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THERMODYNAMIC STATES IN EXPLOSION FIELDS

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Here we investigate the thermodynamic states occurring in explosion fields from the detonation of condensed explosives in air. In typical applications, the pressure of expanded detonation products gases is modeled by a Jones[1]-Wilkins[2]-Lee[3] (JWL) function: $p_{JWL} = f(v, s_{CJ})$; constants in that function are fit to cylinder test data. This function provides a specification of pressure as a function of specific volume, v, along the expansion isentrope ($s = \text{constant} = s_{CJ}$) starting at the Chapman-Jouguet (CJ) state. However, the JWL function is not a fundamental equation[4] of thermodynamics, and therefore gives an incomplete specification of states. For example, explosions inherently involve shock reflections from surfaces; this changes the entropy of the products, and in such situations the JWL function provides no information on the products states. In addition, most explosives are not oxygen balanced, so if hot detonation products mix with air, they after-burn, releasing the heat of reaction via a turbulent combustion process. This raises the temperature of explosion products cloud to the adiabatic flame temperature (~3,000K). Again, the JWL function provides no information on the combustion products states.

This conundrum may be overcome by using the Cheetah code[5] as an equation-of-state module. As inputs, one specifies the chemical composition of the substance and two thermodynamic variables; Cheetah then finds the thermodynamic equilibrium (or constrained equilibrium) solution by minimizing the Gibbs free energy of the system; the output is all thermodynamic variables at that state. This approach was used to analyze the thermodynamic states from the detonation of a C-4 charge ($\rho_0 = 1.6\,g/cc$) and the combustion of the detonation products with air.

Figure 1 depicts the locus of states of the C-4 detonation products in the pressure-specific volume plane. The locus starts at the *Chapman-Jouguet* (CJ) state, and expands down the isentrope ($s_{CJ} = 1.768\,cal/g - K$) to atmospheric pressure. The locus was fit with the following JWL function:

$$p_{PG}^{JWL}(v,T) = A\left(1 - \frac{\omega \cdot v_0}{R_1 \cdot v}\right)e^{-R_1 \cdot v/v_0} + B\left(1 - \frac{\omega \cdot v_0}{R_2 \cdot v}\right)e^{-R_2 \cdot v/v_0} + R_{DP}T/v \qquad (1)$$

where $A = 5.23\,Mbar$, $B = 0.154\,Mbar$, $R_1 = 4.30$, $R_2 = 1.70$ and $R_{DP} = 3.12$ (bar-cc/g-K). Note that for specific volumes larger than ~10 cc/g, the function reduces to the perfect gas law.

Figure 2 presents the same locus in the specific internal energy—temperature plane. Points (red circles) were calculated by the Cheetah code, assuming that the composition of detonation products was frozen for $T<1,800$ K. The solution starts at the *CJ* point ($T_{CJ} = 3,238\,K$) and expands down the isentrope ($s_{CJ} = 1.768\,cal/g - K$) to room temperature. The standard energy of C-4 Reactants and Products at *stp* (1 atm, 298K) are: $u_{F,R}^0 = 73.114$ and $u_{F,P}^0 = -1,173.68\,cal/g$, respectively; their difference is the heat of detonation:

$u_{F,P}^0 - u_{F,R}^0 \equiv \Delta H_d = -1{,}248 \; cal/g$, and is indicated on the figure. Also shown in that figure is the *equilibrium* isentrope (blue curve), which assumes chemical equilibrium at all temperatures. At room temperature, it results in energy of -1,350 cal/g which disagrees with the measured heat of detonation. This effect is typical of condensed explosives; quenching induced by the strong rarefaction created when the DP gases expand from the CJ state stops the kinetic reactions at ~1,800 K. A Constant Volume Detonation (CVD) is represented by the $u = u_{F,R}^0$ line from R to P. It gives a CVD detonation temperature of 2,887 K.

Figure 3 depicts the locus of states for the equilibrium products CP for the stoichiometric combustion of C-4 in air ($\sigma_s = 2.1$). The red line represents isobaric ($p = 1atm$) combustion locus. The standard energy of C4-air Reactants and Products at *stp* are: $u_{CP,R}^0 = +9.677 \; cal/g$ and $u_{CP,P}^0 = -1{,}016.77 \; cal/g$, respectively; their difference is the heat of combustion: $u_{CP,P}^0 - u_{CP,R}^0 \equiv \Delta H_c = -929.04 \; cal/g_m = -2{,}880 \; cal/g_{C4}$, which is indicated on the figure. Adiabatic Combustion (AC) is represented by the $u = u_{CP,R}^0$ line from R to P. It gives an adiabatic combustion temperature of 2,816 K. For temperatures below 3,000 K, these curves are only a function of temperature. Therefore the loci of states in Fig. 3 were fit with quadratic functions of temperature:

$$u_k(T) = a_k T^2 + b_k T + c_k \qquad k=F, A, R, CP \qquad (2)$$

thereby providing a caloric equation of state for the combustion products. In hydro codes, one typically carries the density ($\rho_k = 1/v_k$) and specific internal energy (u_k) as independent variables. Given u_k, the above relation may be inverted:

$$T_k = [-b_k + \sqrt{b_k^2 - 4a_k(c_k = u_k)}]/2a_k \qquad (3)$$

to determine the temperature. Then pressure is calculated from the perfect gas relation:

$$p = RT/v \qquad (4)$$

We will show that the above relation is valid for pressures less than one kilo-bar.

