PROPAGATION OF PHOTODISSOCIATION WAVES IN GASES WITH ALLOWANCE FOR CHEMICAL REACTIONS

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We investigate the process of propagation of a quasimonochromatic pulse of light in a gas mixture in which chemical transformations are possible. The analysis is carried out for the case of chain reactions in a binary gas. We calculate the profile and velocity of the photodissociation wave. We show that allowance for the chain mechanism of chemical transformations leads to an increase of the velocity and to a broadening of the profile of the wave.

1. INTRODUCTION

PHOTODISSOCIATION waves[1, 2] are among the disturbances that can propagate in a gas with supersonic velocity. As follows from [2], a particle-density discontinuity is realized on the front of a photodissociation wave at a length $l \gtrsim 100\, l_0$, where l_0 is the particle mean free path in the unperturbed gas and determines the width of the shock-wave front. At the same time, the photodissociation-wave velocity, which is determined by the pump radiation flux density I_0 and by the absorbing-molecule density A_2^0, can exceed the velocity of the shock wave with equivalent density discontinuity by several orders of magnitude.

As a result of elementary photodissociation acts, the gas molecule A_2 breaks up into two atoms A. Let us assume that a gas consisting of molecules B_2, which are chemically active with respect to the atoms A, are mixed together with the gas A_2 (it is assumed that the absorption bands of the molecules A_2 and B_2 do not overlap). Then, if the products of the chemical interaction of the molecules B_2 and of the atoms A influence effectively the rate of change of the density of the reagent A_2, then we can expect qualitative singularities to appear during the course of propagation of a quasimonochromatic pulse of light in such a binary mixture.

A typical example of a mixture with the indicated properties is a binary gas in which a chain reaction is possible. If a gas mixture A_2-B_2 having a chain transformation mechanism is exposed to light whose frequency corresponds to the spectral absorption band of the molecules A_2, then a simplified scheme of the reactions in the mixture can be represented in the form

$$A_2 + h\nu_0 \xrightarrow{\sigma} 2A, \tag{1.1}$$

$$A + B_2 \xrightarrow{k_1} AB + B, \tag{1.2}$$

$$B + A_2 \xrightarrow{k_2} AB + A, \tag{1.3}$$

$$A, B \xrightarrow{k_3} \text{breaking of chain.} \tag{1.4}$$

Unlike the case when a light pulse propagates in a pure absorbing gas A_2, the presence of the molecules B_2 causes the photon mean free path to increase, i.e., $\lambda > \lambda_0 = 1/\sigma(A_2^0)$, where σ is the photoionization cross section and (A_2^0) is the density of the gas A_2. This circumstance can be understood by taking into account the fact that as the light pulse propagates in the two-component medium, the density of the reagent A_2 decreases not only because of photodissociation, but also because of the chemical reaction (1.3) in the presence of the active center B. For this reason, some of the photons of the beam, which would be completely absorbed in a layer of thickness $\Delta x \approx \lambda_0$ of the pure gas A_2, will not find absorbing partners in the same layer, and will penetrate in the next layer, where it is consumed in photodissociation. Thus, a layer whose longitudinal dimension is $\lambda > \lambda_0$ becomes translucent. The radiation ensures in this case a displacement of a translucent layer in the gas; the thickness of this layer, and consequently its velocity, exceed the corresponding values for the ordinary photodissociation wave and depend on the radiation flux density, on the densities of the initial reagents, and on the characteristic constants of the chemical reactions.

APPROXIMATE RELATIONS FOR THE WAVE VELOCITY

It is easy to obtain an approximate relation for the photodissociation wave velocity with account taken of chain-transformation chemical reactions such as (1.2) and (1.3). Let us consider a flat layer of the binary A_2-B_2 gas of thickness $\Delta x = \lambda$, on which a beam of low-density quanta I_0 is incident. We separate in this layer a volume with unit cross section area, $V = \Delta x$. Obviously, the total number of active centers produced in this volume is equal to double the number of photons penetrating through the unit surface within the time interval Δt, i.e.,

$$[(A)_{\text{eff}} + (B)_{\text{eff}}]\Delta x = 2 I_0 \Delta t, \tag{2.1}$$

where $(A)_{\text{eff}}$ and $(B)_{\text{eff}}$ are the effective densities of the active centers A and B, and A_0 is the radiation flux density.

