

Significance of Some Equations of State Obtained from Shock-Wave Data

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A single Hugoniot curve determined from shock-wave experiments does not provide enough thermodynamic information to specify an equation of state. The assumptions which, along with shock-wave data, are sufficient to determine a complete equation of state are instructive to a serious student of thermodynamics, because they illustrate the significance of the state variables and the relations among them. This paper considers the specific problem of calculating the state variables of shock-induced states and discusses calculations based on the assumption of either constant C_v or constant C_p from a structural point of view. Methods of calculating the state variables are formulated to show how the assumptions make them possible. The assumption of constant C_p specifies implicitly the functional forms of the $(E-p-v)$ and $(p-v-T)$ equations of state. Similarly, the assumption of constant C_v specifies the functional forms of the $(H-p-v)$ and $(p-v-T)$ equations of state. The experimental Hugoniot curve is used as a boundary condition to determine arbitrary functions in these equations of state and to show how the assumptions and the experimental data lead to a complete thermodynamic description of shock-induced states.

INTRODUCTION

TO determine equations of state from shock-wave experiments it is necessary to assume that shocked states lie on equilibrium, thermodynamic surfaces, which are defined by equations of state and which satisfy the thermodynamic identities of Gibbs.¹ This assumption is valid if thermodynamic equilibrium is established behind the shock front. In this case, the shock connects equilibrium states, but the entropy of the shocked state is greater than the entropy of the initial state because the shock process is both adiabatic and irreversible. Also, conditions reached in a shocked state can be attained from the initial state by reversible, nonadiabatic processes, for example, reversible, static, isothermal, compression, followed by reversible addition of heat. To test the validity of the assumption of equilibrium behind the shock, it is necessary to compare equations of state determined from shock-wave experiments with those obtained from static experiments. Although there are not enough data to make a conclusive comparison, it is significant that the 27°C isotherms of Al, Cu, and Zn, calculated by Walsh and Christian²

from shock-wave data, when extrapolated below 100 kbar, are in some agreement with those determined by Bridgman³⁻⁵ in static experiments.

Applying the laws of conservation of mass, momentum, and energy to a steady-state shock moving in stationary material yields the Rankine-Hugoniot jump conditions across the shock front⁶:

$$\text{Mass} \quad \rho_0 U = \rho(U-u), \quad (1a)$$

$$\text{Momentum} \quad p - p_0 = \rho_0 U u, \quad (1b)$$

$$\text{Energy} \quad p u = \rho_0 U (E - E_0 + \frac{1}{2} u^2), \quad (1c)$$

where U is the shock velocity, u , p , $\rho = 1/v$, and E are the particle velocity, the pressure, the density, the specific volume, and the specific internal energy of material behind the shock front, and p_0 , $\rho_0 = 1/v_0$, E_0 , are the values of these quantities ahead of the shock front.

The elimination of U and u from Eq. (1c) gives the Hugoniot equation

$$E - E_0 = \frac{1}{2} (p + p_0) (v_0 - v), \quad (2)$$

that defines all states on the $(E-p-v)$ surface that can be reached from an initial condition (E_0, p_0, v_0)

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¹ J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs: Vol. I, Thermodynamics* (Dover Publications, Inc., New York, 1960).

² J. M. Walsh and R. H. Christian, *Phys. Rev.* **97**, 1544 (1955).

³ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **76**, 55 (1948).

⁴ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **77**, 187 (1949).

⁵ P. W. Bridgman, *Phys. Rev.* **60**, 351 (1941).

⁶ R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Interscience Publishers, Inc., New York, 1948).

by a single shock. If the $E(p,v)$ equation of state is known, Eq. (2) defines the locus of shocked states as a curve in the $(p-v)$ plane

$$\dot{p} = \dot{p}_h(p_0, v_0, v), \quad (3)$$

which passes through the initial state (p_0, v_0) and is called the Hugoniot curve centered at (p_0, v_0) . The entropy increases along the Hugoniot curve as the pressure increases because the shock is irreversible.⁶

The elimination of u from Eqs. (1a) and (1b) gives

$$p - p_0 = (U/v_0)^2(v_0 - v), \quad (4)$$

the equation of a straight line that is called the Rayleigh line. Because the shocked state must satisfy Eqs. (3) and (4), the intersection of the Hugoniot curve centered at (p_0, v_0) and the Rayleigh line passing through (p_0, v_0) defines the thermodynamic state (p, v) behind a shock traveling with constant velocity U in stationary material with pressure p_0 and specific volume v_0 .

