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QUADRACTIC MODEL OF THERMODYNAMIC STATES IN SDF EXPLOSIONS

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ABSTRACT

We study the thermodynamic states encountered during Shock-Dispersed-Fuel (SDF) explosions. Such explosions contain up to six components: three fuels (PETN, TNT and Aluminum) and their products corresponding to stoichiometric combustion with air. We establish the loci in thermodynamic state space that correctly describes the behavior of the components. Results are fit with quadratic functions that serve as fast equations of state suitable for 3D numerical simulations of SDF explosions.

INTRODUCTION

A thermodynamic model of afterburning in explosions was first presented at the 34th ICT Conference on Energetic Materials [1]. Six explosives were investigated: PETN, TNT, an aluminized charge, a polyethylene-based fuel, an IPN-based fuel and a magnesium-based fuel. At the 36th ICT conference, a thermodynamic model of Aluminum combustion in SDF explosions was presented [2]. In these cases, afterburning of the PETN booster charge was neglected on the grounds that it caused little change in the system energy. But subsequently we have realized that it can have a dramatic effect on the combustion cloud temperature, increasing it by a factor of ten, which causes a three-fold increase in the cloud sound speed, and therefore must be taken into account for accurate numerical simulations.

In this paper we extend model to include afterburning of PETN booster explosion products along with the main fuel. We consider the thermodynamic states encountered during Shock-Dispersed-Fuel (SDF) explosions studied by Neuwald et al [3-14]. Typical charge construction is shown in Fig. 1. It begins with a 0.5-g booster charge of PETN ($C_5H_8N_4O_{12}$) at a initial density of $\rho_0 = 1$ g/cc. This can be surrounded by a 1-g shell of TNT ($C_7H_5N_3O_6$, $\rho_0 = 1$ g/cc), or by a thin paper cylinder with the void filled by a loosely packed Aluminum flake (bulk density ~ 0.63 g/cc). There is a need to build a fast and simple Equations of State (EOS) for the detonation products from such explosions, appropriate also during their afterburning/combustion with air. We assume for simplicity that reactions PETN-air, TNT-air and Al-air are parallel and do not interact with each other. This is a reasonable assumption, since as we shall show, the composition of the detonation products are typically frozen for

specific volumes $v > 28 cc/g$. Thus we have six components to consider: three fuels (PETN and TNT detonation products gases, and Aluminum), and their corresponding combustion products (PETN-air, TNT-air, and Al-air). In this paper we establish loci in thermodynamic state space that correctly describes the behavior of these components. Results are fit with quadratic functions formulated to serve as suitable EOS for numerical simulations of SDF explosions [15, 16, 17]. When phase transitions take place in the fuels, the functions are built in a piece-wise manner.

THERMODYNAMIC SPACE

We analyze the detonation and combustion processes occurring in SDF explosions in the $u-T$ plane of specific internal energy versus temperature [1, 2]. Figure 2 provides a typical example for TNT and PETN charges, as calculated by the CHEETAH code of Fried [18]. Curves represent the locus of detonation products states along the expansion isentrope, starting at the Chapman-Jouguet (CJ) point, and expanding to 1 bar. At temperatures above 1,800 K, products are in thermodynamic equilibrium. According to Rhee [19], detonation products composition becomes frozen when temperatures drop below 1,800 K (point F). The horizontal line represents the detonation process as a transformation from reactants to products at constant energy and volume, terminating at point UV. These so-called Constant Volume Explosions (CVE) result in temperatures of 2,700 K and 4,223 K for TNT and PETN respectively. The corresponding heats of detonation are $\Delta H_d = -818$ cal/g and 1,423 cal/g for TNT and PETN, and are indicated in the figure. These theoretical heats of detonation agree with calorimeter measurements of Ornellas [20]. The CJ temperatures are considerably higher due to compressive heating by the detonation (3,186 K and 4,600 K for TNT and PETN, respectively).

Figure 3 presents the loci of states for these fuels and air, extended up to 6,000 K. The detonation products curves represent *composite curves* defined as loci possessing the CJ entropy, with frozen composition below 1,800 K and equilibrium composition above 1,800 K. The air curve corresponds to an equilibrium isobar (10 bars). Also shown is the locus of states for Aluminum. Jumps in the curves correspond to phase changes.

