On the Structure of Plane Detonation Waves

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A steady planar detonation wave, considered to be a shock wave followed by a reaction zone, is studied with both irreversible and reversible first-order reaction kinetics. A perturbation solution with first-order transport effects, valid in the reaction zone for those cases where the ratio of the characteristic collision time to the characteristic chemical time is small compared to one, is presented with sample calculations of temperature and concentration distributions for typical irreversible and reversible reaction cases. Analysis of the solution shows that simple series solutions and hence the given perturbation solutions do not hold near the hot boundary for all possible final Mach numbers. In the irreversible reaction case, the perturbation solution is a valid approximation for final Mach numbers less than $(1 - B)^{\frac{1}{2}}$, where B is the ratio of characteristic times, the approximation becoming less accurate as the Mach numbers tend toward this limiting value. In the reversible reaction case, the perturbation solution is a valid approximation for final Mach numbers up to the Chapman-Jouguet value of unity, if the Mach number is based on the equilibrium speed of sound.

INTRODUCTION

THE gross details of the detonation wave have been the subject of both experimental and theoretical investigation for many years. Thus, such quantities as the wave Mach number for a given heat release, as well as the resulting pressure, temperature, and density ratios are well known. However, it is only recently that serious consideration has been given to the internal structure of the detonation wave. Perhaps the greatest deterrent to such studies has been the complexities involved in a complete description of the chemical kinetics which hold in even the simpler reactions. In fact, only the simplest reaction mechanisms have been employed to date.

Since a complete description of the processes occurring in a stationary detonation wave would involve a simultaneous solution of the conservation equations including transport phenomena, and the equation of state, attempts have been made to postulate relatively simple models in which only the important mechanisms are retained. For example, von Neumann,[1] following Chapman and Jouguet,[2] pictured the wave as being a shock followed by reaction and in his description of the structure, completely neglected any transport effects. No reaction kinetics were employed, the extent of reaction being characterized by a parameter n which varied between zero and one. Von Kármán,[3] in noting the essential differences between the detonation and deflagration wave, considered the same model. In his paper, he also established the form of the parameter to be used in deciding upon the relative importance of the transport terms. The next improvement in the model employed was the consideration of simple reaction kinetics, still with no transport terms. It was argued that since, in gross terms, one could show that the transport terms were small compared to the convective terms, the transport terms could be neglected entirely. Moreover, it was clear that in this case the thickness of the wave and the various property distributions depended on the reaction rate, so attempts were made to consider the chemical kinetics. For example, Brinkley and Richardson[4] and Kirkwood and Wood[5-7] analyzed such cases. Even more recently, Hirschfelder and his group have published a series of papers[8-10] on the structure of the detonation wave wherein the most general model has been considered. That is, not only the reaction terms, but also the transport terms have been included. However, only very simple first-order reactions have been studied, for obvious reasons.

[1] J. von Neumann, "On the theory of stationary detonation waves," Ballistic Research Laboratories, Aberdeen Proving Ground, File No. X122, September 20, 1948.
[2] D. L. Chapman, Phil. Mag. **47**, 90 (1899); E. Jouguet, J. Mathematique **6**, No. 1, 347 (1905) and **6**, No. 2, 6 (1906).
[3] T. von Kármán, Aerotecnica, **33**, 80 (1953).
[4] S. Brinkley and J. Richardson, "On the structure of plane detonation waves with finite reaction velocity," Fourth Symposium on Combustion, Cambridge, Massachusetts 1952, pp. 450–457.
[5] J. G. Kirkwood and W. W. Wood, J. Chem. Phys. **22**, 1915 (1954).
[6] W. W. Wood and J. G. Kirkwood, J. Chem. Phys. **25**, 1276 (1956).
[7] W. W. Wood and J. G. Kirkwood, J. Chem. Phys. **29**, 957A (1958).
[8] J. O. Hirschfelder and C. F. Curtiss, J. Chem. Phys. **28**, 1130 (1958).
[9] B. Linder, C. F. Curtiss, and J. O. Hirschfelder, J. Chem. Phys. **28**, 1147 (1958).
[10] C. F. Curtiss, J. O. Hirschfelder, and M. P. Barnett, J. Chem. Phys. **30**, 470 (1959).

In this paper, as in those by Hirschfelder *et al.*, mentioned in the foregoing, a steady-state plane detonation wave is considered. As mentioned in the first of these papers,[8] for final Mach numbers less than unity, it is not possible to compare the theoretical solutions with experimental detonations initiated at a wall; since no limitations on the final Mach number are given by the hydrodynamic boundary conditions in the steady-state condition assumed, other criteria must be employed to rule out those Mach numbers which are physically unattainable. Recently, Nicholls[11] and Gross[12] have shown that it is possible to attain steady planar detonation waves in the laboratory, so it might be possible to compare theoretical solutions with their results. However, at the present time, it is not possible to establish definitely the fact that strong detonations were attained.

The purpose of this paper is to present an approximate analytical solution to essentially the same mathematical problem solved numerically by Hirschfelder and co-workers. In the event that there is a relatively small coupling between the shock and reaction zone, it is found that this can be accomplished by means of a perturbation solution.[13] The model chosen is that of a shock followed by reaction, so that in zeroth order, that is, with no molecular transport effects, it is essentially the von Neumann model.

