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# CRANFIELD

Reaction-Resisted Shock Fronts

- by -

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# SUMMARY

It is shown that shock waves whose structure is determined solely by the effects of chemical reactions (reaction-resisted shock fronts) are possible and completely analogous to relaxation - resisted waves. A single dissociation reaction is considered and numerical results indicate that such waves could be observed experimentally. Bulk viscosities equivalent to reaction effects are possibly 10<sup>2</sup> or more times shear viscosity values. (Examples are based on Lighthill's ideal dissociating gas).

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a, a e f	Equilibrium and frozen speeds of sound			
с	Atom mass fraction			
c <sub>e</sub> (p,s)	Equilibrium atom mass fraction evaluated at local p and s			
c'	See equation 19			
D	Dissociation energy per unit mass			
h	Enthalpy per unit mass			
k <sub>f</sub> , k	Specific reaction rate constants			
M <sub>e</sub> , M <sub>f</sub>	Equilibrium and frozen Mach numbers			
р	Pressure			
R	Universal gas constant			
8	Entropy per unit mass			
т	Absolute temperature			
u	Gas velocity			
Wa	Molecular weight of molecules			
ж	Streamwise co-ordinate			
$\gamma_{\rm e}, \gamma_{\rm f}$	Equilibrium and frozen "polytropic exponents", see equations 30, 31			
ĸ	Equivalent bulk viscosity			
λ	See equation 22			
μ	Shear viscosity			
$\mu_{a}, \mu_{m}$	Chemical potentials, atoms and molecules respectively			
P	Density			
σ	See equation 12			
τ, τ',τ"	See equations 16, 18 and 28			
Suffixes , and 2 apply to far upstream and far downstream conditions, respectively.				

# LIST OF SYMBOLS

#### 1. Introduction

Inviscid flow theory shows that a plane compression wave in a gas will always steepen until, finally, the physically impossible condition is reached wherein three different values of pressure, gas velocity, etc. are predicted to occur at one point in the flow field at one and the same time. Before this state is reached of course, inviscid flow theory begins to lose validity and it becomes necessary to include the effects of viscosity and heat conduction. The diffusive effects of these phenomena act in such a way as to halt the convective steepening of the wave and eventually a shock front will be formed (so-called diffusion-resisted waves). The width of such a shock front is measured in units of  $\mu/\rho u$  ( $\mu$ ,  $\rho$ , u are shear viscosity, density and velocity, respectively).

At least, this is true if viscosity and heat conduction are the only dissipative effects present in the gas. If the gas is polyatomic, relaxation of the internal degrees of freedom provides a further mechanism which will exert its influence on shock structure. Ordinarily, this influence is confined to regions behind the thin, viscosity-resisted wave (the relaxation zone), except for rapidly relaxing modes like rotation. In the latter cases, where the relaxation time may be less than ten molecular collision time intervals, the effective "viscosity" of the mode remains comparable with  $\mu$ , and can frequently be included as a bulk viscosity factor, merely serving to widen the diffusion-resisted wave. For the modes with much longer relaxation times (many hundreds or thousands of collisions), the effective viscosity is very much greater and, as a direct result of the dispersive character of a relaxing gas, the possibility arises that a compression wave can be entirely resisted by relaxation effects alone. For this to happen, the equilibrium Mach number of the shock front must be less than the appropriate frozen to equilibrium sound speeds ratio. These facts, and the analysis to support them, have been given by Lighthill (1956), who called the resulting waves "fully-dispersed" shock waves.

In broad terms, the dispersive power of a relaxing gas is measured by the sound speeds ratio mentioned above, whilst its absorptive power depends both on this and on the relaxation time. When a gas is reacting chemically, dispersion and absorption are still present and behave in a very similar way to that encountered in relaxing gases. However, the sounds speed ratio has the possibility of being much larger in a reacting than in a relaxing gas and, furthermore, the appropriate "chemical times" are larger, or certainly no smaller, than many practically encountered vibrational relaxation times. For these reasons we might speculate that "reaction-resisted" shock fronts can occur in chemically reacting gases and it is the purpose of the present paper to prove that this is indeed so. It is also shown that reaction-resisted waves may be two or even more, orders of magnitude thicker than diffusion-resisted waves, i.e. of thickness  $10^2 \ \mu/\rho u$  or more.

