Thermodynamic Solution for Combustion of PETN/TNT Products with Air

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Introit

We consider the explosion of a 1.5-g spherical PETN/TNT charge in air in a 6.6-l calorimeter [1]. The hot detonation products are rich in fuel ($C_{(s)}$, CO and H_2), and when they mix with air, they release 2,500 cal/g (in addition to the 1,100 cal/g released by the detonation) by a non-premixed turbulent combustion process [2]. Here we trace the evolution of combustion in *Thermodynamic State Space*—to elucidate the mechanisms (constraints) that control this process. The analysis is formulated in the *Le Chatelier* plane of Oppenhiem [3], i.e., specific-internal-energy versus temperature diagram, shown in Fig. 1. The thermodynamic properties of the components *k* (Fuel-*F*, Air-*A*, Reactants-*R*, and Products-*P*) were computed by the Cheetah code [4], and fit with quadratics to establish the Equations of State (EOS) of the components:

$$u_{k}(T_{k}) = a_{k}T_{k}^{2} + b_{k}T_{k} + c_{k} \qquad (k = F, A, R, P)$$
(1)

These quadratic EOS functions (curves in Fig. 1) well approximate the thermodynamic values (circles in Fig. 1) and fully characterize the thermodynamic behavior of the system [4]. Combining this with a combustion model, we find a *combustion locus* in thermodynamic space; we show that this locus is a strong attractor to numerical simulations of the combustion field.

Thermodynamics

We divide the process into two steps: (i) mixing: of F and A to form R; (ii) combustion: material transformation from R to P in a thermodynamically-isolated chamber. Mixing is governed by:

Mass:
$$Y_F + Y_A = 1$$
(2)

Volume:
$$Y_F \cdot v_F + Y_A \cdot v_A = v_c \tag{3}$$

Energy:
$$Y_F \cdot u_F + Y_A \cdot u_A = u_c(\sigma_c)$$
(4)

where the specific volume of the chamber is given by $v_c = V_c/(m_F + m_A)$, and $\sigma_c = Y_A/Y_F = 5.37$ represents the chamber air/fuel ratio. Given the initial conditions ($T_A = 300K \& T_F = 3,070K$), the constraint (4) specifies the chamber energy: $u_c(\sigma_c) = -45 \ cal/g$ and reactants temperature $T_R = 1,032 \ K$. Fuel and air combine in σ_c proportions to form reactant $R(\sigma_c)$. Combustion at constant energy and volume (UV) is expressed by:

Mass: $Y_R + Y_P = 1 \tag{5}$

Volume:
$$Y_R \cdot v_R + Y_P \cdot v_P = v_c \tag{6}$$

Energy:
$$u_p = u_R = u_c(\sigma_c) \tag{7}$$

Constraint (7) provides the *combustion locus*: $u_p = u_R = u_c(\sigma_c)$ depicted in Fig. 1 as the R-P line.

Gas Dynamics

We model evolution of the combustion field in the limit of large Reynolds and Peclet numbers. Then the flow field is governed by the multi-component gas-dynamics for the mixture (*m*):

Mass:
$$\partial_t \rho_m + \nabla \cdot (\rho_m \mathbf{u}) = 0$$
 (8)

Mom

nentum:
$$\partial_t \rho_m \mathbf{u} + \nabla \cdot (\rho_m \mathbf{u} \mathbf{u}) = -\nabla p_m$$
 (9)

Energy:
$$\partial_t \rho_m(u_m + \mathbf{u} \cdot \mathbf{u}/2) + \nabla \cdot \rho_m(u_m + \mathbf{u} \cdot \mathbf{u}/2)\mathbf{u} = -\nabla \cdot (p_m \mathbf{u})$$
 (10)

