However, it would appear that, for the metals, γ_G tends to increase with increase of temperature while, for the carbides, γ_G tends to decrease.

The increase in γ_G with temperature is probably not real because, as discussed in Section 4. A.c., the formula $\gamma_G = V_{00} \alpha / \beta_{00} C_V$ is valid only as an approximation, especially at higher temperatures.

Table 5-2
 γ_G FROM THERMAL EXPANSION DATA AT ZERO PRESSURE

Material	Temp $^{\circ}\text{K}$	$\alpha \times 10^{+5}$ $(^{\circ}\text{K})^{-1}$	C_V cal (gm-atm $^{\circ}\text{K}$) $^{-1}$	V_{00}/β_{00} cal (gm-atm) $^{-1}$	γ_G
Al	273	7.01	5.496	1.73×10^5	2.20
	293	7.01	5.606		2.17
	296	7.01	5.603		2.17
	298	7.01	5.602		2.17
	303	7.48	5.623		2.31
	373	7.48	5.837		2.22
	436	8.47	5.997		2.44
	573	8.47	6.252		2.34
	708	9.92	6.385		2.69
	773	9.92	6.491		2.64
Be	303	3.35	3.88	1.46×10^5	1.26
	373	3.35	4.45		1.10
	573	4.91	4.97		1.44
	673	4.82	5.42		1.30
	873	5.59	5.78		1.41
	1073	5.99	6.03		1.45
	1273	6.46	6.28		1.50
W	298	11.23	5.89	7.08×10^5	1.35
	400	11.76	5.96		1.40
	500	12.28	6.04		1.44
	600	12.80	6.11		1.48
	700	13.32	6.18		1.53
	800	13.85	6.26		1.57
	900	14.37	6.33		1.61

Table 5-2 (continued)

Material	Temp °K	$\alpha \times 10^{+5}$ (°K) ⁻¹	C _V cal (gm-atm °K) ⁻¹	V ₀₀ /B ₀₀ cal(gm. atm) ⁻¹	γ _G
	1000	14.89	6.40		1.65
	1200	15.93	6.54		1.72
	1400	16.98	6.67		1.80
	1600	18.02	6.81		1.87
	1800	19.07	6.93		1.95
	2000	20.11	7.07		2.01
Ta	298	1.80	6.018	5.68 x 10 ⁵	1.70
	400	1.80	6.198		1.65
	700	1.94	6.388		1.74
	1200	2.24	6.516		1.95
	1600	2.67	6.658		2.28
	2000	2.66	6.893		2.19
	2400	3.10	7.288		2.42
	3000	3.66	8.998		2.31
WC	298	1.35	9.816	9.82 x 10 ⁵	1.35
	400	1.35	11.324		1.17
	600	1.50	12.582		1.17
	800	1.35	13.231		1.00
	1000	1.50	13.698		1.08
	1200	1.49	14.088		1.04
	1400	1.94	14.436		1.32
	1600	1.64	14.757		1.09

Table 5-2 (concluded)

Material	Temp °K	$\alpha \times 10^{+5}$ (°K) ⁻¹	C_V cal (gm-atm °K) ⁻¹	V_{00}/β_{00} cal (gm. atm) ⁻¹	γ_G
SiC	298	1.20	6.389	6.65×10^5	1.24
	300	1.20	6.443		1.24
	500	1.50	9.321		1.07
	700	1.50	10.321		.97
	900	1.64	10.898		1.00
	1200	1.64	11.505		.95
	1400	1.79	11.836		1.01
	1600	1.94	12.135		1.06
	1800	1.64	12.411		.88

The tendency for γ_G to decrease with increasing temperature in the case of the carbides, however, is difficult to explain.

It is reported (Reference 18, p. 351) that, for beryllium, γ_G , calculated using a variation of the Grüneisen formula used here, gives an indication of becoming negative at very low temperatures.

C. γ_2 FOR ALUMINUM AND TUNGSTEN BY THE METHOD OF BEECROFT AND SWENSON (Reference 2)

a. Calculations

The method of calculating γ_2 from

$$P_T = \frac{\gamma_2}{V} E_T$$

was discussed in Section 4.A.e. The method has been applied to both aluminum and tungsten in this study.

The validity of this method rests on the temperature independence and linear volume dependence of compressibility. For aluminum the temperature and volume dependency of compressibility was checked by plotting compressibilities at different temperatures vs volume (Figure 5-2). As can be seen from the figure, compressibility may be taken to a first approximation, in the pressure range from 1 atm to about 30 kb and in the temperature range 20°C - 435°C, as independent of temperature and a linear function of volume.

Tungsten compressibility data, which was available at room temperature only, was found to be rather unusual in that it increased with decreasing volume (Figure 5-3). This behavior certainly would not be expected for a metal, and it would be interesting to examine this behavior further.

The results of the calculations for aluminum are shown in Figures 5-4 through 5-8 and for tungsten in Figure 5-9.

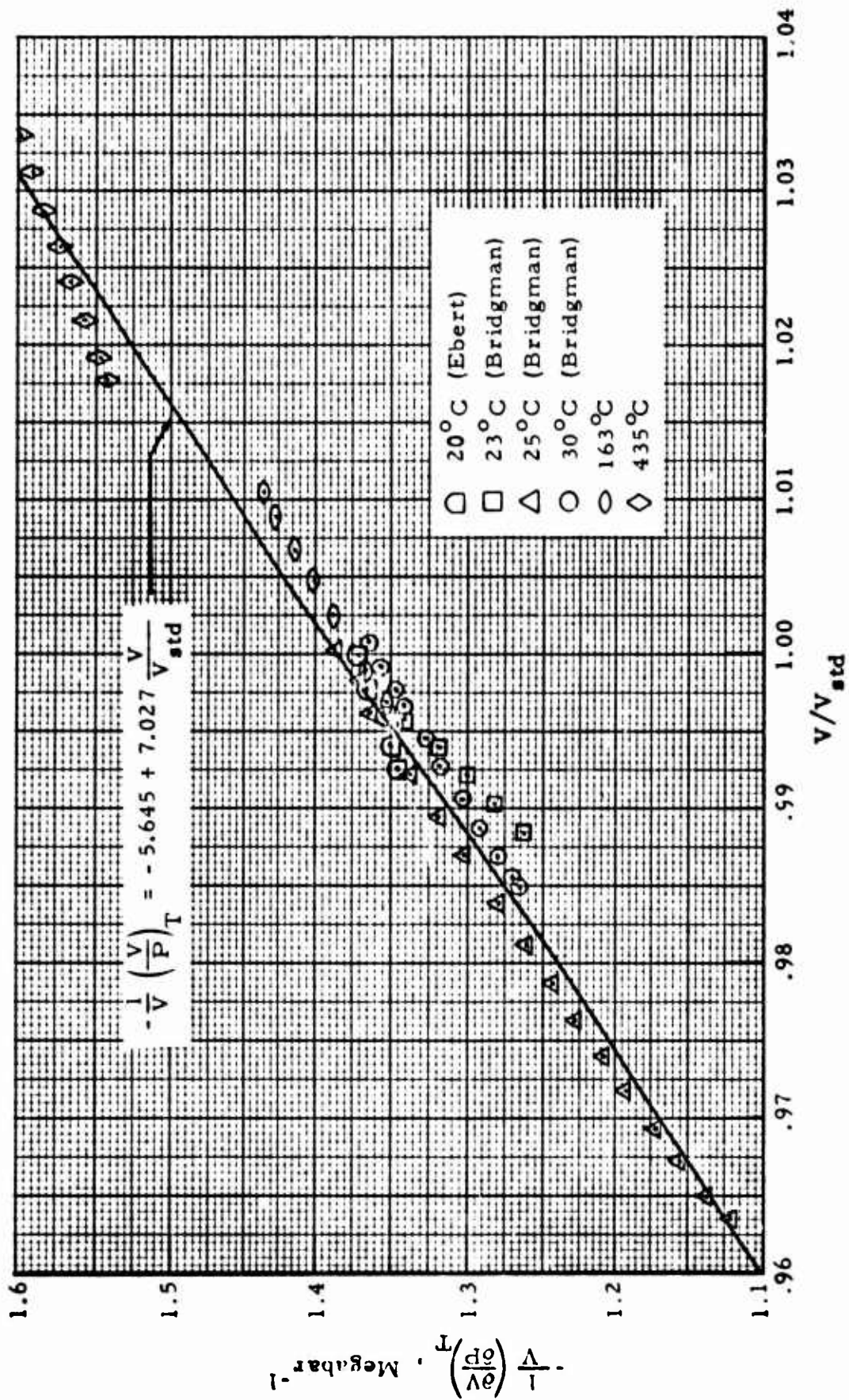


Figure 5-2 - Compressibility of Aluminum as a Function of Volume Ratio - (V_{std} is the Volume at 1 Atmosphere and 20°C)