Further, if it is assumed that the rate constant for the production of active centers B (reaction (1.2)) is much smaller than the rate constant for their annihilation (reaction (1.3)), then the balance condition for the atoms B is written in the form

$$k_1(A)(B_2)=k_2(B)(A_2); \qquad (2.2)$$

where A, B, A_2, and B_2 are the densities of the particles of the corresponding type. For the same reason, we can put $(B)_{\text{eff}} \approx 0$ in (2.1), corresponding to a slow production and rapid annihilation of active centers B. We thus obtain from (2.1)

$$(A)_{\text{eff}}=2I_0/D, \qquad (2.3)$$

where $D = \Delta x/\Delta t$ is the wave velocity.

Taking (2.2) into account, the equation for the rate of change of the density of the reagent A_2 is

$$\frac{1}{c}\frac{\partial(A_2)}{\partial t}=-\sigma(A_2)\left[I_0+\frac{k_1}{\sigma}(A)\frac{(B_2)}{(A_2)}\right].$$

By virtue of this, we can conceive of a situation in which the photodissociation of the molecules A_2 in the volume B occurs, as it were, upon absorption of photons whose flux density, with allowance for (2.3), is

$$I_{0\,\text{eff}}=I_0+\frac{2k_1}{\sigma}\frac{I_0}{D}\frac{(B_2{}^0)}{(A_2{}^0)}$$

Equating the number of photons "entering" the volume V within a time Δt to the number of absorbing particules in the given volume, we get

$$\left[I_0+\frac{2k_1}{\sigma}\frac{I_0}{D}\frac{(B_2{}^0)}{(A_2{}^0)}\right]\Delta t=(A_2{}^0)\Delta x. \qquad (2.4)$$

Putting, as before, $D = \Delta x/\Delta t$, we obtain with the aid of (2.4) an equation connecting the velocity with the parameters of the system. The solution of this equation takes the form

$$D/D_0={}^1\!/_2+[{}^1\!/_4+2k_1(B_2{}^0)/\sigma I_0]^{1/2}, \qquad (2.5)$$

where $D_0 = I_0/(A_2^0)$ is the velocity of the usual dissociation wave, $(I_0/(A_2^0) \ll c$, and c is the speed of light). From (2.5) we can draw the physically understandable conclusion that an increase of the rate of the chain reaction increases the velocity of the photodissociation wave. In the limiting case when $2k_1(B_2^0) \gg \sigma I_0$ we get

$$D/D_0 \approx [2k_1(B_2{}^0)/\sigma I_0]^{1/2}. \qquad (2.6)$$

3. INITIAL EQUATIONS, CASE OF EQUAL BINARY MIXTURE COMPONENT DENSITIES

Having made the preliminary estimate, let us proceed directly to an investigation of the photodissociation wave with allowance for the chemical reactions (1.1)–(1.4). To describe such a wave, we start from a system of equations consisting of the one-dimensional radiation-transfer equation and the kinetic equations. Without allowance for the chain-breaking reactions (1.4), the system takes the form

$$\begin{gathered}
\left(\frac{1}{c}\frac{\partial}{\partial t}+\frac{\partial}{\partial x}\right)I=-\sigma I(A_2),\\
\frac{\partial(A_2)}{\partial t}=-\sigma I(A_2)-k_2(B)(A_2),\\
\frac{\partial(B_2)}{\partial t}=-k_1(A)(B_2),\\
\frac{\partial(A)}{\partial t}=2\sigma I(A_2)-k_1(A)(B_2)+k_2(B)(A_2),\\
\frac{\partial(B)}{\partial t}=k_1(A)(B_2)-k_2(B)(A_2),
\end{gathered} \qquad (3.1)$$

where I is the radiation-flux density and A, B, A_2, and B_2 are the densities of the components. The initial and the boundary conditions of the system (3.1) are

$$\left(1-\frac{D}{c}\right)\frac{dI}{dx'}=-\sigma I(A_2),$$

$$D\frac{d(A_2)}{dx'}=\sigma I(A_2)+k_2(B)(A_2),$$

We seek a solution of the initial system in the form of a stationary wave with velocity D to be determined; this form of solution, if its existence is rigorously established, will be obviously valid for optically thick layers of a gas medium. Thus, by assumption, the particle densities and the radiation flux density depend only on the argument $x' = x - Dt$. Then the system (3.1) takes the form

$$\begin{gathered}
D\frac{d(B_2)}{dx'}=k_1(A)(B_2),\\
D\frac{d(A)}{dx'}=-2\sigma I(A_2)+k_1(A)(B_2)-k_2(B)(A_2),\\
D\frac{d(B)}{dx'}=-k_1(A)(B_2)+k_2(B)(A_2).
\end{gathered} \qquad (3.2)$$