PHYSICAL CONCEPTS

In any aerodynamic flow in which reaction occurs, attention must be given to the mechanism by which continuous ignition of the combustible gases may occur. For example, in a deflagration it is clear that the molecular transports of mass (in the form of active radicals) and energy, from the burned to the unburned gases, are the mechanisms by which the reaction is sustained. In the detonation wave, however, two possibilities present themselves. First the initial compression in the shock part of the wave increases the temperature and pressure to relatively high values in a distance of the order of a few mean free paths. Following this, the main part of the reaction occurs and molecular transport, while occurring, may or may not be important. The picture seen by an observer moving with the mass average velocity of the gas in the reaction zone, would differ from that seen by an observer in a deflagration, only in the higher relative velocity of random motion of the molecules. If this higher temperature is high enough to initiate a reaction immediately, then transport of mass or energy from the burned gases will contribute a negligible portion to the reaction rate. If, however, the temperature, and thus the reaction rate, is low enough that the energy transferred from the unburned gas is a significant fraction of the energy released by the reaction, then, of course, the transport effects must be included. Hence, it seems clear that in a gross manner of speaking, for relatively small heat releases, and thus relatively low wave Mach numbers, with corresponding small temperature increase across the shock portion of the wave, the transport terms should be more important than in these waves where the heat release is relatively very large, the wave Mach number is large, and hence, the temperature at the beginning of reaction is much greater. Of course, these remarks are made with the tacit assumption that the activation energy remains essentially the same for the two examples mentioned.

A comparison of values characteristic of the various processes occurring in the wave can be made in terms of length or time. In this case, as both von Kármán[3] and Hirschfelder[10] point out, one can define a characteristic collision time, equivalent to the average time between collisions, and a characteristic chemical time, equivalent to the time between collisions resulting in reaction, for example. For most cases, $t_c \ll t_{ch}$, the collision time is usually far less than the chemical time. In other words, the number of collisions resulting in reaction is generally far less than the number of collisions. In fact, it would seem physically impossible to set $t_{ch} < t_c$. Generally, it is not enough to compare t_c and t_{ch} alone since roughly the same values hold whether one considers a deflagration or a detonation. Thus, in comparing deflagration and detonation waves, von Kármán[3] evaluates the ratio of the previously noted characteristic time ratio to the square of the Mach number. However, since the Mach number in the reaction zone of the detonation wave is of the order of one, it is necessary to consider only the characteristic time ratio in this case, as will be shown in later calculations.

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[11] J. A. Nicholls, E. K. Dabora, and R. L. Gealer, "Studies in connection with stabilized gaseous detonation waves," Seventh Symposium on Combustion, Oxford, England, September 1958, pp. 766–772.

[12] R. A. Gross, ARS Journal, January 1959, pp. 63–64.

[13] Upon submission of this paper, it was learned that similar solutions had been found simultaneously by Dr. W. W. Wood at the Los Alamos Scientific Laboratory. See Rept. No. GMX-10-38-A, "On perturbation solutions for Navier Stokes detonations based on the von Neumann solution as the zeroth-order approximation."

DETONATION WAVE EQUATIONS

A stationary plane detonation wave is considered in a one-dimensional flow. There are no external forces, and bulk viscosity is neglected. The reaction is a first-order reaction with no change in molecular weight. Hence, a binary mixture of perfect gases with constant specific heats is employed. Diffusion is neglected, so that this forms the counterpart of the "thermal model" studied in deflagration problems. This assumption is not necessary for the calculations to be performed. Indeed, the comparison of the limits of this solution with those obtained with diffusion included, leads to a slight change in form, but not in functional dependence. The diffusion is neglected, then, only for the greater simplicity in computation obtained.

With the foregoing assumptions, the equations which hold in the detonation wave are (see reference 14, for example),

$$\rho u = \rho_f u_f = m \tag{1a}$$

$$\frac{4}{3}\mu \frac{du}{dx} = m(u - u_f) + P - P_f \tag{1b}$$

$$\frac{\lambda}{m}\frac{dT}{dx} = C_P(T - T_f) - \frac{1}{2}(u - u_f)^2 + (\epsilon_1 - \epsilon_{1f})Q - (P - P_f)\frac{1}{\rho} \tag{1c}$$

$$m\frac{d\epsilon_1}{dx} = w_1 \tag{1d}$$

$$p = \frac{\rho R_0 T}{\mathfrak{M}}, \tag{1e}$$

where the subscript f refers to the hot boundary, or final conditions, Q is the heat released by the reactant in cal/g, and ϵ_1 is the mass fraction of the reactant, ρ_1/ρ. $\mathfrak{M}$ is the molecular weight.