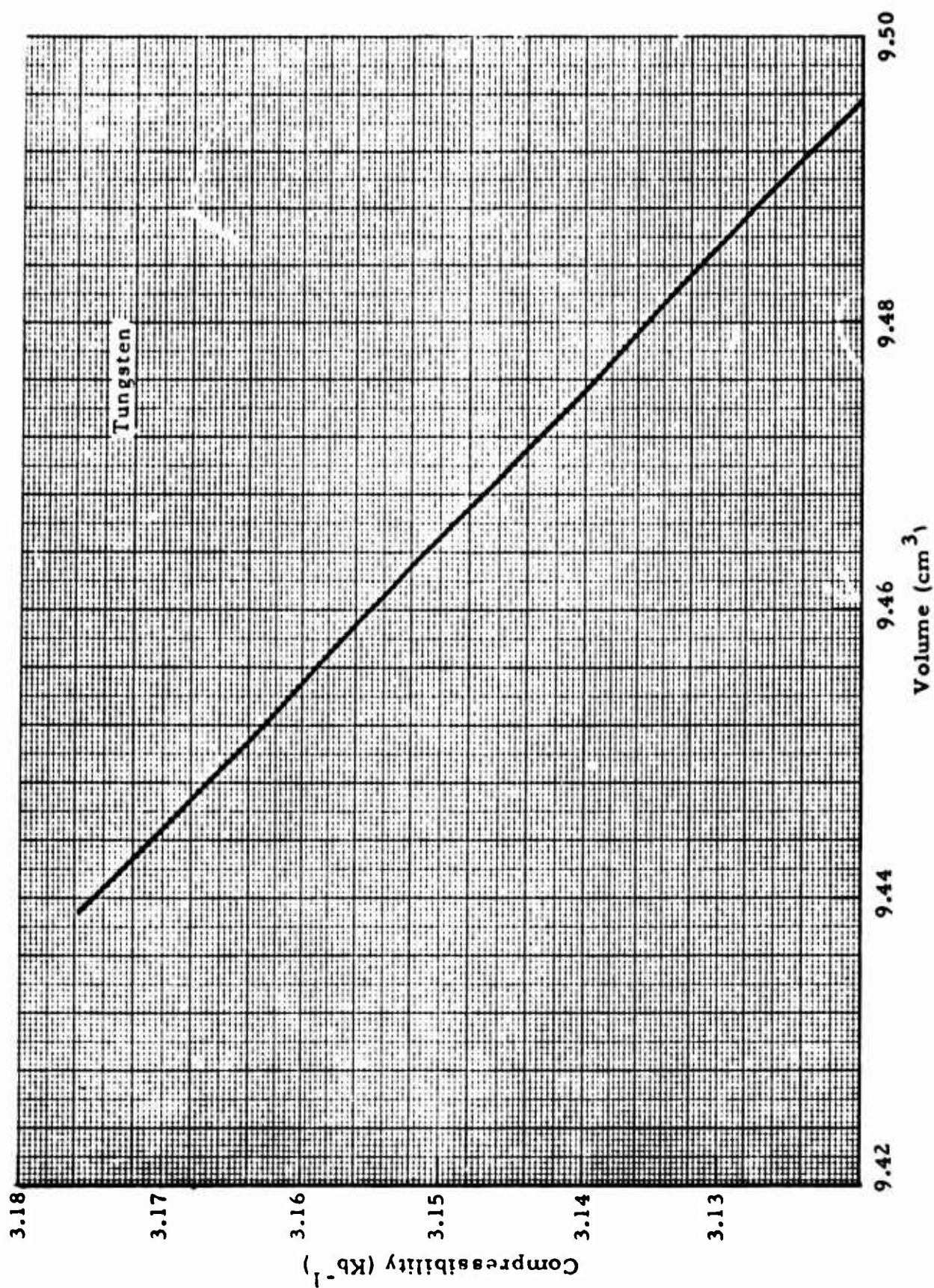


Figure 5-3 - Compressibility vs Volume for Tungsten at 25°C

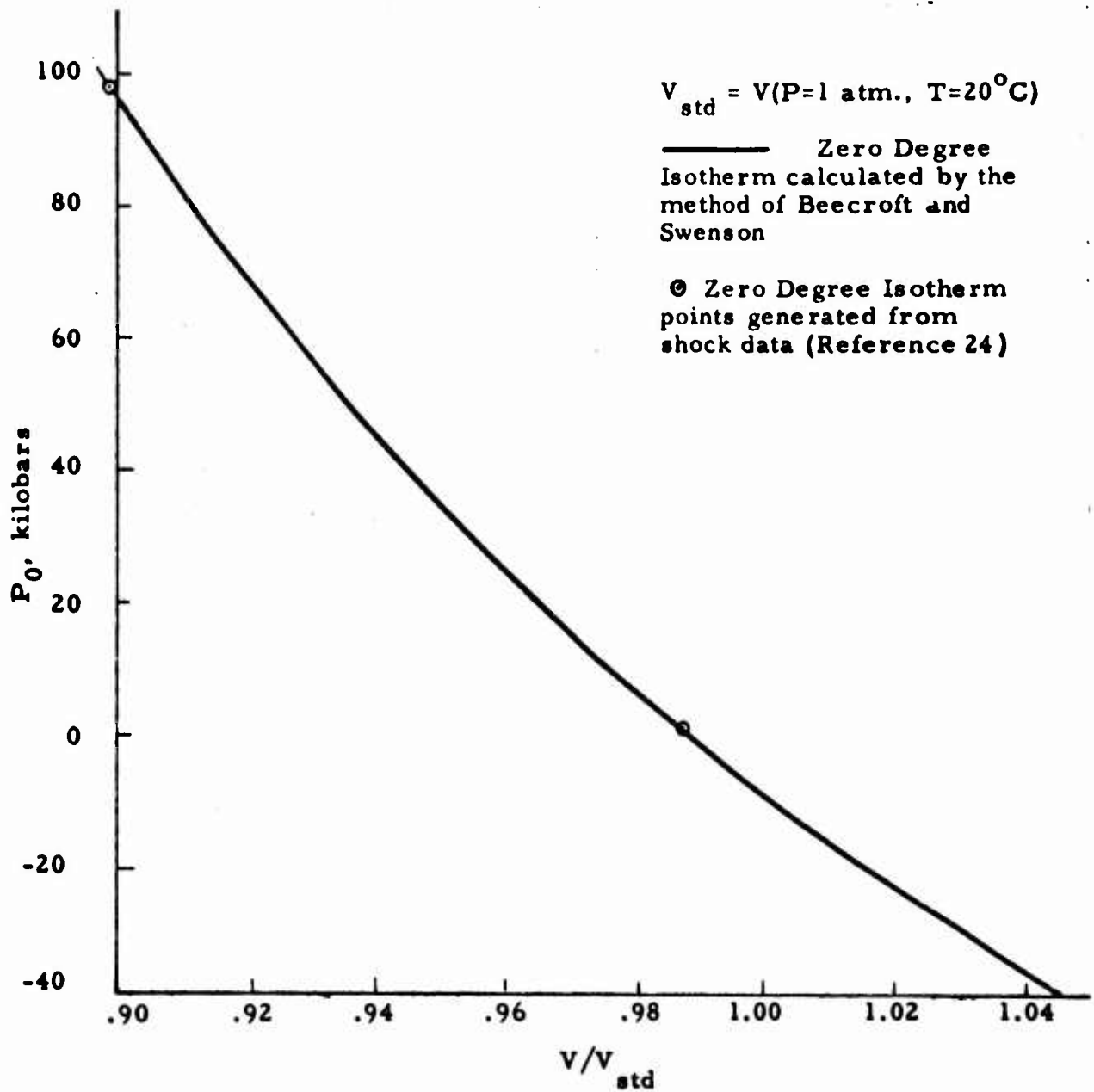


Figure 5-4 - Zero Degree Isotherm for Aluminum

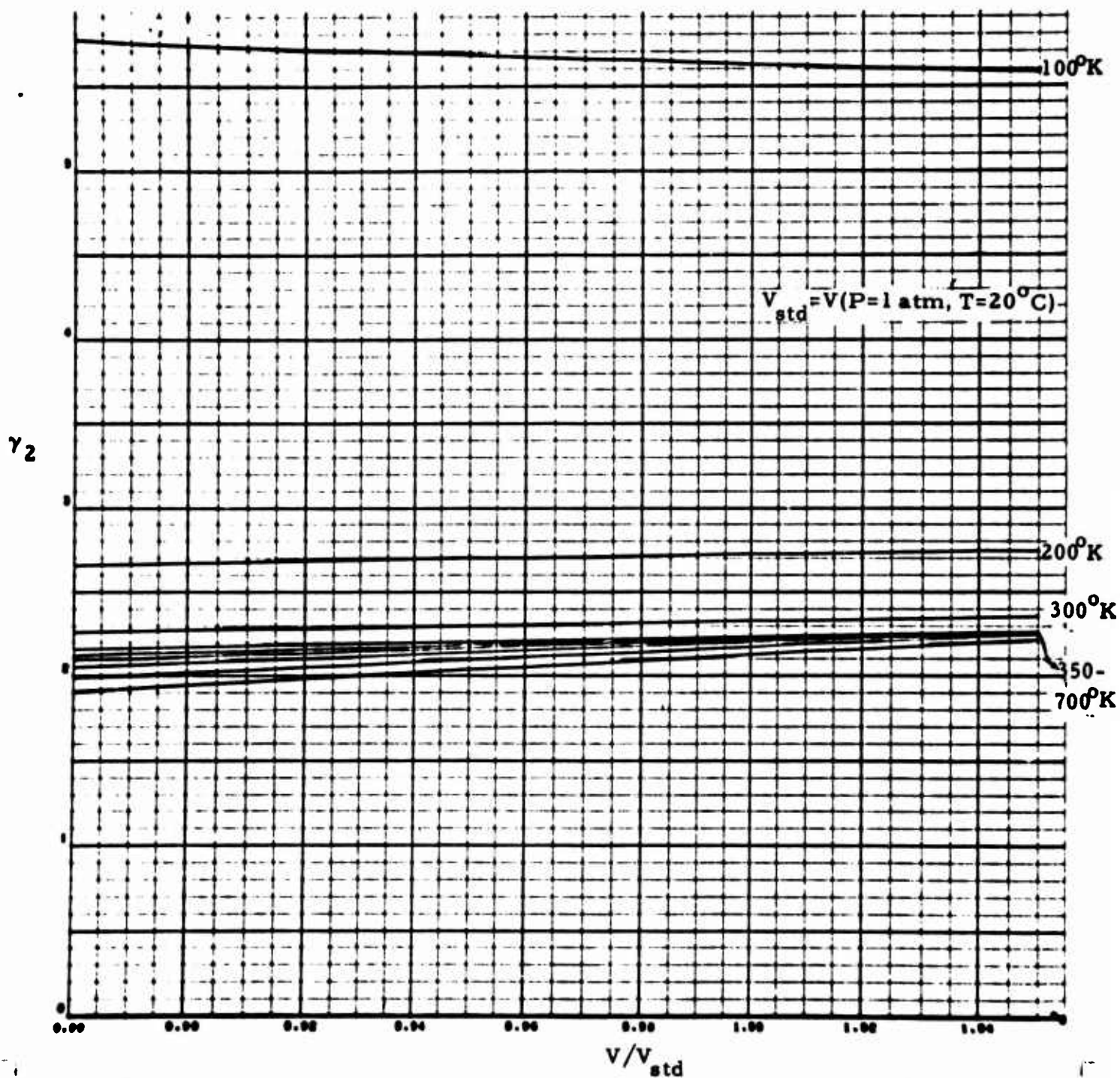


Figure 5-5 - Variation of γ_2 as a Function of Volume and Temperature for Aluminum (for specific temperatures in the 350° - 700°K range, see Figure 5-6)

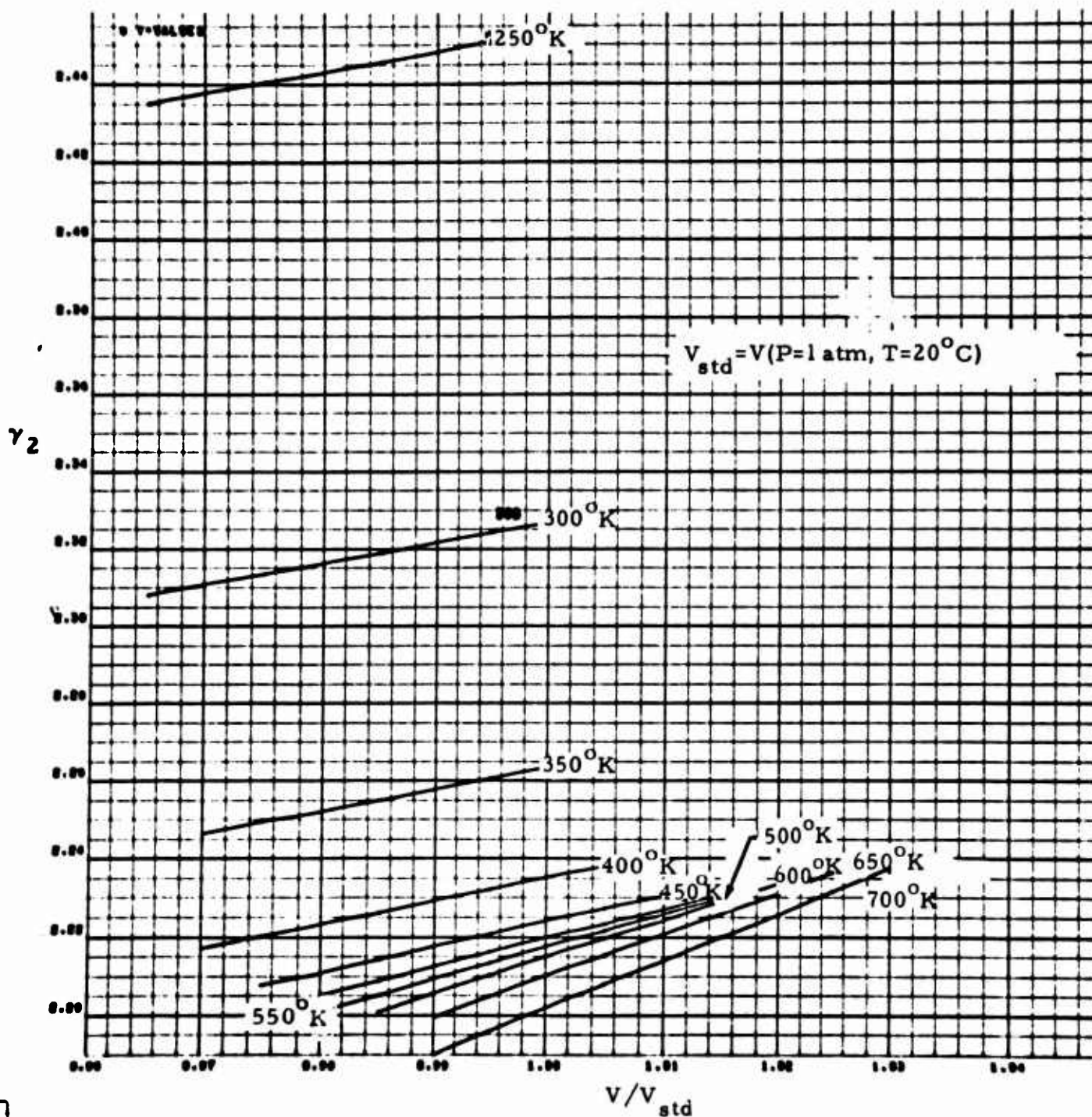


Figure 5-6 - Variation of γ_2 as a Function of Volume and Temperature for Aluminum - Scale Expanded

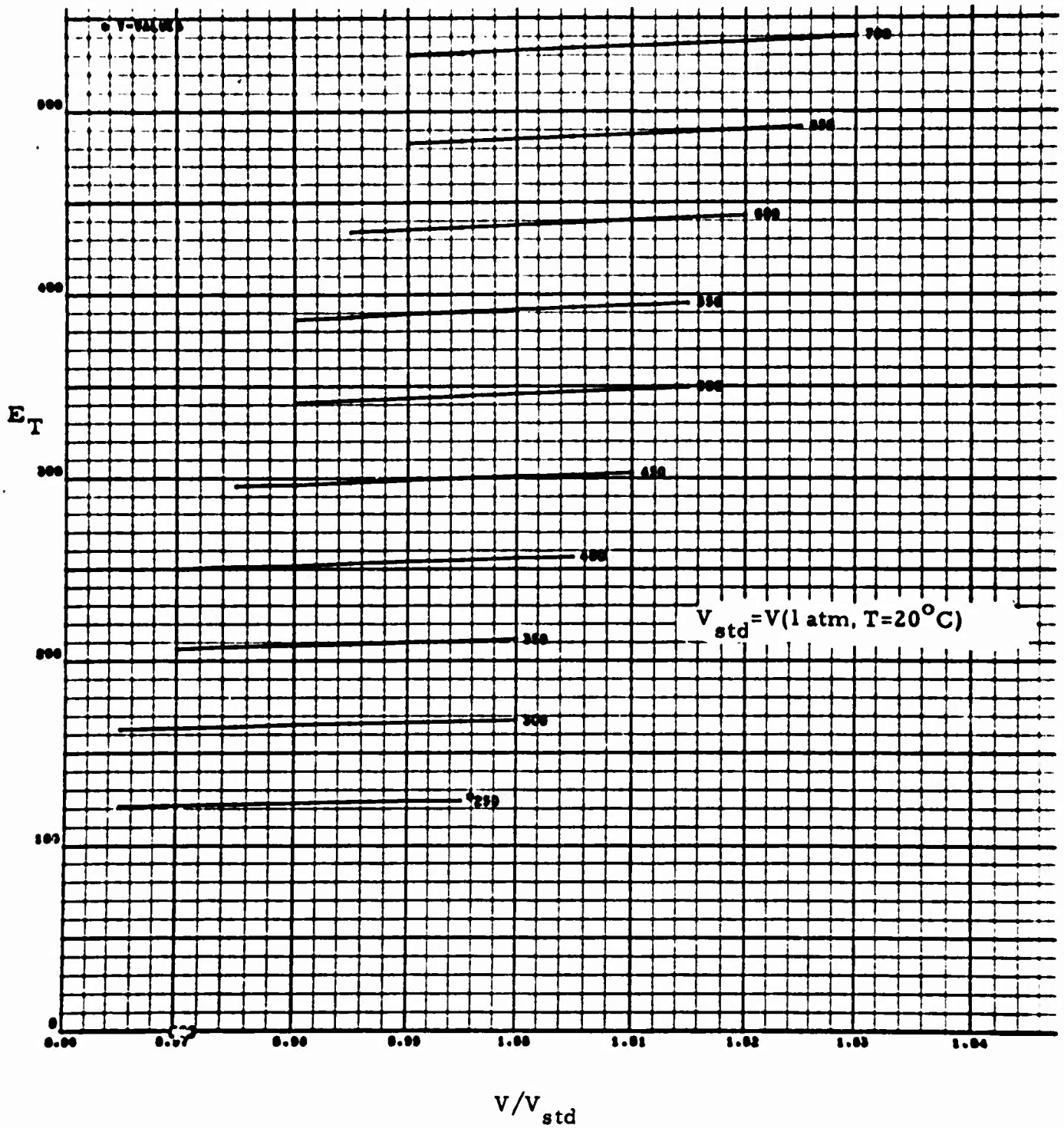


Figure 5-7 - Thermal Energy as Function of Temperature and Volume for Aluminum

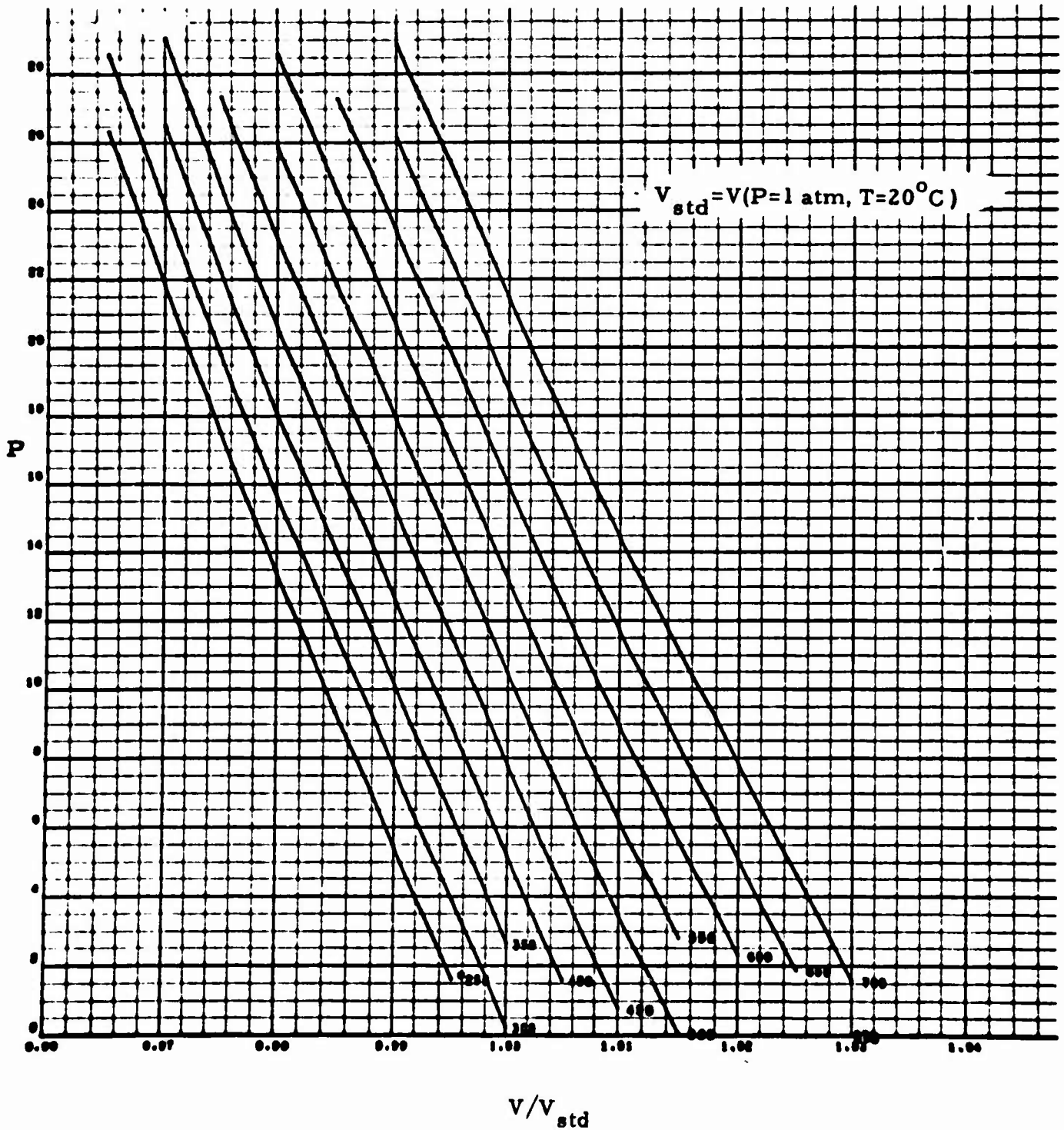


Figure 5-8 - Pressure as Function of Temperature and Volume for Aluminum

b. Discussion of Results

In Figure 5-4 is shown the calculated zero-degree isotherm. It can be seen that the calculated curve agrees excellently with the zero-degree values generated from shock data (Reference 24, p. 214).

In Figures 5-5 and 5-6 are shown the calculated γ_2 values for aluminum at different temperatures as a function of volume. In Figure 5-6 the scale expanded to show more detail. The greatest change in γ_2 occurs below 300°K. The γ_2 curve at 100°K is very interesting. The γ_2 values at this temperature are surprisingly high. In an attempt to obtain more reasonable values at 100°K, the integration interval was decreased in the computation of energy from the specific heat curve. However, the difficulty persisted, causing us to examine more closely the applicability of the basic assumptions of the method to metals less compressible than sodium. These assumptions are that the compressibility is a linear function of volume and independent of temperature. For aluminum, these conditions are only approximately fulfilled as shown in Figure 5-2. We may conclude then that the method of Beecroft and Swenson is very sensitive to the slope of the compressibility vs volume curve, and the accuracy of γ_2 values calculated by it is doubtful in cases where the linear volume dependence and temperature independence of compressibility does not rigorously hold. Thus, the γ_2 values given in Figures 5-5, 5-6 and 5-9 for aluminum and tungsten probably are not very accurate, especially those for tungsten. For tungsten compressibility data were found for only one temperature, so that the assumption of volume linearity and temperature independence of compressibility is rather far fetched.

Figures 5-7 and 5-8 show the variation of the thermal energy and the total pressure with volume and temperature. They are included in this report for general information purposes.

