of 11 605.6°K),

$$p_1(V_s)=-2.467+6.769\eta-6.956\eta^2+3.040\eta^3-0.3869\eta^4,$$
$$a(V_s)=-0.2267+0.2712\eta,$$
$$b(V_s)=0.08316-0.07804\eta^{-1}+0.03068\eta^{-2},$$

with $\eta=V_s^0(T^0)/V_s=\rho/\rho_0$ being the compression of the material relative to its normal crystal density of 2.25 g/cc. The numerical coefficients were obtained by fitting expression (2) to points on the shock Hugoniot of graphite[15] and to the compressibility and thermal expansion coefficient at normal density. The range of applicability is $0.95<\eta<2.5$, $0<T<2$.

## 2. THEORY

If solid carbon is considered, expressions are needed for the thermodynamic functions of both gas and solid phases; these may be derived by standard thermodynamic methods, and are summarized here.

For the gaseous component with equation of state (1),

$$E=\sum x_i(E^0-H_0^0)_i+\sum x_i(H_0^0)_i +RT[\alpha T(F-1)/(T+\theta)], \quad (3a)$$

$$S=\sum x_i(S^0)_i-R[\sum x_i \ln x_i+\ln(p/p^0)] +R[\ln F-(e^{\beta x}-1)/\beta+\alpha T(F-1)/(T+\theta)], \quad (3b)$$

$$\mu_i=(F^0-H_0^0)_i+(H_0^0)_i+RT\ln(x_ip/p^0) -RT[\ln F-(e^{\beta x}-1)/\beta-\kappa k_i(F-1)/k], \quad (3c)$$

where the gas imperfection factor $F$ is defined in Eq. (1) and should not be confused with the (Gibbs) free energies $F^0$ and $F_s'$.

For the solid with equation of state (2),

$$E=(H^0-H_0^0)+H_0^0-(pV_s)^0 +\int_{V_s^0}^{V_s}[b(V)T^2-p_1(V)]dV, \quad (4a)$$

$$S=S^0+\int_{V_s^0}^{V_s}[a(V)+2b(V)T]dV, \quad (4b)$$

$$\mu=(F^0-H_0^0)+H_0^0+F_s', \quad (4c)$$

where

$$F_s'=pV_s-(pV_s)^0-\int_{V_s^0}^{V_s}[p_1(V)+a(V)T+b(V)T^2]dV.$$

For chemical equilibrium,

$$\ln\Pi_g(n_i)^{\nu_i}=\ln K_p(T)-(\textstyle\sum_g\nu_i)\ln(p/n_gp^0) +(\textstyle\sum_g\nu_i)\left(\ln F-\dfrac{e^{\beta x}-1}{\beta}\right) -\dfrac{\sum_g\nu_ik_i}{k}(F-1)-\dfrac{\nu_sF_s'}{RT}, \quad (5)$$

where

$$RT\ln K_p(T)=-\sum\nu_i(F^0-H_0^0)_i-\sum\nu_i(H_0^0)_i$$

(one such equation for each independent chemical reaction).

In Eqs. (3) to (5) $E$, $S$, and $\mu$ are internal energy, entropy, and chemical potential, respectively. A superscript 0 refers to the reference state (ideal gas or real solid at pressure $p^0$ and temperature $T$),[16] with $H_0^0$ being the enthalpy of formation from the elements at absolute zero; $x_i$ and $n_i$ are the mole fraction and number of moles of component $i$; and $n_g=\sum_g n_i$. In Eq. (5) the $\nu_i$'s are the coefficients of the chemical reaction, positive for products and negative for reactants, and the subscript $g$ for a sum indicates it is for gaseous components only.

The thermodynamic state of the detonation products is defined by the Hugoniot equation[17]

$$h\equiv E-E_0-\tfrac{1}{2}(p+p_0)(V_0-V)=0, \quad (6)$$

and the Chapman-Jouguet condition[18]

$$(\partial p/\partial V)_S=-(p-p_0)/(V_0-V). \quad (7)$$

In (6) the subscript 0 refers to the undetonated explosive, $E_0$ being given by the expression

$$E_0=(\Delta H_f)_e+\textstyle\sum_j N_j[H^0(T_0)-H_0^0]_j-p_0V_0, \quad (8)$$

where $(\Delta H_f)_e$ is the molar enthalpy of formation of the explosive at $T_0$, and $N_j$ is the number of moles of element $j$ in one mole of explosive.

## 3. CALCULATIONS

The detonation products were assumed to be made up of the following chemical components:

$$(1)\ H_2,\quad (2)\ CO_2,\quad (3)\ CO,\quad (4)\ H_2O,\quad (5)\ N_2,\quad (6)\ NO,\quad (7)\ C\ (\text{graphite}). \quad (9)$$

Oxygen was not included, since none of the explosives considered was more oxygen rich than RDX, which balances to $N_2$, $H_2O$, CO. In some preliminary calculations on IBM-CPC equipment some of the components considered by Brinkley, *et al.*,[10,11] *viz.*, $NH_3$, $CH_4$, and OH, were also included; these were found to be present in small though not negligible amounts. For

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[15] J. M. Walsh, private communication. The measurements were made by a dynamic method similar to that used for aluminum, copper, and zinc by J. M. Walsh and R. H. Christian [Phys. Rev. 97, 1544 (1955)].

[16] In evaluating the thermodynamic functions for the solid we neglected $(pV_s)^0$ and approximated $V_s^0(T)$ by $V_s^0(25°C)$. The resulting error was less than that of the analytic fits used for $(H^0-H_0^0)$ and $S^0$.

[17] See, for example, R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Interscience Publishers, Inc., New York, 1948), p. 204.

[18] In the usual statement of the C−J condition, $(\partial p/\partial V)_S$ is to be evaluated for equilibrium composition. However, Kirkwood and Wood [J. Chem. Phys. 22, 1915 (1954)] have recently shown that this derivative should be evaluated with frozen composition. Our calculations have used the older statement of the C−J condition, but there is very little difference between the two, at least for our equation of state. Check calculations showed that the use of the correct C−J condition would decrease $p_{CJ}$ by less than 1% at the lowest loading density of interest ($\rho_0=1.2$) and make almost no change at high loading density.