

What exactly is meant by the positiveness of the expression $[C + B(ds/dq)]$ can be made clear by specializing the preceding theorem to the case of an ideal dissociating gas as introduced by Lighthill.⁵

For an ideal dissociating gas, we have, using Capioux and Washington,⁶ (under usual notations)

$$A = (\partial p / \partial \rho) S, \alpha^* = a_f^2 = RT \{ [(1 + \alpha^*)^2 / 3 + (1 + \alpha^*) \}$$

$$B = (\partial p / \partial S) \rho, \alpha^* = (\rho T / 3)(1 + \alpha^*)$$

$$C = (\partial p / \partial \alpha^*) \rho, S = (\rho / 3)(1 + \alpha^*)(\mu_1 - \mu_2) + \rho \{ RT - (D/3)(1 + \alpha^*) \}$$

where μ_1 and μ_2 are the chemical potentials of the atoms and molecules, respectively and α^* is the mass-fraction.

Further from the second law of thermodynamics we write

$$TdS = dh - (1/\rho)dp - (\mu_1 - \mu_2)d\alpha^*$$

Substituting the values of A, B, C and $ds/d\alpha^*$ from the preceding Eq. (16), we get

$$du/d\alpha^* = -\{ \hat{C} / [3(\hat{C}^2 - a_f^2)\rho] \} (3RT - D\alpha^* - D) \quad (17)$$

Conclusion

In the terminology of Capioux and Washington⁶ the first term in the bracket of Eq. (17), i.e. $3RT$ corresponds to a "sensible" internal energy e_s , and the second term ($D\alpha^*$) is taken as e_c , the internal energy of chemical bonding. Keeping this terminology in view we state the following theorem on simple waves in ideal dissociating gasdynamics: if the ratio of the difference of sensible internal energy e_s and the chemical bond energy e_c to the dissociation energy D per unit mass is such that it exceeds unity then the particle speed u , decreases or increases as the dissociation variable increases, according as the flow is supersonic or subsonic.

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Calculated Pulsating One-Dimensional Detonations with Induction-Zone Kinetics

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Nomenclature

- a = sound speed
 C = specific constant—pressure heat capacity

- D = detonation velocity
 E^\dagger = activation energy
 E^* = reaction rate parameter
 f = D^2/D_{CJ}^2 , degree of overdrive
 k = rate multiplier
 p = pressure
 Q = heat release parameter
 r = reaction rate
 R = specific gas constant
 x = distance
 t = time
 T = absolute temperature
 v = specific volume
 ε = reaction rate parameter
 γ = isentropic exponent
 λ = degree of reaction
 ρ = density

Subscripts

- 0 = initial state
1, 2 = species 1 and 2

ONE-DIMENSIONAL pulsating detonations similar to those previously reported¹ for first-order Arrhenius kinetics have been calculated for more realistic kinetics: a simple mockup of the branching-chain mechanism characterizing a large class of gaseous fuel/oxygen systems. The previous work used an idealized model of a gaseous detonation system consisting of a mixture of two polytropic gases with the same heat capacity and molecular weight, one transformed into the other by a first-order Arrhenius reaction. It was inspired by a linear analysis of the hydrodynamic stability of the one-dimensional steady solution in the piston-supported (overdriven) regime. This analysis² showed that the steady solution is, for some values of the parameters, unstable to one-dimensional perturbations as well as to three-dimensional ones; hence the interest in the simpler one-dimensional time-dependent calculation. This calculation gave in the unstable case a strongly pulsating detonation, with peak-to-peak front pressure amplitude not much less than the pressure of the unstable steady solution.

The computer program³ for the one-dimensional time-dependent calculation considers a single chemical reaction and assumes constant heat capacities. Our mockup of the branching-chain mechanism is constructed within this constraint. An accurate description requires much more detail: perhaps ten or more elementary chemical reactions and a comparable number of chemical species with temperature-dependent heat capacity. A computer program for calculating the one-dimensional steady solution with such a realistic representation is available at this laboratory; some results obtained with it are presented below for comparison.