Figure 4 presents the Combustion Products (CP) curves for PETN/TNT composite charges. The CP curves correspond to stoichiometric mixtures of TNT-air ($\sigma_s = 3.35$) and PETN-air ($\sigma_s = 0.482$) where the combustion products are in thermodynamic equilibrium at a pressure of 10 bars. Horizontal lines represent adiabatic combustion (i.e., material transformations from reactants to products at constant energy and volume); their intersection

with their products curve establishes the adiabatic combustion temperature (T_c) indicated on the abscissa: 2,900 K for TNT-air and 3,175 K for PETN-air, respectively. The corresponding Heats of Combustion are $\Delta H_c = -840.5$ cal/g$_{\text{TNT}}$ and $\Delta H_c = -1{,}371$ cal/g$_{\text{PETN}}$ for TNT and PETN; these theoretical values agree with calorimeter measurements of Ornellas [20].

Figure 5 presents the Combustion Products (CP) curves for Al-SDF charges. The curves correspond to stoichiometric mixtures of PETN-air ($\sigma_s = 0.482$) and Al-air ($\sigma_s = 4.03$). As in Fig. 4, they represent loci of equilibrium states along the 10-b isobar. Horizontal lines correspond to adiabatic combustion; their intersection with their own products curve establishes the adiabatic combustion temperature (T_c) indicated on the abscissa: 3,175 K for PETN-air and 4,120 K for Al-air, respectively. The Heat of combustion is $\Delta H = -1{,}473$ cal/g$_{\text{Al}}$ for Al-air.

QUADRATIC MODEL

These states have been fit with quadratic functions:

$$u_k(T) = a_k T^2 + b_k T + c_k \qquad (k = A, DP, R, P) \qquad (1)$$

These functions (curves) do an excellent job at fitting the computed thermodynamic states (data points) as demonstrated in Fig. 2. (see Appendix for values of a_k, b_k, c_k). Given the internal energy and composition Y_k in a cell, (1) can be solved to find the temperature. For a pure cell ($Y_k = 1$) one finds:

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

For computational cells containing a mixture of components, the *Intensive-variable Addition Law* is used to calculate the mixture energy:

$$u_m = \sum_k Y_k u_k = a_m T_m^2 + b_m T_m + c_m \qquad (3)$$

The mixture temperature is calculated from the inversion of (3):

$$T_m = [-b_m + \sqrt{b_m^2 - 4a_m(c_m - u_m)}]/2a_m \qquad (4)$$

while the mixture properties are determined from:

$$a_m = \sum_k Y_k a_k\,,\ b_m = \sum_k Y_k b_k\,,\ c_m = \sum_k Y_k c_k\,,\ R_m = \sum_k Y_k R_k \qquad (5)$$

For pure cells ($Y_k = 1$) the pressure is calculated from the following:

$$p_k = \begin{cases} \rho_k R_k T_k & k = A,R,P \\ p_{JWL}(\rho, \mathrm{T}) & k = DP \end{cases} \tag{6}$$

In the above, the detonation products (DP) are described by the JWL function:

$$p_{JWL}(\rho,T) = A\left[1 - \frac{\omega}{R_1 \mathrm{v}}\right]\exp(-R_1 \mathrm{v}) + B\left[1 - \frac{\omega}{R_1 \mathrm{v}}\right]\exp(-R_2 \mathrm{v}) + \rho R_{DP} T \tag{7}$$

where v represents the specific volume ratio: $\mathrm{v} = v/v_0 = \rho_0/\rho$. In [14] we showed that for PETN and TNT, $p_{JWL} v/RT = 1$ when $\mathrm{v} > 28$, so the exponential terms are only important during the initial expansion phase.

In mixed cells, the mixture pressure is calculated from the mixture temperature by the *Law of Additive Pressures* [21]:

$$p_m = \sum_k p_k(V_m, T_m) \tag{8}$$

where $p_k(V_m, T_m)$ denotes the pressure that would be exerted by component k if it existed alone at the temperature and volume of the mixture.

