INFLUENCE OF NONEQUILIBRIUM CHEMICAL REACTIONS ON THE DECAY OF AN ARBITRARY DISCONTINUITY

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Experiments [1, 2] show that in a shock tube in which the driven gas is a gas mixture reacting with heat release, after rupture of the diaphragm a compression shock forms near the contact surface and propagates through the reacting mixture, which is compressed in the shock wave.

We will examine the beginning of the decay process of an arbitrary discontinuity, when the driven gas is a chemically reacting mixture, and the driver gas is an inert gas. As in the problem of the effect of relaxation oscillation on the decay of an arbitrary discontinuity [3], we will use the series expansion method. The analysis is developed for the slow reaction

$$A_2 + B_2 \to 2AB \tag{1}$$

without taking oscillation relaxation into account.

If this reaction involves heat release, then compression waves will propagate in both directions from the contact surface, the shock wave formed upon rupture of the diaphragm will be decelerated, while, in the further process, fusion of the compresion waves leads to the appearance of a compresion shock.

If the reaction involves heat absorption, then rarefaction waves will propagate in both directions from the contact surface, the latter will be accelerated, and the shock wave will be decelerated. This analysis is extended to cover the case of a shock wave reflected from the end face of the tube in a reacting mixture.

Let the diaphragm exhibit, at the initial moment of time, a discontinuity of the constant parameters

$$\begin{gathered}\theta_1 = \theta_+, \quad P_1 = P_+, \quad V_1 = 0,\\ \theta_2 = \theta_-, \quad P_2 = P_-, \quad V_2 = 0,\\[1ex] \begin{matrix}\mu_1 = \mu_+, & \gamma_1 = \gamma_+, & x \geqslant 0\\ \mu_2 = \mu_-, & \gamma_2 = \gamma_{1-}, & x \leqslant 0\end{matrix} \left(\gamma = \frac{c_p}{c_v}\right).\end{gathered} \tag{2}$$

The low-pressure chamber ($x \geq 0$) is filled with a stoichiometric mixture of two gases—A_2 and B_2. The formation of the AB component that begins after the passage of a shock wave through the mixture, will be treated in accordance with the Arhenius law [4]

$$\frac{dn\,(AB)}{dt} = A\, n\,(A_2)\, n\,(B_2) \exp\left(-\frac{E}{R\theta}\right). \tag{3}$$

Excitation of oscillatory degrees of freedom of the diatomic gas molecules of A_2, B_2, and AB will be neglected. Then, for the specific enthalpies we have

$$\begin{gathered}h\,(A_2) = \frac{7}{2}\frac{R\theta}{\mu\,(A_2)},\\ h\,(B_2) = \frac{7}{2}\frac{R\theta}{\mu\,(B_2)}, \quad h\,(AB) = \frac{7}{2}\frac{R\theta}{\mu(AB)} - Q_0.\end{gathered} \tag{4}$$

In the expressions (2) through (4) use is made of the following notation: θ is temperature, P pressure, V velocity, μ molecular weight, c_p and c_v are specific heats, x is the distance from the diaphragm t time, n the number of molecules per unit volume, A a constant, E the activation energy, R the gas constant, and Q_0 the thermal effect of the reaction ($Q_0 > 0$ for $Cl_2 + H_2$ 2HCl and $Q_0 < 0$ for, say, $N_2 + O_2 \to 2NO$).

We note that, regardless of the quantity of newly formed component AB, the molecular weight of the mixture will be constant:

$$\mu_1 = {}^1/_2\, [\mu\,(A_2) + \mu\,(B_2)]. \tag{5}$$

If viscosity and heat conductivity are not considered, the one-dimensional steady flow resulting from the discontinuity of the initial parameters (2) is described on each side of the contact surface by the equations

$$\begin{gathered}\frac{\partial \rho_i}{\partial t} + \frac{\partial \rho_i V_i}{\partial x} = 0, \quad \frac{\partial V_i}{\partial t} + V_i \frac{\partial V_i}{\partial x} = -\frac{1}{\rho_i}\frac{\partial P_i}{\partial x},\\ \frac{\partial h_i}{\partial t} + V_i \frac{\partial h_i}{\partial x} = \frac{1}{\rho_i}\left(\frac{\partial P_i}{\partial t} + V_i \frac{\partial P_i}{\partial x}\right),\end{gathered} \tag{6}$$

where, with allowance for (4) and (5),

$$\begin{gathered}\rho_1 = \frac{P_1\mu_1}{R\theta_1}, \quad h_1 = \sum C\,(k)\, h\,(k) = \frac{7}{2}\frac{R\theta_1}{\mu_1} - Q_0 C,\\ \rho_2 = \frac{P_2\mu_2}{R\theta_2}, \quad h_2 = \frac{\gamma_2}{\gamma_2 - 1}\frac{R\theta_2}{\mu_2}\end{gathered} \tag{7}$$

(ρ is density and C the mass of AB).