The equation of state and rate used in the present time-dependent calculation are

$$pv = T, \quad E = (C - 1)T - \lambda Q; \quad C = C_1 + \lambda(C_2 - C_1) \quad (1)$$

$$r = k\rho(\lambda + \varepsilon)(1 - \lambda)e^{-E^\dagger/T - E^*\lambda}$$

The system is a mixture of two species with constant heat capacities C_1 and C_2 . Other symbols are the same as in Ref. 1, with the exception of the dimensionless constants ε and E^* here introduced into the rate. As before, p , v , and T are in units of their values in the initial state, E and Q are in units of RT_0 , and C is in units of R . The unit of time is the time required for a particle in the steady solution to react to $\lambda = \frac{1}{2}$ after it is shocked. The distance unit is a_0 times the time unit. The half-reaction-zone length is the distance of the $\lambda = \frac{1}{2}$ point from the steady shock.

All of the calculations reported here are started from an approximate steady-solution configuration, generated by programming the piston to follow the velocity history of a particle passing through the desired steady solution, specified by the final constant piston velocity approached in this prescription. This final piston velocity or the corresponding steady detonation velocity D is the single problem parameter characterizing the boundary conditions. We measure it by the "degree of over-

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drive" $f = D^2/D_{CJ}^2$. The rate multiplier k has no effect on stability, serving merely to set the time scale. In each calculation its value is chosen to place unit time at $\lambda = \frac{1}{2}$.

Several known detonable gas mixtures whose ignition is governed by a branched chemical chain reaction are composed of hydrogen or unsaturated hydrocarbons as fuel and oxygen as oxidizer.⁴ We center our attention on the specific system $2H_2 + O_2 + 9Ar$ at $p_0 = 0.1$ atm and $T_0 = 300^\circ K$, whose three-dimensional detonation structure has been well-characterized.⁵ We calculate its one-dimensional, steady Hugoniot behavior for Chapman-Jouguet (*CJ*) and overdriven waves, and the *CJ* reaction-zone pressure profile, using standard thermochemical data and a system of reaction steps⁶ and temperature-dependent rate coefficients derived from recent chemical kinetics sources.⁷⁻⁹ The *CJ* profile is shown as curve 1 of Fig. 1. Since there are many reactions there is no time unit which corresponds directly to the choice of unit time at $\lambda = \frac{1}{2}$ used for the one-reaction model; we have selected the half-pressure point: $p(t = 1) = \frac{1}{2}(p_n + p_{CJ})$, where p_n and p_{CJ} are the von Neumann and *CJ* pressures. The distance unit, a_0 times this time unit, is about 1 cm for this profile.

The early reaction is dominated by a branching chain mechanism, resulting in the induction period in which reaction grows exponentially but remains macroscopically negligible. The main reaction zone which follows is strongly exothermic. The rate-determining steps at $p_0 = 0.1$ atm are termolecular recombination reactions, and, at this initial pressure, this portion of the profile, hereafter called the exothermic zone, is much longer than the induction zone. As the initial pressure is increased, the exothermic zone becomes shorter relative to the induction zone. Less is known in detail about the chemistry of hydrocarbon-oxygen systems, but they do have a similar induction zone with about the same temperature dependence, and an exothermic zone whose length is more nearly equal to that of the induction zone.

The thermochemistry of the reaction products changes rapidly with temperature above the *CJ* point. The important effect is not the change in the frozen-composition heat capacity, which increases only slightly, but the shift in the equilibrium degree of dissociation of the reaction products. This reduces the net exothermicity, and becomes large enough at a degree of overdrive of $f \approx 2$ to reduce it to zero, so that the Hugoniot for no reaction and for equilibrium composition cross at this point in the $p-v$ plane.

Our parametric fluid model for the time-dependent calculation, Eqs. (1), has too few parameters to reproduce all of this behavior correctly, but we have achieved a reasonable representation of it by making the reaction proceed unidirectionally to nominal completion but formulating the exothermicity as $Q - (C_2 - C_1)T$ and introducing an artificially large difference between C_2 and C_1 : $C_2 = 6$, $C_1 = 3$, compared to both approximately 3 in the real system. These round-number values were chosen so that, in conjunction with the realistic value of D_{CJ} , they produce the approximately correct von Neumann and *CJ*

pressures shown in Fig. 1. This matching of the *CJ* pressure by adjusting Q and C_2 necessarily also yields a match to the equilibrium sound speed (and thus the $p-v$ slope of the equilibrium Hugoniot) at the *CJ* point. It also yields a close match to the higher temperature states along the strong detonation branch of the equilibrium Hugoniot, including its crossing of the no-reaction Hugoniot. This is accomplished at the expense of an unrealistically large heat capacity and potential exothermicity below the *CJ* temperature. One consequence of this is a somewhat reduced frozen sound speed in the reaction products, but this seems not to be a serious concession, since in typical finite amplitude disturbances (rarefaction and compression waves) the bulk of the energy is propagated at the equilibrium sound speed.³ Trial time-dependent calculations with C_2 only slightly larger than C_1 gave results qualitatively similar to those with the larger difference.