We consider only plane waves in one dimension and, treating the flow as steady, find the conditions under which a purely reaction-resisted shock is possible. In this we follow Lighthill, but the method used here differs slightly from his in that here we start from the inviscid, non-heat conducting differential equations governing the gas flow, whereas Lighthill's analysis started from the integrated forms of these equations. Briefly, the reason is that, in the reacting case, the behaviour of the concentrations is a little more difficult to handle than is that of the internal mode temperature in the relaxation problem.

In the analysis to follow, relaxation effects are ignored (but commented upon in Section 5) and the reaction is assumed to be the dissociation and recombination of a symmetrical diatomic molecule. That is to say,

$$A_m + A_o \stackrel{k_f}{\longleftrightarrow} 2A_a + A_o$$
 (1)

A and A are chemical symbols for molecules and atoms, respectively, and (in the pure gas mixture) the "catalyst" in this reaction, A<sub>o</sub>, may be either A<sub>m</sub> or A<sub>a</sub>. Either is assumed to be equally effective.  $k_f$  and  $k_r$  are the appropriate rate constants. In examples below numbers are used which are appropriate to an oxygen-like ideal dissociating gas (Lighthill, 1957).

## 2. The Basic Equations

The mass conservation equation in steady one-dimensional flow is simply

$$\rho u = Q$$
 (2)

where Q is a constant, or, in differential form,

$$u \frac{d\rho}{dx} + \rho \frac{du}{dx} = 0.$$
 (3)

Since  $\rho$  is a function of pressure, entropy and mass fraction of atoms (p, s and c, respectively) we can write

$$u \frac{d\rho}{dx} = \left(\frac{\partial\rho}{\partial p}\right)_{s,c} u \frac{dp}{dx} + \left(\frac{\partial\rho}{\partial s}\right)_{p,c} u \frac{ds}{dx} + \left(\frac{\partial\rho}{\partial c}\right)_{p,s} u \frac{dc}{dx} .$$
(4)

The energy equation is

$$\rho u \frac{dh}{dx} - u \frac{dp}{dx} = 0, \qquad (5)$$

where h is the specific enthalpy, and the entropy equation becomes

$$T u \frac{ds}{dx} + (\mu_a - \mu_m). u \frac{dc}{dx} = 0.$$
 (6)

( $\mu_{a}$  and  $\mu_{m}$  are the chemical potentials, per unit mass, for atoms and molecules,

respectively). Making use of the results in equations 4 and 6, and manipulating some of the thermodynamic derivatives which appear in the course of the analysis it can be shown that equation 3 leads to

$$u \frac{dp}{dx} + \rho a_f^2 \frac{du}{dx} + \rho a_f^2 \sigma u \frac{dc}{dx} = 0.$$
 (7)

(Details of the derivation of this equation can be found in Clarke, 1958). The quantity  $a_s^2$  is identifiable with the frozen speed of sound and

$$a_{f}^{2} = \left(\frac{\partial p}{\partial \rho}\right)_{S,C}$$
(8)

The momentum equation in a one-dimensional steady flow is

$$\rho u \frac{du}{dx} + \frac{dp}{dx} = 0 , \qquad (9)$$

which can be integrated at once to give

$$p + \rho u^2 = F = p + Qu \tag{10}$$

where F is a constant. Alternatively equation 9 can be used as it stands to eliminate u (dp/dx) from equation 7, resulting in

$$(a_f^2 - u^2)\frac{du}{dx} + a_f^2 \sigma u \frac{dc}{dx} = 0.$$
 (11)