For the driven gas, in addition to (6), from (3) we have

$$\frac{\partial}{\partial t}(\rho_1 C) + V_1 \frac{\partial}{\partial x}(\rho_1 C) = \frac{AN}{4\mu_1}\rho_1^2 (1 - C)^2 \exp\left(-\frac{E}{R\theta_1}\right) \tag{8}$$

(N is the Avogadro's number).

Let us pass to the independent variables t and ψ and introduce the dimensionless parameters

$$\begin{gathered}\tau = \frac{t}{t_0}, \quad \zeta = \frac{(R_0\theta_0)^{1/2}}{P_0 t_0}\psi, \quad p = \frac{P}{P_0},\\ T = \frac{\theta}{\theta_0}, \quad u = \frac{V}{(R_0\theta_0)^{1/2}}, \quad Q = \frac{Q_0}{R_0\theta_0},\\ \psi = \int_{x_*(t)}^{x} \rho_i dx \qquad \left(R_0 = \frac{R}{\mu_1}, \quad t_0 = \frac{4R\theta_0}{ANP_0}\exp\frac{E}{R\theta_0}\right),\end{gathered} \tag{9}$$

where $x_*(t)$ is a coordinate of the contact surface and P_0 and θ_0 are certain constants to be determined.

Then, taking (7) and (9) into account, the expressions (6) and (8) will take the form

$$\frac{T}{p}\frac{\partial p}{\partial \tau}-\frac{\partial T}{\partial \tau}+p\frac{\partial u}{\partial \zeta}=0,\quad \frac{\partial u}{\partial \tau}=-\frac{\partial p}{\partial \zeta},$$

$$\frac{7}{2}\frac{\partial T}{\partial \tau}-\frac{T}{p}\frac{\partial p}{\partial \tau}=Q\frac{\partial C}{\partial \tau},$$

$$\frac{\partial}{\partial \tau}\left(\frac{p}{T}C\right)=\left[\frac{p}{T}(1-C)\right]^2\exp\frac{E}{R\theta_0}\left(1-\frac{1}{T}\right). \qquad (10)$$

Linearizing near these constants, and expressing the solution in the form

$$T=1+\sum \tau^n T_n(z),\qquad p=1+\sum \tau^n p_n(z)\qquad (n=0,1,2,\ldots)$$
$$u=u^\circ+\sum \tau^n u_n(z),\quad C=\sum \tau^n C_n(z),\quad z=\zeta/\tau, \qquad (11)$$

from (10) we obtain n systems of ordinary differential equations for determining T_n, p_n, u_n, and C_n:

$$nu_n-zu_n'+p_n'=0,\quad {}^5\!/_7(np_n-zp_n')+u_n'={}^2\!/_7Qf_n,$$

$$T_n'-(n/z)T_n={}^2\!/_7(p_n'-n/zp_n-Qf_n/z),$$

$$C_n'-(n/z)C_n=-f_n/z\qquad (f_0=0,\quad f_1=1,$$

$$f_n=(E/R\theta_0-2)T_{n-1}-2p_{n-1}-2C_{n-1}\ \text{for}\ n\geqslant 2). \qquad (12)$$

From (12) for n = 0, we obtain

$$p_0=\text{const},\quad u_0=\text{const},\quad C_0=\text{const}=0,\quad T_0=\text{const}. \qquad (13)$$

From (12) and (13) it can be seen that for n = 0 the flow parameters in the reacting mixture are "frozen." Assuming in (13) that $T_0 = p_0 = u_0 = C_0 = 0$, we will take for the constants θ_0, P_0, $V_0 = u^\circ(R_0\theta_0)^{1/2}$ the corresponding parameters behind a shock wave propagating at a constant velocity V_0°, associated with the decay of an arbitrary discontinuity [5] calculated for initial conditions (2) without considering the chemical reaction. Here, the temperature of the driver gas at the contact surface will be denoted by θ_*.

Then, the boundary conditions for (12) at the contact surface will be

$$u_n=-Gp_n\quad \text{at}\quad z=0, \qquad (14)$$

and at the shock wave

$$u_n=Dp_n,\quad T_n=Fp_n,\quad C_n=0\quad \text{at}\quad z=U, \qquad (15)$$

where

$$U=\frac{V_0^\circ-V_0}{(R_0\theta_0)^{1/2}},\qquad G=\left(\frac{\theta_*\mu_1}{\gamma_2\theta_0\mu_2}\right)^{1/2},\qquad M_0=\frac{V_0^0-V_1}{(\gamma_1R_0\theta_1)^{1/2}},$$
$$D=\frac{1+M_0^2}{2M_0^2}\left(\frac{\theta_1}{\gamma_1\theta_0}\right)^{1/2}\frac{P_0}{P_1},\qquad F=\frac{\gamma_1-1}{\gamma_1+1}\left(1+\frac{1}{\gamma_1M_0^2}\right)\frac{\theta_1P_0}{\theta_0P_1}.$$