The parameter values we use are: $Q = 32$, $C_1 = 3$, $C_2 = 6$, $E^\dagger = 30$, $\epsilon = 10^{-4}$, $E^* = 0$, and $E^* = 9$. The activation energy is that reported by White⁴ for the induction zone. The steady

Table 1 Shock-pressure behavior

E^*	f	Amplitude ^a	Period	
			Time	Space ^b
9	1.000	2.0	3.1	9.6
0	1.225	30.0	7.0	28.0
0	1.250	4.5	1.7	5.5
0	> 1.500	stable

^a Peak-to-peak in pressure.

^b In half-reaction-zone lengths for the steady solution.

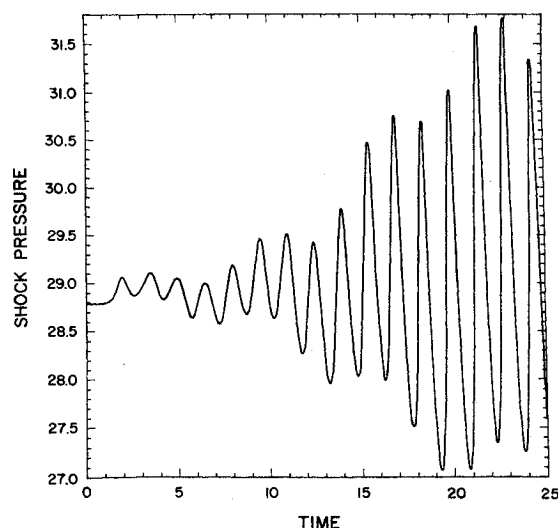


Fig. 2 Small-period oscillation at $f = 1.3$ for $\epsilon = 10^{-4}$, $E^* = 0$.

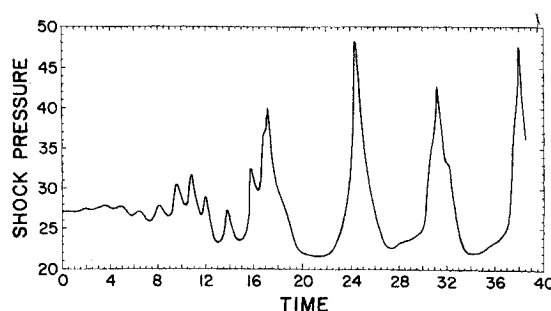


Fig. 3 Long-period pulsation at $f = 1.225$ for $\epsilon = 10^{-4}$, $E^* = 0$. Note the change in vertical scale from Fig. 2.

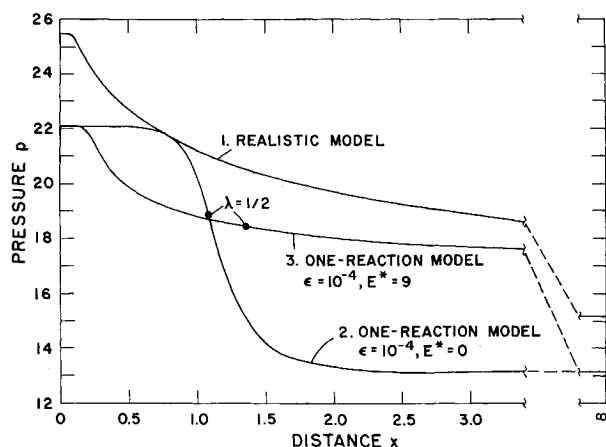


Fig. 1 Calculated Chapman-Jouguet steady-solution profiles.

profiles calculated with these in Eqs. (1) are shown as curves 2 and 3 of Fig. 1. That for $E^* = 9$ represents roughly the hydrogen/oxygen system at $p_0 = 0.1$ atm; that for $E^* = 0$ is more like a hydrocarbon system, or hydrogen/oxygen at higher density. Note that the distance scale for these would be considerably shortened had the half-pressure point chosen for curve 1 been used instead of $\lambda = \frac{1}{2}$ to set the time unit.