The quantity  $\sigma$  which appears here and in equation 7 above, is a purely thermodynamic function. In general, for the dissociating diatomic gas,

$$\sigma = \rho \frac{\beta_{f}}{C_{pf}} \left(\frac{\partial h}{\partial c}\right)_{p,T} + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial c}\right)_{p,T}, \qquad (12)$$
  
$$\beta_{f} = \left(\frac{\partial \rho^{s^{s}}}{\partial T}\right)_{p,c}; \quad C_{pf} = \left(\frac{\partial h}{\partial T}\right)_{p,c}.$$

If we treat the gas as an ideal dissociating gas (Lighthill, 1957),  $\sigma$  can be evaluated analytically. We find that

$$\sigma = \left[ DW_{2}/RT + 1 \right] \left[ 4 + c \right]^{-1} - \left[ 1 + c \right]^{-1}, \qquad (13)$$

where D is the dissociation energy per unit mass,  $W_2$  is the molecular weight of the molecules and R is the universal gas constant. We note for future reference that the combination  $a_f^2 \sigma$  has the following value for an ideal dissociating gas,

$$a_{f}^{2}\sigma = \left[D(1+c)/3\right] - RT/W_{2}, \qquad (14)$$
  
e  $a_{f}^{2} = \left[(4+c)/3\right](p/\rho)$  and  $p = \rho(1+c)(R/W_{2})T).$ 

The atom continuity equation, with atoms being produced according to the reaction described in the Introduction, can be written in the form

$$\tau = u \frac{dc}{dx} = K(1 - c) - c^2$$
 (15)

where  $\tau$  is the "chemical time"

$$\tau = W_2^2 / 4k_r \rho^2 (1 + c)$$
 (16)

and

(sinc

$$K = (W_2 k_f / 4 \rho k_r) .$$
 (17)

 $k_f$  and  $k_r$  are the forward (dissociation) and reverse (recombination) specific reaction rate constants measured in terms of moles per unit volume (raised to appropriate powers) per unit time, respectively. We shall shortly demonstrate that a reactionresisted shock wave is necessarily a weak wave. In that event, the mass fraction c will not change greatly from the free stream to downstream regions, and it seems legitimate to linearise the reaction rate term on the right-hand side of equation 15. Indeed we shall go a little further and assume a constant value for the chemical time (and write it as  $\tau'$ ), so that equation 15 now appears in the form

$$\tau' u \frac{dc}{dx} = c_e(p, s) - c. \qquad (18)$$

 $c_e$  is an arbitrarily chosen local equilibrium value and  $c_e(p, s)$  above indicates that we have chosen local pressure and entropy for the evaluation of  $c_e$ . We shall subsequently be able to evaluate both the difference  $c_e(p, s)$  -c and c itself, so that  $\tau'$  can be found from the mean value of  $\left[\kappa(1-c)-c^2\right]/\left[c_e(p, s)-c\right]$  across the shock wave.

It is rather more convenient to work in terms of the quantity c', defined as

$$c' = c - c_{0}(p, s)$$
 (19)

Then equation 18 can be written as

$$\tau' u \frac{dc'}{dx} + \tau' u \frac{dc_e}{dx} + c' = 0.$$
 (20)

Now we may write

$$u \frac{dc_e}{dx} = \left(\frac{\partial c_e}{\partial p}\right) u \frac{dp}{dx} + \left(\frac{\partial c_e}{\partial s}\right) u \frac{ds}{dx}$$

$$\lambda u \frac{dp}{dx} + \left(\frac{\partial c}{\partial s}\right)_{p} \cdot (\mu_{a} - \mu_{m}) T^{-1} \cdot (c'/\tau'), \qquad (21)$$

by using equations 6 and 18. We have written

equation 20 in the form

$$\lambda = \left(\frac{\partial c_e}{\partial p}\right)_{s}$$
(22)

for brevity. It has been shown elsewhere (Clarke, 1958, 1960) that  $(\mu_a - \mu_m)T^{-1}$  is of order  $(R/W_2)c'$  and that the derivative  $(\partial c_e/\partial s)_p$  is less than order  $(W_2/R)$ . Consequently it is legitimate to use equation 21, together with these results, to write

$$t' u \frac{dc'}{dx} + \tau' \lambda u \frac{dp}{dx} + c' = 0$$
 (23)

The approximation involved in neglecting the last term in equation 21 when this result is used in equation 20 is no worse than that leading to the linear rate law involved in equation 20.