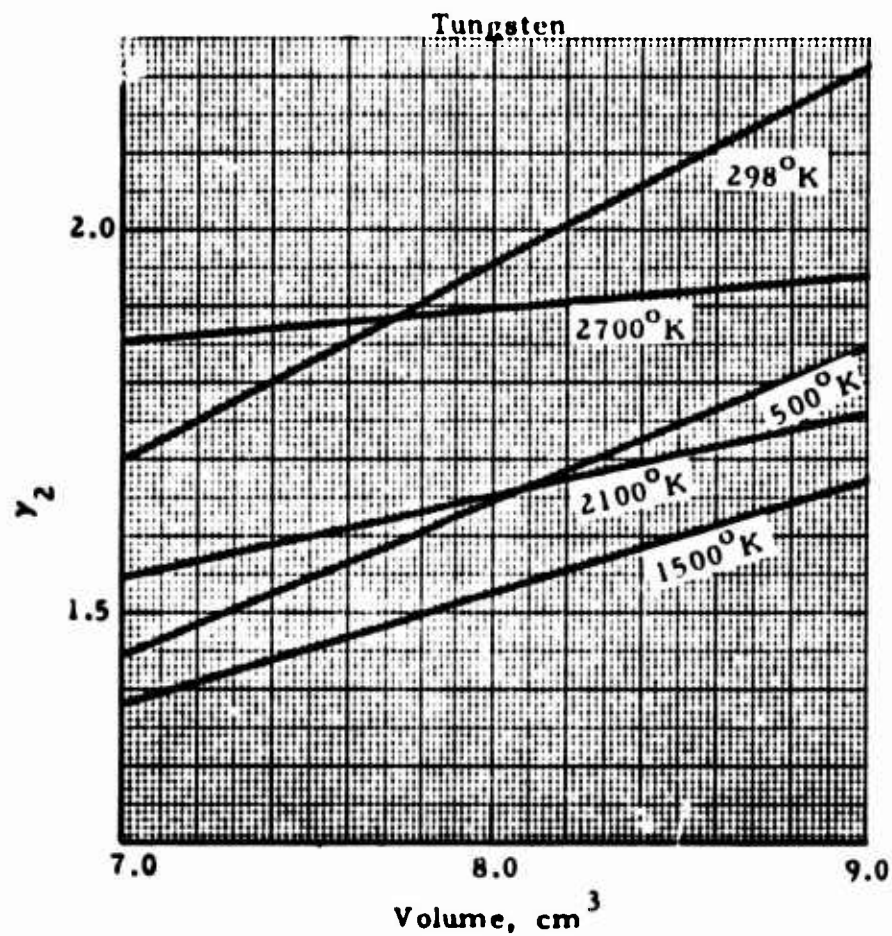


Figure 5-9 - γ_2 Values for Tungsten as Calculated by the Method of Beecroft and Swenson

D. GRÜNEISEN'S PARAMETER FOR ALUMINUM, BERYLLIUM, AND TUNGSTEN FROM SHOCK DATA

A comparison has been made of the Grüneisen parameter as computed by several different methods from experimental P-V data. These results have been plotted as a function of volume ratio in Figures 5-10, 5-11 and 5-12 for aluminum, beryllium and tungsten, respectively. All of the curves were plotted from data presented in Reference 15 with the exception of the curve labeled "Walsh, et al" which was computed from the polynomial least square curve fit data presented in Table III of Reference 24.

In the Beers report (Reference 15) the experimental shock Hugoniot data (or the isothermal P-V data in the case of Bridgeman's data) were fitted to two different mathematical models which will be referred to as the Murnaghan equation and the linear equation. The Murnaghan equation has the form

$$P = A \left[\left(\frac{V_{0H}}{V} \right)^K - 1 \right] \quad (1)$$

For each material, values of A and K were chosen to minimize the error between the mathematical expression and the experimental data.

The linear model assumes a linear relationship between the shock velocity and particle velocity leading to an equation of the form

$$U_s = C_0 + S U_p \quad (2)$$

Again, for each material, values of C_0 and S were chosen to minimize the error between the linear model and the experimental data. By combining Equation 2 and the Rankine-Hugoniot relations the following equation is formed.

$$P = \frac{C_0^2 (V_{0H} - V)}{\{V_{0H} - S(V_{0H} - V)\}^2} \quad (3)$$

Equations 1 and 3 represent two different analytical expressions for the same experimental P-V data.

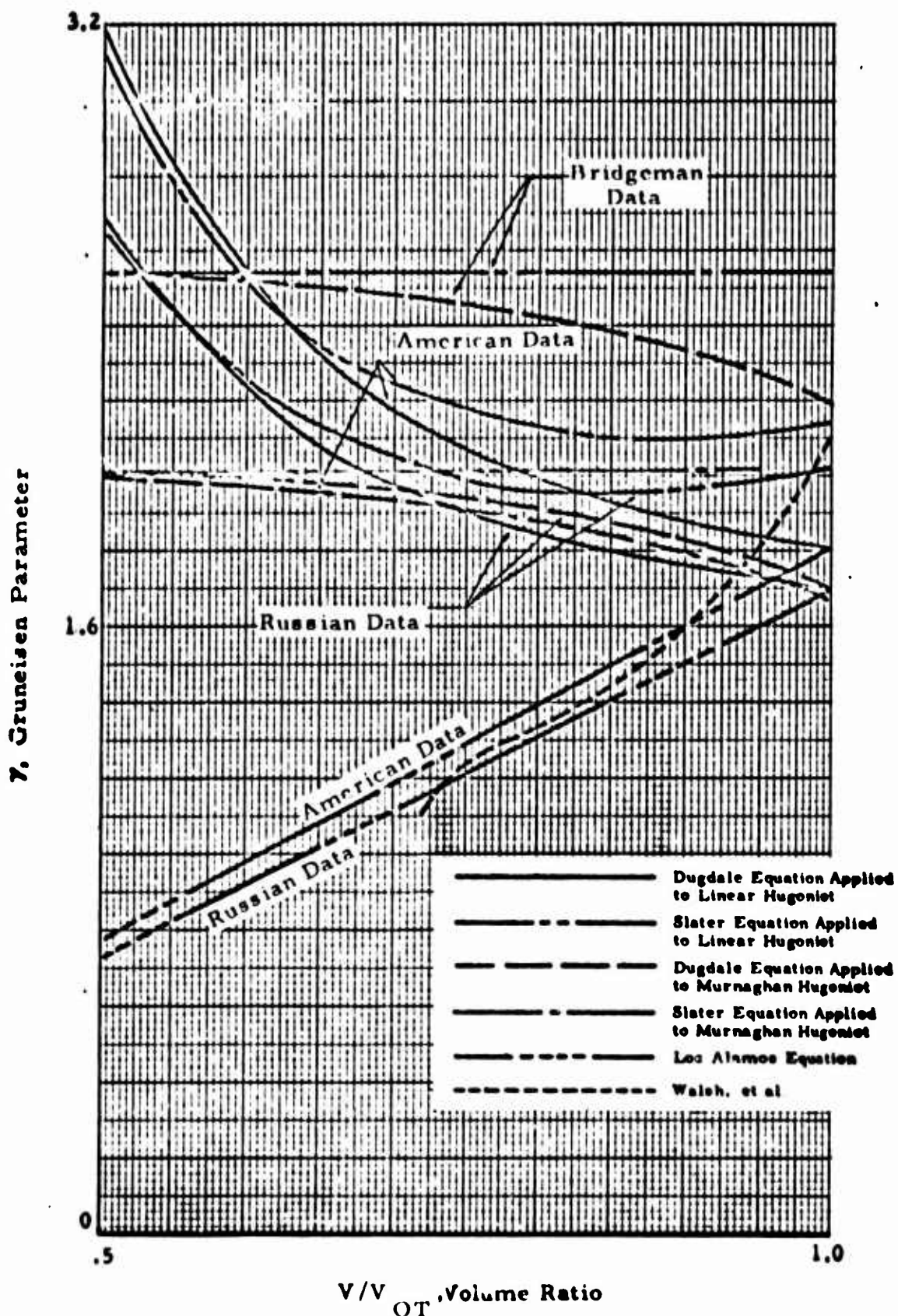


Figure 5-10 - Comparison of Aluminum Grüneisen Parameter as Computed by Several Different Methods

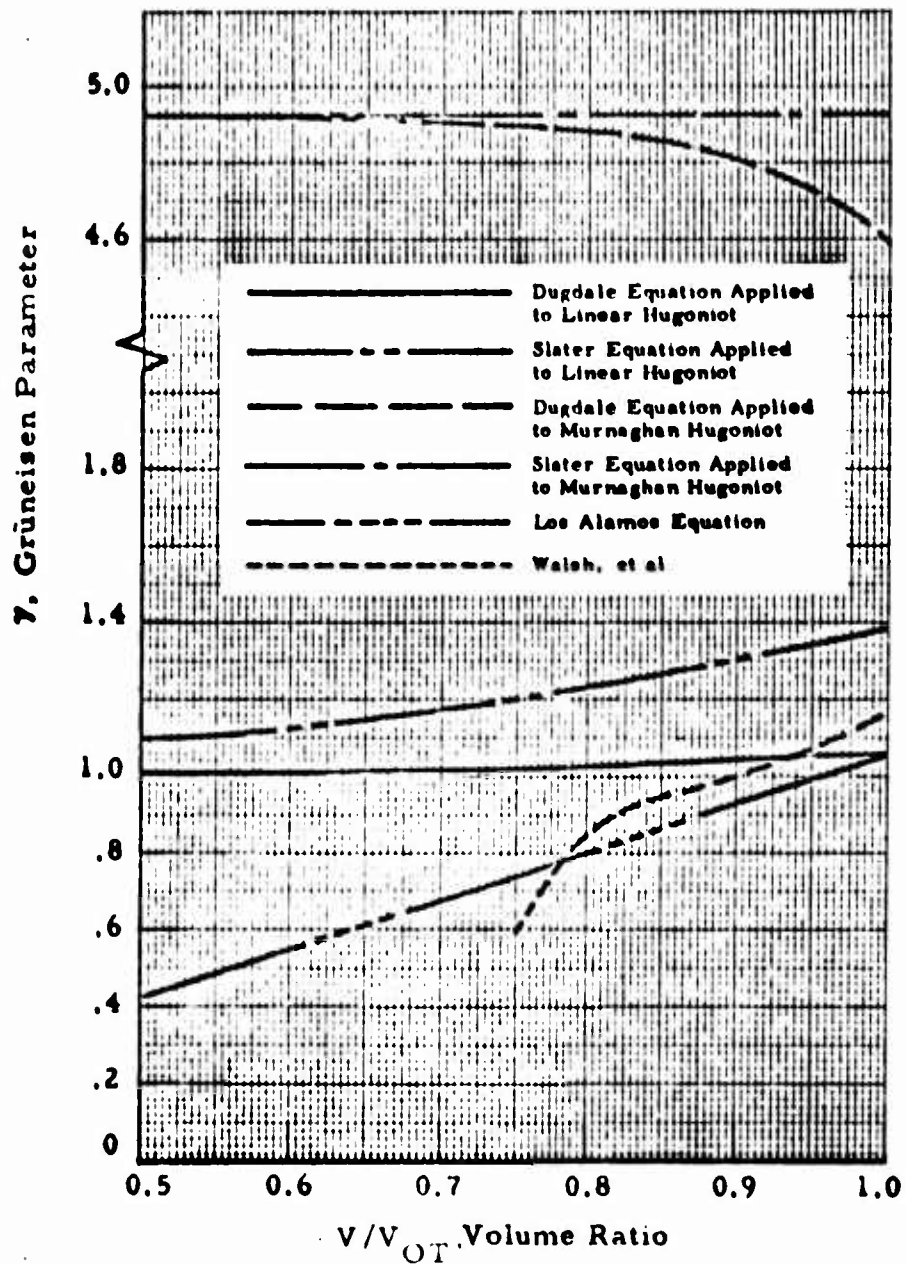


Figure 5-11 - Comparison of Beryllium Grüneisen Parameter as Computed by Several Different Methods

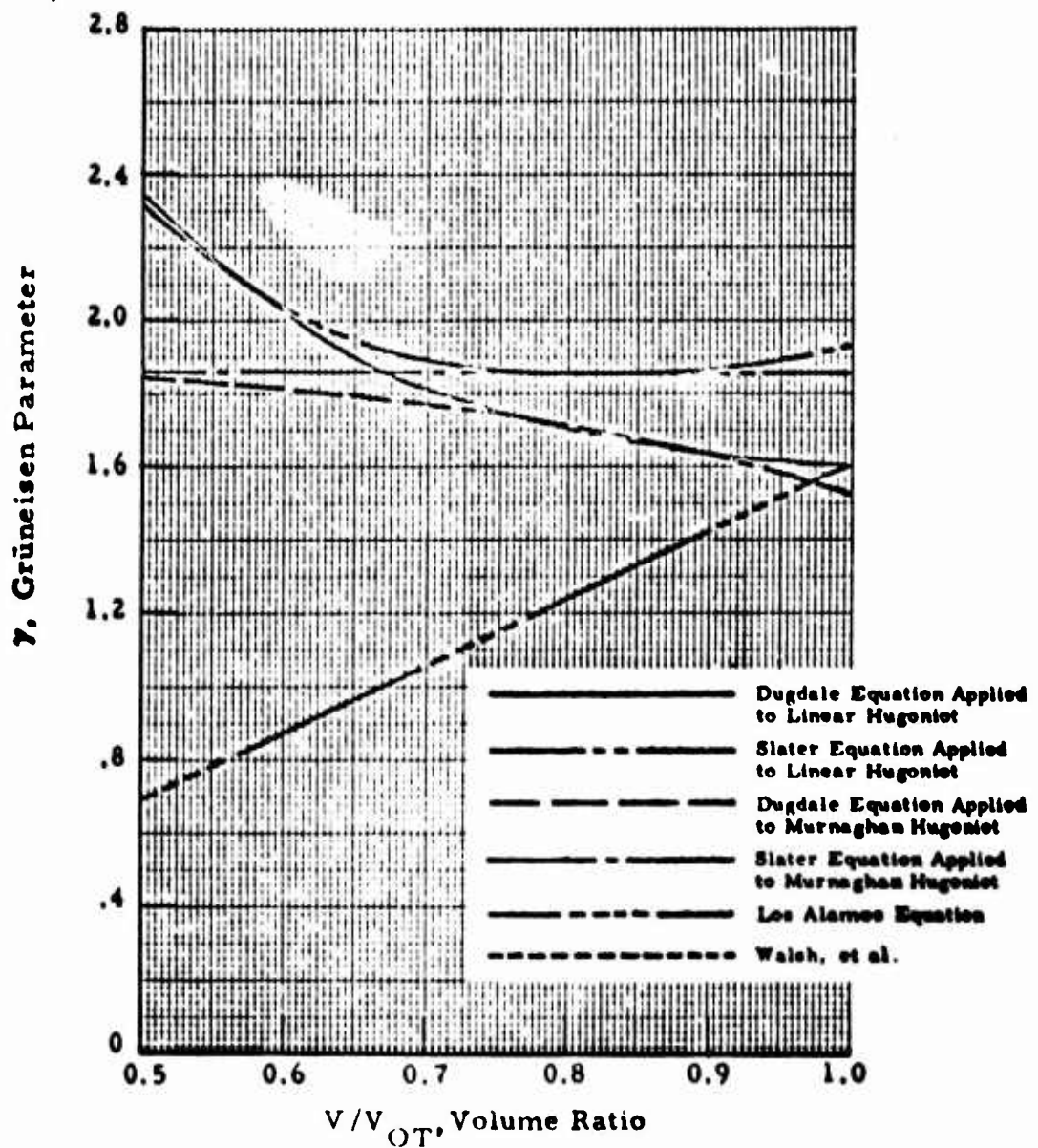


Figure 5-12 - Comparison of Tungsten Grüneisen Parameter as Computed by Several Different Methods

In the Beers report, the Slater formula and the Dugdale-MacDonald formula were applied directly to Equations 1 and 3 to obtain values of the Grüneisen parameter. The application of the Slater and Dugdale-MacDonald formulas to Rankine-Hugoniot and to non-zero isothermal data is not theoretically correct, since the derivations of both formulas were based on isentropic P-V relationships. However, for very small compressions the slope and curvature of the Rankine-Hugoniot curve approach that of an isentrope, which suggests that the Beers approximation of the Grüneisen parameter may be fairly good for small compressions.

The Grüneisen parameter computed by Walsh, et al, (Reference 24) was obtained by generating a zero-degree isotherm using experimental shock data and commonly available material properties. The Slater formula was then applied to the zero-degree isotherm to obtain the Grüneisen parameter. Since the zero-degree isotherm is also an isentrope this method is compatible with the assumptions inherent in the Slater formula.

