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EQUATION OF STATE FOR DETONATION PRODUCTS

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The concepts of hydrodymanics and thermodynamics as they apply to equations of state for explosive products are collected and discussed. The physics behind the behavior of dense gases is considered. Some ideas about applications are presented. This paper is intended as an introduction to the subject of equation of state for detonation products.

I. INTRODUCTION

The concepts and formulas that are pertinent to the development and use of an equation of state for explosive products gases, taken from hydrodynamics, thermodynamics, and the physics of gases are collected and discussed in this paper. Perhaps having them collected in one place will help clarify the confusing subject usually called "equation of state" by those who work with explosives.

The second and third sections are devoted to the equations of hydrodynamics and their solutions. The fourth section presents thermodynamics for use with hydrodynamics, and the fifth a discussion of incomplete equations of state as they are used for explosives. The sixth section presents the simple physical principles that determine the general form for an equation of state. Sections seven, eight, and nine discuss engineering applications, the choice of a fitting form for an equation of state, and the calibration of the fitting form.

This paper is intended to be an introduction to the mysteries of the subject, and is certainly not the final description of all the intricacies.

II. EQUATIONS OF HYDRODYNAMICS

The equations for the conservation of mass, momentum, and energy, for flow in one dimension, can be written as

$$\dot{v} - v u_x = 0 \qquad (2\text{-}1)$$

$$\dot{u} + v p_x + A = 0 \qquad (2\text{-}2)$$

$$\dot{\overline{\left(E + \frac{1}{2}u^2\right)}} + v(pu)_x = B \qquad (2\text{-}3)$$

where v is the specific volume, u is the particle velocity, p is the pressure, and E is the specific internal energy. The dot denotes the total time derivative such that $\dot{v} = \partial v/\partial t + u\,\partial v/\partial x$, and $u_x = \partial u/\partial x$ is a partial derivative. In Eq. (2-3) the term $E + 1/2u^2$ is the sum of the internal and kinetic energies, and is the total specific energy of the fluid element. The term A in Eq. (2-2) represents nonequilibrium processes that transfer momentum, usually viscous effects. The term B in Eq. (2-3) represents nonequilibrium processes that transfer energy, usually viscous and thermal diffusion processes.

In addition to these equations, there is an equilibrium equation of state for the material

$$E = E(p,v) \qquad (2\text{-}4)$$

that describes the equilibrium material properties. The equilibrium equation of state can be used to expand the term in $\dot{E}$ in Eq. (2-3) as

$$\dot{E} = E_p\dot{p} + E_v\dot{v} \ , \qquad (2\text{-}5)$$

where

$$E_p = (\partial E/\partial p)_v \ , \quad E_v = (\partial E/\partial v)_p \ . \qquad (2\text{-}6)$$

Equation (2-3) can be written, after doing the indicated differentiation and substituting terms from Eqs. (2-1), (2-2), and (2-5), as

$$\dot{p} + \frac{v(E_v + p)}{pE_p}(p/v)\dot{v} = (v/E_p)(uA + B)/v \ . \tag{2-7}$$

The coefficients that describe the material properties have their own special names. The coefficient (v/E_p) is called the Gruneisen gamma and is represented as

$$v/E_p = \Gamma \quad . \tag{2-8}$$

The coefficient $v(E_v + p)/pE_p$ is called the adiabatic gamma and is written

$$v(E_v + p)/pE_p = \gamma \quad . \tag{2-9}$$

With these definitions, Eq. (2-7) becomes

$$\dot{p}/p + \gamma\dot{v}/v = \Gamma(uA + B)/pv \quad . \tag{2-10}$$

The conservation equations, Eqs. (2-1), (2-2), and (2-3), can now be replaced by

$$\dot{v} - vu_x = 0 \tag{2-11}$$

$$\dot{u} + vp_x + A = 0 \tag{2-12}$$

$$\dot{p}/p + \gamma\dot{v}/v = \Gamma(uA + B)/pv \quad . \tag{2-13}$$

All the description of the material is given in the two derivatives, γ and Γ. If the two derivatives are given as functions of p and v, the equations are a complete set of three equations with three dependent variables.

III. SOLUTIONS OF THE EQUATIONS

The equations of hydrodynamics have simple solutions for special cases, and these solutions allow some insights into the physical meaning of the various terms in the equations.

Let us first consider the important case of a steady shock wave propagating in the material. Steady means independent of time, and thus the partial derivatives with respect to time in Eqs. (2-1), (2-2), and (2-3) are all zero. The equations become

$$uv_x - vu_x = 0 \tag{3-1}$$

$$uu_x + vp_x + A = 0 \tag{3-2}$$

$$uE_x + u^2u_x + vup_x + vpu_x = B \quad . \tag{3-3}$$

The first equation can be immediately integrated to give u/v = constant. If we require that the shock wave be localized near x = 0 with the material flowing in the positive direction from negative values of x at velocity u_0, and set the specific volume in the undisturbed material at v_0, then the solution is

$$u/v = u_0/v_0 \quad . \tag{3-4}$$

For the solution of the next two equations more information about A and B is needed. In the Navier-Stokes equations,

$$A/v = -\frac{\partial}{\partial x}\left[(4/3)\mu u_x\right] \tag{3-5}$$

$$B/u = (v_0/u_0)\frac{\partial}{\partial x}\left[(4/3)\mu uu_x + kT_x\right] \tag{3-6}$$