The reaction rate term, w_1, is written for a first-order reaction, either reversible or irreversible. Thus, for the irreversible case,

$$A_1 \rightarrow A_2$$
$$w_1 = -\frac{\rho}{\tau}\epsilon_1 \exp\left(-\frac{A}{R_0 T}\right) \tag{2}$$

while for the reversible case,

$$A_1 \rightleftharpoons A_2$$
$$w_1 = -\frac{\rho}{\tau}\exp\left(-\frac{A}{R_0 T}\right)\cdot\left[\epsilon_1 - (1 - \epsilon_1)\exp\left(-\frac{Q\mathfrak{M}}{R_0 T}\right)\right], \tag{3}$$

where τ, a characteristic time in the reaction, is the inverse of the steric factor, assumed to be the same for both the forward and reverse reactions in the reversible case. A is the activation energy.

Since, in Eqs. (1), x does not appear explicitly, it is convenient to transform these equations such that a dimensionless velocity,

$$v = 1 - u/u_f \tag{4}$$

is the new independent variable. The following dimensionless variables and parameters are also introduced:

$$\theta = 1 - T/T_f, \qquad \Gamma = (\gamma - 1)/\gamma,$$
$$q = Q/(C_P T_f), \qquad \theta_a = A/(R_0 T_f),$$
$$N = \gamma M_f^2, \qquad B = \frac{\lambda_f}{C_P \tau P_f}\exp\left(-\frac{A}{R_0 T_f}\right), \tag{5}$$

where M_f is the Mach number at the hot boundary. The parameter B is of the order of the maximum value of the ratio of characteristic times mentioned, i.e.,

$$B \sim (t_c/t_{ch})_{\max} \tag{6}$$

since $(1/\tau)\exp(-\theta_a)$ is of the order of the maximum reaction rate and $\lambda_f/(C_v P_f)$ is of the order of the characteristic time between collisions at this same state point. $(1/\tau)\exp(-\theta_a)$ is essentially the maximum reaction rate because this rate term is that where the relative mass concentration is unity and the temperature is at its final value which is the maximum temperature or close to the maximum temperature, depending on the strength of the wave.

IRREVERSIBLE REACTION

In terms of the just mentioned parameters, the transformed equations, for the case of an irreversible reaction are as follows:

$$\frac{d\epsilon_1}{dv} = -B\frac{(1 - \theta)\epsilon_1 \exp(-\theta_a\theta/(1 - \theta))}{[\theta - Nv^2 + (N - 1)v]}, \tag{7}$$

$$\frac{d\theta}{dv} = N(1 - v)\frac{[\theta(1 - \Gamma) - \epsilon_1 q + (\Gamma N/2)v^2 + \Gamma v]}{[\theta - Nv^2 + (N - 1)v]}, \tag{8}$$

where $\tilde{P}_r = \frac{4}{3}C_v\mu/\lambda$, the reduced Prandtl number, has been assumed to be one. Also, λ, the thermal conductivity has been assumed to vary linearly with the temperature, and the speed of sound is taken to be $(\gamma R_0 T/\mathfrak{M})^{\frac{1}{2}}$. The boundary conditions

[14] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

are simply that at the hot boundary, where $v = 0$, $\epsilon_1 = \theta = 0$.

In view of the fact that the irreversible mechanism gives physically realizable results for B small compared to one, it is in order to compute a perturbation solution for the part of the wave in which reaction occurs, with B as the small parameter. In this event, the proper perturbation expansions are as follows:

$$\theta = \theta^{(0)} + B\theta^{(1)} + B^2\theta^{(2)} + \cdots$$
$$\epsilon_1 = \epsilon_1^{(0)} + B\epsilon_1^{(1)} + B^2\epsilon_1^{(2)} + \cdots . \tag{9}$$

Employing these expansions in Eqs. (7) and (8), one can show that the zeroth- and first-order functions are

$$\theta^{(0)} = (1 - N)v + Nv^2, \tag{10a}$$

$$\epsilon^{(0)} = q\epsilon_1^{(0)} = [1 - N(1 - \Gamma)]v + \left(\frac{2 - \Gamma}{2}\right)Nv^2, \tag{10b}$$

$$\theta^{(1)} = -\left(\frac{d\epsilon^{(0)}}{dv}\right)^{-1}(1 - \theta^{(0)})\epsilon^{(0)} \cdot \exp\left(-\frac{\theta_a\theta^{(0)}}{1 - \theta^{(0)}}\right), \tag{10c}$$

$$\epsilon^{(1)} = q\epsilon_1^{(1)} = -\theta^{(1)} \cdot \left[\frac{d\theta^{(0)}}{dv}\frac{1}{N(1 - v)} - (1 - \Gamma)\right]. \tag{10d}$$

The zeroth-order solutions are those which hold for the well-known case of negligible transport effects, while the first effects of the transport properties are given by the inclusion of $\epsilon^{(1)}$ and $\theta^{(1)}$. While the conditions that $\epsilon^{(1)}$ and $\theta^{(1)}$ must vanish at both hot and cold boundaries are met at the hot boundary, they are not precisely met at the cold boundary, i.e., immediately after the shock. Just as in combustion theory, because of the form of the reaction rate employed, a finite reaction rate exists at any temperature greater than absolute zero. Hence, the cold boundary condition is only approximately satisfied since $B\theta^{(1)}$, for example, does not vanish but is very small compared to $\theta^{(0)}$ at the cold boundary. Higher-order terms would show the same behavior.