The Los Alamos equation is based on the linear equation and the Dugdale-MacDonald formula. Using Equation 3 and the Dugdale-MacDonald formula, the Grüneisen parameter and the slope of the Grüneisen parameter with respect to volume are computed for zero compression. The Grüneisen parameter at other volumes is then computed by the following equation

$$\gamma = \gamma_{0H} - (V_{0H} - V) \left(\frac{\partial \gamma}{\partial V} \right)_{P=0} \quad (4)$$

The following two expressions were obtained from Reference 13.

$$\gamma_{0H} = 2S - 1 \quad (5)$$

$$\left(\frac{\partial \gamma}{\partial V} \right)_{P=0} = \frac{1}{V_{0H}} \left(S^2 - \frac{S}{3} + \frac{5}{9} \right) \quad (6)$$

Substitution of Equations 5 and 6 into Equation 4 leads to Equation 7 which is called the Los Alamos equation in the Beers report.

$$\gamma = \left(\frac{V}{V_{0H}} - 1 \right) \left(S^2 - \frac{S}{3} + \frac{5}{9} \right) + (2S - 1) \quad (7)$$

The only experimental data required to compute the Grüneisen parameter by this equation are the shock and particle velocities which makes it attractive for materials for which limited information is available.

Equation 5 has been verified by independent derivation. However, an attempt to derive Equation 6 resulted in the following expression:

$$\left(\frac{\partial \gamma}{\partial V}\right)_{P=0} = \frac{1}{V_{0H}} \left(-S^2 + \frac{2}{3}S + \frac{5}{9} \right) \quad (8)$$

Until the discrepancy between Equation 6 and Equation 8 is resolved, the validity of Equation 7 is in doubt.

E. γ_2 USING MURNAGHAN'S EQUATION

One of the methods investigated as a means of evaluating the Grüneisen parameter involves the use of the Murnaghan equation to represent P-V-T behavior. The basic assumption inherent in the Murnaghan equation is that the isothermal bulk modulus of a material is a linear function of pressure (see Reference 26). From this basic assumption the following P-V relationship along an isothermal can be derived.

$$P = \frac{B_{0T}}{B'_{0T}} \left[\left(\frac{V_{0T}}{V} \right)^{B'_{0T}} - 1 \right] \quad (9)$$

in which

P = pressure

V = volume

B = bulk modulus

B' = rate of change of bulk modulus with pressure

and the subscript 0T indicates that the value of the variable should be taken at 0 pressure and the temperature of the isothermal. Thus, a complete P-V-T relationship exists for a substance when B, B' and V are known as a function of temperature.

The objective of this investigation was to evaluate the Grüneisen parameter, γ_2 , as a function of volume, V , and temperature, T . The basic equation used in this evaluation is

$$\gamma_2 = \frac{V(P - P_0)}{E - E_0} \quad (10)$$

in which E is energy at the specified volume and temperature, and E_0 and P_0 are the energy and pressure at zero degrees absolute. At a given temperature the numerator of Equation (10) can be expressed in terms of V and T by use of Equation (9). It remains to express $(E - E_0)$ in terms of V and T .

The path followed (1-2-3-4) in evaluating $(E - E_0)$ and the subscripts used in the following equations are illustrated in Figure 5-13. The energy difference between 0 and 00 is

$$E_{00} - E_0 = \int_{V_{00}}^{V_0} P(V) dV \quad (11)$$

From 00 to 0T the change in energy is

$$E_{0T} - E_{00} = \int_0^{T_1} C_p(T) dT \quad (12)$$

and from 0T to PT

$$E_{PT} - E_{0T} = \int_{V_{0T}}^{V_{PT}} T \left(\frac{\partial P}{\partial T} \right)_V dV - \int_{V_{0T}}^{V_{PT}} P(V) dV$$

But

$$\left(\frac{\partial P}{\partial T} \right)_V = \alpha B$$

in which

α = coefficient of thermal expansion

B = isothermal bulk modulus

If the assumption is made that αB is a function of temperature only (Reference 2)

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha_{0T} B_{0T}$$

and

$$E_{PT} - E_{0T} = T \alpha_{0T} B_{0T} (V_{PT} - V_{0T}) - \int_{V_{0T}}^{V_{PT}} P(V) dV \quad (13)$$

The sum of Equations (11), (12) and (13) is the energy difference $E - E_0$ in Equation (10). $P(V)$ along the two isothermals in Figure 5-13 can be expressed in terms of Equation (9) when the appropriate subscripts are used.

These equations were programmed and γ_2 was computed for sodium and aluminum. Input data for these computations are presented in Table 5-3 and Figures 5-14 through 5-18.

Volume expansivity data are given in Table 5-3 for a number of materials. The numbers appearing in Table 5-3 are coefficients determined by least squares techniques for the following polynomial:

$$\frac{V - V_{std}}{V_{std}} = 0.01 (A + BT + CT^2 + DT^3) \quad (14)$$

in which

V = volume

V_{std} = volume at $293^\circ K$

T = temperature, $^\circ K$

The data from which the coefficients were determined were obtained from Reference 2 for sodium and from References 8 - 10 for the other materials.

In the computation of γ_2 a value of $23.66 \text{ cm}^3/\text{mole}$ was used for the standard volume of sodium, and a value of $9.998 \text{ cm}^3/\text{mole}$ was used for aluminum.

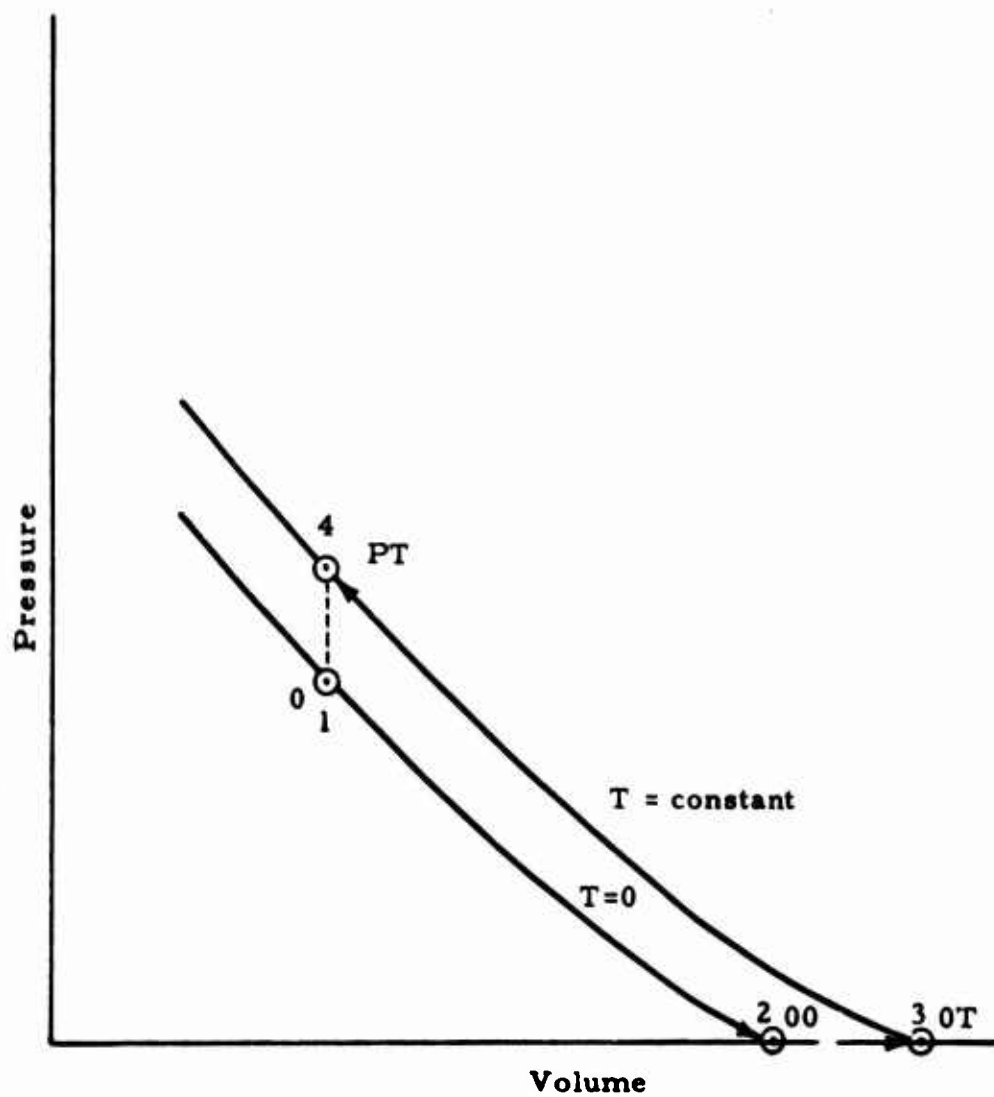


Figure 5-13 - Path Followed in Evaluating Energy Difference Term in Equation (10)

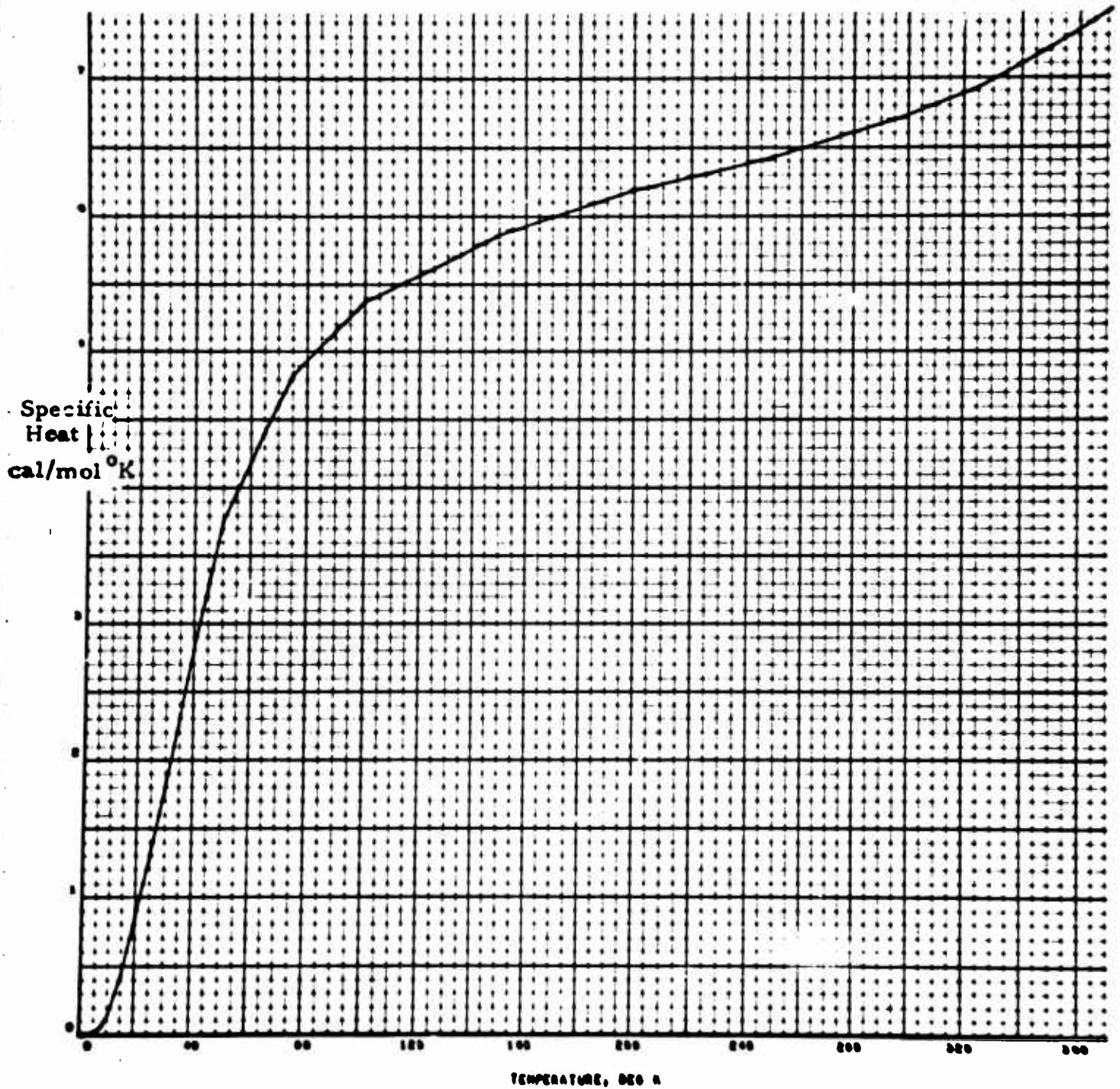


Figure 5-14 - Specific Heat of Sodium (From Reference 14)

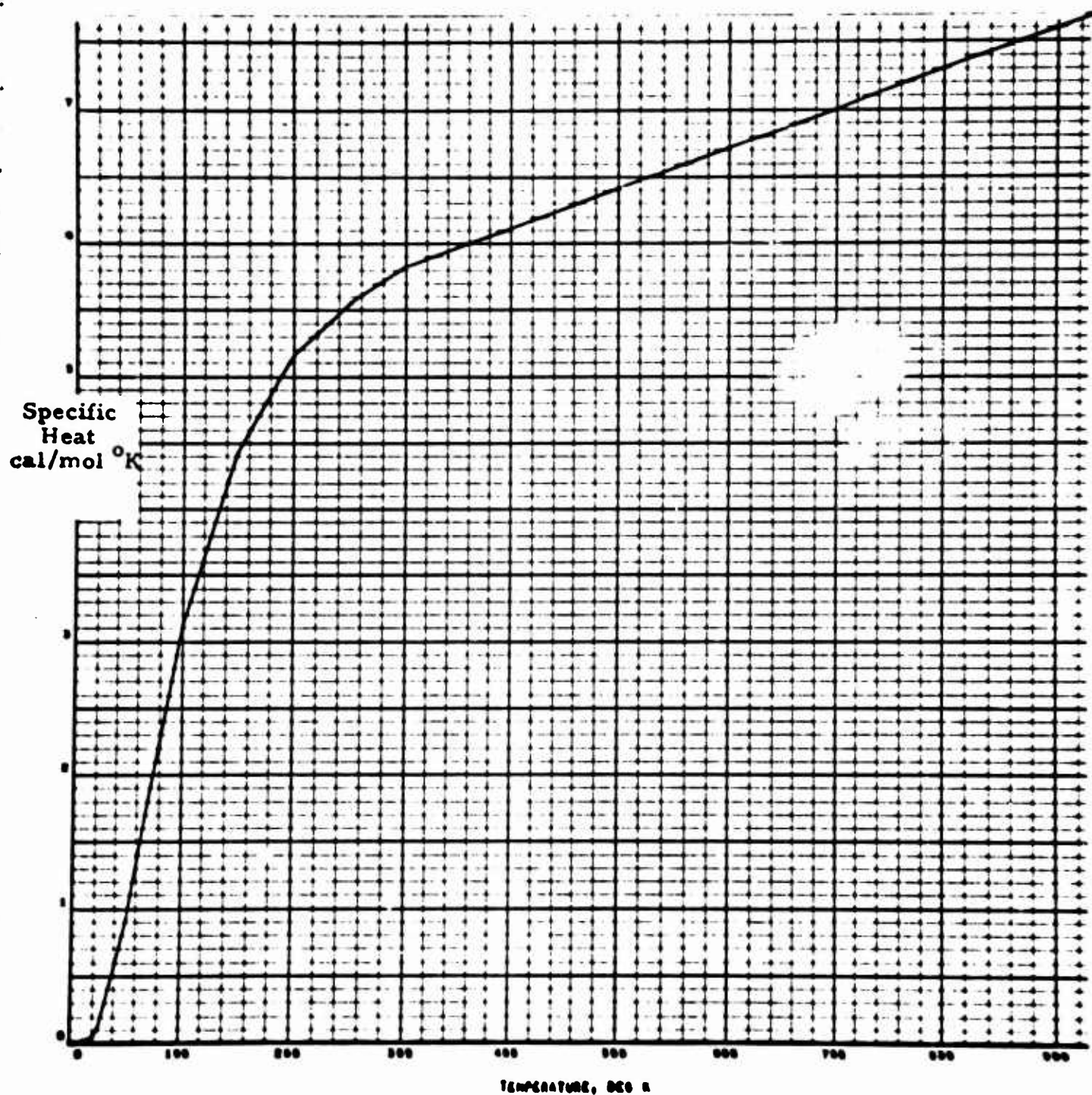


Figure 5-15 - Specific Heat of Aluminum (From Reference 14)