Equation (3-2) can be written, using Eq. (3-4) and (3-5), as

$$(u_0/v_0)u_x + p_x - \frac{\partial}{\partial x}\left[(4/3)\mu u_x\right] = 0 \tag{3-7}$$

and immediately integrated to give, with the boundary conditions imposed,

$$p - p_0 = \rho_0u_0(u_0 - u) + (4/3)\mu u_x \ . \tag{3-8}$$

where $\rho_0 = 1/v_0$. After dividing by u, and using Eq. (3-1) to eliminate u_x/u, one can write Eq. (3-3) as

$$E_x + uu_x + vp_x + pv_x$$

$$= (v_0/u_0)\frac{\partial}{\partial x}\left[(4/3)\mu uu_x + kT_x\right], \tag{3-9}$$

and this can be integrated to give, with the boundary conditions imposed,

$$(E + pv) - (E_0 + p_0v_0) = \frac{1}{2}(u_0^2 - u^2)$$

$$+ (v_0/u_0)\left[(4/3)\mu uu_x + kT_x\right] \quad . \tag{3-10}$$

Far from the shock in the region of large positive x, the terms in Eqs. (3-8) and (3-10) containing derivatives have decreased to zero, and the Eqs. (3-4), (3-8), and (3-10) can be written as the usual jump conditions for a steady shock wave. These are

$$v/v_0 = u/u_0 \qquad (3\text{-}11)$$

or

$$v/v_0 = 1 - (u_0 - u)/u_0 \qquad (3\text{-}12)$$

for the conservation of mass, from Eq. (3-4). Equation (3-12) is written to correspond to the more familiar form in laboratory coordinates, where the mass velocity is $(u_0 - u)$. Equation (3-8) becomes

$$p - p_0 = \rho_0 u_0 (u_0 - u) \quad , \qquad (3\text{-}13)$$

already in its familiar form. It can also be written, using Eq. (3-12) to eliminate $(u_0 - u)$, in its Rayleigh line form as

$$p - p_0 = \rho_0^2 u_0^2 (v_0 - v) \quad . \qquad (3\text{-}14)$$

Equation (3-10) can be written in its several familiar forms as

$$(E+pv) - (E_0+p_0v_0) = \frac{1}{2} u_0^2 - \frac{1}{2} u^2 \qquad (3\text{-}15)$$

$$E - E_0 = \frac{1}{2} (u_0-u)^2 + p_0(v_0-v) \qquad (3\text{-}16)$$

$$E - E_0 = \frac{1}{2} (p+p_0)(v_0-v) \quad . \qquad (3\text{-}17)$$

Equation (3-16) is obtained from (3-15) by substituting $p = p_0 + (u/v)(u_0 - u)$, which is obtained from Eqs. (3-13) and (3-11). Equation (3-17) is obtained from (3-16) by substituting for one of the terms $(u_0 - u)$ from Eq. (3-13), and for the other one in the squared term from Eq. (3-12). These equations describe the conditions far from the shock wave, relating the properties on the two sides of the shock.

The details of the shock itself can be obtained by integrating Eqs. (3-8) and (3-10), considering them as the differential equations that describe the shock itself. Some additional assumptions about the equation of state and the values of the shear viscosity μ and thermal conductivity k are required. The problem is well treated by Hayes (1).

The jump in entropy is also interesting. The equations show that the entropy is increased by the dissipative processes in the shock. From the first law of thermodynamics

$$TdS = dE + pdv \quad , \qquad (3\text{-}18)$$

one can write

$$TS_x = E_x + pv_x \quad . \qquad (3\text{-}19)$$

Using Eqs. (3-7) and (3-9) to substitute for terms on the rhs, one finds

$$S_x = - (v/T) \frac{\partial}{\partial x} \left[(4/3)\mu u_x\right]$$

$$+ (v_0/u_0)(1/T) \frac{\partial}{\partial x} \left[(4/3)\mu u u_x + kT_x\right] \qquad (3\text{-}20)$$

The equation can be simplified to

$$\rho_0 u_0 S_x = (4/3)\mu(u_x)^2/T + (k/T) \frac{\partial}{\partial x}(T_x) \quad . \qquad (3\text{-}21)$$

Integration then gives

$$\rho_0 u_0 (S - S_0) = \frac{k}{T} \left(\frac{\partial T}{\partial x}\right) \Big|_{x_0}^{x} + \int_{x_0}^{x} \frac{k}{T^2} \left(\frac{\partial T}{\partial x}\right)^2 dx + \int_{x_0}^{x} (4/3)\mu \frac{(u_x)^2}{T} dx \quad . \qquad (3\text{-}22)$$

While the first term on the rhs is zero far from the shock, the two integral terms are positive contributions to the entropy.