In the 50–500-kbar regime, shock-induced states of liquids and solids, which are assumed to lie on equilibrium thermodynamic surfaces, are incompletely defined thermodynamic systems because not enough experimental data are available to determine equations of state. The experimental Hugoniot curve is determined in a domain of the $(p-v)$ plane where no equation of state is known and the change in internal energy along it is given in terms of the mechanical state variables by the Hugoniot equation. However, because the pressure-specific volume-temperature $(p-v-T)$ and $(E-p-v)$ equations of state are not known, neither the values of the thermodynamic variables, temperature T and specific entropy S , of shocked states along the Hugoniot curve, nor the values of the state variables off the Hugoniot curve can be calculated without making assumptions.

The problem of evaluating the state variables of shocked states is instructive to a student of thermodynamics because it demands a working knowledge of thermodynamic identities and introduces him to a region of the $(p-v)$ plane where equation of state problems arise because of strong interatomic and intermolecular forces. However, it is more instructive to present structural aspects of the problem by so formulating it to give some

insight into the more general thermodynamic question: what additional data are required to completely characterize an incompletely defined thermodynamic system? The problem of evaluating the thermodynamic state variables along the Hugoniot curve is considered to specify precisely how shocked states are incompletely defined when a Hugoniot curve is known. The models specified by the assumption of either constant specific heat at constant volume C_v or constant specific heat at constant pressure C_p are discussed because they have been used to calculate the state variables of shocked states.^{2,7-11}

To show the full significance of the assumptions they are combined with the general relationships of thermodynamics to derive additional properties of the models which are implicitly assumed, but at first sight may not be obvious. This structural point of view is adopted to show how the induced properties of the model, together with the assumptions, determine a logical way to solve the problem, and why the original assumptions are sufficient for its solution.

Illustrative examples are provided by reformulating the work of Walsh and Christian² on metals and Rice and Walsh¹¹ on water. The assumptions and the experimental Hugoniot data are sufficient to determine a complete equation of state over the domain of the $(p-v)$ plane specified by the Hugoniot curve. The assumptions determine functional forms of equations of state and also allow shock temperature to be calculated along the Hugoniot curve. The Hugoniot curve is used to obtain the arbitrary functions in the equations of state and to characterize the models completely.

HUGONIOT CURVE IN THE $(p-v)$ PLANE

Consider a typical Hugoniot curve 01A in the $(p-v)$ plane as shown in Fig. 1. It gives the locus of all possible states attainable by passing a one-dimensional shock wave into a fluid at a given initial pressure p_0 and specific volume v_0 . The intersection of the Rayleigh line 0a whose equa-

⁷ R. H. Christian, UCRL-4900 (1957).

⁸ A. W. Campbell, W. C. Davis, and J. R. Travis, *Phys. Fluids* **4**, 498 (1961).

⁹ M. W. Evans, *J. Chem. Phys.* **36**, 193 (1962).

¹⁰ C. L. Mader, *Phys. Fluids* **6**, 375 (1963).

¹¹ M. H. Rice and J. M. Walsh, *J. Chem. Phys.* **26**, 824 (1957).

tion is $p - p_0 = (U_1/v_0)^2(v_0 - v)$ and the Hugoniot curve defines the shocked condition (p_1, v_1) at 1 behind a stepshock with velocity U_1 . The change in internal energy across the shock front is given by $E_1 - E_0 = \frac{1}{2}(p_1 + p_0)(v_0 - v_1)$ which is the area of the trapezoid 0123 with bases p_1 and p_0 and altitude $v_0 - v_1$.