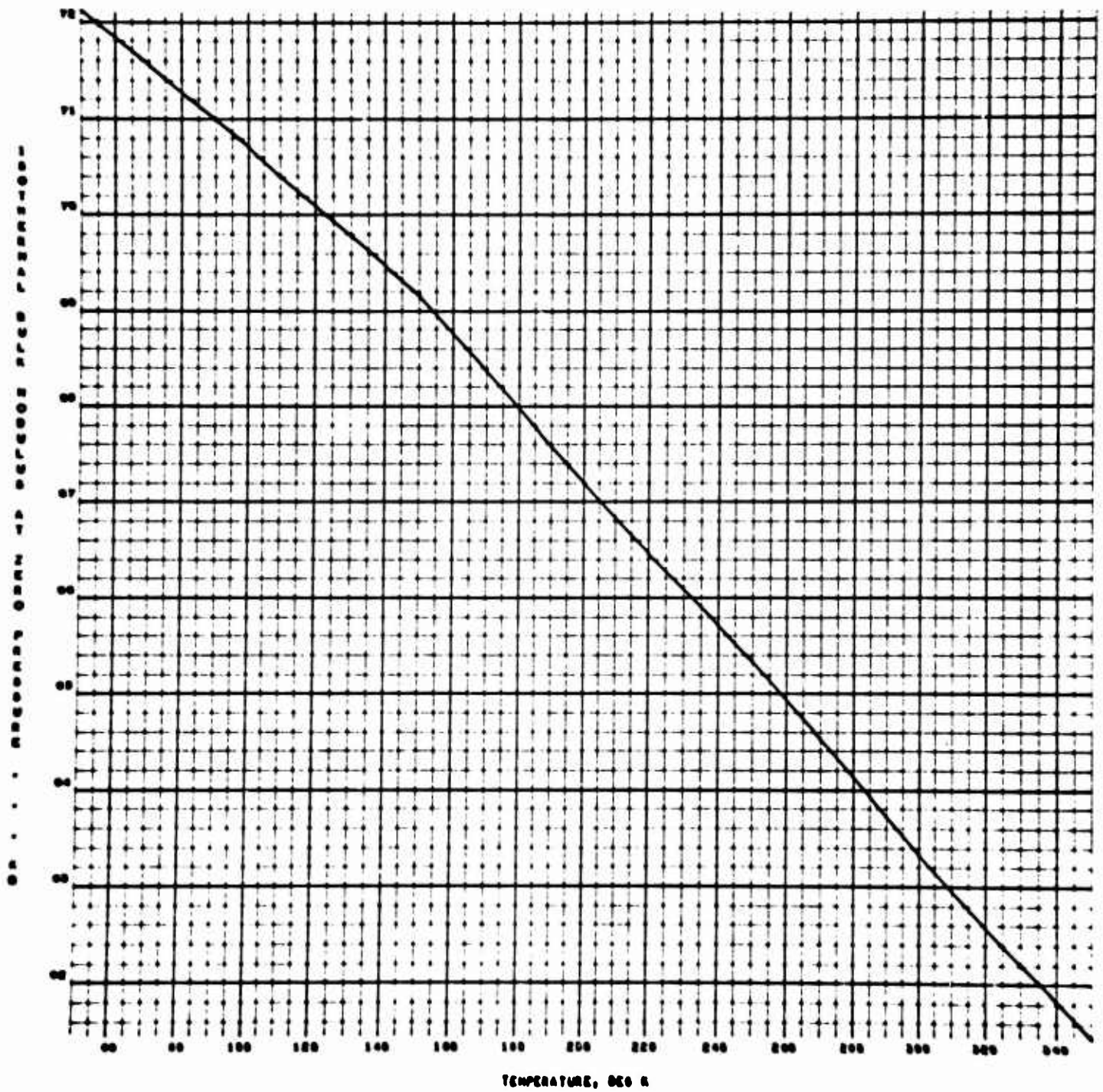


Figure 5-16 - Isothermal Bulk Modulus of Sodium (From Reference 2)

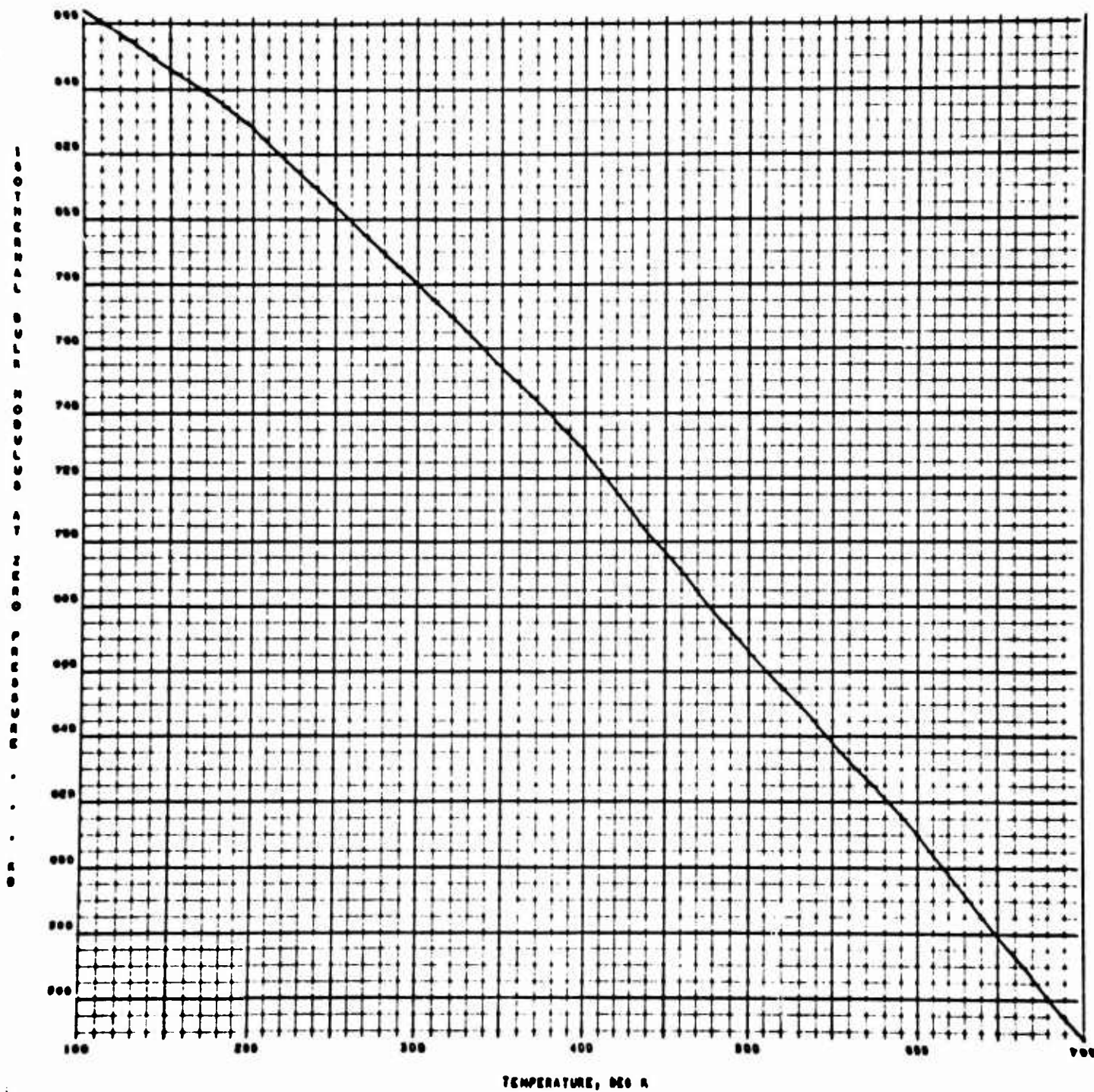


Figure 5-17 - Isothermal Bulk Modulus of Aluminum (From Reference 28)

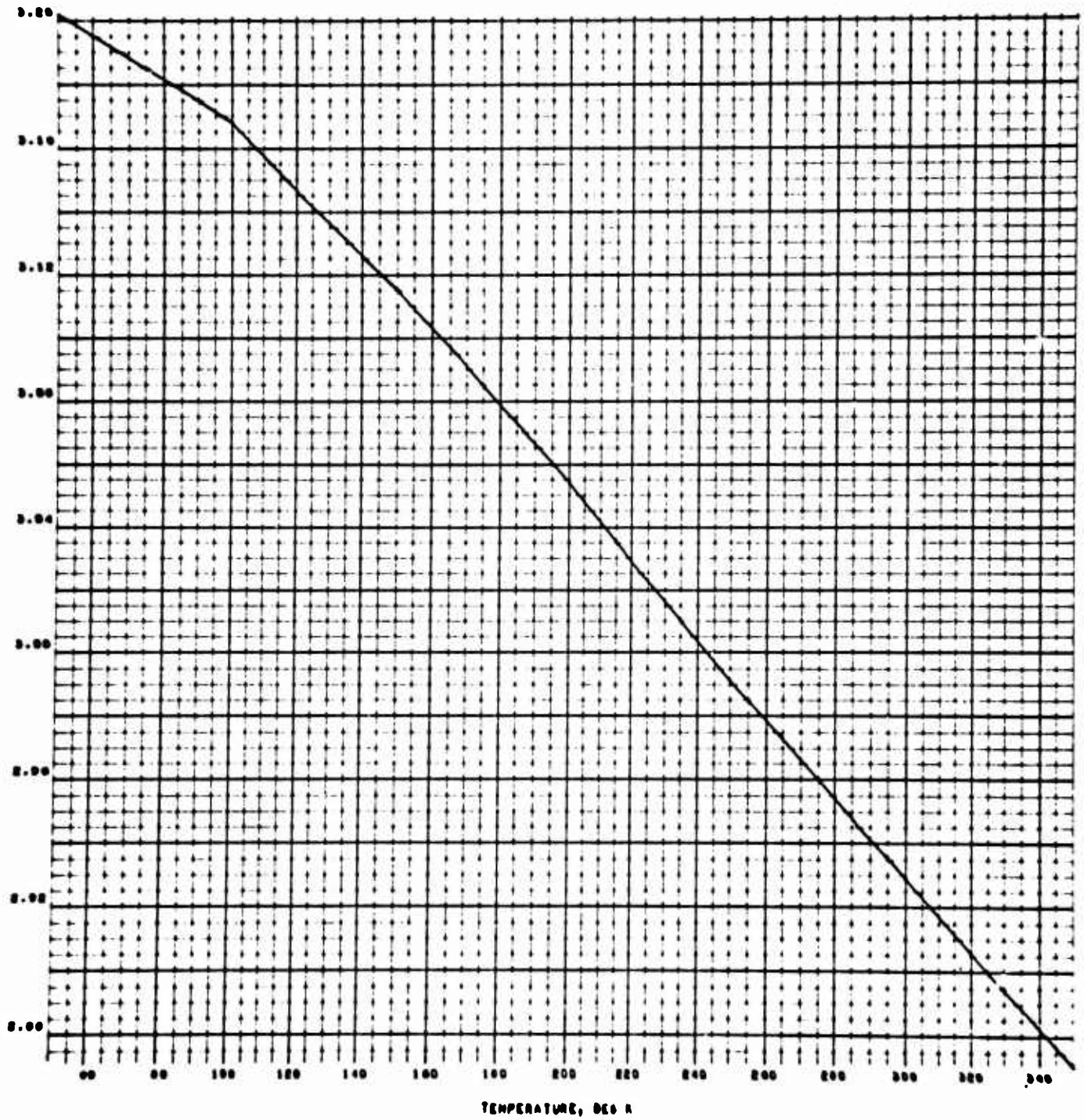


Figure 5-18 - Pressure Derivative of Isothermal Bulk Modulus of Sodium (from Reference 28)

Table 5-3
VOLUME EXPANSIVITY DATA

Material	A	$B \times 10^3$ (°K) ⁻¹	$C \times 10^8$ (°K) ⁻²	$D \times 10^{11}$ (°K) ⁻³
Na	-4.14	-1.88	8660	-10700
Al	-1.36	2.53	797	297
Be	-1.40	4.59	-1.25	92.7
W	-0.404	1.28	2.11	4.69
Ta	-0.593	2.04	-2.17	7.67
WC	-0.424	1.43	-13.1	11.4
SiC	-0.384	1.32	-15.4	-0.13

The pressure derivative of isothermal bulk modulus for aluminum used in the computations has a constant value of 5.55. This value was obtained from Reference 29. Both the isothermal bulk modulus and the pressure derivative of isothermal bulk modulus for aluminum were derived by ultrasonic techniques.

The computed values of γ_2 for sodium and aluminum are plotted in Figures 5-19 and 5-20, respectively. For small compressions the results are similar to the results obtained by the Beecroft and Swenson method. Again, the γ_2 curve for aluminum at 100°K is unrealistically high. Of greater interest are the negative values obtained for γ_2 at high compressions. Although Pautamo in Reference 27 refers to negative values of the Grüneisen parameter, it seems more likely in this case that the negative values are due to assumptions inherent in the method and in limitations of the input data.

Pressure curves corresponding to the γ_2 curves are shown in Figures 5-21 and 5-22.

