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PRODUCTS

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EQUATION OF STATE FOR DETONATION PRODUCTS

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To be useful, an equation of state for detonation products must allow rapid computation. The constraints applied by this requirement have surprising thermodynamic effects. Some of these are discussed here. A simple, complete equation of state is proposed, and its properties are discussed. With the form assumed here, all the useful integrals (except the Riemann integral) can be written simply and explicitly, so the behavior of the important variables can be easily seen. The complete equation of state is calibrated for PBX9404 and PBX9501.

INTRODUCTION

The words in the title of this paper deserve some comment. "Equation of state" means, by convention, some calibrated fitting form, describing material properties in some limited region, that allows a user to compute, in reasonable approximation, the behavior of a physical system. The knowledge of the material properties is always incomplete, and the calibration is an approximation; the computation is also an approximation to the solution of the equations used; and the description of the physical system is an approximation too. In addition the problems to be solved, and the judgment of what constitutes a reasonable approximation, are various, and change as computer power changes, and as the sophistication of the physical devices and of the investigators changes.

"Detonation products" usually means that the working fluid formed by the explosive is considered as a high-density gas, without rate processes, and without solid inclusions or other inhomogeneities. Real detonation products are a mixture of several gases, among which the equilibrium composition shifts as the state changes, with rates that control the shifts, and with varying amounts of solid particles entrained by the gases as they move. Sometimes the usual assumptions lead to important failures of the approximation to agree with physical reality.

In the past, few problems involving the temperature and other thermal properties were attempted, and a complete equation of state was not necessary. Also, problems where equations of state for mixtures, such as mixtures of reacted and unreacted explosive, are required were not attempted. Now these problems are major research subjects, and good equations of state are needed. Possible forms will be proposed for consideration.

It is essential that users of proposed "equations of state for detonation products" understand as much as possible about the details of the approximations and their effects on the computed results. All the above assumptions are accepted as the basis for what follows in this paper.

USEFULNESS OF AN EQUATION OF STATE

A calibrated fitting form will be useful for computation only if it allows the calculation to proceed at high speed. A hydrodynamics code, for example, calls the equation of state at every time step for pressure as a function of specific volume and specific internal energy, and pressure must be given as an explicit function without extensive computation. Otherwise, the calculation is slowed and becomes uneconomical. Other codes may require different variables, but the speed requirement always remains important.

A practically useful fitting form must have only a few, say a dozen or less, calibration constants, and only a few, say three or four, terms to compute. Iteration to find a solution must be avoided.

As an example of how the requirements of speed affect provides a physical constraint, we consider here an equation of state proposed for a description of detonation products to be used with an equation of state for unreacted explosive to give a description of the mixture of these. It is convenient, almost essential, that the equation of state can be written as $p(E,v)$, and can be inverted to $E(p,v)$. A linear relationship between pressure and specific internal energy, of the form

$$p = \alpha(v) + \beta(v)E \quad (1)$$

where p is the pressure, E is the specific internal energy, and $\alpha(v)$ and $\beta(v)$ are fitting forms for the variation with volume v , satisfies this requirement. Grüneisen gamma is defined as

$$\Gamma = v \left(\frac{\partial p}{\partial E} \right)_v \quad (2)$$

and for the description in Eq. (1) it is a function of volume only. One consequence of this linear relationship between p and E is that the thermodynamic identity

$$\frac{v}{TC_v^2} \left(\frac{\partial C_v}{\partial v} \right)_s = \left(\frac{\partial \Gamma}{\partial E} \right)_v \quad (3)$$

where T is the temperature and C_v is the specific heat, requires that the specific heat be constant along any isentrope, although it can be different on different isentropes. The form of Eq.(1), chosen for simplicity, has important physical consequences.

An equation of state should be consistent with the results of thermodynamics, in order to ensure that the functions are truly state functions, and do not depend upon the path to a point in state space. The discussion above shows that, for example, one cannot choose the Grüneisen gamma a function of volume only, and then choose the specific heat to be a function of entropy and volume.