First, making no assumptions, let us decide what information about the thermodynamic variables, temperature T and specific entropy S , of shocked states can be obtained from a Hugoniot curve. The equations which govern changes in the thermodynamic variables along the Hugoniot curve are obtained from the Hugoniot equation and the general relationships of thermodynamics. Differentiating the Hugoniot equation with $p_0 = 0$ gives the change in internal energy along the Hugoniot curve as

$$dE = \frac{1}{2}(v_0 - v)dp - \frac{1}{2}p dv. \quad (5)$$

The combination of Eq. (5) with the thermodynamic identities

$$dE = TdS - pdv = (\partial E / \partial T)_v dT + (\partial E / \partial v)_T dv \quad (6)$$

gives the following differential equations for the entropy and temperature along the Hugoniot curve

$$TdS = C_v dT + T(\partial p / \partial T)_v dv = \frac{1}{2}(v_0 - v)dp + \frac{1}{2}p dv, \quad (7)$$

where

$$(\partial E / \partial T)_v = C_v \text{ and } (\partial E / \partial v)_T = T(\partial p / \partial T)_v - p.$$

Although the right-hand side of Eq. (7) can be evaluated from the experimental Hugoniot curve, the equations can only be integrated if the $(p-v-T)$ equation of state is known. However, if the $(p-v-T)$ equation of state is known, the temperature along the Hugoniot curve can be calculated directly without integrating and the entropy can then be calculated from Eq. (7). Therefore, it is necessary to know the $(p-v-T)$ equation of state to calculate values of temperature and entropy along the Hugoniot curve.

It is useful to consider other paths between the states $0(p_0, v_0, T_0)$ and $1(p_1, v_1, T_1)$, in particular, $01'1$ and $00'1$ for which the temperature is constant along $01'$ and $0'1$ and the volume constant along $1'1$ and $00'$. Integrating from 0 to 1 along

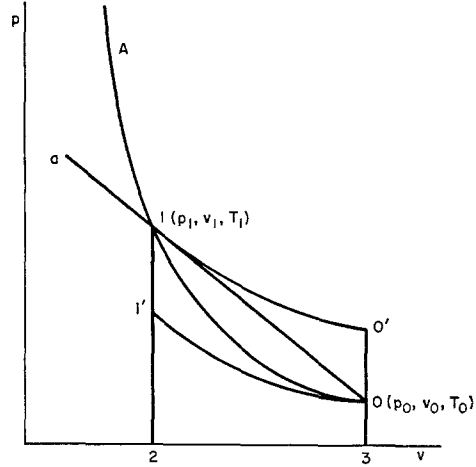


FIG. 1. A typical Hugoniot curve of a fluid in the $(p-v)$ plane.

$01'1$ and $00'1$ gives the equation

$$\begin{aligned} \Delta E &= \int_{T_0}^{T_1} C_v(T, v=v_1) dT \\ &\quad + \int_{v_0}^{v_1} \left[T_0 \frac{\partial p(T=T_0, v)}{\partial T} \Big|_v - p \right] dv \\ &= \int_{T_0}^{T_1} C_v(T, v=v_0) dT \\ &\quad + \int_{v_0}^{v_1} \left[T_1 \frac{\partial p(T=T_1, v)}{\partial T} \Big|_v - p \right] dv. \quad (8) \end{aligned}$$

It follows from Eq. (8) that because the specific heat is, in general, a function of volume, the increase in thermal energy between any two states depends upon the process used to bring about the change of state.

Consequently, it is not possible from a known Hugoniot curve in the $(p-v)$ plane to estimate what fraction of the internal energy increase is thermal, let alone estimate values of the thermodynamic variables along the curve. To obtain any useful information from the Hugoniot curve it is thus necessary to make assumptions about the equation of state of the material.