At this point, although it has nothing to do with finding special solutions to the equations, let us look briefly at the viscous terms in the equations, represented by A and part of B in Eqs. (2-2) and (2-3) or (3-2) and (3-3). Often writers use the term "viscous pressure," usually denoted by q, and it is identified with the terms in Eqs. (3-5) and (3-6) as

$$q = - (4/3)\mu u_x \quad . \qquad (3\text{-}23)$$

For numerical solution of the equations, artificial viscosity is used to make the solutions of the equations stable to perturbations by numerical noise. Many different forms have been used for q. We see that q has the dimensions of pressure, and that the coefficient of u_x in Eq. (3-23) must be a product of density, velocity, and distance. The important distance for numerical stability is the mesh spacing Δx for the calculation, and the density ρ must be the local density, but the velocity term can be chosen to make the numerical oscillations damp in optimal fashion. Some popular choices are the Landshoff form

$$q \sim -\rho c \Delta x u_x \qquad (3\text{-}24)$$

using the sound velocity, the Richtmyer-von Neuman or quadratic form

$$q \sim -\rho(\Delta x u_x)\Delta x u_x \qquad (3\text{-}25)$$

using $\Delta x u_x$ as a velocity, and the Harlow or PIC form

$$q \sim -\rho u \Delta x u_x \qquad (3\text{-}26)$$

using the local particle velocity. In a numerical calculation all three forms may be used in linear combination, with dimensionless multipliers chosen for optimum damping.

Now let us turn away from the strong shock wave, and look for solutions corresponding to the propagation of an infinitesimal disturbance, a sound wave. We wish to consider a uniform medium with no strong gradients, so the viscous and heat conduction terms are negligible. We use Eqs. (2-11), (2-12), and (2-13), rewritten here as

$$\dot{v} - v u_x = 0 \qquad (3\text{-}27)$$

$$\dot{u} + v p_x = 0 \qquad (3\text{-}28)$$

$$\dot{p}/p + \gamma \dot{v}/v = 0 \quad . \qquad (3\text{-}29)$$

We look for solutions for infinitesimal waves moving at constant velocity c without change of shape, described by

$$v = v_0 + v_1 f(x-ct) \qquad (3\text{-}30)$$

$$u = 0 + u_1 f(x-ct) \qquad (3\text{-}31)$$

$$p = p_0 + p_1 f(x-ct) \quad , \qquad (3\text{-}32)$$

where v_1, u_1, and p_1 are very small. Differentiating, and neglecting terms higher than first order in the small perturbations, we find

$$\dot{v} = -c v_1 f' \qquad (3\text{-}33)$$

$$u_x = u_1 f' \qquad (3\text{-}34)$$

$$\dot{u} = -c u_1 f' \qquad (3\text{-}35)$$

$$p_x = p_1 f' \qquad (3\text{-}36)$$

$$\dot{p} = -c p_1 f' \quad . \qquad (3\text{-}37)$$

Substituting these values into the original differential equations gives

$$c v_1 + v_0 u_1 = 0 \qquad (3\text{-}38)$$

$$c u_1 - v_0 p_1 = 0 \qquad (3\text{-}39)$$

$$p_1 + (\gamma p_0/v_0) v_1 = 0 \quad . \qquad (3\text{-}40)$$

From Eqs. (3-38) and (3-39) we find

$$c^2 = -v_0^2 p_1/v_1 \quad , \qquad (3\text{-}41)$$

corresponding to the usual definition

$$c^2 = -v^2(\partial p/\partial v)_S \qquad (3\text{-}42)$$

if p_1 and v_1 are infinitesimals. Using Eqs. (3-40) and (3-41) we find

$$\gamma = c^2/p_0 v_0 \quad , \qquad (3\text{-}43)$$

corresponding to the usual definition, after we substitute from Eq. (3-42),

$$\gamma = -(v/p)(\partial p/\partial v)_S \quad . \qquad (3\text{-}44)$$

Thus we have shown that our equations describe a medium that transmits sound waves and the γ, defined by Eq. (2-9), is simply the square of the dimensionless sound speed.

In Eqs. (3-27) through (3-29) the dissipative terms A and B were neglected. Inclusion of these terms allows for dissipation of energy, and therefore attenuation of sound. For most cases of physical interest, the damping is small. The sound velocity remains that for the nondissipative case. Discussions of the damping are given by Bond, Watson, and Welch (2), and by Lighthill (3).

IV. THERMODYNAMICS FOR HYDRODYNAMICS

Compressible flows usually contain large regions where the flow is approximately isentropic separated from other isentropic regions by small regions where the flow is strongly nonequilibrium and nonisentropic. The natural thermodynamic potential to describe such flows is the specific internal energy E, written as

$$E = E(S,v) \qquad (4\text{-}1)$$

where S is the specific entropy and v is the specific volume. For the regions of isentropic flow the potential E is a function only of volume.

The differential expansion of Eq. (4-1) is

$$dE = T\,dS - p\,dv \qquad (4\text{-}2)$$

where

$$T = (\partial E/\partial S)_v \quad \text{and} \quad p = -(\partial E/\partial v)_S \qquad (4\text{-}3)$$

The independent variables S and v, and the variables obtained from the first partial derivatives, are the variables of thermodynamics.

The derivatives of these variables can be expressed as second derivatives of the potential. There are three independent second derivatives, so all the derivatives can be expressed in terms of three independent second derivatives. In what follows, we use the subscript notation for differentiation, so that, for example,

$$E_{vv} = (\partial^2 E/\partial v^2)_S \qquad (4\text{-}4)$$

and the independent variable held constant is obvious from the context. The definitions used here are

$$\gamma = vE_{vv}/p = -(v/p)(\partial p/\partial v)_S \qquad (4\text{-}5)$$

$$\Gamma = -vE_{Sv}/T = -(v/T)(\partial T/\partial v)_S$$

$$= -(v/T)(\partial p/\partial S)_v \qquad (4\text{-}6)$$

$$g = pvE_{SS}/T^2 = pv/C_vT \quad . \qquad (4\text{-}7)$$

These three partial derivatives form the standard set for hydrodynamics; all other thermodynamic first derivatives can be written in terms of them.