It is easy to ascertain that the system (3.2) has the following two integrals:

$$\begin{gathered}
2(A_2)-2(B_2)+(A)-(B)=C_1,\\
(A_2)-(B_2)+(A)-\frac{I}{D}\left(1-\frac{D}{c}\right)=C_2,
\end{gathered} \qquad (3.3)$$

where C_1 and C_2 are constants determined from the condition for $x' \to +\infty$, with $C_1 = 2C_2 = 2[(A_2^0) - (B_2^0)]$. For the density of the product of the chain reaction, the particle-conservation conditions yield

$$(AB)=2(A_2{}^0)-2(A_2)-(A)=2(B_2{}^0)-2(B_2)-(B).$$

It follows from (3.3) that

$$(A)+(B)=\frac{2I}{D}\left(1-\frac{D}{c}\right),$$

$$(A_2)=(A_2{}^0)-(B_2{}^0)+(B_2)+(B)-\frac{I}{D}\left(1-\frac{D}{c}\right). \qquad (3.4)$$

Using (3.4) and introducing the dimensionless quantities

$$b_2=\frac{(B_2)}{(B_2{}^0)},\quad b=\frac{(B)}{(B_2{}^0)},\quad u=\frac{I(1-D/c)}{(B_2{}^0)D},\quad \eta=x'\frac{k_1(B_2{}^0)}{D},$$

$$\alpha=\frac{\sigma}{k_1}\frac{D}{1-D/c},\quad \Delta=\frac{(A_2{}^0)}{(B_2{}^0)}-1,\quad \mu=\frac{k_1}{k_2}\ll 1,$$

we obtain a system equivalent to (3.2):

$$\begin{gathered}
\frac{du}{d\eta}=-\alpha u(b_2+b-u+\Delta),\\
\frac{db_2}{d\eta}=b_2(2u-b),\\
\mu\frac{db}{d\eta}=-\mu b_2(2u-b)+b(b_2+b-u+\Delta).
\end{gathered} \qquad (3.5)$$

Inasmuch as μ is a small parameter, the phase volume $(u, b_2, b, \dot{u}, \dot{b}_2, \dot{b})$ breaks up into regions of "slow" motions (the first two equations of the system (3.5)) and "fast" motions (the third equation).[3] Therefore, in accordance with the general procedure, we can put[1]

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[1] It is easy to show that the "fast" motions are always stable; naturally, it is necessary to take into account here the fact that in the laboratory system the events are observed in opposite sequence compared with an observer taht registers the events in a system connected with the wave. It is necessary to put formally $\eta \to -\eta'$.

$$\mu b_2(2u-b)=b(b_2+b-u+\Delta), \tag{3.6}$$

from which we obtain for the dimensionless density of the active centers B, which follows in a quasistationary manner the variation of the variables b_2 and u, we obtain

$$b=-{}^1/_2[b_2(1+\mu)-u+\Delta]+\{{}^1/_4[b_2(1+\mu)-u+\Delta]^2+2\mu b_2u\}^{1/2}. \tag{3.7}$$

For simplicity let us consider the case of equal concentrations of the reagents A_2 and B_2, i.e., $\Delta = 0$.

Introducing the substitution $z = b_2(1+\mu)/u$, we can obtain from (3.5) with the aid of (3.6) and (3.7) the following equation:

$$\frac{dz}{du}=-z-\frac{1}{2\alpha\mu'}(1-z+[(z-1)^2+8\mu' z]^{1/2}), \tag{3.8}$$

here $\mu' = \mu/(1+\mu)$. Integration of (3.8) yields

$$\left[1+\frac{(2-\alpha)(1-2\alpha\mu')}{\alpha(1-\alpha\mu')}-q_2\right]\ln\left(z+\frac{2-\alpha}{\alpha(1-\alpha\mu')}\right)$$
$$+[4\mu'-q_1]\ln(\sqrt{Z}+z-1+4\mu')-\ln[(z+1)\sqrt{Z}+1+z^2+4\mu' z]$$
$$+q_2\ln\left[\sqrt{Z}+q_2+\frac{q_1}{q_2}\left(z+\frac{2-\alpha}{\alpha(1-\alpha\mu')}\right)\right]+\frac{2}{\alpha}(2-\alpha)\ln u=C,$$
$$Z=(z-1)^2+2\mu' z, \tag{3.9}$$
$$q_1=-\frac{2-\alpha\mu'(4+\alpha)+4\alpha^2\mu'^2}{\alpha(1-\alpha\mu')},\qquad q_2=[q_1^2+8\mu'(1-\mu')]^{1/2}.$$