In the first approximation it is assumed that the internal energy is separable into two independent parts: one a function of temperature only and the other a function of volume. This is

expressed mathematically by the equation

$$E(T,v) = {}^1E(T) + {}^2E(v), \quad (9)$$

from which it is obvious that the specific heat at constant volume is, in general, only a function of temperature and that $(\partial E/\partial v)_T$ is, in general, only a function of volume. It follows from the identity

$$(\partial C_v/\partial v)_T = T(\partial^2 p/\partial T^2)_v \quad (10)$$

that, for a material obeying Eq. (9), the following equation is also satisfied

$$(\partial^2 p/\partial T^2)_v = 0. \quad (11)$$

Integrating Eq. (11) gives a van der Waals-type equation of state of the form

$$p = (\partial p/\partial T)_v T + g(v), \quad (12)$$

where either

$$(\partial p/\partial T)_v = \text{a constant} \quad (12')$$

or

$$(\partial p/\partial T)_v = f(v) \text{ a function of } v, \quad (12'')$$

and $g(v)$ is an arbitrary function of v .

It should be noted that assuming the specific heat at constant volume either to be constant or to be only a function of temperature is necessarily equivalent to specifying a $(p-v-T)$ equation of state given by Eq. (12). Physically, this means that the pressure is the result of two mechanisms acting independently. The contribution from the attractive and repulsive forces is given by the $g(v)$ term and is temperature-independent, while the pressure exerted by the thermal motion is given by $f(v)T$.

THERMODYNAMIC PROPERTIES OF THE CONSTANT C_v MODEL

It follows from the assumption of constant C_v that the general $(p-v-T)$ equation of state has the form

$$p = f(v)T + g(v), \quad (13)$$

and also that the $(E-p-v)$ equation of state obtained by integrating the identity

$$(\partial E/\partial p)_v = C_v/f(v) \quad (14)$$

has the form

$$E = [C_v/f(v)]p + g^1(v), \quad (15)$$

where $g^1(v)$ is a function of v related to $g(v)$. The assumption of constant C_v is thus equivalent to assuming a Mie-Grüneisen type of equation of state. The corresponding $(S-v-T)$ and $(E-v-T)$ equations of state are given by

$$S - S_i = C_v \ln(T/T_i) + \int_{v_i}^v f(v)dv \quad (16)$$

and

$$E - E_i = C_v(T - T_i) - \int_{v_i}^v g(v)dv \quad (17)$$

The elimination of T from Eqs. (13) and (17) defines the relationship between $g^1(v)$ and $g(v)$, and the elimination of T from Eqs. (16) and (17) gives the complete $E(S,v)$ equation of state. Thus for a given value of C_v the constant C_v model is completely defined over a domain of the $(p-v)$ plane by the knowledge of the functions $g(v)$ and $f(v)$ over the domain and a point $(E_i, S_i, T_i, p_i, v_i)$ within the domain. However, for the construction of the isentropes and isotherms, it is sufficient to know $g(v)$ and $f(v)$, i.e., the $(p-v-T)$ equation of state and a point (T_i, p_i, v_i) . The isentrope in the $(p-v)$ plane through the point (T_i, p_i, v_i) is constructed from Eqs. (13) and (16). Setting $\Delta S = 0$ in Eq. (16) defines the temperature as a function of volume along the isentrope and the corresponding pressure is calculated from Eq. (13). An isotherm through each point of this isentrope can then be constructed directly from Eq. (13). The isotherms define new starting points for isentropes and by repeating this procedure the isentropes and isotherms covering the domain can be constructed.

It is interesting to reformulate some of the earlier work of Walsh and Christian² in which the Hugoniot curves of Al, Cu, and Zn were measured experimentally and used with the assumptions of constant C_v and constant $(\partial p/\partial T)_v$ to determine neighboring isotherms and isentropes.