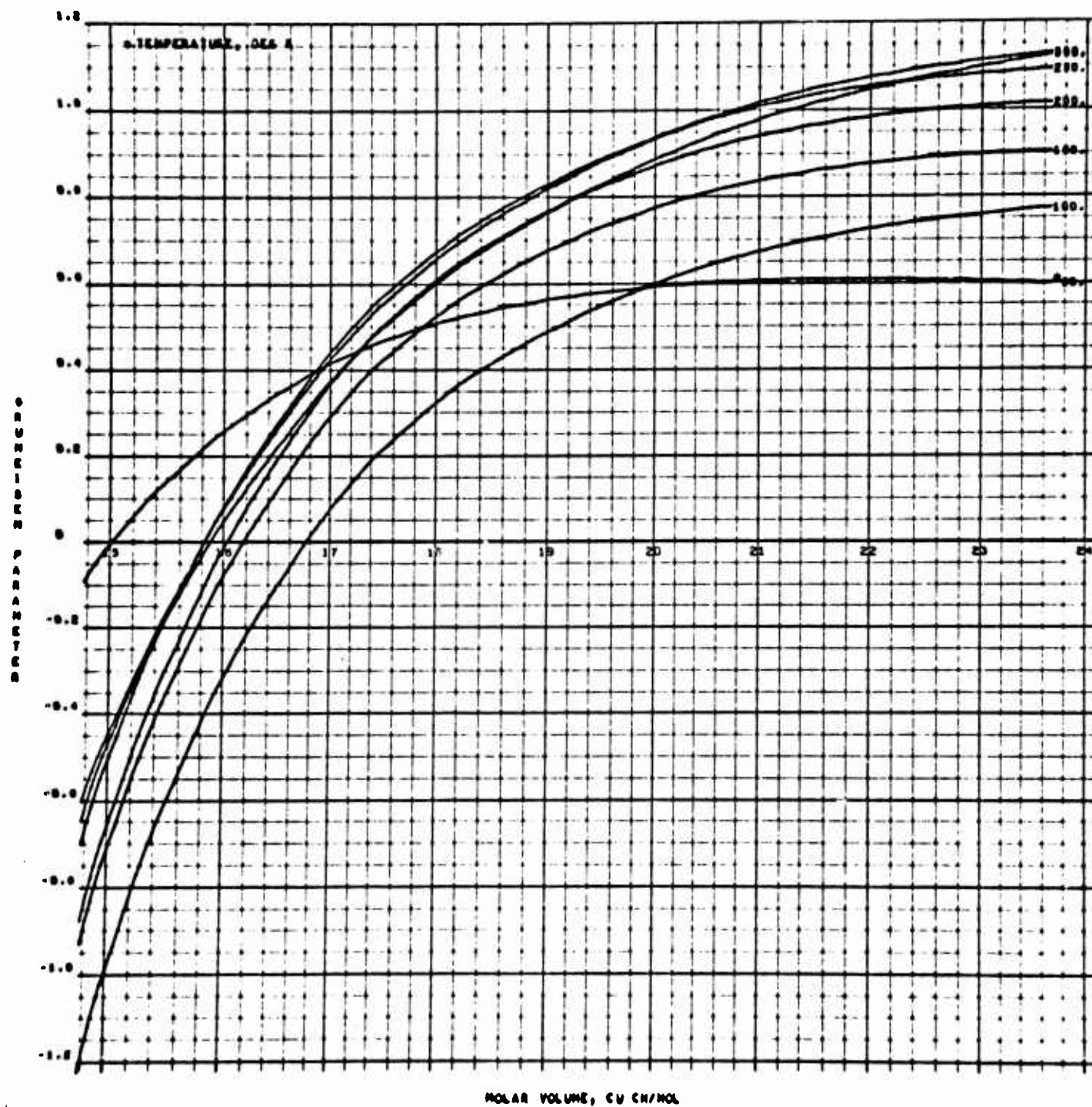


Figure 5-19 - γ_2 as a Function of Volume and Temperature for Sodium

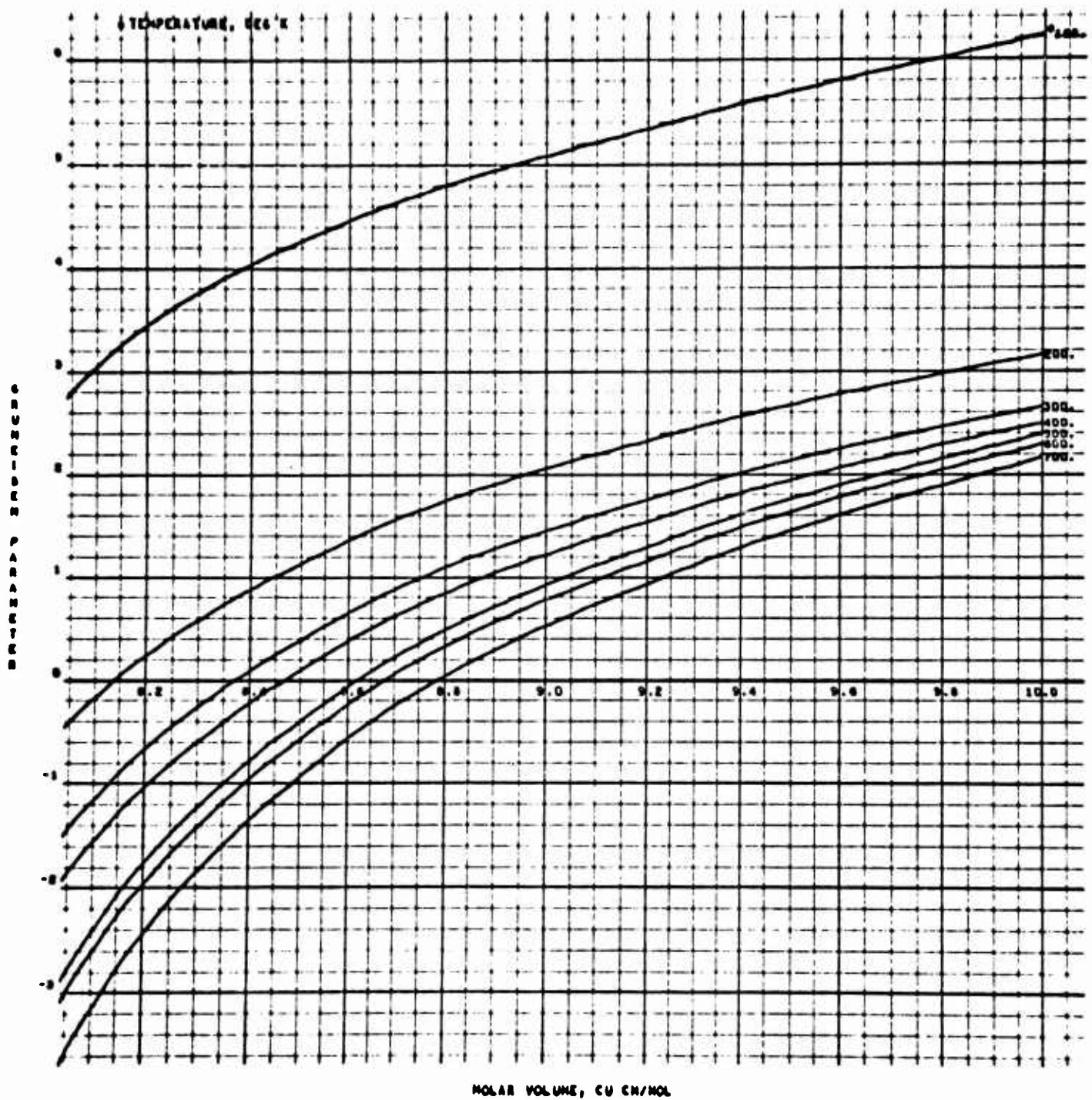


Figure 5-20 - γ_2 as a Function of Volume and Temperature for Aluminum

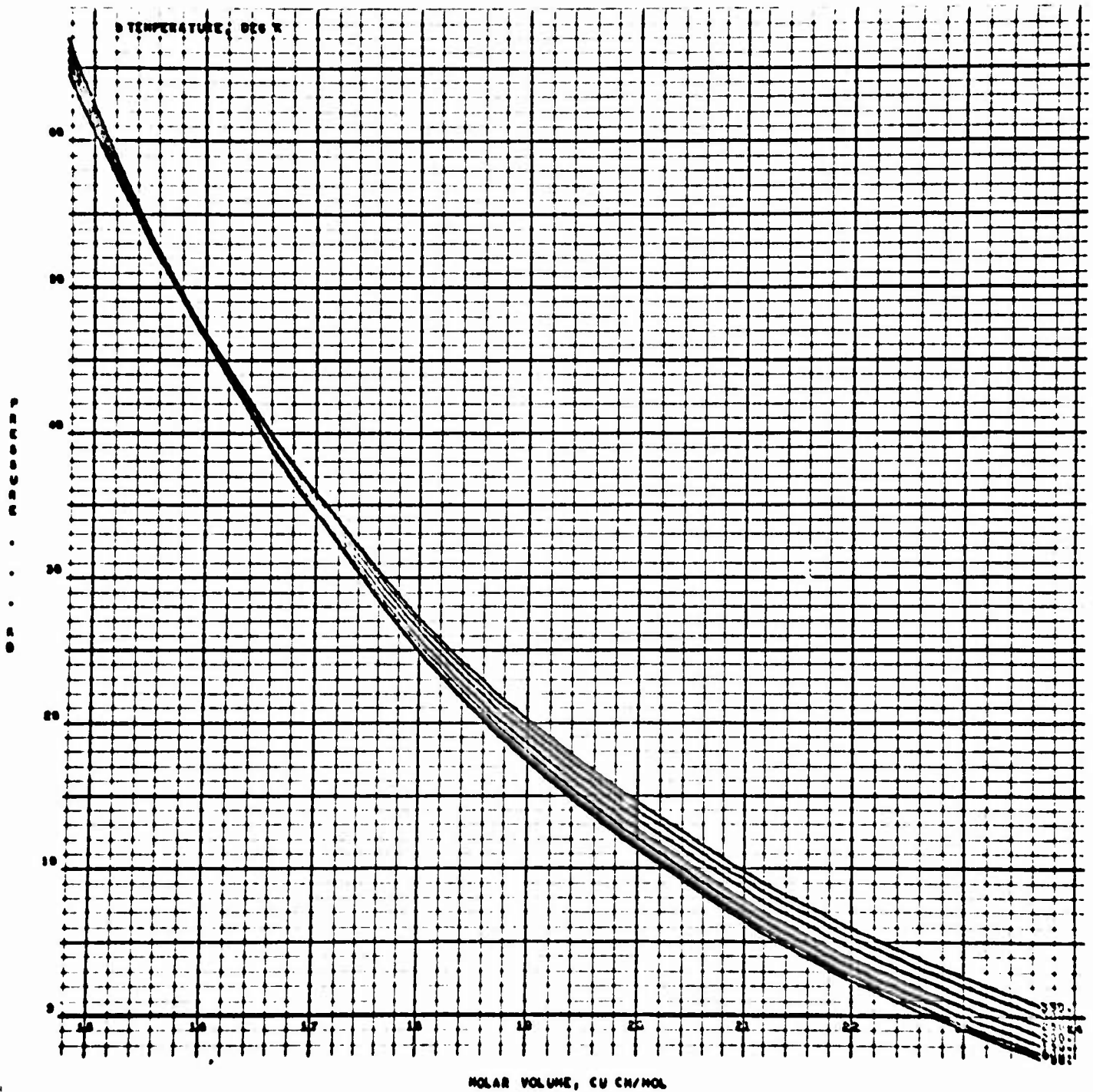


Figure 5-21 - Pressure as a Function of Volume and Temperature for Sodium

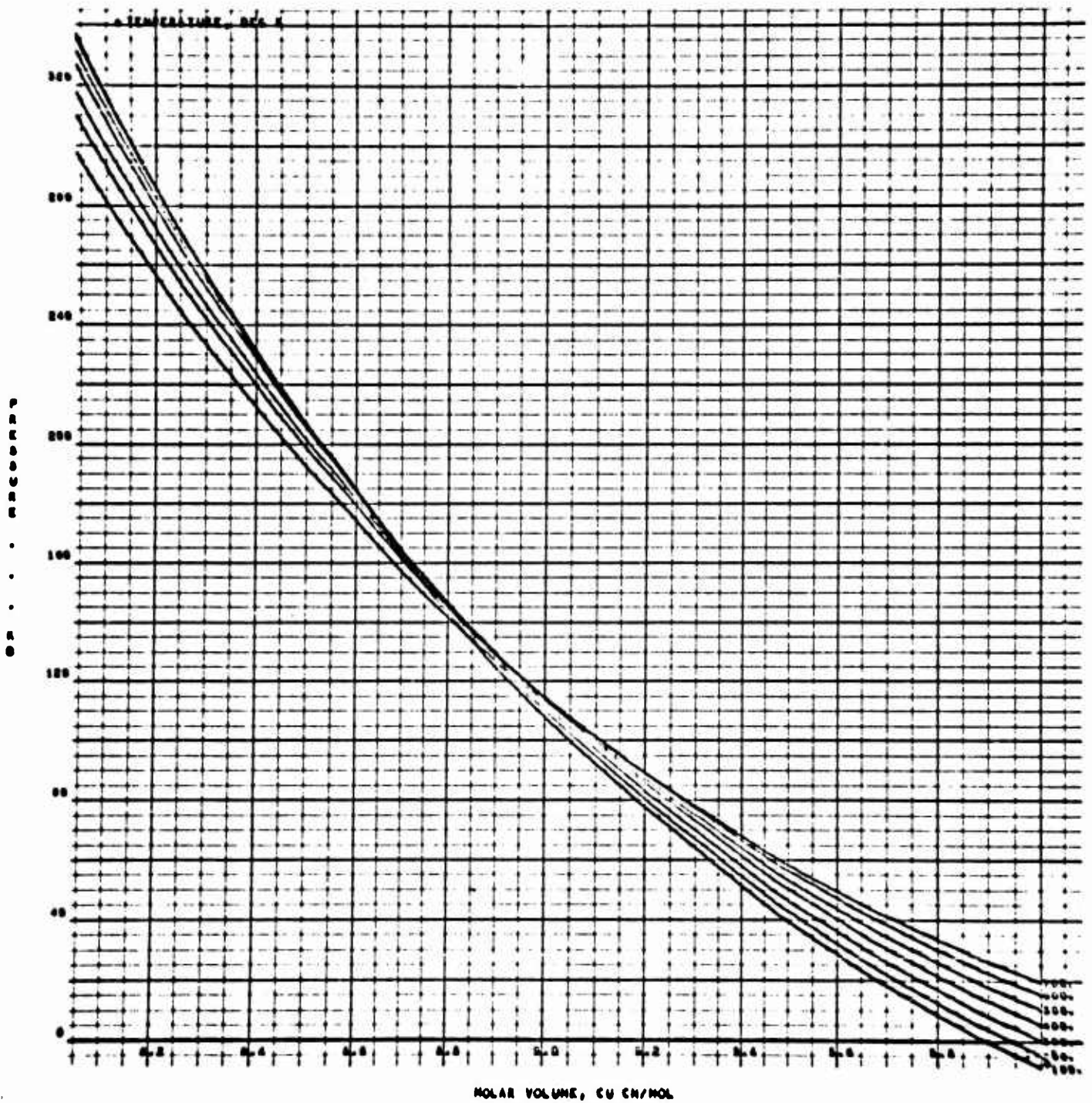


Figure 5-22 - Pressure as a Function of Volume and Temperature for Aluminum

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Section 6 FOAMED AND DISTENDED MATERIAL

A. HIGH PRESSURE REGION

A shock adiabat of a foam suitable for discussion in the high pressure region is shown by the dotted line in Figure 6-1. The solid line represents the shock adiabat of solid, compacted material.

The volume V_f is the volume of the foam and V_{OH} the volume of non-porous material. The volume V_{OH} contains the same amount of mass as volume V_f ; the densities, however, are different. In other words, a foam or original volume V_f is crushed to volume V_{OH} at P essentially equal to zero.

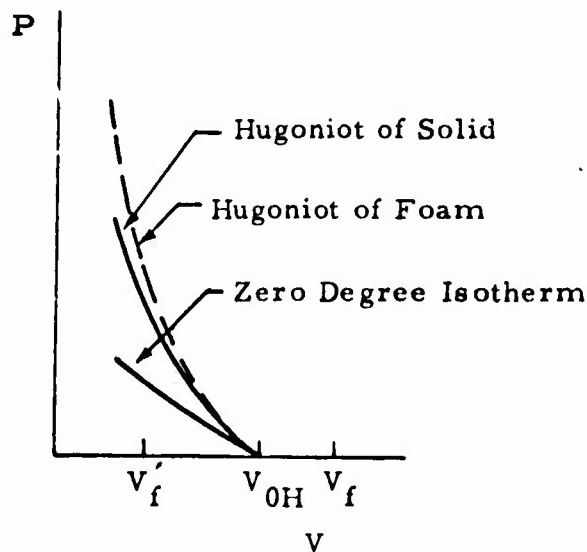


Figure 6-1 - P vs V Curve to Illustrate Relationship between Shock Compression of Compacted Solid and of Foam

The different shock adiabats follow from the fact that a shock compression of a foam is a more irreversible process than the corresponding compression of a compacted solid.

At volume V_f' , the shocked compacted solid and the shocked foam have the same static energy. This is given by the zero degree isotherm at volume V_f' . The difference in internal energy, therefore, is caused by a greater thermal energy in the shock foam, i.e.,

$$E_H - E_f' = \Delta E_{\text{thermal}}$$

Similarly, the difference in pressure at volume V_f' is the result of a difference in thermal pressure:

$$P_H - P_f' = \Delta P_{\text{thermal}}$$

The Grüneisen parameter γ_3 therefore can be determined from

$$\gamma_3 \approx V_f' \left(\frac{\Delta P_T}{\Delta E_T} \right)_{V_f'}$$

The preceding discussion was taken mainly from Krupnikov, Brazhnik, and Krupuikova, 1962; Zel'dovich and Rayzer, 1965, p. 874; and Morgan, Rockowitz, and Atkinson, 1965.

The experimental data for tungsten foams and for aluminum foams (Morgan, Rockowitz, and Atkinson, 1965, p. 95), can be represented to a first approximation by the equation

$$E_T = g(V P_T) + h(V P_T)^2$$

where g and h are constants. The Grüneisen parameter, therefore, can be represented as

$$\gamma_3 = v \left(\frac{\partial E_T}{\partial P_T} \right)_V = \frac{1}{g + 2hVP_T}$$

Because E_T is a function of VP_T only, γ_3 is a function of E_T only.

The Grüneisen parameter γ_3 determined in this fashion for aluminum foams shows a dependence on the thermal energy. This is shown in Figure 6-2.

It should be pointed out that the reproducibility and validity of shocked foam data is still questionable. (See Morgan, Rockowitz and Atkinson, 1965, p. 107, and McQueen, 1964, p. 69.)