Components:

$$\partial_t Y_k + \mathbf{u} \cdot \nabla Y_k = \alpha_k \dot{Y}_s$$
 with $\sum_k Y_k = 1$ (11)

where k = F, A, P and $\alpha_k = \{-1, -\sigma_s, (1 + \sigma_s)\}$ denotes the stoichiometric source/sink coefficients based on the stoichiometric air/fuel ratio: $\sigma_s = 2.77$. The term \dot{Y}_s embodies kinetic effects. Here it is modeled by the fast-chemistry, large-Damköhler-number limit which is consistent with the gas dynamic model (8-11). This system is closed by Equations of State (EOS) for components-k(A1, A2, A5 & A7) of Fig. 2, while mixture EOS is based on the mixing laws for perfect gases:

Mixture EOS:
$$T_m = [-b_m + \sqrt{b_m^2 - 4a_m(c_m - u_m)}]/2a_m \& p_m = \rho_m R_m T_m$$
 (12a,b)

Mixture Properties:
$$a_m = \sum_k Y_k a_k$$
, $b_m = \sum_k Y_k b_k$, $c_m = \sum_k Y_k c_k$, $R_m = \sum_k Y_k R_k$ (13a,b,c,d)

The above model equations (8-11) were integrated using a high-order Godunov scheme, and Adaptive Mesh Refinement (AMR) was used to follow the thin reaction zones on the grid. We simulated the explosion and combustion of 1.5-g PETN/TNT charge in a 6.6-l cylinder; details of this numerical simulation are described in a companion paper of this Colloquium [5].

Projection

The numerical solution was projected from physical space to Thermodynamic space via the following volume-averaging operators:

Mass:
$$\overline{M}_m(t) = \sum_k \overline{M}_k(t)$$
 where $\overline{M}_k(t) = \int_{V_c} \rho_k(t, \mathbf{x}) dV$ (14a,b)

Amagat's Law:	$\overline{V}_m(t) = \sum_k \overline{V}_k(t)$	where $\overline{V}_k(t) = \int_{V_c} N_k(t, \mathbf{x}) dV / N_m$	(15a,b)
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Dalton's Law:
$$\overline{p}_m(t) = \sum_k \overline{p}_k(t)$$
 where $\overline{p}_k(t) = \int_{V_c} p_k(t, \mathbf{x}) dV / V_c$ (16a,b)

Specific Energy:
$$\overline{u}_m(t) = \sum_k \overline{u}_k(t)$$
 where $\overline{u}_k(t) = \int_{V_c} \rho_k(t, \mathbf{x}) u_k(t, \mathbf{x}) dV / \overline{M}_k(t)$ (17a,b)

Specific Entropy:
$$\overline{s}_m(t) = \sum_k \overline{s}_k(t)$$
 where $\overline{s}_k(t) = \int_{V_c} \rho_k(t, \mathbf{x}) s_k(t, \mathbf{x}) dV / \overline{M}_k(t)$ (18a,b)

Temperature:
$$\overline{RT}_m(t) = \sum_k \overline{R_k T_k}(t)$$
 where $\overline{R_k T_k}(t) = \int_{V_c} \rho_k(t, \mathbf{x}) R_k T_k(t, \mathbf{x}) dV / \overline{M}_k(t)$ (19a,b)

where V_c denotes the volume of the chamber.

Solution

Temporal Space

The evolution of the mean thermodynamic variables from the numerical solution (averaged over V_c) is presented in temporal space in Figs. 3 and 4. While *component variables* in general change over time due to combustion, conserved variables such as the *mixture mass, volume* and *energy* remain constant—thereby illustrating conservation principles (2)-(7) for the system. In addition, Figs. 3b and 3d illustrate Amagat's Law of partial volumes and Dalton's Law of partial pressures, respectively, for the mixture.

Thermodynamic Space

The mean solution is presented in Thermodynamic Space in Figs. 5-8. In this depiction, time appears only implicitly as the evolution parameter that links corresponding thermodynamic values, depicted as data points (circles) on those figures. Figure 5 presents the evolution of numerical solution in the u-T plane. Computed points for fuel, air and products lie on the F, A and P lines corresponding to the equation of state functions (1). Computed points for the mixture rapidly (by 0.1 ms) approach the combustion locus: $u_c = -45 \ Cal/g$ denoted as the R-P curve. Figure 6 presents the numerical solution in the p-v plane. Computed points for the mixture lie along the combustion isochor: $v_c = 690 \ cc/g$ (red curve R-P). Figure 7 presents the numerical solution and products isochor. Figure 8 presents the numerical solution in the s-T plane. While the reactants and products entropies obey the usual logarithmic dependence on temperature, the mixture entropy exhibits a *linear* dependence on temperature—in accordance with the linear mixing laws (18)-(19) of perfect gases.