It is important to note that in adopting equation 23 as the atom continuity equation we have not in any sense "linearised" the problem. We have merely made as convenient an approximation to the dissipation effect as possible. The convective, steepening effect, remains with us in the presence of the ud/dx operators etc.

## 3. The Fully Dispersed, Reaction-Resisted, Wave

The chemical reaction rate equation (equation 15 or its "linear" version equation 18) shows that  $u dc/dx \Rightarrow 0$  as equilibrium is approached. The shock transition takes place between two states of equilibrium and we must have  $du/dx \Rightarrow 0$ on either side of the wave. Also, u dc/dx must remain finite everwhere. In order for the solution of the equations in the preceding section to be meaningful in the present context, clearly du/dx must remain finite during the transition from one equilibrium state to the other. It follows at once from equation 11 that u must be less than  $a_f$ 

everwhere. Since u decreases and  $a_f$  increases in passing, with the flow, through the shock front, it is sufficient to specify that  $u_1 < a_{f_1}$  (suffix 1 signifying the "upstream" equilibrium state).

Using equations 18 and 19 with equation 11 we have

$$(a_{f}^{2} - u^{2}) \frac{du}{dx} - a_{f}^{2} \sigma \frac{c'}{\tau'} = 0. \qquad (24)$$

Equations 10 and 23 show that

$$\tau' u \frac{dc'}{dx} - \tau' \lambda \rho u^2 \frac{du}{dx} + c' = 0.$$
 (25)

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and elimination of c' between these two equations leads to an equation in derivatives of u only.

$$\tau' u \frac{d}{dx} \left\{ (a_{f}^{2}\sigma)^{-1} (a_{f}^{2} - u^{2}) \frac{du}{dx} \right\}$$
  
+  $(a_{f}^{2}\sigma)^{-1} \left\{ a_{f}^{2} - u^{2} (1 + \rho a_{f}^{2}\sigma \lambda) \right\} \frac{du}{dx} = 0$  (26)

Equation 26 is still somewhat awkward to handle as it stands and we intend to make two more approximations, which are not, however of a very drastic nature. In the first place we recall the result in equation 14. The dominant term there is D/3, since  $DW_2/R$  is  $\approx 6 \times 10^{40}$ K for a typical gas (oxygen, for example) of the type that we are considering. Typically, T may be of order  $4 \times 10^{30}$ K in the "interesting" dissociation range and we are concerned with relatively small variations of T about the mean value through the wave (of order  $10^{20}$ K say, but see the example below). Variations of c will also be small and we may fairly take the term  $(a_f^2 \sigma)^{-1}$  as constant

#### in equation 26.

It has been shown (Clarke, 1958) that, if all of  $\rho$ ,  $a_f$ ,  $\sigma$  and  $\lambda$  are evaluated in an equilibrium state, then  $1 + \rho a_f^2 \sigma \lambda$  is equal to the square of the ratio of frozen to equilibrium sound speeds in that state. In equation 26,  $\rho$ ,  $a_f$  and  $\sigma$  are evaluated at actual values of the thermodynamic variables, which are not equilibrium values in general.  $\lambda$  is evaluated in terms of c (p, s). We remark that the maximum value of the sound speeds ratio squared seems to be about 1.4, roughly speaking, whence it follows that any variations in the product  $\rho a_f^2 \sigma \lambda$  are relatively (about 0.4 : 1) less important here. In fact it seems reasonable, firstly to treat  $1 + \rho a_f^2 \sigma \lambda$  as constant everywhere and secondly, to write it as  $(a_f/a_e)^2$ , where  $a_f$  is the equilibrium sound speed. This latter approximation becomes exact far in front of and far behind the wave.