DISCUSSION OF ASSUMPTIONS

We ask the question: *"what is the locus of thermodynamic states that properly describes expanded detonation products (DP) gases?"* This is explored in Fig. 6 for PETN. The black curve is the loci of states with the CJ entropy $S_{CJ} = 1.96$ cal/g where the species are in chemical equilibrium. Its value at room temperature does not agree with the heat of detonation $\Delta H_d = -1{,}490$ cal/g as measured in a calorimeter [20]. The red curve represents an isentrope ($S_{CJ} = 1.96$ cal/g) with a fixed composition ϕ_k^F (equal to the species composition of the CJ isentrope state at $T_F = 1{,}800$ K). The green curve represents an isobar (p=10 bar) with the same fixed composition ϕ_k^F. Both curves agree with the measured heat of detonation $-1{,}490$ cal/g. Below 3,500 K, the isobar locus is identical to the isentrope locus (both with ϕ_k^F), proving that the specific internal energy is only a function of temperature $u = f(T, \phi_k^F)$ in this temperature regime. This is a property of a perfect gas. In other words, the detonation products behave as a calorically-perfect gas over the range $300K < T < 3{,}500\mathrm{K}$. Above 3,500 K, the specific internal energy of the detonation products is a function of two thermodynamic variables: $u = g(T, v)$. Since temperatures are rarely above 3,500 K (except at shock convergence points), we ignored these imperfect gas effects and defined the u-T relation for

PETN and TNT for T>3,500 K as the equilibrium isentrope (thereby avoiding the two-dimensional fits required to represent $u = g(T,v)$).

The loci of states for Combustion Products from a stoichiometric mixture of PETN detonation products gases with air is presented in Fig. 7. The Products curves are equilibrium isobars. Below 3,500 K, the curves are identical, proving that the Products behave as a perfect gas for T<3,500 K. For T>3,500 K we used the 10-bar curve to define the $u - T$ Products relation: $u = f(T, p = 10\,bar)$.

CONCLUSIONS

We have established the locus of thermodynamic states encountered in SDF explosions. For the detonation products gases, the locus is a composite CJ isentrope (with fixed composition below 1,800 K and equilibrium composition above 1,800 K). For the combustion products, the locus is the 10-bar equilibrium isobar. By CHEETAH code calculations we have proven that both the Detonation Products and the Combustion Products behave as calorically-perfect gases for temperatures below 3,500 K.

These loci were fit with quadratic functions suitable for defining the equations of state needed in numerical simulations of SDF explosions.

This formulation allows both the afterburning of the booster charge and the combustion of the fuel in SDF explosions (i.e., two combustion processes). This Model can accommodate additional combustion processes, such as the combustion of hydrocarbon clouds interacting with SDF explosions. It is therefore an extension and generalization of the thermodynamic modeling presented in the previous ICT conferences [1, 2].

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Table 1. Air EOS (10 bar): Piece-wise Quadratic Model\

Region *i*	a_A^i	b_A^i	c_A^i
1 (300—2,340K)	2.02768 E-5	0.16498	-71.9172
2 (2,340—3,700K)	1.34322 E-4	-0.41045	658.24424
3 (3,700—4,150K)	7.01281 E-5	0.11507	-403.36139
4 (4,150—4,530K)	-1.02084 E-4	1.53731	-3,340.674
5 (4,530—6,000K)	4.04923 E-5	0.11381	198.38643

Table 2. PETN detonation products EOS (CJ isentrope): Piece-wise Quadratic Model

Region *i*	a_{DP}^i	b_{DP}^i	c_{DP}^i
1 (300—2,340K)	3.31674 E-5	0.20867	-1,890.164
2 (2,340—3,700K)	5.97088 E-5	0.0377	-1,634.868
3 (3,700—4,150K)	1.9052 E-4	-0.89226	20.04935
4 (4,150—4,530K)	2.28177 E-4	-1.20053	651.0422
5 (4,530—6,000K)	1.78281 E-4	-0.774255	-248.616

Table 3. PETN-air combustion products EOS (10 bars): Piece-wise Quadratic Model

Region *i*	a_{CP}^i	b_{CP}^i	c_{CP}^i
1 (300—2,340K)	4.745 E-5	0.1549	-1,555.6
2 (2,340—3,700K)	4.6038 E-4	-1.7722	711.74
3 (3,700—4,150K)	4.9083 E-4	-1.841	558.87
4 (4,150—4,530K)	-6.1549 E-4	7.3463	-18,515.0
5 (4,530—6,000K)	-2.8216 E-4	3.8022	-9,254.5