In this case the model is specified by the assumptions of constant C_v and $(\partial p/\partial T)_v$, and the model constant b is defined by the equation

$$b = (\partial p/\partial E)_v = (\partial p/\partial T)_v/C_v. \quad (18)$$

The $(p-v-T)$, $(E-p-v)$, and $(S-v-T)$ equations of

state are given by the equations

$$p = bC_p T + g(v), \quad (13')$$

$$E = (p/b) + g^1(v), \quad (15')$$

and

$$S - S_i = C_p \ln(T/T_i) + bC_p(v - v_i). \quad (16')$$

The knowledge of p , v , and T along any one curve in a domain of the $(p-v)$ plane is sufficient to determine the unknown function $g(v)$ and the $(p-v-T)$ equation of state over the domain. Walsh and Christian calculated the temperature along the Hugoniot curve to determine the $(p-v-T)$ equation of state, but here an alternative method is presented. As temperature is known as a function of volume along an isentrope from Eq. (16'), it is sufficient to determine the position of an isentrope in the $(p-v)$ plane in order to determine the $(p-v-T)$ equation of state and completely characterize the model. Over the domain of the $(p-v)$ plane specified by the experimental Hugoniot curve, the $(E-p-v)$ equation of state is determined by combining Eqs. (2) and (15') to determine the function (vg^1) . The position of the isentrope through the initial condition is calculated with the $(E-p-v)$ equation of state by integrating the first law with $dS=0$. The $(p-v-T)$ equation of state follows from this isentrope and Eq. (13'). Thus the determination of the experimental Hugoniot curve through the known initial condition $(E_0, S_0, T_0, p_0, v_0)$ allows the evaluation of the arbitrary function $g^1(v)$ in Eq. (15), and the calculation of the position of the isentrope through the initial condition, and thus is sufficient to define the model completely. For this model the pressure difference between isotherms whose difference in temperature is equal will be equal and independent of volume (see Fig. 1).

THERMODYNAMIC PROPERTIES OF THE CONSTANT C_p MODEL

The assumption of constant C_p is equivalent to assuming that the enthalpy H is separable into two independent parts: one a function of temperature and the other a function of pressure. The thermodynamic identity

$$(\partial C_p / \partial p)_T = -T(\partial^2 v / \partial T^2)_p \quad (19)$$

applied to the model gives the equation

$$(\partial^2 v / \partial T^2)_p = 0, \quad (20)$$

which determines the form of the $(p-v-T)$ and $(H-p-v)$ equations of state. Integrating Eq. (20) gives

$$v = (\partial v / \partial T)_p T + \Phi(p), \quad (21)$$

with either

$$(\partial v / \partial T)_p = \text{constant} \quad (22)$$

or

$$(\partial v / \partial T)_p = \eta(p),$$

where $\Phi(p)$ and $\eta(p)$ are arbitrary functions of p , and integrating the thermodynamic identity

$$(\partial H / \partial v)_p = C_p / \eta(p) = \epsilon(p) \quad (23)$$

gives the $(H-p-v)$ equation of state as

$$H = [C_p / \eta(p)]v + \Phi^1(p), \quad (24)$$

where $\Phi^1(p)$ is a function of p related to $\Phi(p)$. The equation of state

$$v = \eta(p)T + \Phi(p) \quad (25)$$

and the relationships of thermodynamics give the equations

$$H - H_i = C_p(T - T_i) + \int_{p_i}^p \Phi(p) dp, \quad (26)$$

$$S - S_i = C_p \ln(T/T_i) - \int_{p_i}^p \eta(p) dp, \quad (27)$$

which define the implicit assumed properties of the constant C_p model. The functions $\Phi(p)$, $\eta(p)$, and a known point $(H_i, S_i, T_i, p_i, v_i)$ in a domain of the $(p-v)$ plane completely define the model over this domain. Thus a knowledge of either the pressure, volume, and temperature along any two curves in the $(p-v)$ plane, or one of the functions and the pressure, volume, and temperature along any one curve is sufficient to define the model.

It is interesting to reformulate the work of Rice and Walsh¹¹ on water and determine the $(p-v-T)$ equation of state by integrating along the Hugoniot curve to calculate shock temperature. The assumption of a constant C_p model with $C_p = 0.86$ cal/g·deg for $p \geq 25$ kbar was

based on the low-pressure work of Kennedy.¹² Rice and Walsh determined $(\partial H/\partial v)_p$ at different pressures by an elegant reflected-shock technique in which points on Hugoniot curves centered on the incident Hugoniot were measured. The analytic fit for $\epsilon(p)$ in the range 25–250 kbar is given by

$$\log_{10}\epsilon = 2.17943 + 0.0030338p, \quad (28)$$

with ϵ and p in kilobars. Although the constancy of C_p necessitates that, generally, $(\partial H/\partial v)_p$ is only a function of pressure, the converse is not necessarily true (see Appendix).