In Reference 1 an equation of state was proposed with p a quadratic function of E . This form could also be inverted easily to either $p(E,v)$ or $E(p,v)$ so it could be useful. It can be seen from Eq(3) that this form would allow variation of C_v with v . Unpublished work has shown that it cannot be calibrated for the thermal properties over a large region, and is of limited use. An equation of state with p depending on E and $E^{3/2}$ could be inverted and might be useful.

In what follows, the argument is restricted to a linear relationship between p and E .

COMPLETE EQUATION OF STATE

Calibration measurements for detonation products are usually made on the principal isentrope, the isentrope that passes through the CJ state. Suppose the isentrope is given, so that $p^S(v)$, $E^S(v)$ are known, and that Grüneisen gamma $\Gamma(v)$ is also known. The

superscript S denotes values on the principal isentrope. (Grüneisen gamma might be determined by measuring two distinct isentropes. See Eq. (2).) It is implicit that the temperature $T^S(v)$ can be inferred from Grüneisen gamma, defined by Eq. (2) and its equivalent,

$$\Gamma = -\frac{v}{T} \left(\frac{\partial T}{\partial v} \right)_s \quad (4)$$

by integration, but a constant of integration must be furnished. Assume further that

$$C_v = \text{constant} \quad (5)$$

and

$$\Gamma = \Gamma(v) \quad (6)$$

independent of E or S , not just on the principal isentrope but everywhere.

Then from Eq.(2), using Eq.(6), the pressure is given by

$$p(E, v) = p^S(v) + \frac{\Gamma(v)}{v} (E - E^S(v)) \quad (7)$$

This is the incomplete equation of state required for hydrodynamic codes.

The temperature, with the assumption of Eq.(5), is

$$T = T^S(v) + \frac{E - E^S(v)}{C_v} \quad (8)$$

and, at constant volume

$$dE = TdS \quad (9)$$

Using Eq.(8) and integrating Eq.(9) gives

$$E(S, v) = E^S(v) + C_v T^S(v) \left[\exp\left(\frac{S - S^S}{C_v}\right) - 1 \right] \quad (10)$$

where S is the entropy, and S^S is the value of the entropy on the principal isentrope. Eq.(10) is the complete equation of state, from which all the properties of the material, including for example Eq.(7), can be derived.

For convenient reference, the assumptions and results are collected here:

Assumptions

$$p^S(v), E^S(v), \text{ and } T^S(v) \text{ are given} \quad (11)$$

$$C_v \text{ is constant} \quad (12)$$

$$\Gamma = \Gamma(v) \quad (13)$$

Results

$$E(S, v) = E^S(v) + C_v T^S(v) \left[\exp\left(\frac{S - S^S}{C_v}\right) - 1 \right] \quad (14)$$

$$p(E, v) = p^S(v) + \frac{\Gamma(v)}{v} (E - E^S(v)) \quad (15)$$

$$T(S, v) = T^S(v) \exp\left(\frac{S - S^S}{C_v}\right) \quad (16)$$

$$T(E, v) = T^S(v) + \frac{E - E^S(v)}{C_v} \quad (17)$$

$$\gamma(p, v) = -\frac{v}{p} \cdot \frac{dp^S}{dv} + \left(1 - \frac{p^S}{p}\right) \cdot \left(\Gamma + 1 - \frac{v}{\Gamma} \cdot \frac{d\Gamma}{dv}\right) \quad (18)$$

$$g(p, v) = \frac{pv}{C_v T^S(v) + (p - p^S(v))v / \Gamma(v)} \quad (19)$$

where γ is the adiabatic gamma, sometimes called the dimensionless sound speed since $\gamma = c^2/pv$, and g is the dimensionless reciprocal specific heat, defined as $g = pv/C_v T$.