Table 4. TNT detonation products EOS (CJ isentrope): Piece-wise Quadratic Model

Region *i*	a_{DP}^i	b_{DP}^i	c_{DP}^i
1 (300—2,340K)	5.3244 E-5	0.17393	-941.33
2 (2,340—3,700K)	7.9903 E-5	0.035886	-760.12
3 (3,700—4,150K)	0	1.80555	-6211.8
4 (4,150—4,530K)	4.5108 E-4	-2.7713	5,014
5 (4,530—6,000K)	2.578 E-3	-22.917	52,697

Table 5. TNT-air combustion products EOS (CJ isentrope): Piece-wise Quadratic Model

Region *i*	a_{CP}^i	b_{CP}^i	c_{CP}^i
1 (300—2,340K)	3.5282 E-6	0.25361	-949.3
2 (2,340—3,700K)	2.5302 E-4	-0.80169	168.08
3 (3,700—4,150K)	-6.1238 E-5	1.5345	-4,178
4 (4,150—4,530K)	-3.9217 E-4	4.2413	-9,713.6
5 (4,530—6,000K)	2.7654 E-5	0.2432	-195

Table 6. Al inert EOS: Piece-wise Quadratic Model

Region *i*	a_{Al}^i	b_{Al}^i	c_{Al}^i
1-5 (300—6,000K)	0	0.28128	-8.3895

Table 7. Al-Air combustion products EOS (10 bar): Piece-wise Quadratic Model

Region *i*	a_P^i	b_P^i	c_P^i
1 (300—2,340K)	1.76153E-5	0.20186	-1,553.62
2 (2,340—3,700K)	1.49115 E-5	0.2502	-1,554.5182
3 (3,700—4,150K)	0.00113	-7.95255	13,553.8
4 (4,150—4,530K)	0.00826	-67.29752	137,084.51
5 (4,530—6,000K)	5.03544 E-5	-0.07059	1,216.0279

Table 8. Molecular mass for components

Component	**condition**	**MW** (g/mole)
Air	p=10 bars, $T < 3{,}000K$	28.85
PETN detonation products	isentrope, $T = 1{,}800K$	28.76
PETN-air combustion products ($\sigma_s = 0.482$)	p=10 bars, $T_a = 3{,}200K$	27.75
TNT detonation products	isentrope, $T = 1{,}800K$	26.93
TNT-air combustion products ($\sigma_s = 3.35$)	p=10bars, $T_a = 2{,}900K$	29.65
Al-air combustion products ($\sigma_s = 4.03$)	p=10bars, $T_a = 4{,}120K$	40.78