At the cold boundary of the reactive region, θ, ϵ, and v are all positive, being those values which may be found by applying the shock wave relations across a shock traveling at the detonation wave propagation Mach number. Moreover, according to the perturbation solution, ϵ and θ both are zero when v is zero, so that no negative values of v exist between the cold and hot boundaries. Since $\epsilon^{(0)}$ is always positive or zero, and since succeeding terms are assumed to be small compared to a given term, ϵ must be positive no matter how many terms are included, if the perturbation solution is to be valid. In the irreversible case, of course, $\epsilon_1 > 0$ is a physical necessity.

It can be seen from Eqs. (10) that near the hot boundary, i.e., as $v \to 0$, both θ and ϵ are proportional to v, at least to first order. Furthermore, when $1 - N(1 - \Gamma) = 0$, which corresponds to the Chapman-Jouguet case of $M_f^2 = 1$, $\epsilon^{(0)} \sim v^2$, while $\epsilon^{(1)} \sim v$, which indicates that the perturbation solution breaks down. Hence, it is necessary to examine solutions near the hot boundary, in order to determine whether there is a range of final Mach numbers for which a perturbation solution is not valid in this region.

First, it is of interest to calculate the limiting values of $d\epsilon_1/dv$ and $d\theta/dv$ at the hot boundary. Thus, if

$$a_1 = \lim_{v \to 0}\frac{d\theta}{dv}, \tag{11}$$

$$b_1 = \lim_{v \to 0} q\frac{d\epsilon_1}{dv}; \tag{12}$$

and, since by L'Hospital's rule,

$$\lim_{v \to 0}\frac{\theta}{v} = a_1;$$

$$\lim_{v \to 0} q\frac{\epsilon_1}{v} = b_1.$$

Then, at the limit, Eqs. (7) and (8) can be shown to reduce to

$$b_1(a_1 + N - 1 + B) = 0 \tag{13}$$

$$a_1(a_1 + N - 1) = N[a_1(1 - \Gamma) - b_1 + \Gamma]. \tag{14}$$

Since it is desired, at this point, to consider only those solutions for which ϵ_1 and θ can be expanded in powers of v and thus are linear functions of v in the small, and since $v \geq 0$, and $\epsilon_1 \geq 0$, it is clear that $b_1 \geq 0$ is a necessary condition which must be met if the perturbation solutions are to be valid. In fact, since

$$b_1 = \sum_0^\infty B^n(d\epsilon^{(n)}/dv)_{v=0} \quad \text{and} \quad (d\epsilon^{(n)}/dv)_{v=0} \neq 0$$

in general, then $b_1 = 0$ implies that as $v \to 0$, several terms of the perturbation expansion must be of the same absolute order of magnitude, so that the

fundamental condition of the perturbation solution is violated. Here, of course, b_1 is the coefficient of the first term of an expansion of ϵ in powers of v about the point $v = 0$. If $b_1 \neq 0$, then Eqs. (13) and (14) may be solved for a_1 and b_1. Thus,

$$a_1 = -(N - 1 + B) \tag{15}$$

$$b_1 = [(B + N)/N][1 - B - N(1 - \Gamma)]. \tag{16}$$

Equation (15) specifies that if a critical N is defined as

$$N_c = \gamma M_{f_c}^2 = 1 - B, \tag{17}$$

then $a_1 \lesseqgtr 0$ as $N \gtreqless N_c$. The critical final Mach number, M_{f_c}, can be shown to be that Mach number above which a temperature maximum exists in the wave. Thus, since $v \geq 0$, then as $v \to 0$, $dv/dx \lesseqgtr 0$, or $du/dx \geq 0$. Hence, $a_1 \lesseqgtr 0$ implies $dT/dx \lesseqgtr 0$ near the hot boundary. Figure 1 indicates the

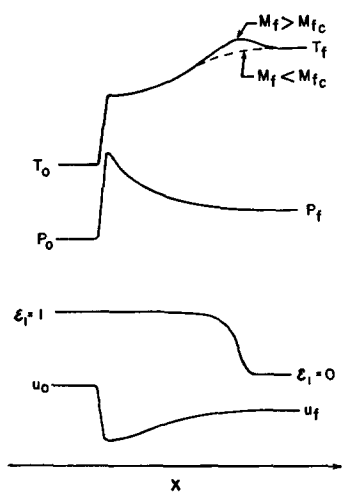

FIG. 1. Variation of properties through a detonation wave.

cases mentioned with the corresponding ranges of the final Mach number. It is interesting to note that, according to Eq. (17), the inclusion of transport properties changes the critical final Mach number from its classical value of $\gamma^{-\frac{1}{2}}$ by a factor $(1 - B)^{\frac{1}{2}}$. For the generally accepted values of $B \ll 1$, the difference from the classical value is relatively small.

From Eq. (16), it can be seen that the condition $b_1 > 0$ imposes a condition on the final Mach number. Thus, for $b_1 > 0$,

$$\begin{aligned} N &< (1 - B)/(1 - \Gamma), \\ M_f &< (1 - B)^{\frac{1}{2}}. \end{aligned} \tag{18}$$

That is, the perturbation solution in this region can be expected to be valid only in the final Mach number regime given by Eq. (18). Certainly, it is not valid for $M_f \geq (1 - B)^{\frac{1}{2}}$. It should be noted that this range does not include the Chapman-Jouguet wave ($M_f = 1$). In fact, near the hot boundary, one should expect the approximation to be less accurate as the Mach number approaches the limiting value of $(1 - B)^{\frac{1}{2}}$.