Rewriting Eq. (28) formally as

$$\epsilon(p) = \exp(n + mp), \quad (28')$$

and substituting in Eq. (25) gives

$$(\partial v/\partial T)_p = C_p/(e^{n+mp}); \quad (29)$$

and the $(p-v-T)$ and $(S-p-T)$ equations of state above 25 kbar are given by

$$v = [C_p T/(e^{n+mp})] + \Phi(p) \quad (30)$$

$$S - S_i = C_p \ln(T/T_i) + (C_p/m)$$

$$\times [\exp - (n + mp) - \exp - (n + mp_i)], \quad (31)$$

where the point (S_i, T_i, p_i) lies on the 25-kbar isobar. Now the calculation of temperature along the initial Hugoniot curve above 25 kbar is sufficient to determine the $(p-v-T)$ equation of state, the isentropes, and the isotherms. The shock temperature is calculated in the 25–250 kbar range by an analogous method to the one used by Walsh and Christian for metals. The general differential equation for temperature along the Hugoniot curve,

$$C_p dT - T(\partial v/\partial T)_p dp = \frac{1}{2}[(v_0 - v)dp + p dv] \quad (32)$$

combined with Eqs. (29) becomes

$$dT - T dp \exp - (n + mp) = (1/2C_p)[(v_0 - v)dp + p dv]. \quad (33)$$

Equation (33) has a simple integrating factor,

$$R(p) = \left(\exp - \int \frac{dp}{\exp(n + mp)} \right) = \exp[(1/m) \exp - (n + mp)] \quad (34)$$

¹² G. C. Kennedy, Am. J. Sci. 248, 540 (1950).

and the shock temperature is given by

$$TR(p) - T_h R(p_i) = \frac{1}{2C_p} \int_{p_i=25 \text{ kbar}}^{p \leq 250 \text{ kbar}} R(p)[(v_0 - v)dp + p dv]. \quad (35)$$

The temperature T_h at 25 kbar on the Hugoniot curve is calculated from the equation

$$v_p - v_{iso} = (\partial v/\partial T)_{p=25 \text{ kbar}}(T_h - T_{iso}), \quad (36)$$

where v_{iso} and T_{iso} lie on the 175°C isotherm determined by Bridgman.¹³

The temperatures calculated from Eq. (35) are obviously found to be in good agreement with those calculated by Rice and Walsh. The isotherms intersecting the Hugoniot in the 25–250 kbar region now follow directly from Eq. (30) and the isentropes intersecting the Hugoniot curve are calculated from Eqs. (30) and (31) by the method described previously.

APPENDIX

To show that the equation

$$(\partial H/\partial T)_p/(\partial v/\partial T)_p = (\partial H/\partial v)_p = F(p) \quad (23')$$

does not imply that

- (1) C_p is a constant or that
- (2) $(\partial v/\partial T)_p$ is only a function of p ,

consider the following equations:

$$H = \theta(p)f(T) + \Phi(p) + C_1, \quad (37)$$

$$v = \gamma(p)f(T) + \epsilon(p) + C_2, \quad (38)$$

where $\theta(p)$, $f(T)$, $\Phi(p)$, $\gamma(p)$, and $\epsilon(p)$ are general functions and do not refer to earlier equations. Obviously, C_p is not constant and $(\partial v/\partial T)_p$ is not only a function of p . However, an equation of type (23') is satisfied,

$$(\partial H/\partial T)_p/(\partial v/\partial T)_p = \theta(p)f'(T)/\gamma(p)f'(T) = F(p), \quad (23')$$

with the condition $\theta'(p)f'(T) = -\gamma(p)Tf''(T)$ specified by the thermodynamic identity

$$(\partial C_p/\partial p)_T = -T(\partial^2 v/\partial T^2)_p. \quad (19)$$

¹³ P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 399 (1942).