Accepting these approximations, the gas velocity u satisfies the differential equation

$$\tau'\left(\frac{a_e}{a_f}\right)^2 u \frac{d}{dx} \left\{ \left(a_f^2 - u^2\right) \frac{du}{dx} \right\} + \left(a_e^2 - u^2\right) \frac{du}{dx} = 0.$$
 (27)

We note that although  $(a_f/a_o)^2$  is treated as a constant here, so that we shall write

$$\tau' \left(\frac{a}{a_f}\right)^2 = \tau'' = constant$$
 (28)

in what follows, a, and a separately will vary from one side of the wave to the other.

It can be shown that

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$$a_{f}^{2} = \frac{4+c}{3} \cdot \frac{p}{\rho}$$
 (29)

for the ideal dissociating gas, but it is quite consistent with the previous approximations to write

$$a_{f}^{2} = \gamma_{f} \frac{p}{\rho}$$
(30)

and also

$$a_e^2 = \gamma_e \cdot \frac{p}{\rho} , \qquad (31)$$

and to treat  $\gamma_f$  and  $\gamma_e$  hereafter as constants, (or better still, as constant suitable mean values).

Proceeding on this basis we find from equation 10 that

$$a_{f}^{2} = \gamma_{f} \left(\frac{F}{Q} - u\right)u, \qquad (32)$$

with a similar result for  $a_e^2$ . Then equation 27 can be integrated once to give

$$\tau''(a_{f}^{2}-u^{2})\frac{du}{dx}+\gamma_{e}\frac{F}{Q}u-(\gamma_{e}+1)\frac{u^{2}}{2}=Constant \qquad (33)$$

Since  $a_f^2 - u^2 \neq 0$  and we expect to find  $du/dx \neq 0$  upstream and downstream of the wave, the integration constant can be found when  $u = u_q$ , the upstream value (which we can take as given at  $x = -\infty$ ). Then clearly the term

$$-(\gamma_{e}+1)\frac{u^{2}}{2}+\gamma_{e}\frac{F}{Q}u-\gamma_{e}\frac{F}{Q}u_{1}+(\gamma_{e}+1)\frac{u_{1}^{2}}{2}$$
(34)

must be zero again (at  $x = +\infty$ ), where  $u = u_2$ , say. It follows that we can now write equation 33 as

$$\tau'' \left\{ \gamma_{\rm f} \; \frac{\rm F}{\rm Q} \; u - (\gamma_{\rm f} + 1)u^2 \right\} \frac{\rm du}{\rm dx} = \frac{(\gamma_{\rm e} + 1)}{2} \; (u - u_{\rm s})(u - u_{\rm g}). \tag{35}$$

Making use of the fact that

$$u_{n}\left\{\frac{\gamma_{f}}{\gamma_{f}+1}, \frac{F}{Q}-u_{n}\right\} = \frac{a_{fn}^{*}-u_{n}^{*}}{\gamma_{f}+1}; n = 1 \text{ or } 2$$

equation 35 can be integrated to give the result

$$\left(\frac{a_{f_1}^2 - u_1^2}{u_1 - u_2}\right) \log (u_1 - u) - \left(\frac{a_{f_2}^2 - u_2^2}{u_1 - u_2}\right) \log (u - u_2) = (\gamma_e + 1) \frac{x}{2\tau''} + (\gamma_f + 1)u + \text{Const.}$$
(36)

The constant here is arbitrary and merely serves to locate the origin of x. This result may be compared with Lighthill's (1956) result for the relaxation resisted shock. Not unnaturally, in view of the constant  $\gamma_{p}$  and  $\gamma_{p}$  assumptions implied in

equations 30 and 31, the results are similar: in fact the term  $(\gamma_f + 1)u$  does not appear in Lighthill's equation, but since u is restricted to an even smaller range of variation, in his case no serious error would be incurred by writing  $u = u_i$  there and absorbing  $(\gamma_f + 1)u_i$  in the arbitrary constant.