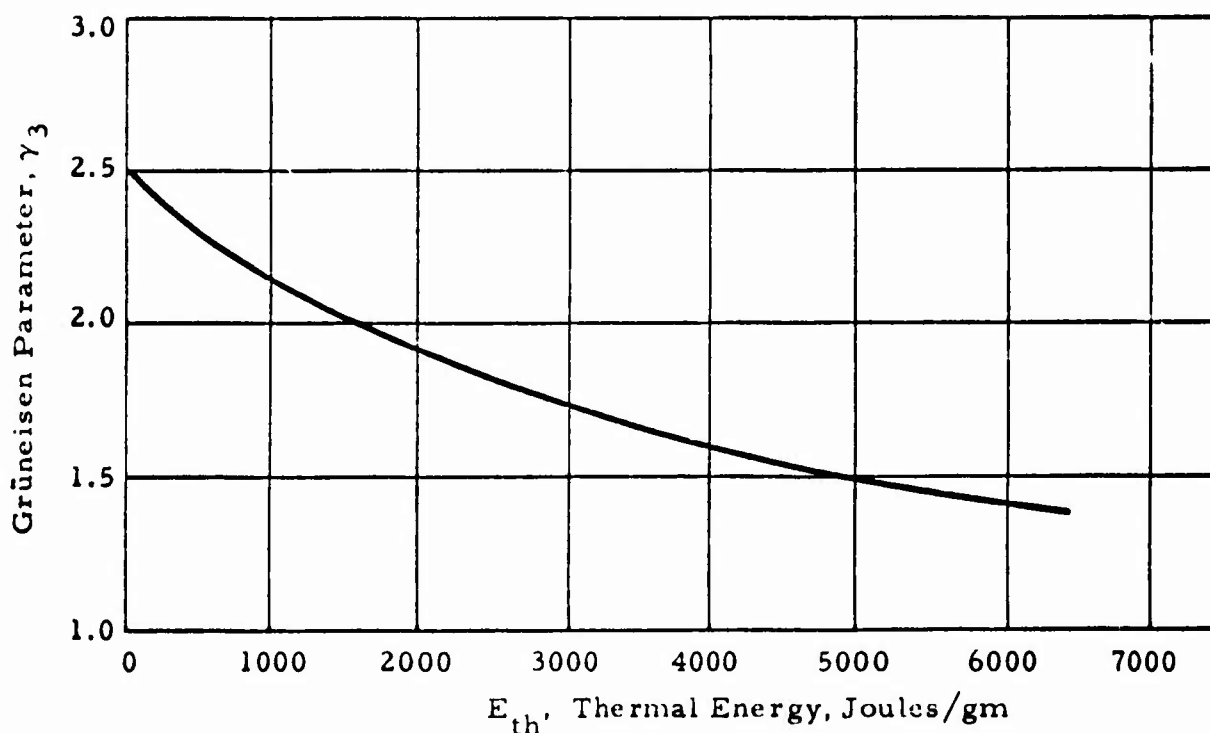


Figure 6-2 - Grüneisen Parameter as a Function of Thermal Internal Energy for Aluminum (From Morgan, Rockowitz, and Atkinson, 1965, p. 104)

Russian workers (see Al'tshuler, 1965) have expanded the Mie-Grüneisen equation of state to take into account electronic contributions at high temperatures and pressures. Their equation is essentially

$$P - P_0 = \frac{\gamma_a}{V} E_{T_a} + \frac{\gamma_e}{V} E_{T_e}$$

where the subscripts a and e refer to atomic and electronic contributions. The γ_e parameter apparently varies rather slowly with density, going from 1/3 for an isolated atom at zero pressure to the limit 2/3 for an ideal Fermi-Dirac gas (Brush, 1967).

In connection with the equation of state in foams, Bjork, et. al., (1967) modified existing equations of state to agree with experiments conducted by the Russians on porous samples and to fit other available data. In this treatment the electronic thermal contribution to pressure and energy are included. The equation was incorporated into a hydrodynamic code by constructing a table consisting of a matrix of pressure elements P_{ij} , where i and j correspond to certain values of η and E. The hydrodynamic code could then compute the pressures it needed by two-way interpolation in the table. It appears that no allowance for the variation of γ_a with temperature has been made.

Figure 6-3 shows a comparison of PV curves generated by this treatment with experimental data.

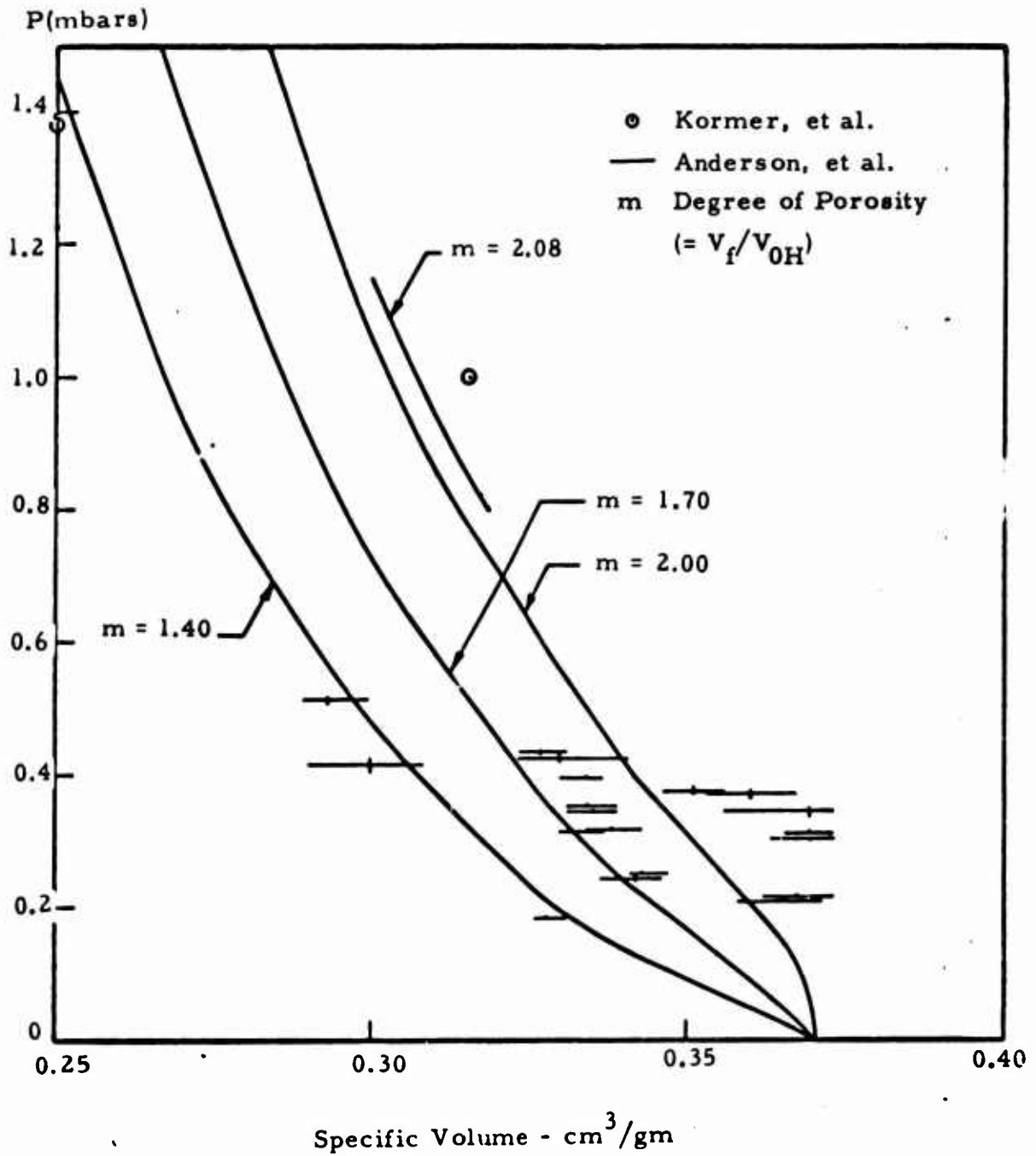


Figure 6-3 - Comparison of Aluminum Hugoniot with Experimental Data (Bjork, et al., 1967)

B. COMPLICATIONS CAUSED BY STRESS ANISOTROPY AND HYSTERESIS EFFECTS

a. Introduction

The preceding discussion concerned situations where the pressure could be considered to be the same as a hydrostatic pressure and the states of the materials before and after shock or hydrostatic compression to be those of thermodynamic equilibrium. Actually, one or the other of these two assumptions often break down in practice and may lead to unpredictable shock behavior patterns. For example, in foams and solid ductile materials, shock compression at low pressures may exhibit a shock front which splits into two fronts (Dudley, 1966; Rempel, 1963) — the first front known as the elastic precursor and the second as a plastic shock wave. Experimental confirmation of various mathematical models for such behavior has been good in some cases and not so good in others.

Attention was focused, in reviewing these mathematical models, on how the equations of state were formulated for foams in the low pressure regions, especially for the BCD part of the shock compression P-V curve which is well approximated as shown in Figure 6-4.

It became apparent almost immediately that no clear, systematic treatment of the basic thermodynamics and physics of hysteresis effects exists. The formulation in the literature of equations of state for materials displaying hysteresis effects are extremely difficult to understand and evaluate because most of these formulations are "couched in terms of elasticity theory and dislocation concepts" (passage in quotes taken from Fitzgerald, who is quoted again in the next paragraph). The same criticism may be made of many current explanations of mechanical behavior. Fitzgerald (1966) neatly sums up the confusion:

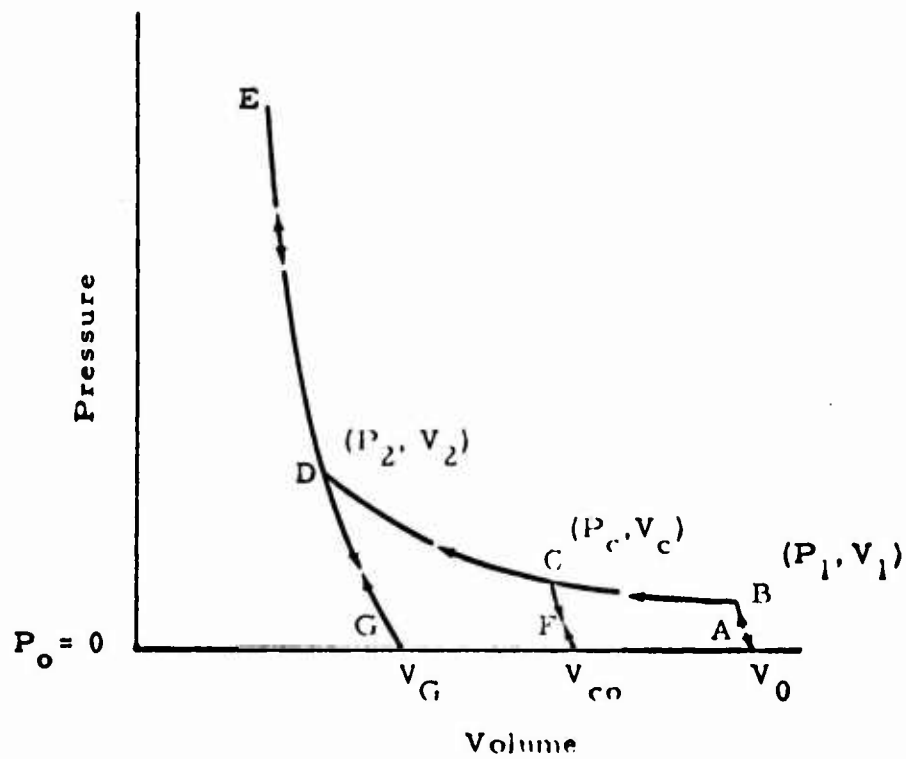


Figure 6-4 - Assumed P-V Diagram in Phasetransition Procedure
(Linde and Schmidt, 1966)

"Current explanations of mechanical properties of solids are generally couched in terms of elasticity theory and dislocation concepts. The latter are employed chiefly in attempts to explain obvious nonelastic behavior such as plastic deformation, but even in this case elastic ideas prevail to a surprising extent. That is, calculations of the forces or interactions between dislocations and/or other crystal lattice defects are often made in terms of linear, elastic continuum surrounding the imperfections. Thus a clearly nonelastic phenomenon like plastic slip is treated in terms of linear elastic concepts and constants. After thirty years, this approach has led to no numerical calculations in agreement with measured values of any nonelastic quantity, except through the arbitrary assignment of values to one or more constants, and even qualitative provisions for the existence of certain well-known classes of mechanical behavior are missing."

Fitzgerald goes on to develop a treatment of mechanical properties in terms of wave mechanics, which leads directly to

"predictions of nonelastic audiofrequency resonances in vibration experiments and to anticipation of acoustic emission, simple and quantitative explanations of hypervelocity impact phenomena, stress-strain relations for poly and single crystals, sliding friction and the formation of crystal mosaics. Also obtained is the correct form of the stress-strain law for cubic metals and its variation with single-crystal orientation, temperature, parity, sample size and various kinds of sample pretest treatment."

If the above claims are really true, Fitzgerald's approach is a great advance. Fitzgerald's work certainly appears very promising and should be explored in more detail. However, a great need still exists for a clarification of irreversible processes in terms of classical thermodynamics and basic physics. Bridgman's work (1950) in this direction indicates that such an approach can yield much insight and information simply and directly.

At the very least, such an approach would enable explorations of the limits of applicability of classical thermodynamics and basic physics and, thus, provide a firm basis for decisions on approximations in practical calculations and the need in certain cases for more complicated theories, such as Fitzgerald's or irreversible thermodynamics. Regardless of the light such an approach can throw on irreversible processes, a clarification

of the various definitions of "state" is imperative if equations of state are to be formulated at all.

In this report only a beginning of a clarification of irreversible processes and definitions of "state" in terms of classical thermodynamics and physics can be attempted because of time limitations. However, from the following discussion, it will be obvious that the classical approach is far from exhausted or completely understood.

b. Classification of Mechanical Processes and Stresses

First of all, it is necessary to clearly separate elastic, reversible behavior from irreversible, hysteresis type behavior and internal stresses from external stresses. Elastic or reversible displacements are those in which no work is dissipated as heat. In an elastic displacement, the displacing force can be reversed at any point in the displacement and the material brought back to the original state. All irreversible displacements involved work dissipation, and reversal of the displacement force may or may not bring the material back to its original state. Also, a consideration in classifying hysteresis behavior is whether the process approaches reversibility if done slowly enough. We believe that mechanical hysteresis behavior probably can be classified according to one of five or six general classes or combination thereof, according to how the original state can be restored and whether time is a factor or not. However, in the short time that was available, we are not sure that we have completely covered every possibility or that each of the five types is indeed unique.

The type of hysteresis most pertinent to the case of a foam collapsing, either by fracture or flow, is one in which the initial cannot be restored by reversal of displacement force, and no matter how slowly the force is increased the collapse can never be reversible.

In this respect the collapse of a solid foam has much in common with the crystallization of a subcooled liquid. A subcooled liquid like a foam is a metastable equilibrium state. If the subcooled liquid is catalyzed or suddenly jarred, the solid phase appears and increases irreversibly until equilibrium is established. If a subcooled liquid is cooled slowly, a critical temperature, called the temperature of maximum subcooling, is reached, and the solid phase suddenly precipitates and continues to grow until equilibrium is established. Although nothing has been found in the literature about what would happen to a subcooled liquid if the pressure were gradually increased at constant temperature, it is most probable that a critical pressure exists, for as Bridgman notes (1935, p. 9) an increase of pressure is equivalent to a decrease in temperature in some respects.

The analogy of a subcooled liquid and a solid foam is further strengthened by the fact that a metal powder sinters slowly at moderate temperatures but increases with a rise in temperature. At the Tammann temperature (near $0.5 T_m$) the sintering rate accelerates markedly (Gregg, 1961, p. 155).

The thermodynamic characterization of metastable states will be discussed later. We now turn our attention to stress as a state variable.

If a hydrostatic pressure P is applied to an elastic solid, say a cube of material is immersed in oil which is in turn compressed by a piston, the work done on the solid will be given by $-PdV$, where dV is the change in volume of the solid. The work will be $-PdV$, even if the cube deforms anisotropically as long as the deformation is elastic. In other words the compression may be more in one direction than in the others, and the cube may be deformed say to a rectangular block. Since the process is reversible, the internal P will be the same as the external applied P . If we further assume that the temperature is constant, the state of the solid material may be characterized by two independent state variables P and T .

Let us now consider the same cube as above, but to one face a tension stress τ is applied as in Figure 6-5 below (Reiss, 1965).

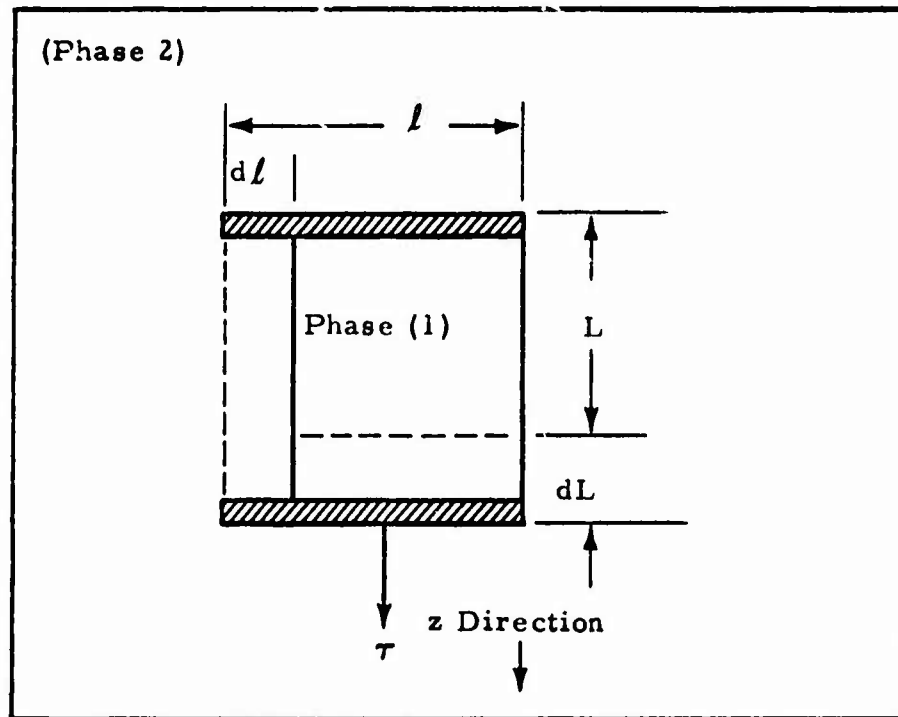


Figure 6-5 - Deformable Isotropic Solid Solution, Phase (1)
Surrounded by a Fluid Solution, Phase (2)

The actual stress in the z direction will be

$$\tau_z = \tau - P$$

The work done as a result of reversible application of tension is

$$W = (\tau - P) l^2 dL + 2PL l dl$$

or

$$W = P dV^{(1)} - \tau l^2 dL$$

where the superscript (1) refers to the volume change of the solid cube.