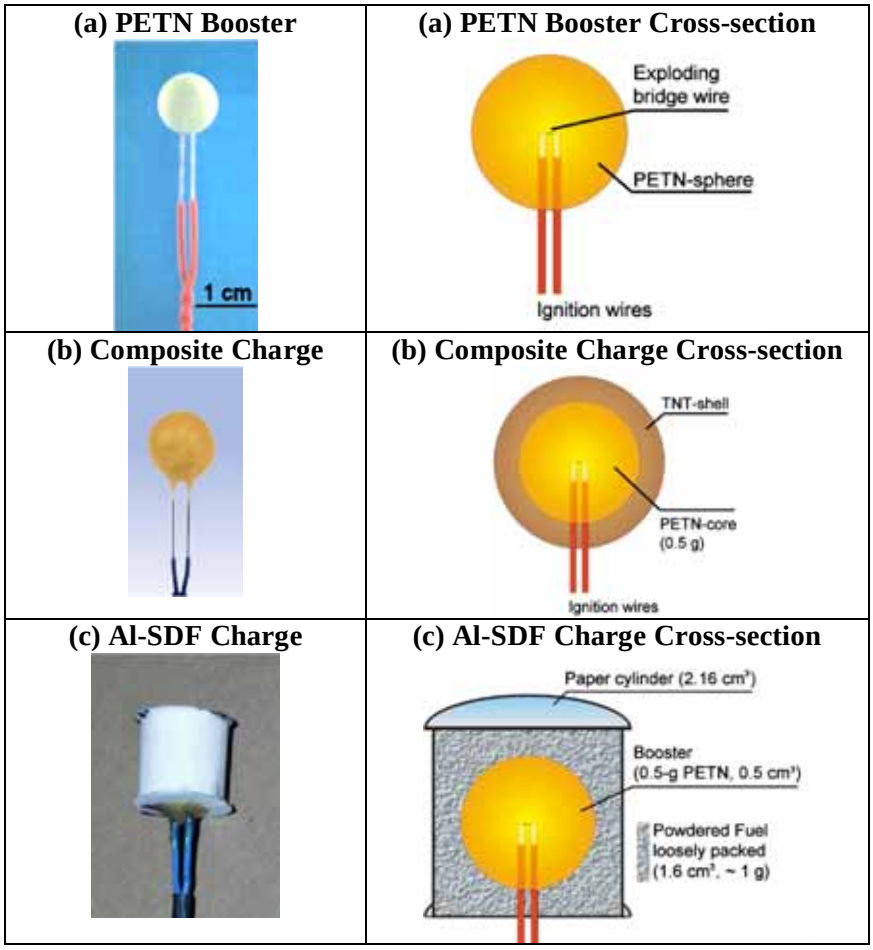

Figure 1. Charge construction: (a) 0.5-g PETN booster charge; (b) composite charge (0.5-g PETN booster + 1-g TNT shell); (c) Al-SDF charge (0.5-g PETN booster + 1-g Aluminum).

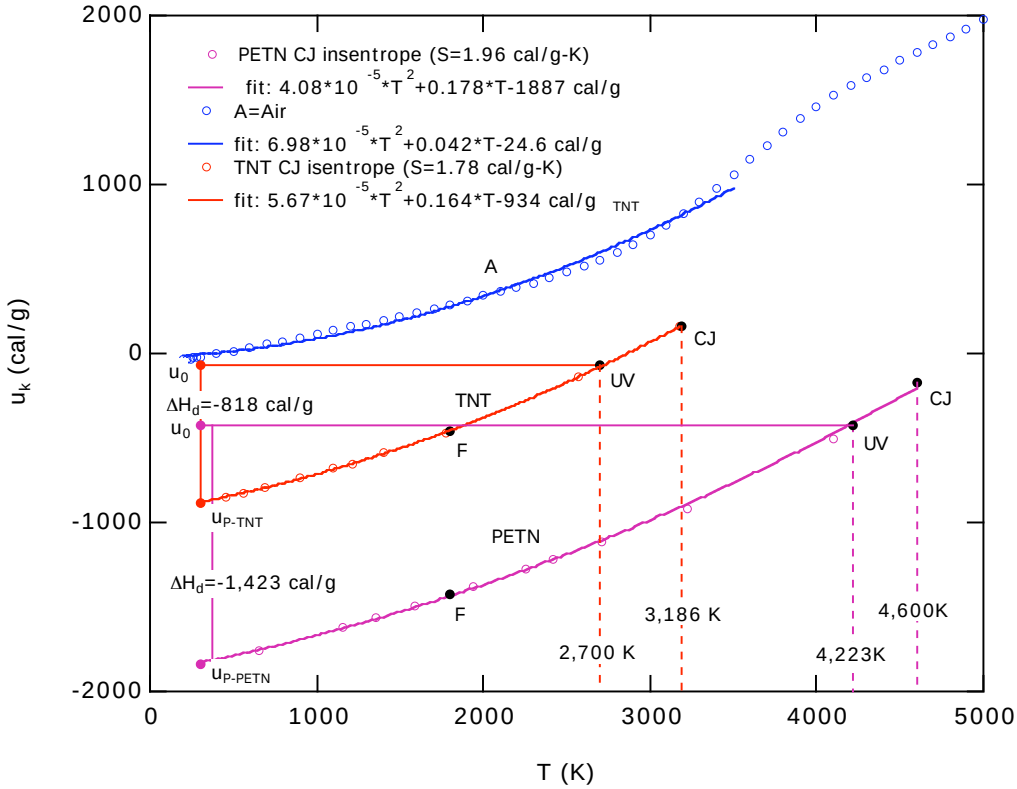

Figure 2. Detonation products loci for TNT and PETN charges ($\rho_0 = 1 g/cc$). Curves TNT and PETN represent the locus of detonation products states along the expansion isentrope, starting at the CJ point, and expanding to 1 bar. Products composition becomes frozen for T<1,800 K (below point F).