We reiterate Lighthill's remarks here, that the coefficients  $(a_{fn}^2 - u_n^2)(u_1 - u_2)^{-1}$ (where n = 1 or 2) are the scale factors for the rate of change of u near the head and tail of the shock front. In particular we see that if  $u_1 * a_{f_1}$ , the changes in u with x in the head of the wave become extremely rapid. Since  $u_1$  will approach  $a_{f_1}$  before  $u_2 * a_{f_2}$ , it follows that the fully-dispersed wave begins to break down near the head first, this part of the wave being governed by relaxation\* or viscous effects. Some examples of the velocity profile through a fully dispersed wave are given below (see also Griffith and Kenny, 1957). Once the velocity profile has been found, the density profile follows at once from equation 2.

The variation of the concentration difference c' follows from equations 24, 28 and 33, which give

$$c' = -\frac{(\gamma_e + 1)}{2 a_e^2 \sigma} (u_1 - u) (u - u_2).$$
 (37)

With the assumptions of constant  $\gamma_e$  and  $\gamma_f$  it follows that we may, as with  $a_f^2 \sigma$ , treat  $a_e^2 \sigma$  as constant. Whence the maximum value of c'occurs when  $2u = u_1 + u_2$  and has the value

$$c'_{\max} = -\frac{(\gamma_e + 1)}{8 a_{e_1}^2 \sigma_1} (u_1 - u_2)^2$$
(38)

We can find the velocity increment  $u_1 - u_2$  by solving the quadratic equation obtained on setting expression 34 equal to zero. Thus

$$u_{1} - u_{2} = \frac{2(u_{1}^{2} - a_{e}^{2})}{(\gamma_{e} + 1)u_{1}} = \frac{2(a_{e}^{2} - u_{2}^{2})}{(\gamma_{e} + 1)u_{2}}$$
(39)

See below

and it follows from equations 38 and 39 that

$$c'_{\max} = -\frac{\left(M_{e_1} - M_{e_1}^{-4}\right)^2}{2\sigma_1(\gamma_e + 1)}$$
 (40)

If we take  $M_{e_1} = 1.2$  (about the maximum possible) and  $\sigma_1 \approx 1$  (which is conservatively small for a large part of the dissociation range), then  $c'_{max} \sim 0.04$ , which is small enough for a linear rate law approximation to appear reasonable.

It is interesting to observe that c' (at a given u) is independent of the reaction rate (as summarised in the chemical time  $\tau'$ ). Since the significant thickness of the shock is clearly measured in some multiple of  $\tau' u_i$  (see equation 36), the entropy and reaction equations show that the entropy rise is independent of  $\tau'$ . In other words, the connection between initial and final equilibrium states is independent of the shock structure and merely requires that some dissipative mechanism shall be present to resist the convective steepening effects. That mechanism is provided by the chemical reactions in this case.

We may use the result in equation 21 (neglecting the last term there) in order to estimate the changes in  $c_e(p,s)$ . Assuming a suitable mean value for  $\lambda$  ( $\lambda_1$  will do as a first approximation) we can readily show that

$$c_{(p,s)} - c_{\alpha} \approx \lambda_{(p-p_{\alpha})} = \lambda_{Q} (u_{\alpha} - u), \qquad (42)$$

using the momentum equation (equation 10). The maximum value of  $c_e - c_1$  occurs when  $u = u_2$  (since u decreases monotonically). Whence equations 39 and 42 show that

$$(c_e(p,s) - c_1)_{max} = c_2 - c_1 \approx 2\lambda_1 \cdot \frac{\gamma_e P_1}{\gamma_e + 1} (M_{e1}^2 - 1) \cdot (43)$$

The value of  $p_1\lambda_1$  can be found in Clarke (1960) and is very roughly of order  $(RT_1/W_2D)$ , or about 10<sup>-1</sup>, to give it some numerical magnitude. Thus with  $M_{e1} = 1.2$  it follows that  $c_2 - c_1 \sim 0.04$ .<sup>\*</sup> Changes in atom mass fraction are therefore extremely small throughout the wave and the assumptions involving constant  $\gamma_f$ ,  $\gamma_e$ ,  $a_f^2\sigma$  etc. are apparently quite justifiable. (Note that  $p_2\rho_1/p_1\rho_2 = 1 + (2/\gamma_e + 1)(M_{e1} - M_{e1}^{-1})(\gamma_e M_{e1} - M_{e1}^{-4})$  $= T_2/T_1(1 + c_2/1 + c_1)$  so that T varies only a little across the wave too).