Model

The above comparisons suggest the following model for the thermodynamic solution of combustion in a chamber (denoted by subscript c):

Temperature:	$T_c(t) = T_R + Y_P(t)[T_P - T_R]$	(20)
1		· /

Pressure: $p_c(t) = p_R + Y_P(t)[p_P - p_R]$ (21)

Entropy:
$$s_c(t) = s_R + Y_P(t)[s_P - s_R]$$
(22)

Here the model parameters ($T_R = 1,032K \& T_P = 2,249K$; $p_R = 4.40 bars \& p_P = 8.98 bars$; $s_R = 0.25 cal/g - K \& s_P = 0.78 cal/g - K$) come from the thermodynamic solution, while the products function $Y_P(t)$ comes from the gas-dynamic solution. In the present case, the products function is well approximated by the exponential:

Products:
$$Y_{p}(t) = 1 - e^{-1.2t}$$
 (23)

This model is depicted in Fig. 9. One can see that the numerical solution (circles) lies close to the model functions (20)-(22), thereby validating the model of this process.

Assessment

To assess the validity of the model, we have compared the theoretical model predictions with experimental data; results are shown in Table 1. For the 0.5-g PETN booster charge, the model predicts 2.75 bars versus the measured value of 2.66 bars; their ratio suggests that 97% of the charge detonated. For the composite charge (0.5-g PETN + 1.0-g TNT) in nitrogen, the model predicts 4.4 bars versus the measured value of 3.6 bars; their ratio suggests that 82% of the charge detonated. For the composite charge in air, the model predicts 8.98 bars versus the measured value of 8.35 bars; their ratio suggests that 93% of the charge was consumed by combustion during the course of the experiment.

CASE	\overline{p}_c (bars)	$\varepsilon_p ~(\%)$	T (K)
PETN booster charge:			
experiment (in N_2)	2.66 ± 0.07	97%	—
Thermodynamic Model (in N_2)	2.75	—	
PETN/TNT Composite charge: experiment (in N_2) Thermodynamic Model (in N_2) experiment (in air) Thermodynamic Model (in air)	3.60±0.2 4.40 8.35±0.28 8.98	82% — 93% —	 1,032 K 2,249 K

Table 1. Comparison of experimental data with theoretical predictions.

Résumé

Mixing and combustion in a thermodynamically-isolated chamber is controlled by u_c : the initial energy in the system. It establishes not only the initial state (temperature) of the reactants and the final state (temperature) of the products, but also the locus of combustion states in *thermodynamic space*. Implementing the quadratic EOS model for stoichiometric combustion in the multi-component gas dynamic conservation laws allows one to simulate the evolution of combustion in *physical space*. Note that combustion in physical space always occurs under locally stoichiometric conditions ($\sigma_s = 2.77$), while the combustion locus represents global combustion effects for the chamber (i.e., at the chamber stoichiometry: $\sigma_c = 5.37$). The most important contribution of this paper is that we show that the gas dynamic solution, when projected from physical space to thermodynamic space, rapidly approaches the combustion locus is a *strong attractor* for this reactive system. This model is especially useful in cases where the kinetics of the system is not known.

Acknowledgements

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. It was sponsored by the Defense Threat Reduction Agency under IACRO # 05-4071.