Eliminating p_n and u_n, respectively, in the first two equations of (12) we obtain

$$(1-{}^5\!/_7z^2)u_n''+{}^5\!/_72(n-1)zu_n'-{}^5\!/_7n(n-1)u_n={}^2\!/_7Qf_n',$$
$$(1-{}^5\!/_7z^2)p_n''+{}^5\!/_72(n-1)zp_n'-{}^5\!/_7n(n-1)p_n=$$
$$={}^2\!/_7Q[zf_n'-(n-1)f_n. \qquad (16)$$

We will obtain a solution for n = 1. From (16) it follows that

$$u_1=a_1(1-\sqrt{{}^5\!/_7}z)+b_1(1+\sqrt{{}^5\!/_7}z),$$

$$p_1=A_1(1-\sqrt{{}^5\!/_7}z)+B_1(1+\sqrt{{}^5\!/_7}z). \qquad (17)$$

We will determine the arbitrary constants a_1, b_1, A_1, and B_1 by making use of (14), the first condition in (15), and the first two equations in (12):

$$A_1=\frac{U}{7}\frac{(\sqrt{{}^5\!/_7}-G)Q}{\sqrt{{}^5\!/_7}({}^5\!/_7U+D+G+GDU)},\qquad B_1=\frac{\sqrt{{}^5\!/_7}+G}{\sqrt{{}^5\!/_7}-G}A_1,$$

$$a_1=\sqrt{{}^5\!/_7}A_1-{}^1\!/_7\sqrt{{}^7\!/_5}Q,\qquad b_1=-\sqrt{{}^5\!/_7}B_1+{}^1\!/_7\sqrt{{}^7\!/_5}Q. \qquad (18)$$

Substituting (18) and (17), we get

$$p_1=L_1Q(1+Gz),\qquad u_1=L_1Q[-G+({}^2\!/_7L_1^{-1}-{}^5\!/_7)z],$$
$$L_1={}^2\!/_7U({}^5\!/_7U+D+G+GDU)^{-1}. \qquad (19)$$

Now, from the third and fourth equations of (12) we obtain, respectively,

$$T_1={}^2\!/_7Q(1+L_1+d_1z),\qquad C=1+d_1^\circ z. \qquad (20)$$

The constants d_1 and d_1° can be determined from the second and third condition of (15), namely

$$d_1={}^7\!/_2U^{-1}({}^5\!/_7L_1+GUL_1-{}^2\!/_7),\quad d_1^\circ=-U^{-1}. \qquad (21)$$

A solution for n = 2, 3, ..., is readily obtained in same manner.

Since U, G, D, F are positive values, it is readily seen from (19) through (21) that for Q > 0 the velocity of the shock wave increases:

$$V^\circ=V_0^\circ+\tau p_1S,\qquad S=\sqrt{\gamma_1R_0\theta_1}\frac{\gamma_1+1}{4\gamma_1}\frac{P_0}{P_1M_0}. \qquad (22)$$

The pattern is reversed for Q < 0. Let us now examine the characteristics of the system of equations (10) that originate at the contact surface

$$\frac{d\zeta}{d\tau}=\sqrt{{}^7\!/_5}\frac{p}{\sqrt{T}}\approx\sqrt{{}^7\!/_5}\left(1+\tau p_1-\frac{1}{2}\tau T_1\right). \qquad (23)$$

Integrating (23) with allowance for (19) through (21), we obtain

$$\zeta=\sqrt{{}^7\!/_5}(1+\alpha_1Q\tau)\left[(\tau-\tau_0)+Q\frac{\alpha_1+\alpha_2}{2}(\tau^2-\tau_0^2)\right], \qquad (24)$$

$$(\alpha_1=\sqrt{{}^7\!/_5}(L_1G-{}^1\!/_7d_1),\quad \alpha_2={}^1\!/_7\sqrt{{}^7\!/_5}(1-6L_1),\quad \alpha_1>0,\quad \alpha_2>0),$$

the equation for the characteristic originating at the point $\zeta = 0$, $\tau = \tau_0$.

Let us find the point of intersection of this characteristic with the characteritisc that originates in $\zeta = 0$, $\tau = \tau_0 + \Delta\tau_0$, and then assume that $\Delta\tau_0$ tends to zero. We see then that for Q > 0 the characteristics (23) intersect starting with

$$\tau_*\approx[Q(\alpha_1+\alpha_2)]^{-1}.$$

Hence, for Q > 0, compression waves propagate from the contact surface, while from Q < 0 the waves are rarefaction waves. The relations derived are also applicable to the analysis of flows of a reacting gas mixture behind a reflected shock, if the reaction in the mixture sets in after the shock wave has passed through it.

For this purpose, it is necessary to take for the constants P_0, θ_0, V_0 the corresponding values of the parameters behind the reflected shock, computed without considering the chemical reaction, and also to take $G = 0$ everywhere starting with (14) and to take in (15) the velocity of the reflected wave for $V_0°$ and the velocity of the gas behind the incident shock wave for V_1.

The above discussion shows that it is possible to obtain a second compression shock upon ignition of gas mixtures by shock waves, and to calculate the subsequent flow within the limits of one-dimensional steady gas motion, taking into account the nonuniformities of the physicochemical processes.

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