It should be emphasised that these estimates are quite crude, so that not too much significance should be attached to the similarity between  $c_2 - c_1$  and  $c'_{max}$ .

#### 4. Numerical Example

To illustrate the results just obtained we consider the following situation. The upstream (suffix<sub>1</sub>) flow is assumed to be at a pressure of one atmosphere and a temperature of 4,250 K. With an oxygen-like Lighthill gas, it follows that  $c_1 = 0.78$ . Also  $(a_{f_1}/a_{e_1})^a = 1.35$ . We may therefore take  $\gamma_f = 1.59$  and  $\gamma_e = 1.18$ . The value of  $p_1 \lambda_1$  for these conditions is 0.086.

By a suitable choice of the constant in equation 36 the velocity profile equation can be written in non-dimensional form as

$$(M_{f_{1}}^{-2} - 1)\log(1 - u/u_{1}) - (M_{f_{2}}^{-2} - 1)\log(u/u_{1} - u_{2}/u_{1}) - (\gamma_{f} + 1)(u/u_{1})$$

$$= (\gamma_{e} + 1)(1 - u_{2}/u_{1})(\gamma_{f}/\gamma_{e})(x/2\tau'u_{1}) .$$

$$(44)$$

The ratio  $(u/u_{4})$  calculated from this expression is plotted against  $(x/\tau' u_{4})$  in Fig. 1, for two values of  $M_{e_{1}}^{2}$ , namely 1.1 and 1.2. The sharpening up of velocity variations in the head of the wave as  $M_{e_{1}}^{2} * (a_{f_{4}}/a_{e_{1}})^{2}$  is apparent, as is the decrease in wave width in terms of  $(x/\tau' u_{4})$  units under the same conditions. Under the chosen conditions  $u_{4} = 1.6 \times 10^{5}$  cm/sec when  $M_{e_{4}}^{2} = 1.1$  and  $1.67 \times 10^{5}$  cm/sec. when  $M_{e_{1}}^{2} = 1.2$ . The wave thickness is roughly given by  $(x/\tau' u_{4}) \sim 10$ , so that practical wave thickness will be  $\sim 1.6 \tau'$  cm. if  $\tau'$  is measured in microseconds. In fact it would seem that  $\tau'$ is in the region of  $1\mu$  sec for oxygen dissociation in the range of variables considered in the present example (see below). It seems that measurable profiles could therefore occur with a judicions choice of initial conditions.

(If we choose to define wave thickness as the change in  $x/\tau' u_1$  in going from velocity  $u_1 - 0.05 (u_1 - u_2)$  to velocity  $u_2 + 0.05 (u_1 - u_2)$  we find that  $\Delta (x/\tau' u_1) = 15.23$  at  $M_{e_1}^2 = 1.1$  and = 7.69 at  $M_{e_1}^2 = 1.2$ ).

Some values of mass fraction c and the equilibrium mass fraction  $c_e(p,s)$  have also been calculated for the one case of  $M_{e_1}^2 = 1.1$ , using equations 37 and 42. They are plotted in Fig. 1 as a difference from  $c_1$  (which equals 0.78).

The temperature change through the wave whose equilibrium Mach number is  $\sqrt{1.1}$  can be found from the expression at the end of the previous section, and turns out to be given by  $(T_2/T_1) - 1 = 0.0195$ . The small variations of both c and T through this wave are ample confirmation that some of the averaging approximations made in the analysis are justifiable.