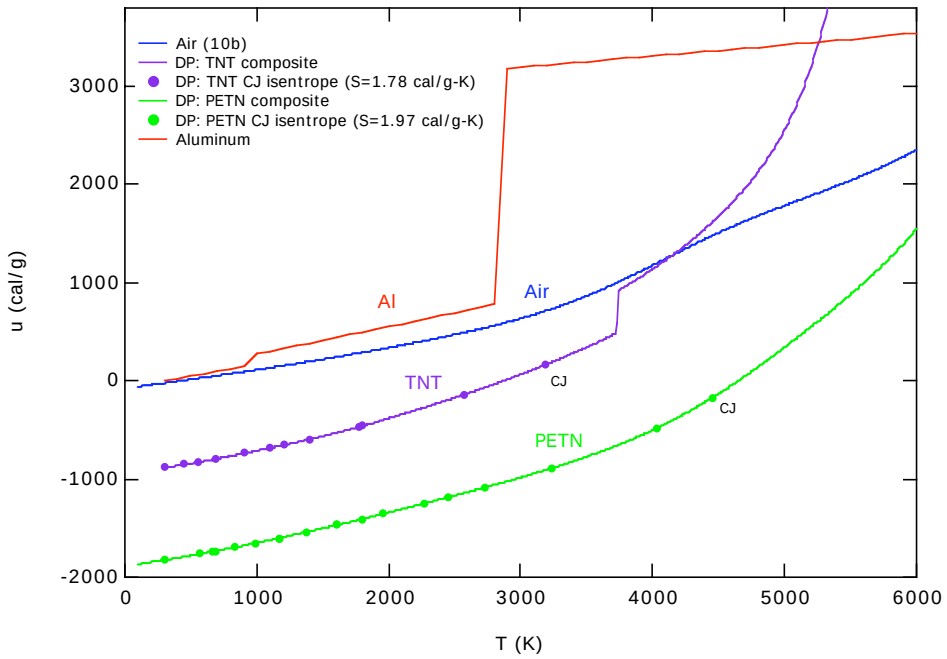

Figure 3. Loci of thermodynamic states for various fuels (Al; TNT and PETN isentropes) and air.