The change in internal energy of the material as the result of the applied stress

$$dE = TdS - PdV^1 - \tau l^2 dL$$

Thus the energy is now a function of three independent state variables. The above system discussion illustrates Reiss' clarification of the differences between stable thermodynamic equilibrium and metastable equilibrium. According to Reiss, a system is in equilibrium if no discernable changes occur during the time span in which we are interested. However, every state of equilibrium is subject to constraints and the number of constraints on a system determine the number of state variables which must be specified in order to characterize the equilibrium. Furthermore, the ways in which a system can do work is determined by the number of constraints. Thus, in the above example, we have three constraints — the thermostat holding the temperature at T , the piston holding the pressure at P , and the applied tensile stress. Release of any one of these constraints, holding the other two constant, enables the system to do a unique kind of work.

According to Reiss, the only difference between metastable equilibrium and stable equilibrium is the number of state variables involved. This view greatly simplifies the understanding of metastable and stable equilibria. However, a corresponding clarification of unstable and neutral equilibria still remains for the future.

A further shortcoming of Reiss' work is that he fails to clarify internal and external constraints. In an externally constrained system at equilibrium, such as discussed previously, the internal and external intensive parameters are the same. Thus the pressure is the same in the system and its surroundings, as are temperature and stress.

Internal constraints arise from activation energy barriers. Edelglass (1966, p. 226) presents a discussion of activation energies and their relationship to reversible and irreversible processes, which is very instructive. A brief summary of his discussion is presented in the next paragraph.

Graphically, the free energies of the various states may be represented as shown in Figure 6-6.

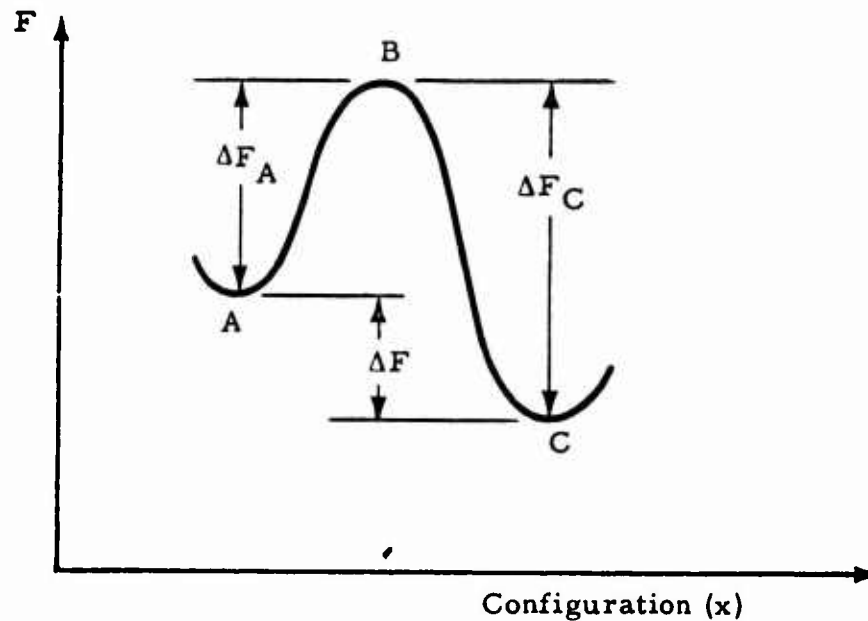


Figure 6-6 - Free Energy vs Configuration Paths for Irreversible "Reactions"

The states A, B, and C are the metastable, activated and stable equilibria states. The activated state B is a state of "unstable" equilibria. The term "unstable" is put in quotes because it is not clear whether the activated unstable state ("The activated complex is stable for atomic displacements in all directions but one." — Glasstone, et al., p. 185) is the same as unstable equilibrium usually referred to in thermodynamic texts. The term ΔF is the free energy change for the transformations $A \rightarrow C$ or $C \rightarrow A$, while ΔF_A is the free energy of activation for $A \rightarrow B$ and ΔF_C for $C \rightarrow B$. Thus, once A has passed over B and fallen into state C, there is little chance it will cross the barrier B to go back to A, and

the resultant reaction will be $A \rightarrow C$, or an irreversible change at a rate which is determined by the frequency of passage over the barrier B.

Contrast this behavior to a reversible change, whose free energy vs. configuration path may be represented as shown in Figure 6-7.

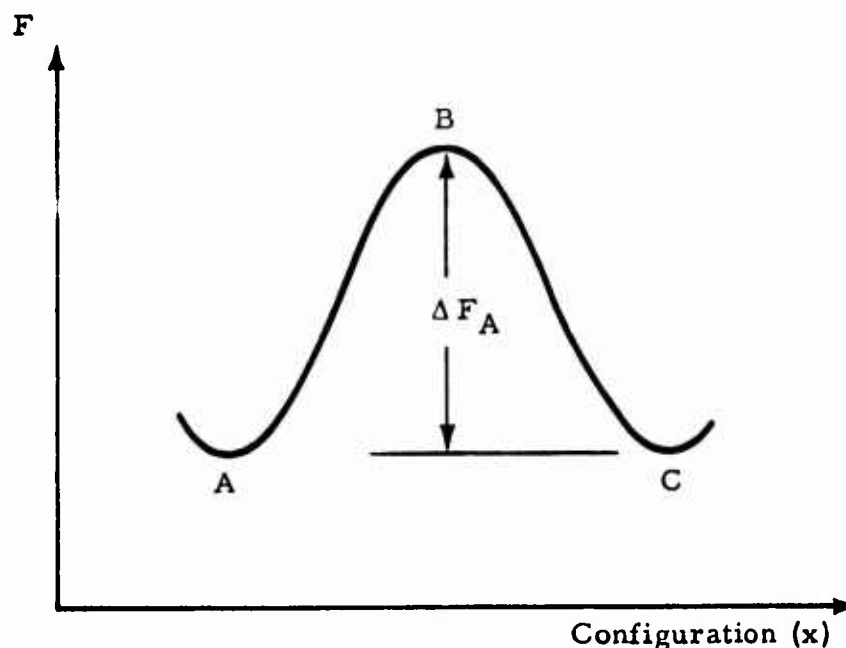


Figure 6-7 - Free Energy vs Configuration Paths for Reversible "Reactions"

Here, the change of $A \rightarrow C$ is just as great as $C \rightarrow A$.

Under stress the above figure assumes the form of the preceding one, so that there is a net flow in the direction of the force. This will result in a strain that is rate controlled, and the rate will have an exponential temperature dependence. If the stress is sufficient to overcome the barrier, the strain deformation will no longer be temperature dependent (Edelglass, p. 228).

More discussion of the above type processes would point out many more interesting aspects of rate controlled phenomena in solid behavior.

In connection with metastable equilibria, the question arises as to which equilibria — stable or metastable — will be more stable under certain conditions. This question arises because apparently there are temperatures where a solid powder, which we would classify as a metastable equilibria, is more stable than a solid crystal, a stable equilibrium case. Huettig (Kingston and Huettig, 1951) suggests that above $T = 893^{\circ}\text{K}$ powdered gold is more stable than solid crystal gold (mp. 1337°K). If it is really the case, interesting ramifications may result in real situations such as an X-ray burst powdering a missile casing. The above situation is perhaps analogous to the case of rapid cooling of liquids. If certain liquids such as glycerol are cooled rapidly, they may be taken down to temperature far below (even below their temperature of maximum subcooling) the melting point of their solid phases and remain in their metastable states at that temperature indefinitely (Walton, 1966).

The above brief discussion should be sufficient to illustrate how a unified approach to hysteresis and rate controlled processes in terms of classical thermodynamics and basic physics is evolving. We will now turn our attention to explicit thermodynamic approaches to the problem.

c. Unified Thermodynamic Approaches to Mechanical Hysteresis

In a very remarkable paper, Bridgman (1950) examines some extensions of the methods and definitions of classical thermodynamics to two cases of irreversible mechanical phenomena. In future work we hope to go more fully into his reasoning and deductions. Here only a brief summary is presented of his conclusions about plastic deformation and processes which generate internal disorder.

Consider the deformation of an ideal plastic as shown in Figure 6-8 (Bridgman, 1950).

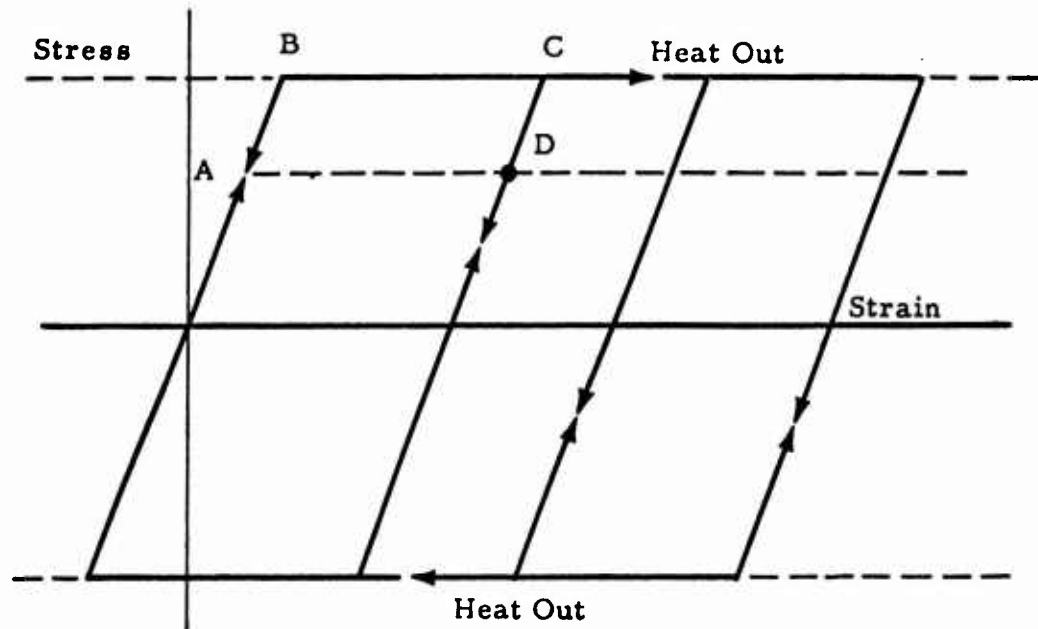


Figure 6-8 - The Stress-Strain Relations in the "Ideal" Plastic Body

In the above figure, the inclined lines correspond to elastic deformation and the horizontal lines to plastic deformation. For a body at point or "state" D, the entropy is the same as point A. In other words, the entropy in the body arising from plastic deformation is zero.

For bodies which can change their internal order, like binary alloys, Bridgman introduces a parameter α , which specifies the degree of internal disorder. He then writes the entropy of the system as

$$S = S(P, T) + S(\alpha)$$

More study of Bridgman's work should reveal how the parameter α can be experimentally determined and how the equation of state for a body at point D in the plastic deformation case can be formulated from experimental stress-strain curves.

In a group of papers (Everett, et al., 1952 and 1953) a unified general approach to hysteresis is also approached. However, only one type of hysteresis is dealt with. This is the kind where a stress cycle returns the material to its original state, but the paths in the forward and reverse directions cannot be made to coincide no matter how slowly the process is carried out. This type of hysteresis is a common phenomena in many fields, such as magnetization of ferromagnetics, solid transitions in crystals and alloys, application of stress to solids, adsorption of gases by solids, etc. Everett and Smith advance a domain theory to explain this type of hysteresis. In this theory the static macroscopic state of a system exhibiting hysteresis is defined at any instant when an internal variable ξ is specified, in addition to the usual external independent variables. The variable ξ represents the fraction of molecules of the system in State II; presumably State II is a metastable state, the rest of the system being in State I. Everett and Smith's treatment will need to be studied in more detail. Their definition of metastable equilibrium is confusing.

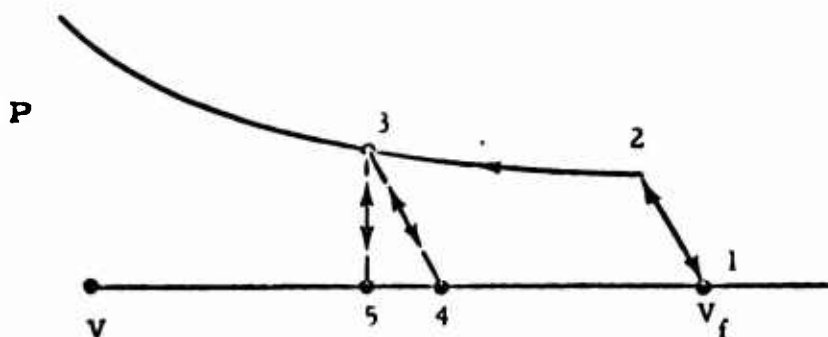
Incidentally, it may be worth mentioning two notes of caution appearing in the literature concerning the application of Onsager's irreversible thermodynamics. Bridgman (1950, p. 63) states:

"As far as I know, however, all the examples treated by the Belgian school are such that some reversible method exists for getting from any state of the system to another, so that the entropy is defined and may be evaluated by conventional methods. The extension of the entropy concept to situations in which the entropy may not be so defined does not appear to have been considered."

Tisza (1966, p. 33) states, "This note is merely a warning that the very simple consideration of irreversibility should not be thoughtlessly applied to situations which in fact involve the question of retrieval."

d. Approximate Calculation of an Equation of State for a Partially Collapsed Foam

A calculation of a γ parameter for foams based on a rigorous application of thermodynamics would obviously involve much more time than is available in the present study. The preceding discussions, however, do suggest that the problem can perhaps lend itself to some approximations. For example, consider the collapsing part of the P-V curve for a foam



where V and V_f represent the volumes of a given mass of compacted solid and of foamed solid ($P = 0$, $T = \text{initial}$). State 3 represents the equilibrium end-point state after application of a pressure P_c . If P_c is released slowly and adiabatically state 3 would relax isentropically to state 4 (assumption). Let us assume that state 3 represents a state containing $(V_5 - V)/(V_f - V)$ parts foamed solid and the rest compacted solid. Let us further assume that state 3, on cooling to room temperature at constant volume, follows the reversible path 3-5. A γ parameter may then be given by

$$\gamma = V \left(\frac{\partial P}{\partial E} \right)_V$$

so that

$$E_3 - E_5 = v \int_0^{P_c} \frac{dP}{\gamma}$$

or assuming γ is independent of pressure

$$E_3 - E_5 = \frac{v}{\gamma} P_c$$

If it is further assumed, as the Russians did (Krupnikov, et al., 1962), that the energy of a foam at initial conditions is little different from that of the compacted solid, then E_5 can be taken as the energy of compacted solid at the initial conditions.

If E_3 can be determined, and it probably can be approximated if heat capacity data on the compacted solid and foam are available, then γ can be calculated.

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Section 7

CONCLUSIONS AND RECOMMENDATIONS

Examination of the theoretical bases of the Mie-Grüneisen equation of state and the results of calculations of the various Grüneisen parameters have shown that its validity cannot be assumed lightly under all conditions.

The study has also shown that a knowledge of the temperature and volume dependence of γ_2 would not only provide a firm basis on which to judge the validity of the Mie-Grüneisen state equation but also would permit direct use of the Mie-Grüneisen type equation of state

$$P - P_0 = \frac{\gamma_2(V, T)}{V} (E - E_0)$$

in shock wave calculations.

Thus, it would be most desirable that methods of obtaining γ_2 from experimental data, both under hydrostatic and shock conditions, be fully explored. In particular, it is suggested that the accuracy of the method of calculating γ_2 originated in this study be evaluated and that γ_2 parameters be calculated for a variety of materials.

It is also recommended that the physical and thermodynamic bases of formulating equations of state be examined more fully. Such an examination should lead to a theoretically sound approach to formulating equations of state for materials characterized by more than two state variables, such as foams and distended materials.

Other desirable work indicated by the study is (a) obtaining more precise values of coefficients of thermal expansion from percent thermal data in the literature, (b) a concentrated examination of the factors involved in obtaining reliable γ values for plastics, (c) a fuller understanding of directional Grüneisen parameters, (d) a fuller understanding of the role of the Grüneisen parameter in phase-change (melting) phenomena, and (3) a fuller consideration of the role of electrons in the thermodynamics of solids.