The value of  $\tau'$  in equation 18 can be obtained via the method proposed in the paragraph following that equation. Carrying out an order of magnitude, slide rule, calculation for the  $M_{e_1}^2 = 1.1$  case using three points at  $u/u_1 = 0.97$ , 0.95 and 0.93 it is found that  $\tau' \sim 10^9/k_r$ , where  $k_r$  is measured in (mole/c.c)<sup>-2</sup> sec<sup>-1</sup>. An acceptable value for  $k_r$  seems to be about  $10^{45}$  in these units, confirming that  $\tau'$  is indeed of the order of 1  $\mu$ sec in the present problem.

## 5. Weak Reaction-Resisted Shocks

Following Lighthill (1956), we may ignore the difference between  $(a_{fi}^2 - u_i^2)$  and  $(a_{fi}^2 - u_i^2)$  when the shock is very weak (i.e.  $M_{ei} \approx 1$ ). We may also write  $(\gamma_f + 1)u \approx (\gamma_f + 1)u_i$  on the right-hand side of equation 36, whence the velocity profile is approximately given by

$$\frac{u_{1} - u}{u_{2}} \simeq \exp\left\{\frac{(\gamma_{e} + 1)(u_{1} - u_{2})x}{2\tau''(a_{f_{1}}^{2} - a_{e_{1}}^{2})}\right\}.$$
(45)

having put  $u_1 \approx a_{e_1}$  in the denominator of the exponential term. The profile of a shock wave of similar velocity amplitude which is resisted by a bulk viscosity  $\kappa_1$  is given by

$$\frac{u_{1} - u}{u_{2} - u_{2}} = \exp\left\{\frac{(\gamma_{e} + 1)(u_{1} - u_{2})x}{2(\kappa_{1}/\rho_{1})}\right\},$$
(46)

assuming the same  $\gamma_e$  in both cases. It follows that the action of the chemical reactions here is similar to that of a bulk viscosity  $\kappa_e$  given by

$$\kappa_1 \simeq \rho_1 \tau'' (a_{f_1}^2 - a_{e_1}^2).$$
 (47)

With the values given in the numerical example above, this implies that  $\kappa_1 \sim 0.3 \tau'$  gm/cm.sec. if  $\tau'$  is measured in microseconds. The ordinary shear viscosity probably has a value of about 10 gm./cm.sec., so that if  $\tau'$  is about 1 µsec., we see at once how very much more powerful the reactions are in resisting the convective steepening than is shear viscosity (and indeed also thermal conduction, which is comparable in effectiveness with the latter).

The strong dependence of  $\kappa_i$  on the difference between  $a_{f_i}^2$  and  $a_{e_i}^2$  is clear from equation 47. An exactly similar result to this holds for relaxation effects in like circumstances (Lighthill, 1956) and we note that, if vibrational relaxation in a diatomic molecule is considered, so that  $\gamma_e = 9/7$  and  $\gamma_f = 7/5$ , the maximum value of  $(a_{f_i}/a_{e_i})^2$  then is only 1.09, compared with 1.35 in our chemical example. It seems reasonable to speculate that vibrational relaxation will not be very significant in a chemically-resisted wave front (under the conditions of our numerical example, anyway) since we do not expect the vibrational relaxation time to be much greater than the chemical time  $\tau'$ . Rather do we expect it to be somewhat smaller than  $\tau'$ ; and it must be remembered too that only 22% of the mixture consists of molecules in this case. When the "chemical  $(a_{f_1}/a_{e_1})^2$ " begins to fall off and the atom mass fraction decreases too it is possible that vibrational relaxations play a larger role in deter-

mining u vs. x profiles. Presumably one must always consider the "secondary" effect which vibrational relaxation may have on the chemical time  $\tau'$ . Such detailed considerations are most interesting, but outside the scope of the present, heuristic, discussion however.

## 6. Conclusions

The foregoing analysis demonstrates that reaction-resisted shock fronts are possible and that their general character is precisely the same as that of Lighthill's fully dispersed, relaxation resisted, shock. This in itself is not perhaps a very startling conclusion; one would suspect as much without the need for analysis to prove the point. However, the numerical orders of magnitude in the present case are interesting since they suggest that a reaction-resisted shock should be observable experimentally without undue difficulty.

7. References

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