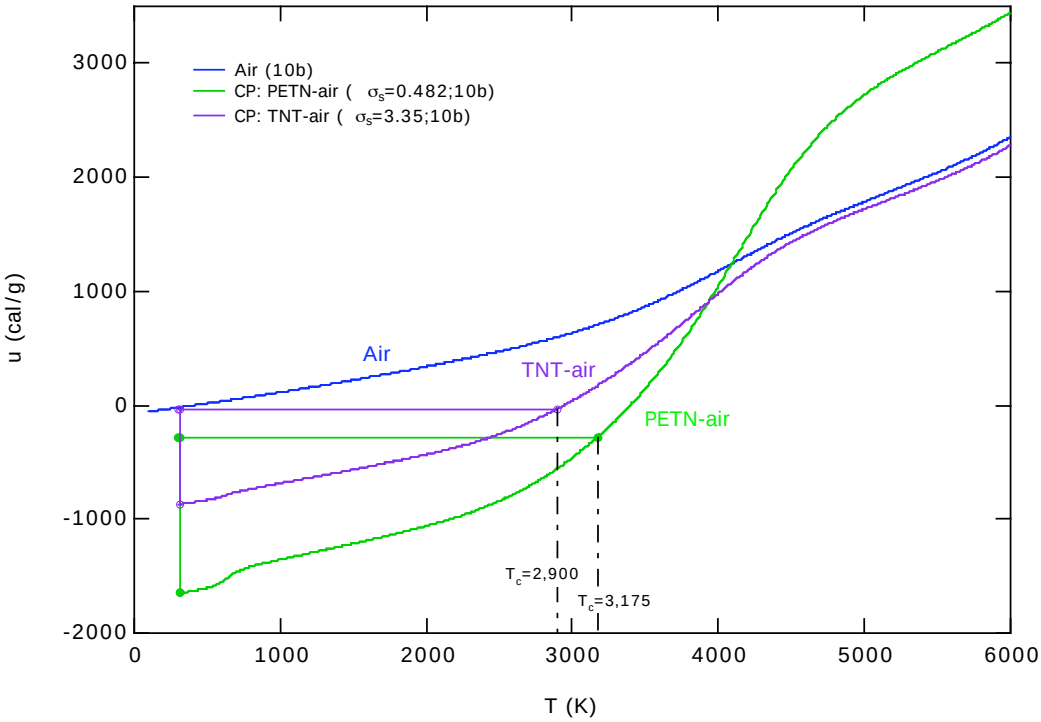

Figure 4. Combustion Products (CP) loci for stoichiometric mixtures of TNT-air ($\sigma_s = 3.35$) and PETN-air ($\sigma_s = 0.482$) in thermodynamic equilibrium (p = 10 bars). Horizontal lines represent adiabatic combustion.

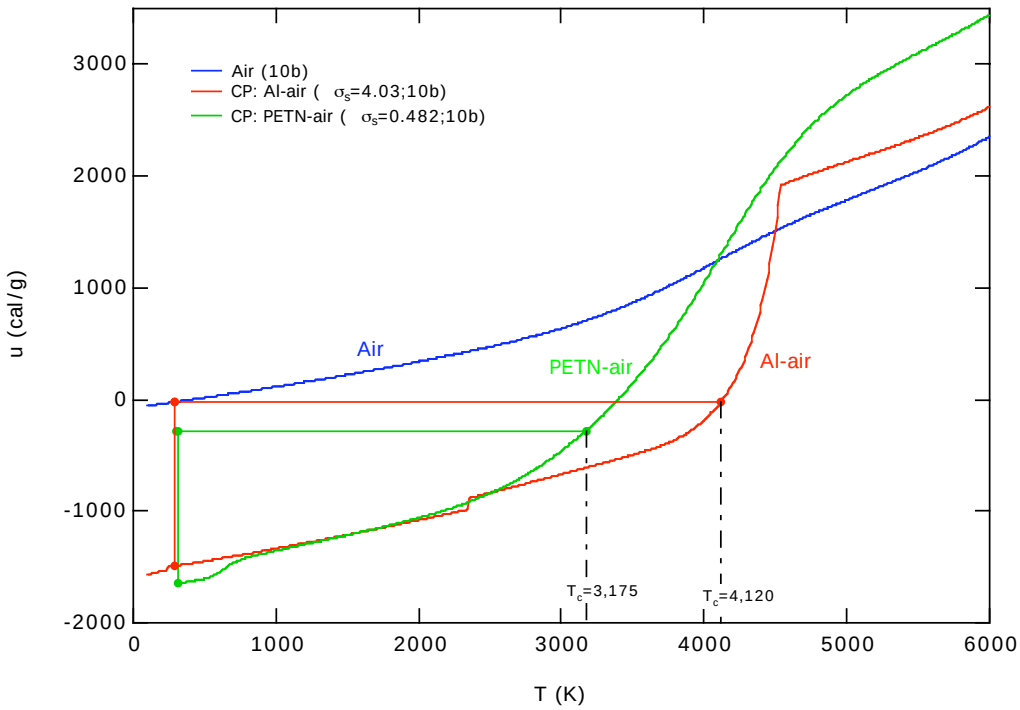

Figure 5. Combustion Products (CP) loci for stoichiometric mixtures of PETN-air ($\sigma_s = 0.482$) and Al-air ($\sigma_s = 4.03$) in thermodynamic equilibrium (p = 10 bars). Horizontal lines represent adiabatic combustion.