The meaning of these second derivatives that form the standard set for hydrodynamics may be made clearer by considering the following expressions:

$$\gamma = -(\partial \ln p/\partial \ln v)_S \qquad (4\text{-}8)$$

$$\Gamma = -(\partial \ln T/\partial \ln v)_S \quad . \qquad (4\text{-}9)$$

Now suppose that γ and Γ are constants. Then one can integrate to find, on an isentrope, that

$$pv^{\gamma} = \text{constant} \qquad (4\text{-}10)$$

$$Tv^{\Gamma} = \text{constant} \quad . \qquad (4\text{-}11)$$

Similarly, one can write

$$\Gamma(TS/pv) = (\partial \ln p/\partial \ln S)_v \qquad (4\text{-}12)$$

$$g(TS/pv) = (\partial \ln T/\partial \ln S)_v \qquad (4\text{-}13)$$

and integrate these to get expressions on the curves of constant volume. (The factor TS/pv enters because we did not use S when we made the second derivatives dimensionless.) Since we do not measure S, perhaps the ratio of the two,

$$T^{\Gamma}/p^{g} = \text{constant} \qquad (4\text{-}14)$$

on a curve of constant volume, is more useful.

In the real physical case γ, Γ, and g are not constants, yet the expressions obtained this way are tangents to the real curves at points where the exponents have the chosen values.

Thermodynamics books usually use another standard set of derivatives, obtained from the Gibbs potential, $G = G(T,p)$, defined as

$$C_p = -TG_{TT} \qquad (4\text{-}15)$$

$$\beta = G_{Tp}/v \qquad (4\text{-}16)$$

$$\kappa_T = -G_{pp}/v \quad . \qquad (4\text{-}17)$$

The reason for this choice is, of course, that many experiments are done with either T or p held constant, and G(T,p) is the natural potential. This usual standard set can be expressed in terms of the hydrodynamic standard set as follows:

$$C_p = (pv/gT)\gamma/(\gamma - \Gamma^2/g) \qquad (4\text{-}18)$$

$$\beta = (\Gamma/gT)/(\gamma - \Gamma^2/g) \qquad (4\text{-}19)$$

$$\kappa_T = p/(\gamma - \Gamma^2/g) \quad . \qquad (4\text{-}20)$$

The denominator in each expression can be shown to be $-(v/p)(\partial p/\partial v)_T$, and it must be positive to ensure mechanical stability (4). For an ideal gas the denominator is one.

The choice of symbols is hopelessly confusing. Various authors use various symbols; worse still, they use the same symbols with different meanings. Until some standardization takes place, readers will just have to resign themselves to being very careful to check the definitions. Perhaps the most bothersome is our definition of the adiabatic gamma. The symbol γ has been widely used for many years to denote the ratio of specific heats; our definition, common in hydrodynamics, is given by Eq. (4-5). The adiabatic gamma and the ratio of specific heats are identical for an ideal gas, but not for real gases, as can be seen by combining Eqs. (4-7) and (4-18).

One higher derivative is important in the context of empirical equations of state. It is called the "fundamental derivative of gas dynamics" by Thompson (5), and is defined as

$$G = \frac{1}{2}\left[\gamma + 1 - (v/\gamma)(\partial\gamma/\partial v)_S\right] \quad . \qquad (4\text{-}21)$$

For ordinary materials, G is positive. Its importance is that when G is positive, compression shock waves form. If G is negative, rarefaction shocks form. For the purposes of this paper, one must be careful not to choose forms for gamma that lead to G less than zero unless rarefaction shocks are desired. G can also be written, using the notation of Eqs. (4-5) through (4-7) as

$$G = -vE_{vvv}/2E_{vv} \quad . \qquad (4\text{-}22)$$

It is often glibly said that the condition for compression shocks to form is that the sound speed must increase with pressure. Really the condition is that higher pressure waves from behind must overtake the front, and they travel at velocity $u + c$ rather than c, and u also increases with pressure. The difference can be made especially clear by relating G to these derivatives. It can be shown that

$$\left(\frac{\partial c}{\partial p}\right)_S = (G - 1)/\rho c \quad , \qquad (4\text{-}23)$$

so the sound velocity increases with pressure only if G is greater than 1. However,

$$\frac{d(u + c)}{dp} = G/\rho c \qquad (4\text{-}24)$$

on the characteristics behind the shock, so compression shocks will form as long as G is greater than zero.

V. INCOMPLETE EQUATION OF STATE

$E = E(S,v)$ is a complete equation of state. All thermodynamic derivatives can be obtained from it. $E = E(p,v)$ is not a complete equation of state, but is very useful for hydrodynamics.

The relationship between $E(S,v)$ and $E(p,v)$ is easy to see. If one has $E(S,v)$, then $-E_v = p(S,v)$. In principle, at least, this expression for p can be inverted to give $S(p,v)$, and then S can be eliminated in $E(S,v)$ to give $E(p,v)$. However, there is no way to go backward; that is, one cannot get back from $E(p,v)$ to $E(S,v)$. Therefore, $E(p,v)$ is incomplete.