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Appendix: Equations of State for the Composite PETN/TNT Charge

FUEL:
$$u_F = 4.5897 \times 10^{-5} \times T^2 + 0.17923 \times T - 1168.3 \text{ (cal/g}_F)$$
 (A1)

AIR:
$$u_A = 1.8611 \times 10^{-5} \times T^2 + 0.16741 \times T - 72.2$$
 (cal/g_A) (A2)

The fuel and air are assumed to mix at frozen composition to form reactants at an air/fuel ratio of $\sigma = Y_A / Y_F$; Reactants properties may be calculated from:

$$u_{R}(\sigma) = (u_{F} + \sigma u_{A})/(1 + \sigma)$$
(A3)

REACTANTS:
$$u_R(\sigma_c) = 4.395 \times 10^{-5} \times T^2 + 0.11775 \times T - 220.1 \text{ (cal/g}_R)$$
 (A4)

REACTANTS:
$$u_R(\sigma_s) = 7.5607 \times 10^{-5} \times T^2 + 0.041931 \times T - 302.32 \text{ (cal/g}_R)$$
 (A5)

where $\sigma_c = 5.367$ and $\sigma_s = 2.773$. The products are assumed to be in thermodynamic equilibrium; at a pressure of 1 bar, a fit to Cheetah calculations gives

PRODUCTS:
$$u_p(\sigma_c, 1 \text{ b}) = 7.454 \times 10^{-5} \times T^2 + 0.060714 \times T - 524.5 \ (cal/g_p)$$
 (A6)

PRODUCTS:
$$u_P(\sigma_s, 1 \text{ b}) = 10.458 \times 10^{-5} \times T^2 + 0.011104 \times T - 848.5 \text{ (cal/g_P)}$$
 (A7)

JWL Parameters: Charge (0.333-PETN; 0.667-TNT) @ $\rho_0 = 1.0$ g/cc, MW=250.658 g/mol A = 5.20719 Mbars, B = 0.13133 Mbars, C = 0.937 $R_1 = 7.00, R_2 = 1.868, \omega = \gamma - 1 = 0.347, \Gamma = 2.659$ $\Delta H_d = -935 \text{ cal/g}_{\text{F}}$ $\Delta H_c = -825.3 \text{ cal/g}_{\text{F}} = -3,113.75 \text{ cal/g}_{\text{F}}$

Chapman-Jouguet jump conditions Shock velocity = 5.42269 km/s Particle velocity=1.48322 km/s Sound speed = 3.93946 km/sE0 = -178.26198 cal/g V_{CI} =0.7265 cc/g T_{CI} =3,628.6 K S_{CI} =1.872 cal/g-K $P_{CI} = 79,380.1$ bars $\Delta H_{CJ} = 1659.51 \text{ cal/g}$ $\Delta E_{CJ} = 262.92 \text{ cal/g}$



Figure 1. Locus of states in the Le Chatelier diagram for the combustion of the detonation products gases generated by the explosion of a composite (PETN/TNT) charge in the 6.6-liter calorimeter. Chamber stoichiometry is $\sigma_c = 5.367$.



Figure 2. Locus of states in the Le Chatelier diagram for stoichiometric combustion ($\sigma_s = 2.773$) of the explosion products from the composite (PETN/TNT) charge in the 6.6-liter calorimeter. The green lines illustrate combustion loci starting at 300K, 1000K and 1500 K.



Figure 3. Evolution of the mean thermodynamic variables of the components in the chamber.

(a) specific internal energies



Figure 4. Evolution of the mean specific internal energies and temperatures of the components in the chamber.



Figure 5. Evolution of the mean thermodynamic solution in the u-T plane. Numerical solution for the mixture is attracted to the Combustion Locus: $u_c = -45 \ Cal/g$ (R-P).



Figure 6. Evolution of the mean thermodynamic solution in the p - v plane. Numerical solution for the mixture rapidly approaches the combustion isochor: $v_c = 690 \ cc / g$ (R-P).



Figure 7. Evolution of the mean thermodynamic solution in the p-T plane. Numerical solution for the mixture rapidly approaches the combustion locus R-P.



Figure 8. Evolution of the mean thermodynamic solution in the s-T plane. Numerical solution for the mixture rapidly approaches the combustion locus R-P.



Figure 9. Comparison of computed mixture environment histories with the analytical chamber model: (a) mass fraction of products produced, (b) temperature, (c) pressure, (d) entropy.