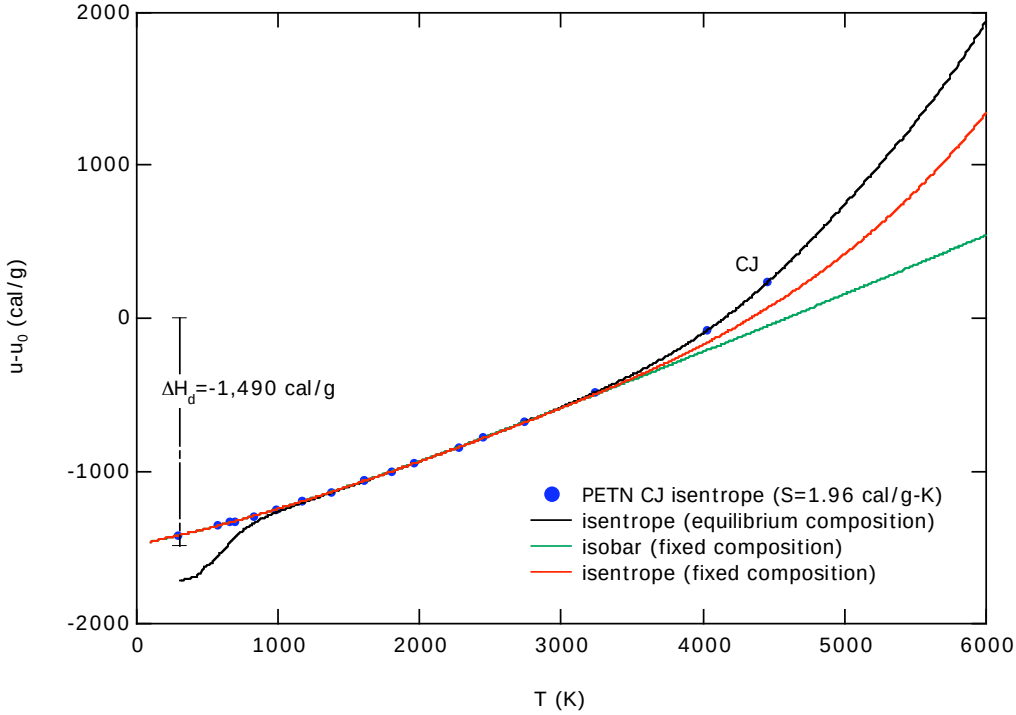

Figure 6. Loci of states for detonation products gases of PETN as calculated by the CHEETAH code.

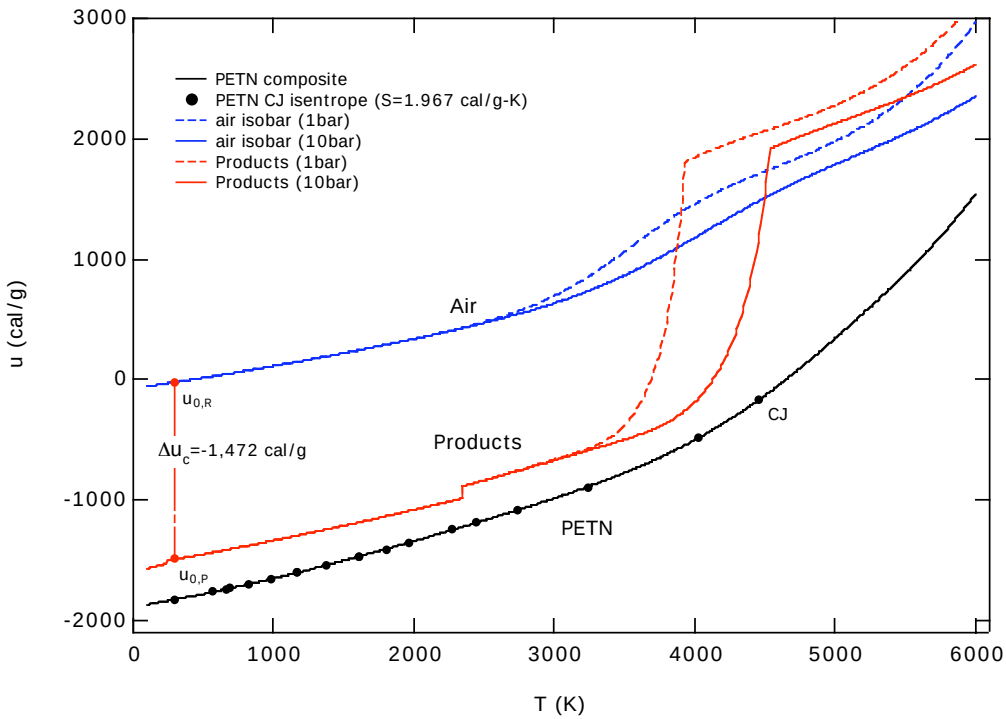

Figure 7. Loci of states for Combustion Products from a stoichiometric mixture of PETN detonation products gases with air, as calculated by the CHEETAH code. Products are assumed to be in thermodynamic equilibrium.