Most of the experiments in hydrodynamics are mechanical experiments. Their variables are p and v. Temperature and entropy are not measured quantities, and they cannot be inferred from $E(p,v)$. On the other hand, the variables that cannot be measured must not be really needed, or they could be measured. For many purposes the incomplete equation of state $E = E(p,v)$ is adequate.

The differential of this incomplete equation of state is

$$dE = E_p dp + E_v dv \quad . \qquad (5\text{-}1)$$

If we use Eq. (5-1) to find the derivative with respect to v at constant S we get

$$(\partial E/\partial v)_S = E_p(\partial p/\partial v)_S + E_v \quad ; \qquad (5\text{-}2)$$

but we know that

$$(\partial E/\partial v)_S = -p \qquad (5\text{-}3)$$

and using this we can rearrange Eq. (5-2) to give

$$-(\partial p/\partial v)_S = (E_v + p)/E_p \quad . \qquad (5\text{-}4)$$

Comparing this result with Eq. (4-5) we find

$$\gamma = v(E_v + p)/pE_p \quad . \qquad (5\text{-}5)$$

Similarly, taking the derivative with respect to S at constant v one can show that

$$(\partial p/\partial S)_v = T/E_p \quad . \qquad (5\text{-}6)$$

Using this result with Eq. (4-6) one finds that

$$\Gamma = v/E_p \quad . \qquad (5\text{-}7)$$

The incomplete equation of state E(p,v) thus gives the adiabatic gamma and the Gruneisen gamma. As shown in Sec. II, it is adequate for simple hydrodynamics.

From the incomplete equation of state, g cannot be determined; however, a differential equation for g can be obtained, and g is thus determined, except for a constant, along an isentrope where γ and Γ are known. The differential equation is obtained by requiring that the partial derivatives of E(S,v) do not depend on the order of differentiation, so that $E_{SvS} = E_{SSv}$. E_{Sv} and E_{SS} are given by Eqs. (4-6) and (4-7). Some manipulation gives the differential equation

$$(v/g)(\partial g/\partial v)_S$$

$$= \Gamma + 1 - \gamma - (\Gamma p/g)(\partial \Gamma/\partial p)_v \quad . \qquad (5\text{-}8)$$

A differential equation for the temperature is also available, so temperature can be determined, within a constant multiplier, along an isentrope. One form of Eq. (4-6) is

$$(v/T)(\partial T/\partial v)_S = -\Gamma \quad . \qquad (5\text{-}9)$$

If Γ is known, this can be integrated immediately, except for the constant.

Expressions for T and g are especially useful for detecting flaws in the choice of a form for an empirical equation of state. One may not know exactly what to expect for T or g, but one can expect them to be smooth, positive, and monotone on the isentrope.

VI. PHYSICAL PRINCIPLES

It was shown in Section II that the adiabatic gamma and the Gruneisen gamma are the important features of the equation of state for hydrodynamics. In Section III it was shown that the adiabatic gamma is the square of the dimensionless sound speed, or

$$\gamma = c^2/pv \quad . \qquad (6.1)$$

Here we ask what we know about the behavior of the adiabatic gamma and the Gruneisen gamma as functions of specific volume along an isentrope.

Molecules interact with each other when the distance between their centers is a few tenths of a nanometer. In a gas at room temperature and pressure the average distance between molecules is about 3 nm, so most of the time a molecule drifts at thermal velocity, unaffected by any other molecule. A disturbance, such as a sound wave, is transmitted through the gas by molecules traveling at thermal velocities, and the velocity of a sound wave is about two-thirds of the average thermal velocity. Collisions are rare events. The details of the molecular interaction have a trivial effect on the velocity of sound.

If the gas, originally at room temperature and pressure, is compressed a thousandfold, so the number of molecules in a cubic centimeter increases from 27 x 10^{18} to 27 x 10^{21}, the average intermolecular spacing decreases from 3.3 nm to 0.33 nm. The effect of a disturbance, a sound wave, is transmitted by molecules that drift a short distance and then collide with another molecule. The motion is then transmitted through the molecule by the electrical forces at nearly the velocity of light. Then there is another thermal drift, but only for a short distance. Thus when the intermolecular spacing is of the same order as the molecular size, the speed of sound increases above the low density value. The change takes place, for ordinary explosive products, at a density near one gram per cubic centimeter. The adiabatic gamma, the square of the dimensionless sound velocity, changes markedly with specific volume in this region.

As compression is continued up the isentrope, the sound velocity continues to increase. Its value depends in detail on the exact form of the molecular interaction. The adiabatic gamma, however, levels off at nearly a constant value. This happens because we have defined gamma by normalizing with respect to pv, as shown in Eq. (6-1). Because of the energy in the molecular interactions, pv/RT increases to large values. For most reasonable forms for the molecular repulsion, the adiabatic gamma seems to be nearly constant at small specific volume. It is easy to show that if the repulsive potential for the interaction energy of two molecules varies inversely as the nth power of the separation, there is an upper bound for the adiabatic gamma,

$$\gamma < 1 + n/3 \quad . \qquad (6\text{-}2)$$

A schematic plot of the variation of gamma with specific volume is shown in Fig. 1. It always has this general shape, but details of the potential, and effects from phase changes and phase separation can cause small perturbations in local regions.

It should be mentioned that this discussion is to be applied to the temperatures and volumes of interest for explosives. That is, regions where the thermal energy of the molecule is much less than its ionization energy. When there is appreciable ionization and dissociation, new effects are important.