The detonation Hugoniot curve is obtained by combining the incomplete equation of state Eq.(15) with the Hugoniot energy and velocity conditions

$$E^H = E_0 + \frac{1}{2} p(v_0 - v) \quad (20)$$

$$u^2 = p(v - v_0) \quad (21)$$

to obtain

$$p^H(v) = \frac{2\Gamma(v)(E_0 - E^S(v)) + 2p^S(v)v}{(\Gamma(v) + 2)v - \Gamma(v)v_0} \quad (22)$$

$$u^H(v) = \sqrt{p^H(v)(v_0 - v)} \quad (23)$$

Thermodynamic identities useful for interpreting plots in $\ln p - \ln v$ space of isentropes, isotherms, and constant energy curves, are

$$-\frac{v}{p} \left(\frac{\partial p}{\partial v} \right)_S = \gamma \quad (24)$$

$$-\frac{v}{p} \left(\frac{\partial p}{\partial v} \right)_E = \gamma - \Gamma \quad (25)$$

$$-\frac{v}{p} \left(\frac{\partial p}{\partial v} \right)_T = \gamma - \Gamma^2 / g \quad (26)$$

$$\frac{T^S}{T_c} = \frac{\left[\frac{1}{2} \left(\frac{v}{v_c} \right)^n + \frac{1}{2} \left(\frac{v}{v_c} \right)^{-n} \right]^{(a/n)(1-b)}}{\left(\frac{v}{v_c} \right)^{k-1+a(1-b)}} \quad (29)$$

$$F(v) = \frac{2a \left(\frac{v}{v_c} \right)^{-n}}{\left(\frac{v}{v_c} \right)^n + \left(\frac{v}{v_c} \right)^{-n}} \quad (30)$$

EXAMPLE

In a paper published at the Tenth Symposium, Davis¹, I calibrated a principal isentrope for PBX9404, and it will be used here as an example. The results of that choice of a fitting form for the isentrope and its calibration gave

$$\frac{p^S}{p_c} = \frac{\left[\frac{1}{2} \left(\frac{v}{v_c} \right)^n + \frac{1}{2} \left(\frac{v}{v_c} \right)^{-n} \right]^{a/n}}{\left(\frac{v}{v_c} \right)^{k+a}} \times \frac{k-1+F}{k-1+a} \quad (27)$$

$$\frac{E^S}{E_c} = \frac{\left[\frac{1}{2} \left(\frac{v}{v_c} \right)^n + \frac{1}{2} \left(\frac{v}{v_c} \right)^{-n} \right]^{a/n}}{\left(\frac{v}{v_c} \right)^{k-1+a}} \quad (28)$$

$$\Gamma(v) = k - 1 + (1-b)F(v) \quad (31)$$

$$E_c = \frac{p_c v_c}{k-1+a} \quad (32)$$

The calibrated values, and the other constants, are given in Table I. Calibration of the principal isentrope is discussed in detail in Reference 1. The entry E_{19} is the cylinder test energy, and e_g , the Gurney energy, is derived from it. The chemical energy of the explosive is e_0 . The constant b has to be recalibrated because it applies off the isentrope, and the equation of state used here is different from the one used in [1]. There are no experimental data for the calibration of T_c and C_v , and they will be discussed below.

TABLE 1

Calibration Input						
Explosive	D (m/s)	p_j (GPa)	ρ_0 (kg/m ³)	E_{19} (MJ/kg)	e_0 (GJ/m ³)	
PBX-9404	8790	35.7	1844	1.620	10.78	
Derived Values						
Explosive	v_0 (m ³ /kg)	v_j (m ³ /kg)	v_7 (m ³ /kg)	γ_j	e_g (GJ/m ³)	
PBX-9404	5.423×10^{-4}	4.064×10^{-4}	37.96×10^{-4}	2.991	7.728	
Calibrated Parameters						
Explosive	k	a	n	v_c (m ³ /kg)	p_c (GPa)	b
PBX-9404	1.3	0.8067	1.4470	8.727×10^{-4}	3.376	0.7
Thermal Parameters						
Explosive	C_v (J/kg K)	R (J/kg K)	T_c (K)	T_j (K)	T_{atm} (K)	
PBX-9404	885	265.5	2295	3787	273	

CALIBRATION

The calibration of the principal isentrope using detonation data is discussed by Davis¹. The choice of Grüneisen gamma is made, first, by choosing it to depend only on v so that the relationship between p and E is linear, and, second, by choosing the form to agree qualitatively with that found from equation of state computations, and, finally, by choosing a form simple enough to make it easy to perform the needed integrations. The constant b is determined by fitting the Hugoniot curve determined by overdriven detonation experiments, but any value in the neighborhood of $b = 0.7$ is satisfactory. Clearly, new measurements on real explosives would improve the calibration.