It is possible to obtain the exact solutions which hold near the hot boundary by considering the linearized equations in this region. The author is indebted to William W. Wood (private communication) for having pointed out that these solutions not only show the range of validity of a simple expansion, but also illustrate the nature of the solution in the region around $v = 0$ for the remaining Mach number range. Thus, if one writes the governing equations, Eqs. (1b), (1c), and (1d), in Lagrangian form and linearizes them with respect to the point $\theta = \epsilon = v = 0$, the result is as follows:

$$d\epsilon/dt = -B\epsilon, \tag{19}$$

$$d\theta/dt = N[\theta(1 - \Gamma) - \epsilon + \Gamma v], \tag{20}$$

$$dv/dt = \theta + (N - 1)v. \tag{21}$$

With the application of the given boundary conditions, the solutions can be written in the following form, where one of the arbitrary constants has been set equal to unity.

$$\epsilon = \exp(-Bt), \tag{22}$$

$$\theta = \frac{N(N - 1 + B)}{(N + B)[N(1 - \Gamma) - 1 + B]} \exp(-Bt) - CN\Gamma \exp\{-[1 - N(1 - \Gamma)]t\}, \tag{23}$$

$$v = -\frac{N}{(N + B)[N(1 - \Gamma) - 1 + B]} \exp(-Bt) + C \exp\{-[1 - N(1 - \Gamma)]t\}, \tag{24}$$

where c is an arbitrary constant. Finally, substituting Eq. (22) in Eqs. (23) and (24), θ and v can be written in terms of ϵ.

$$\theta = \frac{N(N - 1 + B)}{(N + B)[N(1 - \Gamma) - 1 + B]} \epsilon - CN\Gamma\epsilon^{[1 - N(1 - \Gamma)]/B}, \tag{25}$$

$$v = -\frac{N}{(N + B)[N(1 - \Gamma) - 1 + B]} \epsilon + C\epsilon^{[1 - N(1 - \Gamma)]/B}. \tag{26}$$

Thus, as W. W. Wood pointed out, only certain special solutions have power series expansions about the singular point, even though the system is linear. It is clear that for $1 - N(1 - \Gamma) > B$, which is the condition given by Eq. (18), as $\epsilon \to 0$ the linear

term is dominant, while for $1 - N(1 - \Gamma) < B$, the solution for θ and v involve noninteger powers of ϵ, for which a series solution and hence, the perturbation solutions do not hold. At the present time, no approximate solution is known for this Mach number interval, $1 - B < M_f^2 < 1$. In this range of Mach numbers, of course, it is possible that $1 - N(1 - \Gamma) = B/n$, where n is an integer. In this case, for v small enough, $\epsilon \propto v^n$, as seen from Eq. (25). Thus, a series expansion would hold for these discreet values of the Mach number, if the first $n - 1$ coefficients of the series were zero. However, in this event, a perturbation solution would not be applicable near the hot boundary, since enough terms would have to be taken into account to show that the coefficients of v, v^2, v^3, $\cdots$ v^{n-1} canceled out. Thus, as mentioned previously, for the simple case where $b_1 = 0$, successive terms of the perturbation would become of the same order, as $v \to 0$.

At this point, the foregoing results can be compared with those given by Hirschfelder and his group in the first of their very interesting and stimulating series of papers on detonation theory.[8] The first terms of the series expansions, which are essentially Eqs. (25) and (26) with $c = 0$, correspond to Hirschfelder's asymptotic expansion "2" in the section entitled "Nature of the solution near the hot boundary," the only exception being that in the present case, diffusion is not considered. By using the expansions given in that section, it can be shown that the limit on N is, in the notation of this paper,

$$N < 1/(1 - \Gamma)(1 + B) \qquad (27)$$

which reduces to Eq. (18) if $B \ll 1$ is considered. However, it should be noted that the range of Mach numbers over which a series expansion is possible is relatively insignificant for the large values of B considered by Hirschfelder and Curtiss. Thus, their numerical results are calculated for $B > 1$, with $B = 2.5$ corresponding closely to one of their particular solutions. For this value of B and for $\gamma = 1.25$, according to Eq. (27), $N < 0.36$, or $M_f < 0.54$ is the range in which it is possible to consider a series expansion. Of course, for this value of B, the perturbation solution is not proper, since it is based on $B \ll 1$. However, $B = 2.5$ is a seemingly impossible value, as pointed out by Hirschfelder and his group themselves, in the third paper of their series.[10] In this reference, the anomalous condition of $B > 1$ is pointed out, and the possibility of employing more complicated relaxation