The Gruneisen gamma has behavior very similar to that of the adiabatic gamma. At very large specific volume,

$$\Gamma = \gamma - 1 \quad , \qquad (6\text{-}3)$$

so it has a value near 0.3. It increases as the volume decreases, and levels off at 0.6 or 0.7 at small volume. Figure 1 shows a schematic diagram of the usual behavior of the Gruneisen gamma.

VII. ENGINEERING APPLICATIONS

The preceding sections have been devoted to the properties of the thermodynamic equation of state of detonation product gases. The words "equation of state" are often used to denote something very different.

Explosive systems are usually designed with the help of computer programs that solve the hydrodynamic equations. Often the computed system differs markedly from the actual physical system. For example, the shape may be idealized by neglecting glue joints, small voids, or plastic potting compounds. The initiation is usually idealized in important ways and not computed in detail. The chemical reaction zone is not modeled properly. The properties of the material being driven, perhaps metal or rock, are simplified. And in the interest of getting things done, sometimes the mesh size is made large and the computer does not give an accurate solution of the equations. All these defects are accommodated by adjusting the "equation of state."

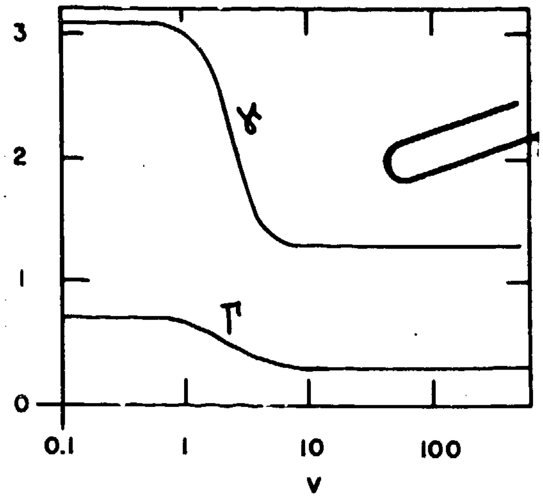

Fig. 1. The dependence of the adiabatic and Gruneisen gammas on specific volume.

A system designer, then, cannot use a real, thermodynamic equation of state. What he needs is an approximate form that will allow him to design a first approximation to the required system using his computer, with all its defects. Then he must test his first design, and use the results to change the "equation of state." Then he must try again. If the requirements have tight tolerances, this iteration can be very expensive and time consuming.

One of the problems with the fitting forms in common use is that they have so many adjustable constants. There are too many ways to adjust the "equation of state" for a good fit to the experiment. An "equation of state" with just one adjustable parameter provides all the necessary adjustment, but still allows the user to make systematic changes: so much positive for this defect, so much the other sign for another, etc.

The one adjustable parameter for a fitting form will probably not be one of the constants in the form but some real physical parameter of importance for the system being designed. For example, for reproducing the results of a cylinder test, the important parameter is the cylinder wall energy at large expansion, and this is the one that must be adjusted. The constants in the fitting form must be varied so that the other calibration parameters are held fixed, and only this energy is changed. For a shock wave in air, the low pressure expansion is important, and for an overdriven or convergent detonation the high pressure region is the one to adjust. The vital thing is to adjust only that important region, and to use only one parameter. In this way, a systematic understanding of the adjustments that correct for various defects can be obtained.

VIII. DESIGNING A FITTING FORM

The usual approach, and the one discussed here, is to find a fitting form for the incomplete equation of state discussed in Section V,

$$E = E(p,v) \quad . \qquad (8\text{-}1)$$

It is convenient and customary to choose a particular isentrope, usually the principal isentrope that passes through the Chapman-Jouguet point, and find a fit for it. Because it is a particular isentrope, any function on the isentrope can be expressed as a function of volume only. Thus on the isentrope the specific internal energy is

$$E_S = E_S(v) \quad , \qquad (8\text{-}2)$$

where the subscript S is used to indicate that the subscripted variable is to be taken on the particular isentrope. The definition of the Gruneisen gamma, given in Eq. (2-8), is

$$\Gamma = v/E_p \quad , \qquad (8\text{-}3)$$

so in the immediate neighborhood of the isentrope the energy may be expanded as

$$E(p,v) = E_S(v)+(v/\Gamma)[p-p_S(v)] \quad . \qquad (8\text{-}4)$$

To make a useful equation of state, it is assumed that Eq. (8-4) applies throughout the region of interest, and that the Gruneisen gamma is a function of volume only,

$$\Gamma = \Gamma(v) \quad . \qquad (8\text{-}5)$$

These two assumptions are not as bad as they might seem, because the entropy produced in shock processes in explosive-driven systems is never large, and the region of interest is a narrow strip always close to the principal isentrope.

Perhaps physical intuition is best for the form of the adiabatic gamma on the principal isentrope, as was discussed in Section VI. If its form is chosen, one has

$$\gamma_S = \gamma_S(v) \quad . \qquad (8\text{-}6)$$

The definition of the adiabatic gamma, Eq. (3-44), can then be written as

$$dp_S/p_S = -\gamma_S dv/v \quad , \qquad (8\text{-}7)$$

and then integration gives

$$p_S = p_S(v) \quad . \qquad (8\text{-}8)$$

The internal energy on the isentrope can be obtained from the first law of thermodynamics with the entropy held constant,

$$dE_S = -p_S dv \quad . \qquad (8\text{-}9)$$

Each integration introduces a constant of integration; the one from the pressure equation, Eq. (8-7), allows one to choose the particular isentrope, making it pass through a chosen p,v point, and the one from the energy equation, Eq. (8-9), sets the zero of energy, usually taken so the energy is zero at infinite volume.