For the complete equation of state C_v and T_c must be chosen. At the present time no real data are available. The choice is governed only by vague ideas about what is probable.

A possible choice can be made by requiring the equation of state to approach the polytropic gas equation of state at large volume, that is, make $p\nu/RT = 1$. It is easy to show that this requirement will be satisfied if C_v is chosen for the high pressure regime, and

$$T_c = \frac{2^{-ab/n}}{k-1+a} \cdot \frac{p_c v_c}{C_v} \quad (33)$$

$$R = (k-1)C_v \quad (34)$$

The value obtained for R may not be in agreement with that for a mixture of the assumed gases in the products. A simple equation of state form cannot be expected to perform well everywhere.

Since it is unlikely that the equation of state will be used in the low pressure regime, if any data are available it is better to calibrate it in the region where it will be used, and accept the fact that it is not calibrated in other regions.

As an example, suppose we choose the values given above for the isentrope, and supplement them with the following: $b = 0.7$, and $C_v = 885$ J/kg K. Then $R = 265.5$ J/kg K, and $T_c = 2295$ K. With these values, the temperature at the CJ state is $T_j = 3787$ K, and at atmospheric pressure on the principal isentrope $T_{atm} = 273$ K. The numbers result from an arbitrary choice, but they are reasonable ones. Increasing the value of b increases T_c and T_{atm} and decreases T_j .

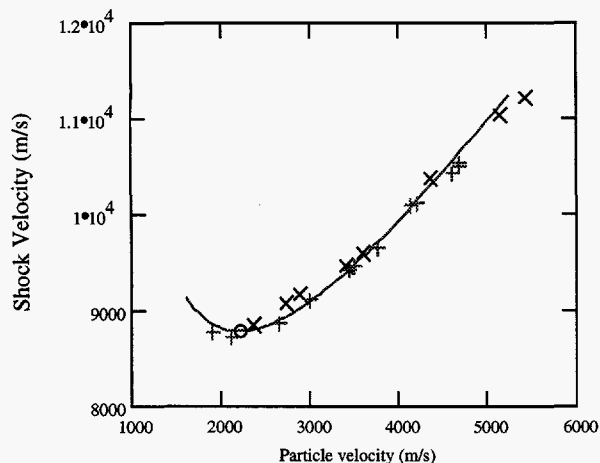


Figure 1. Plot of shock velocity vs particle velocity for overdriven detonations. The x's are for the data for PBX9404 from Green et al., [2], and the +s are for the data for PBX9501 from Hixson et al., [3]. The solid line is calculated from the equation of state calibrated as above. The circle marks the CJ point.

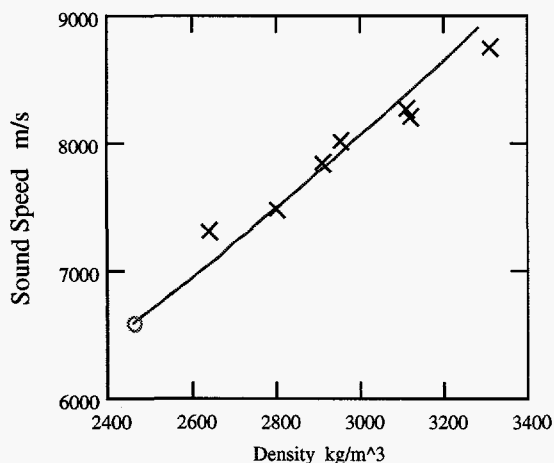


Figure 2. Plot of sound speed along the Hugoniot curve for an overdriven detonation vs density. The x's are data for PBX9501 from Hixson et al.³ The o marks the CJ state. The solid line is calculated from the equation of state as calibrated above.