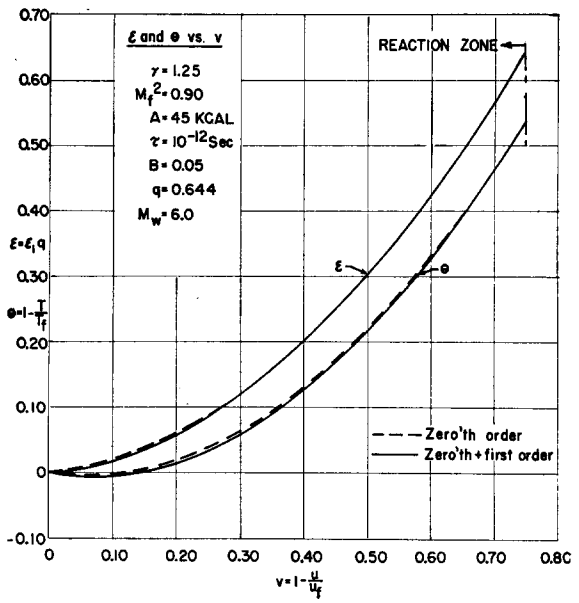

FIG. 2. Perturbation solution of combustible concentration and temperature as functions of velocity in the reaction zone of a detonation wave with a first-order irreversible reaction mechanism; wave Mach number is 6.0.

reactions which might occur during a first-order reaction is discussed. However, it seems more logical to restrict the use of first-order irreversible mechanisms to the more physically realizable values of B. It happens that $B \ll 1$ for those reactants with relatively small heats of formation and relatively high activation energies. For example, for hydrazine, the calculated value of B is 0.002. With such a value, the perturbation solution should be useful up to final Mach numbers very nearly unity.

In view of the foregoing remarks, a calculation of θ and ϵ_1 to first order was made for $B = 0.05$, and $M_f^2 = 0.90$. The results are shown in Figs. 2 and

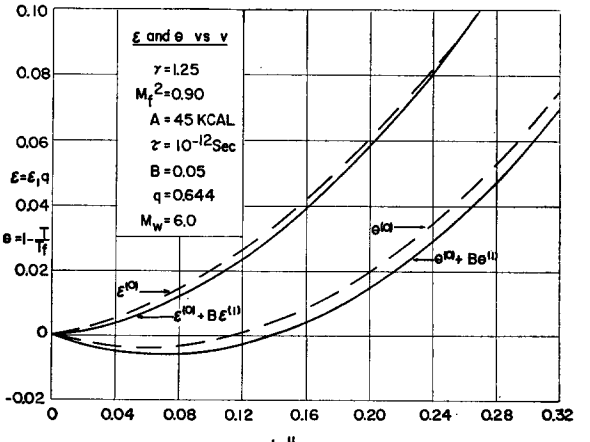

FIG. 3. Perturbation solution from Fig. 2 in the neighborhood of the hot boundary.

3. The differences between the zeroth- and first-order solutions are seen to be relatively small for this case. It is interesting to note that near the hot boundary the solution for ϵ_1 is not as well behaved as the solution for θ. That is, it is only in the calculation for ϵ_1 that the first-order term becomes comparable to the zeroth-order term as $v \to 0$, although a comparison of b_1 with the slope $[d(\epsilon^{(0)} + B\epsilon^{(1)})]/dv$ at the hot boundary, showed good agreement in the example calculations. A glance at Eqs. (25) and (26) explains this behavior, in that, for ϵ small enough, $\theta = \text{const} \times v$ can be written for all Mach numbers, while the linear variation between ϵ and v holds only for the aforementioned range, and becomes increasingly poor as $N(1 - \Gamma) \to (1 - B)$.

REVERSIBLE FIRST-ORDER REACTION

The equations which hold for the reversible first-order reaction mechanism may be written in a form equivalent to Eqs. (7) and (8). In dimensionless form, they are

$$\frac{d\bar{\epsilon}_1}{dv} = -B(1 - \theta) \exp\left(-\frac{\theta_a \theta}{1 - \theta}\right) \frac{\left\{\bar{\epsilon}_1\left[1 + \exp\left(-\frac{q}{\Gamma(1 - \theta)}\right)\right] + \epsilon_{1_f}\left[1 - \exp\left(-\frac{q\theta}{\Gamma(1 - \theta)}\right)\right]\right\}}{[\theta + (N - 1)v - Nv^2]}, \tag{28}$$

$$\frac{d\theta}{dv} = N(1 - v) \cdot \frac{[\theta(1 - \Gamma) - \bar{\epsilon}_1 q + (\Gamma N/2)v^2 + \Gamma v]}{(\theta + (N - 1)v - Nv^2]}, \tag{29}$$

where

$$\bar{\epsilon}_1 = \epsilon_1 - \epsilon_{1_f}. \tag{30}$$

ϵ_{1_f} is the equilibrium value of ϵ_1 at the hot boundary, and the reduced Prandtl number is again assumed to be unity. Since the speed of sound is again taken to be $(\gamma R_0 T/\mathfrak{M})^{\frac{1}{2}}$, the parameter N refers to a Mach number based on the so-called frozen speed of sound.