The program outlined here seems very simple, but when one attempts to carry it through, it quickly becomes apparent that the integrals cannot be expressed in closed form if $\gamma_S(v)$ is chosen with enough complexity to give a reasonable representation of its real form. One response to this difficulty is to let the integrals be expressed as interpolations in tables obtained from numerical integration, or as series expansions. Another possible response is to divide the volume into small intervals with simple fits in each interval. And a third response is to start with the energy represented by a sum of functions, so that

$$E_S(v) = \Sigma a_i \phi_i(v) \quad . \qquad (8\text{-}10)$$

Then by differentiation one finds

$$p_S(v) = - \Sigma a_i \phi_i'(v) \quad , \qquad (8\text{-}11)$$

and

$$\gamma_S(v) = v\, \Sigma\, a_i\phi_i''(v) / \Sigma\, a_i\phi_i'(v) \ . \qquad (8\text{-}12)$$

This form for γ_S can then be fit to the chosen form for $\gamma_S(v)$. The widely used JWL equation of state is of this type.

A form for the Gruneisen gamma must also be chosen. Many workers have chosen it to be constant. It seems that a better choice is to give it the same form as the adiabatic gamma, but with values near those discussed at the end of Section VI.

An expression for the adiabatic gamma off the principal isentrope is obtained by using the definition of gamma, Eq. (2-9), and substituting in the partial derivatives obtained from Eq. (8-4). After simplifying the result by substituting from Eqs. (8-7) and (8-9), the result is

$$\gamma(p,v) = (p_S/p)\gamma_S$$

$$+ (1-p_S/p)(\Gamma+1-d \ln \Gamma/d \ln v). \qquad (8\text{-}13)$$

This expression makes it clear that a discontinuity in the slope of the Gruneisen gamma will lead to a discontinuity in the adiabatic gamma itself. Similarly, Eq. (4-21) shows that a discontinuity in the slope of the adiabatic gamma will lead to a discontinuity in G. Such discontinuities are nonphysical, but it isn't clear what spurious effects might appear in a calculation where an equation of state with discontinuities in the slopes of either of the gammas on the isentrope was used.

Expressions for new isentropes, above or below the principal isentrope, are obtained by integrating Eq. (8-13). Hugoniot curves are obtained by using the equation of state, Eq. (8-4), and the Hugoniot relation

$$E - E_o = \tfrac{1}{2}p(v_o - v) \ , \qquad (8\text{-}14)$$

and eliminating E. Particle velocities on the isentrope are obtained by integrating

$$dp/du = \pm\, c/v = \pm\, (\gamma p/v)^{1/2} \ . \qquad (8\text{-}15)$$

Even for simple choices of functions for the adiabatic gamma, the integration almost always has to be done numerically.

IX. CALIBRATION

The calibration of a fitting form for an equation of state opens opportunity for prejudice and personal preference. There are no absolute rules. The importance of various measurements to the calibration depends on the application.

Calibration of an equation of state begins with the Chapman-Jouguet state. A subscript j denotes that state in what follows. First there is the requirement that the principal isentrope pass through the point p_j, v_j. Then there is the additional requirement that the Rayleigh line and the Hugoniot curve be tangent at that point (the Chapman-Jouguet condition); this requirement is met by requiring

$$p_j = \rho_o D_j^2/(\gamma_j + 1) \qquad (9\text{-}1)$$

and

$$v_j/v_o = \gamma_j/(\gamma_j + 1) \ . \qquad (9\text{-}2)$$

One might proceed, for example, by measuring the detonation velocity and the CJ pressure. Then γ_j can be obtained from Eq. (9-1), and v_j from Eq. (9-2).

The problem with this approach is that apparently no one knows how to measure CJ pressure. One need only thumb through the seven Detonation Symposium volumes to see that there was no more agreement in 1981 than there was in 1951, and that the discussions get more and more complex with time. For calibrating an equation of state, one need only realize that if it made a lot of difference, it would have been measured by now. For many purposes the exact value is not very important. This fact has led to the development of "rules for gamma", that give the value for the adiabatic gamma at the CJ point simply in terms of the initial density of the explosive. A simple rule that works satisfactorily is

$$\gamma_j = 1.6 + 0.8\, \rho_o \ . \qquad (9\text{-}3)$$

The initial density and the measured detonation velocity can then be used with Eqs. (9-1) and (9-2) to find p_j and v_j.

The second thing to get right in the calibration of an equation of state is the amount of energy available for the system under consideration. For almost any system there is a "cut-off pressure", where once the explosive products have expanded to the volume where the pressure reaches this value, little additional work is done on the system. Either the metal or rock breaks, allowing the gases to escape, or the time is too long and the additional acceleration too late, or some other external condition makes the energy remaining in the products useless. For metal systems driven by explosive, the cut-off pressure is about 0.1 GPa in many cases. It has become customary to fix the energy delivered for an expansion down to that pressure with a calibration experiment. Perhaps the best known experiment is the cylinder test (6). For high-density, high-energy explosives the cut-off pressure comes at an expansion of six or seven times the initial volume, and the cylinder test is designed to measure an appropriate value. For other explosives and other uses, alternative tests have been used.