Accuracy comparable to that in the previous work¹ was maintained in the present time-dependent calculations, at the cost of using a net several times finer.

Results

Results are presented in Table 1 and Figs. 2 and 3. The $E^* = 9$ calculation is believed to be near a stability boundary, so that a larger f or larger E^* should stabilize it. For $E^* = 0$, the steady solution is stable at large f , is unstable with small amplitude and high frequency between $f \doteq 1.5$ and $f \doteq 1.25$, and unstable with large amplitude and lower frequency between $f \doteq 1.25$ and $f = 1$. At $f = 1$, an incomplete calculation, carried to a point just beyond the minimum of the valley after the first large peak ($t = 28$ in Fig. 3) suggests that both the period and amplitude are a little larger than at $f = 1.25$.

Discussion

The principal difference between these results and those previously reported is the order of appearance of the high and low-frequency components as f is decreased (for $E^* = 0$). In the previous work the low-frequency components appear first, whereas here the high-frequency components appear first. At $E^* = 9, f = 1$, the oscillation is similar to the high frequency one at $E^* = 0$. From the limited parameter study undertaken, we are inclined to believe that the change in the form of the rate function is more important than the choice of different equation of state parameters in producing this reversal.

Our principal object here is the study of one of the simplest types of instability contained in the equations of reactive flow in the detonation regime. The principal simplifications are the model of the reaction mechanism, the constraint of one-dimensional flow, and the simple rear boundary condition (constant-velocity piston). Although these are such as to preclude any quantitative comparison with experiment, we comment briefly on a few situations in which more realistic one-dimensional calculations of this type may find some application.

The front of an unsupported gas detonation in a tube typically contains transverse waves of complex structure and appreciable amplitude, so that the flow is not one-dimensional. However, a longitudinal period of a sort may be defined, and it may be of some interest to compare it to the one we calculate. In a rectangular tube, the tracks of transverse waves form regular patterns of diamond-shaped cells whose apexes are collision points. Along a line parallel to the tube axis passing through a row of these, the shock pressure history is not unlike that from the unstable one-dimensional calculations. The pressure rises rapidly when two transverse waves collide, then falls below the steady CJ value before being boosted again by the next collision. For the hydrogen/oxygen system of Fig. 1, the measured distance between collisions on such a line⁵ is 0.9 cm, about 0.6 half-reaction zone lengths or 14 induction-zone lengths. The calculated long period of our $E^* = 0$ system, in which the induction zone is about three-quarters as long as the half-reaction zone, is twice as long, about 28 induction-zone lengths.

Within a cell of such a detonation, particularly in its latter part where the decay rate is less and the front is more nearly plane,¹⁰ the growth rate of perturbation seen in our calculations suggests that one-dimensional instability might appear within the cell in some systems. Such a phenomenon has not been observed. Rajan¹¹ has performed a calculation intended to apply to this situation. A fairly realistic reaction model is used, and cylindrical symmetry is assumed, with a piston programmed for the velocity history which would generate a conventional blast wave in the nonreactive case. Although the shock starts at a pressure above

the CJ von Neumann-point value, no shock pressure oscillation appears. Either his system is one-dimensionally stable (as is ours for $E^* > 9$) or the potential instability is damped by the strong rarefaction behind the front. Edwards and Meddins¹² have recently observed interferometrically a different type of "longitudinal instability" in the latter part of a detonation cell, consisting of an apparently approximately steady profile in which a large density peak follows the regular reaction zone. This phenomenon does not appear in our calculations, nor, apparently, in the calculations of Rajan referred to previously. If the mechanism that the authors propose as an explanation is correct, our reaction model is too simple to produce this effect.

Finally, there is the observation of periodic density variations in blunt-body flows in detonable gas mixtures near CJ velocity.¹³ This is probably caused by nearly one-dimensional instabilities of the type we have calculated here, but strongly reinforced by acoustic vibrations between the bow shock and the body.

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Constitutive Equations for Bimodulus Elastic Materials

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I. Introduction

THE bimodulus elastic materials are those which possess different elastic properties in tension and compression. For

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