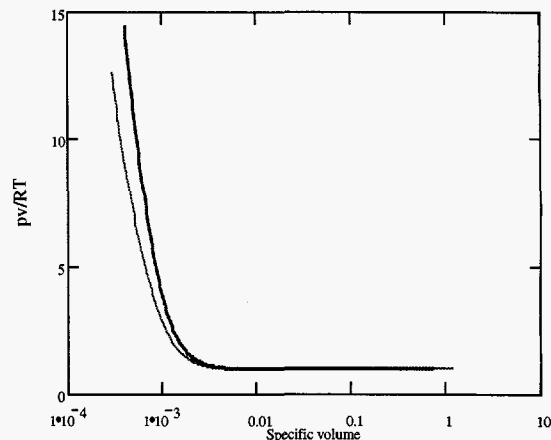


Figure 3. Plot of pv/RT versus specific volume in m^3/kg . The upper curve (the heavier line) begins at the CJ state, $v = 4.064 \times 10^{-4} m^3/kg$, $p = 35.7$ GPa, $T = 3787$ K, where $pv/RT = 14.4$, and ends at $v = 0.716 m^3/kg$, $p = 1$ atm (101325 Pa), and $T = 273$ K. The lower curve begins at the detonation state when the wave speed is 11000 m/s, with $v = 2.952 \times 10^{-4} m^3/kg$, $p = 101.7$ GPa, and $T = 8961$ K, where $pv/RT = 12.6$, and ends at $v = 1.154 m^3/kg$, $p = 1$ atm, and $T = 440$ K.

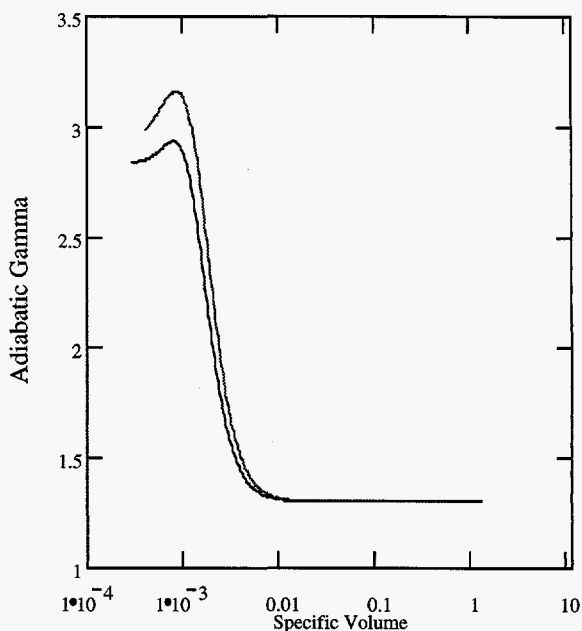


Figure 4. Plot of adiabatic gamma versus specific volume (m^3/kg) for expansion down the isentropes from the CJ state, upper curve, and from the detonation state where wave speed is 11000 m/s, lower curve.

CONCLUSIONS

A complete equation of state for detonation products, simple enough to be practical for computations, is proposed, along with a recipe for calibration. More experience with it is needed to decide what modifications are needed.

The function $F(v)$ of Eq.(30) has been chosen to be physically reasonable, at least qualitatively. Its choice, however, has been strongly influenced by the desire to be able to write out all the integrals explicitly for this example. Calibration was for the high pressure region, and does not extend to low density, below about 100 m³/kg, well enough to model the nonideality of gases in this region.

APPENDIX

Note 1. Eq. (5) is the assumption that C_v is constant, and below that it is used to find $E(S,v)$ as Eq. (10). If instead one assumes that $C_v = C_v^S + \alpha(S - S^S)$, then it is straight forward to show that

$$E = E^S + \frac{C_v^S T^S}{1 + \alpha} \left\{ \left[1 + \frac{\alpha}{C_v^S} (S - S^S) \right]^{\frac{1+\alpha}{\alpha}} - 1 \right\} \quad (35)$$

Note 2. In the example in this paper, $F(v)$ is defined in Eq. (30). It is easy to carry through the procedures of Reference 1 with

$$F(v) = \frac{2ax^{-n}}{x^n + x^{-n}} + \frac{2\alpha(qx)^{-m}}{(qx)^m + (qx)^{-m}} \quad (36)$$

where $x = v/v_c$, and a, n, q, m and α are constants. The equation of state gains flexibility with this change if calibration data are available.

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