The Jacobs engine and the Fickett-Jacobs cycle described by Fickett and Davis (7) make it easy to understand this calibration. Figure 2 is a diagram of the cycle; it is described in the caption. The area between the base line, the Rayleigh line, and the principal isentrope is equal to the maximum useful work that could be obtained from the explosive. Some of that energy is not useful, because the pressure is too low for the application. Therefore, the diagram must be truncated, as shown in Fig. 3, at the limiting useful pressure. For the useful energy calibration, the area to the left of the truncation line must be made proportional to the energy obtained from the test. Several rules for an approximate calibration have been used. The total area is E_0, and the area to the right of the truncation line is E_5, so the rule is

$$E_{test} \sim E_0 - E_5 \quad . \qquad (9\text{-}4)$$

The equation of state parameters are adjusted to satisfy this relationship.

A third calibration point is to set the total energy, E_0, equal to the calculated chemical energy of the explosive. Although it is aesthetically satisfying to have the work available equal to the chemical energy, it is not an important calibration point. In the first place, there is no application of explosives where the energy

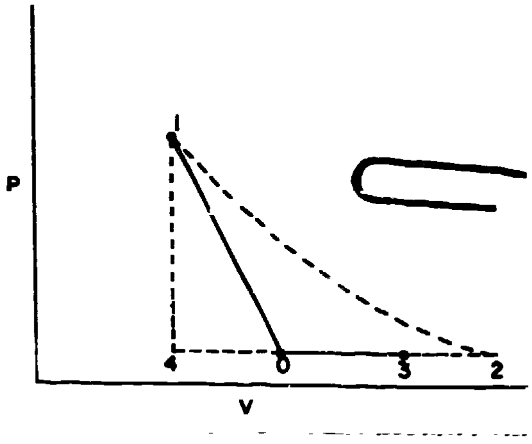

Fig. 2. The Fickett-Jacobs cycle. The initial state, unreacted explosive is at point 0. The CJ state is at point 1. The product gases expand against a piston from point 1 to point 2, doing useful work. The gases are cooled so they contract from 2 to 3, and this energy is lost to the system. The gases are reacted from 3 to 0, back into the original explosive. To get all the gas uniformly into the CJ state, work must be done on it, and this work is represented by the area 0-1-4. The maximum useful output work is the area 0-1-2.

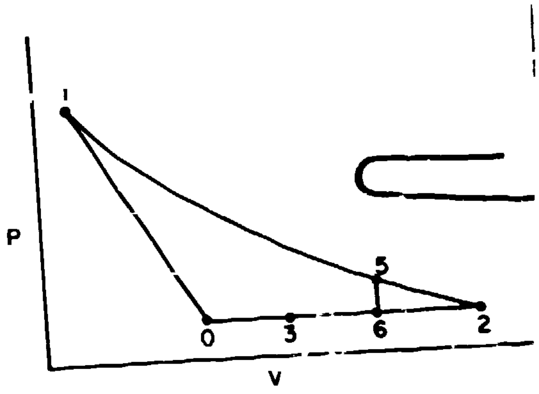

Fig. 3. In most applications of explosives, the product gases do useful work only when their pressure is above some cut-off pressure, shown here at point 5. The useful work is then represented by the area 0-1-5-6-0.

at low pressure is important; if low pressure could do the work, one wouldn't use explosive. And in the second place, heat energy of the explosive is not used (see the segment 2-3 in Fig. 2), and is rejected to the surroundings. Therefore, E_0 is not equal to the chemical energy. It is really more important to get the sound velocity about right at low pressure than to worry about adjusting for the total energy.

These calibrations determine the principal isentrope. The remaining calibration is for the Gruneisen gamma, that influences the values for states off the principal isentrope. Overdriven, colliding, and convergent detonations provide the data for determining Gruneisen gamma. So far, there have been no definitive calibrations. If overdriven detonations are important in the application of the equation of state, Gruneison gamma should be adjusted to fit the data. Otherwise, the choice is not important, and a simple form or even a constant value can be used with little effect on the calculations.

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REFERENCES

1. W. D. Hayes, "The Basic Theory of Gasdynamic Discontinuities," in Fundamentals of Gasdynamics, H. W. Emmons, Ed., Vol. III, High Speed Aerodynamics and Jet Propulsion, Princeton University Press, Princeton, N. J., pp. 416-481, 1958.

2. J. W. Bond, K. M. Watson, and J. A. Welch, *Atomic Theory of Gas Dynamics*, pp. 274-6, Addison-Wesley, Reading, Mass., 1965.

3. J. Lighthill, *Waves in Fluids*, pp. 76-85, Cambridge University Press, Cambridge, Mass., 1979.

4. H. B. Callen, *Thermodynamics*, p. 134, John Wiley and Sons, New York, 1960.

5. P. A. Thompson, *Compressible-Fluid Dynamics*, p. 252 and p. 577, McGraw-Hill, New York, 1972.

6. J. W. Kury et al., "Metal Acceleration by Chemical Explosives," Proceedings Fourth Symposium (International) on Detonation, ACR-126, Office of Naval Research, pp. 3-12, 1965.

7. W. Fickett and W. C. Davis, *Detonation*, Univ. of California Press, Berkeley, California, pp. 35-39, 1979.