A perturbation solution for the condition $B \ll 1$ may be obtained by applying the expansions given in Eq. (9), now for $\bar{\epsilon}$ and θ, to Eqs. (28) and (29). The results for the zeroth- and first-order terms are as follows:

$$\theta^{(0)} = (1 - N)v + Nv^2, \tag{31a}$$

$$\bar{\epsilon}^{(0)} = q\bar{\epsilon}_1^{(0)} = (1 - N(1 - \Gamma))v + [(2 - \Gamma)/2]Nv^2, \tag{31b}$$

$$\theta^{(1)} = -\left(\frac{d\bar{\epsilon}^{(0)}}{dv}\right)^{-1}(1 - \theta^{(0)}) \exp\left(-\frac{\theta_a \theta^{(0)}}{1 - \theta^{(0)}}\right) \cdot\left\{\bar{\epsilon}^{(0)}\left[1 + \exp\left(-\frac{q}{\Gamma(1 - \theta^{(0)})}\right)\right] + \epsilon_{1_f}\left[1 - \exp\left(-\frac{q\theta^{(0)}}{\Gamma(1 - \theta^{(0)})}\right)\right]\right\}, \tag{31c}$$

$$\bar{\epsilon}^{(1)} = q\bar{\epsilon}_1^{(1)} = -\theta^{(1)}\left[\frac{d\theta^{(0)}}{dv}\frac{1}{N(1 - v)} - (1 - \Gamma)\right]. \tag{31d}$$

It is seen that if $\bar{\epsilon}$ is substituted for ϵ, Eqs. (31) are the same as those for the irreversible reaction with the exception of the equation found for $\theta^{(1)}$. The remarks concerning both the cold boundary conditions and the nonnegative values of ϵ and v, made with regard to the irreversible reaction solution can be seen to hold for this solution as well.

In order to find the Mach number limitations of the perturbation solution, the procedure employed in the irreversible reaction problem may be used. Thus, if a_1 and b_1 are defined as in Eqs. (11) and (12), considering $\bar{\epsilon}$ rather than ϵ, then in the limit, Eqs. (28) and (29) become

$$b_1 = -\frac{[b_1 + \epsilon_{1_f}^2 q^2(a_1/\Gamma) \exp(q/\Gamma)]}{[a_1 + N - 1]\epsilon_{1_f}} B \exp(-q/\Gamma) \tag{32}$$

$$a_1 = N\frac{[(1 - \Gamma)a_1 - b_1 + \Gamma]}{[a_1 + N - 1]}. \tag{33}$$

Equation (32) may be simplified by introducing the specific heat ratio of the reacting gas, γ'. As given in reference 14, and in the notation of this paper,

$$\frac{\gamma'}{\gamma} = \frac{1 + \epsilon_{1_f}^2 q^2(1/\Gamma) \exp(q/\Gamma)}{1 + [\epsilon_{1_f}^2 q^2/\Gamma(1 - \Gamma)] \exp(q/\Gamma)}, \tag{34}$$

where the condition of equilibrium at the hot boundary,

$$\epsilon_{1_f} = (1 - \epsilon_{1_f}) \exp(-q/\Gamma) \tag{35}$$

has been used. Defining Γ' similarly to Γ so that

$$\Gamma' = (\gamma' - 1)/\gamma', \tag{36}$$

one can solve Eq. (34) to yield

$$\epsilon_{1_f}^2 q^2(1/\Gamma) \exp(q/\Gamma) = (\Gamma - \Gamma')/\Gamma'. \tag{37}$$

Finally, $\bar{B}$ is defined such that

$$\bar{B} = (B/\epsilon_{1_f}) \exp(-q/\Gamma). \tag{38}$$

$\epsilon_{1_f} \exp(q/\Gamma)$ is of order one, so $\bar{B}$ is of order B. Equations (37) and (38) are substituted in Eq. (32) with the result that

$$b_1(a_1 + N - 1) = -\bar{B}\{b_1 + [(\Gamma - \Gamma')/\Gamma']a_1\}. \tag{39}$$

Thus, Eqs. (33) and (39) may be analyzed to find the desired Mach number range. As in the irreversible case, the perturbation solutions for θ and $\bar{\epsilon}$ are linear in v in the small. Also, since $\bar{\epsilon}$ and v are nonnegative functions, near the hot boundary, $dv/dx \leq 0$ and $d\bar{\epsilon}_1/dx \leq 0$ are conditions which must be met if the perturbation solution is to be valid.

The critical Mach number, i.e., the largest final Mach number which can occur before a temperature maximum exists within the wave can be found by setting $a_1 = 0$. Thus,

$$N_c = (1 - \bar{B}), \tag{40}$$

or

$$M_{f_c} = [(1 - \bar{B})/\gamma]^{\frac{1}{2}},$$

a result similar to the irreversible calculation.