The above relations were used to derive the *Fundamental Equation* for the detonation products and combustion products:

$$u(s,v) = aT_*^2 e^{2s/c_v}(v_*/v)^{2R/c_v} + bT_* e^{s/c_v}(v_*/v)^{R/c_v} + c \qquad (5)$$

where T_* and v_* represent the temperature and specific volume in the reference state denoted by subscript *. Given the fundamental equation: $u(s,v)$ one can use the Maxwell Relations[4] to evaluate the temperature, pressure, specific heat and enthalpy of the products:

$$T(s,v) \equiv \left(\frac{\partial u}{\partial s}\right)_v, \; p(s,v) \equiv -\left(\frac{\partial u}{\partial v}\right)_s, \; c_v(s,v) \equiv \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \Big/ \left(\frac{\partial T}{\partial s}\right)_v, \; h(s,v) \equiv u + pv \quad (6)$$

Summary: the above methodology can be used to specify all thermodynamic states occurring in explosion fields. And it is represented in form suitable for specifying the equations of state for hydro code simulations of explosions. More details, including a description of the historical development of the JWL function and the derivation of the Fundamental Equation (5), will be provided in the paper.

——**WORD COUNT** = 830 words (without figures)——

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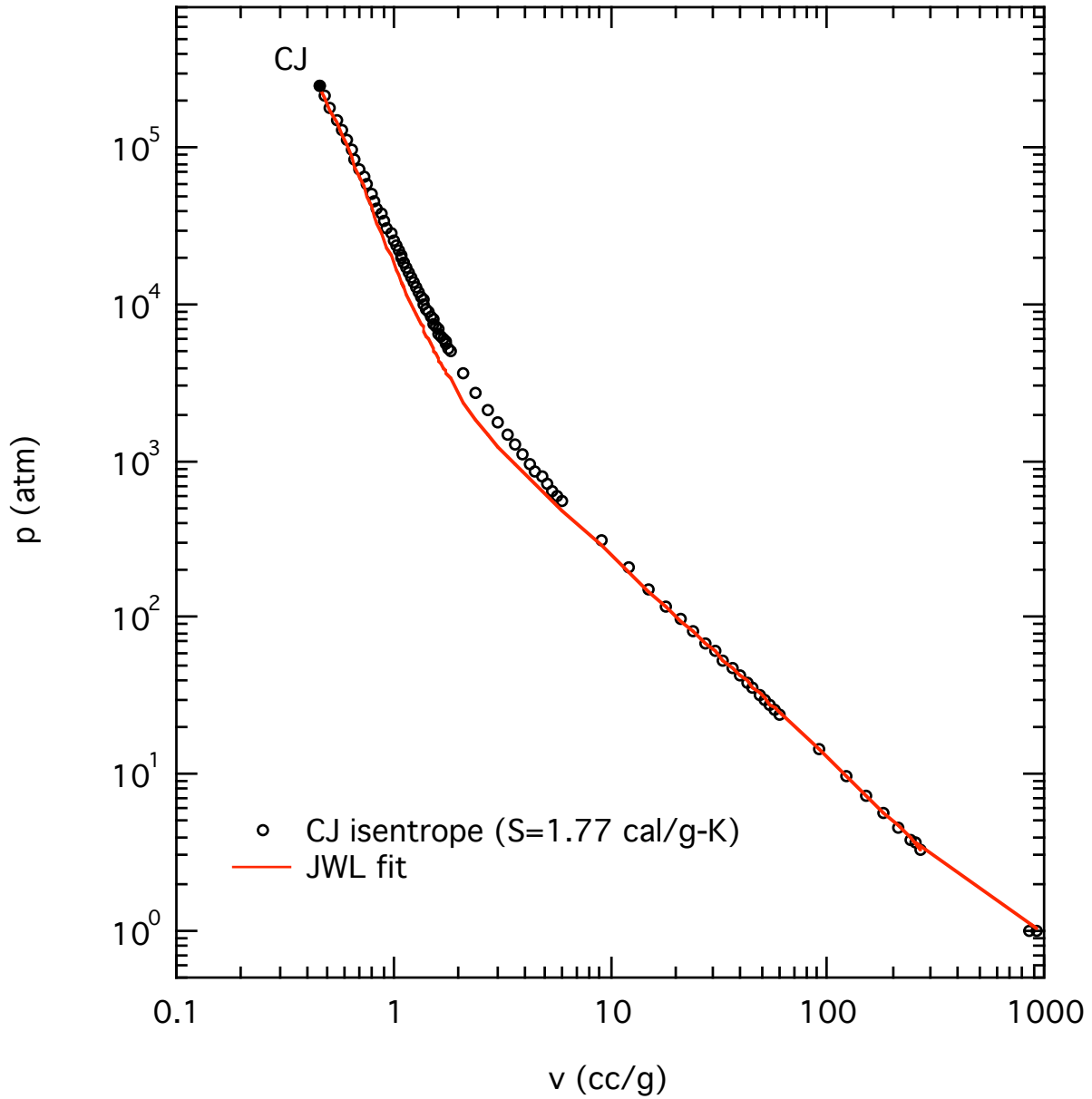
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Figure 1. Pressure-volume diagram depicts the locus of states of the detonation products gases as they expand down the CJ isentrope for a C4 charge. Locus is fit with the JWL function (1).
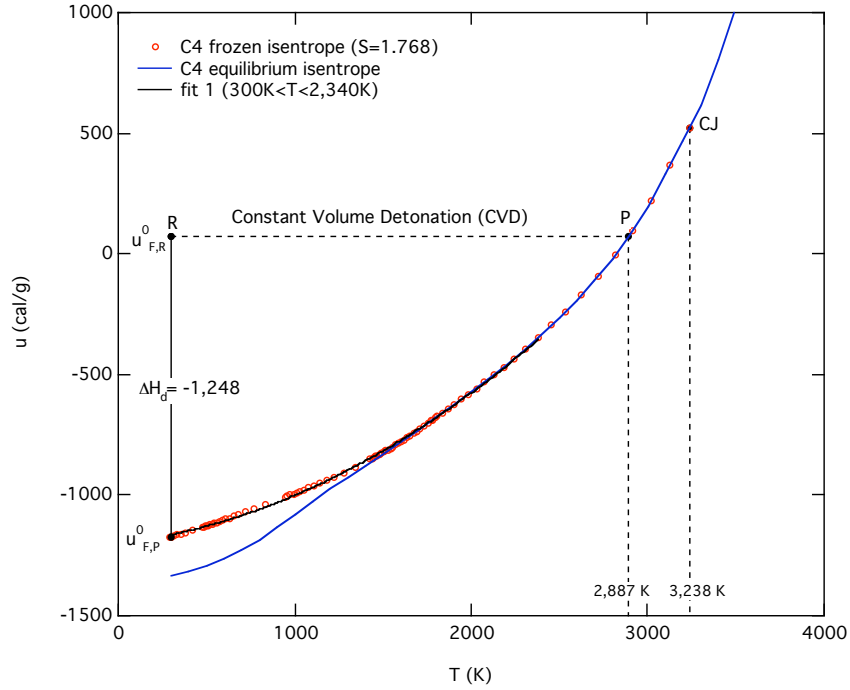
Figure 2. *Le Chatelier* diagram depicting the locus of states of the detonation products of the explosive C-4, starting at the *Chapman-Jouguet* point (*CJ*) and expanding at constant entropy to one atmosphere.
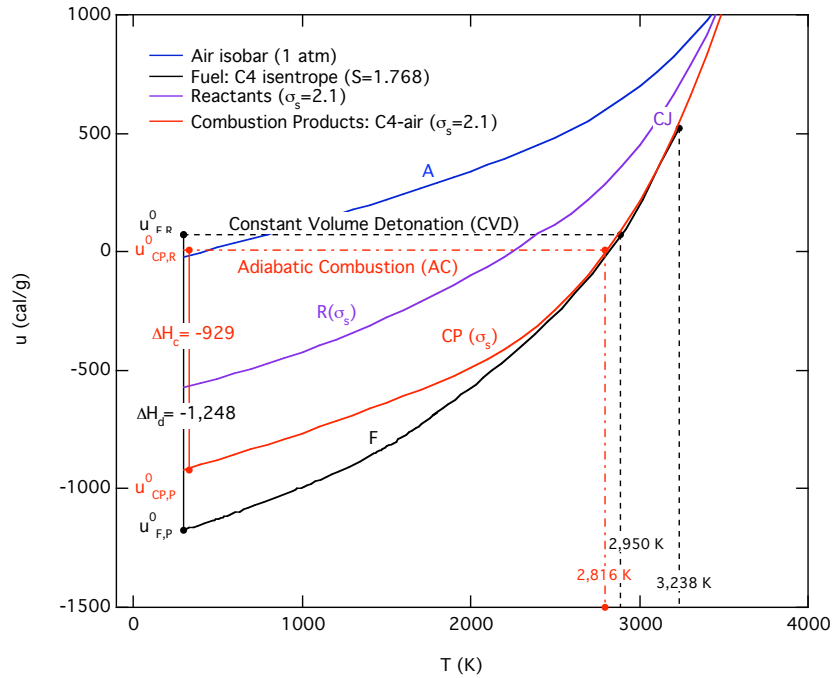

Figure 3. *Le Chatelier* diagram depicting the locus of states for the detonation of a C-4 charge (*curve F*) and its stoichiometric combustion with air (*curve CP*). Also shown are loci of the reactants (*curve R*) and air (*curve A*).