The calculation of the limiting final Mach number is somewhat different from that in the irreversible case. A solution of Eqs. (33) and (39) results in cubic equations for a_1 and b_1. Although no simple solutions were found, the Mach number range may be found by using the conditions noted in the foregoing. In particular, if $dv/dx \leq 0$, and thus $dv/dt \leq 0$ near the hot boundary, then from Eq. (21), which holds for the reversible case also, it can be seen that the equivalent condition at the limit is

$$a_1 + N - 1 \leq 0$$

or, if $\bar{a}_1 = -a_1$,

$$\bar{a}_1 \geq N - 1.$$

Here, $\bar{a}_1 > 0$ since $N > N_c$ corresponds to the Mach number range under consideration. Moreover, since both b_1 and $\bar{B}$ are positive, the foregoing condition applied to Eq. (39) indicates that

$$b_1 - [(\Gamma - \Gamma')/\Gamma']\bar{a}_1 \geq 0. \tag{41}$$

Finally, it may be shown, from Eqs. (33) and (39) that as N increases, b_1 decreases and $\bar{a}_1$ increases. Hence, the maximum Mach number which allows a perturbation solution is given when the equality of Eq. (41) occurs. With this equality, one can show, from Eqs. (33) and (39), that the maximum Mach number is

$$M_f^2 = \gamma'/\gamma. \tag{42}$$

However, if the Mach number is defined in terms of the equilibrium speed of sound, $(\gamma' R_0 T/\mathfrak{M})^{\frac{1}{2}}$, then the limiting condition is, from Eq. (42),

$$M_f' = 1. \tag{43}$$

Hence, the perturbation solution should hold up to the Chapman-Jouguet case, if the Mach number is based on the equilibrium speed of sound. While some controversy has existed in the literature concerning the use of frozen or equilibrium speeds of sound, the latter is now generally accepted as the proper one to use in the definition of the Chapman-Jouguet condition.

It is interesting to note that $b_1 \neq 0$ in the allowable Mach number range for the perturbation solution. Instead, for $0 < b_1 < [(\Gamma - \Gamma')/\Gamma']\bar{a}_1$, $dv/dt > 0$, and since $b_1 > 0$, $d\bar{\epsilon}_1/dt > 0$. Thus, both $\bar{\epsilon}_1$ and v must approach zero from negative values, a condition which is not allowed in the perturbation solution. That is, $\bar{\epsilon}$, initially positive, must remain positive, in accordance with the behavior of $\bar{\epsilon}^{(0)}$.

Example calculations were carried out for a reversible reaction with $q = 0.644$, $B = 0.05$, and $\Gamma = 0.20$. The results are shown in Fig. 4. The limiting case of $M_f' = 1$ was chosen for this example in order to illustrate the difficulties inherent in the perturbation solution near the hot boundary. As $v \to 0$, two terms hardly sufficed to give a proper representation of $\bar{\epsilon}$, since values of $B\bar{\epsilon}^{(1)}/\bar{\epsilon}^{(0)}$ as high

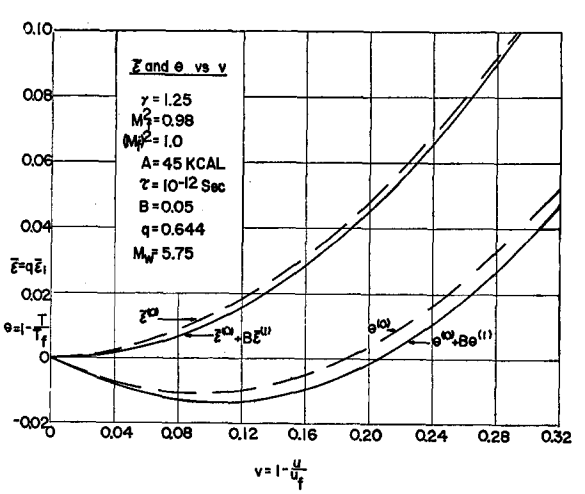

FIG. 4. Perturbation solution of combustible concentration and temperature as functions of velocity in the neighborhood of the hot boundary of a detonation wave with a first-order reversible reaction mechanism; wave Mach number is 5.75.

as 0.50 were calculated. However, a comparison of $d\bar{\epsilon}/dv$ at the hot boundary with the corresponding b_1 showed good results so that at least with the numerical values chosen, the third- and higher-order terms contribute very little to the solution. For v far from zero, of course, the transport effects are seen to be small, and the perturbation solution is evidently valid.

CONCLUSION

A perturbation solution is a relatively simple and accurate solution for the concentration and temperature profiles, for $B \ll 1$. However, its use is restricted to Mach number ranges which do not include the classical Chapman-Jouguet case for irreversible reactions, but which do include the Chapman-Jouguet case for reversible reactions, if the final Mach number is based on the equilibrium speed of sound.

In view of the physical interpretation of the perturbation parameter B, it seems clear that within the given final Mach number range, a perturbation solution should hold for most reactions. Thus, detonations traveling through most reactive mixtures should have relatively small coupling between the shock and reactive zones.

The first-order reaction rate mechanism is difficult to justify mechanistically. The explanation accepted by most kineticists is that initially a relatively fast second-order reaction produces active reactant particles which then decompose slowly at a rate which is first order. Thus, the over-all rate controlling reaction is first order. Generally, the pre-decomposition reactions are not taken into account in simplified combustion or detonation wave treatments so that with a given set of parameters, it is possible to calculate reaction zones of the order of a mean free path in thickness, with $B \geq 1$. However, postulating such a rate would seem to give results of doubtful practical value, since, in such a case, there would be no way of producing the necessary supply of active particles such that the decomposition was still the slowest rate controlling part of the reaction.

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