Taking into account the smallness of the parameter μ and retaining in (3.9) terms up to first order inclusive, we obtain

$$F_1^{[2/\alpha-\mu(2-\alpha)]}F_2^{2\mu(2-\alpha)}F_3^{-1}u^{2(2-\alpha)/\alpha}=\text{const}, \tag{3.10}$$
$$F_1=\sqrt{Z}[4+\alpha(z-1)]+\alpha(z-1)^2+4(z-1)(1+\mu\alpha)+\frac{4}{\alpha}(2+\mu\alpha)^2,$$
$$F_2=\sqrt{Z}+z-1+4\mu,\ F_3=\sqrt{Z}(z+1)+1+z^2+4\mu z.$$

The value of the constant in the integral (3.10) is determined from the conditions as $\eta \to \pm\infty$. In the case $\eta \to \infty$ we have $b_2 \to 1$, $u \to 0$, and $z \to \infty$, and in the case $\eta \to -\infty$ we have $b_2 \to 0$, $u \to i_0(1-D/c)/N_0D$ ($N_0 = (A_2^0) = (B_2^0)$), and $z \to 0$. We thus have

$$[2^{2/\alpha-1+\mu(2-\alpha)}\alpha^{2/\alpha-\mu(2-\alpha)}]_{+\infty}=\Bigg[2^{6/\alpha-1+\mu(2-\alpha)}\alpha^{-2/\alpha+\mu(2-\alpha)}\mu^{2\mu(2-\alpha)}.$$
$$\times\left(\frac{I_0(1-D/c)}{N_0D}\right)^{4/\alpha-2}\Bigg]_{-\infty}=\text{const}. \tag{3.11}$$

Relation (3.11) determines the implicit dependence of the wave velocity D on the system parameters. Let us establish this dependence for the limiting $\mu \to 0$. If we introduce the notation

$$y=\frac{DN_0}{I_0(1-D/c)},\qquad \xi=\frac{2k_1N_0}{\sigma I_0},$$

then (3.11) takes the form

$$y=\xi^{\xi/(2\xi-y)}. \tag{3.12}$$

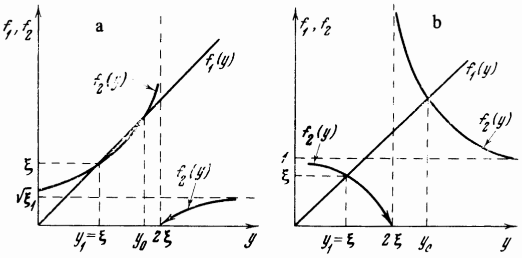


FIG. 1. Graphical determination of the roots of Eq. (3.12); $f_1(y) = y$, $f_2(y) = \xi^{\xi/(2\xi-y)}$.

The transcendental equation (3.12) was investigated graphically (see Figs. 1a and b). This equation admits of two roots corresponding to the intersection of the functions: $f_1(y) = y$, $f_2(y) = \xi \exp \xi/(2\xi - y)$. Obviously, Eq. (3.12) is satisfied by the root $y_1 = \xi$. For the second root y_0 it is easy to show that: (1) if $\xi < 1$, then $y_0 > 1$; (2) if $1 < \xi < e$, then $\xi < y_0 < 2\xi$; (3) if $\xi > e$, then $\sqrt{\xi} < y_0 < \xi$. When $\xi = 1$ we have $y_0 = 2$, when $\xi = e$ we obtain $y_0 = y_1 = e$, and when $\xi \gg 1$ we have $y_0 = \sqrt{\xi}$. The latter agrees, when the inequality $\sqrt{N_0/I_0} \gg c^{-1}\sqrt{2k_1/\sigma}$ is satisfied, with the approximate relation (2.6), which is valid when $c \to \infty$.

In the limiting case $\xi \to 0$, when the chain reaction does not affect significantly the change of the density of the reagent A_2, we have $y_0 = 1$, i.e., the wave velocity D tends to the velocity of the ordinary dissociation wave, $D = D_0 = cI_0/(I_0 + cN_0)$.

A numerical calculation yields the following values for the root y_0 at fixed ξ:

ξ:	0	0,5	1	e	10	20	100
y_0:	1	1,67	2	e	4,36	5,75	11,5

From the obtained value of y we determine the wave velocity as follows:

$$\frac{D}{D_0}=y\frac{cN_0+I_0}{cN_0+yI_0}. \tag{3.13}$$

It follows from (3.13) that large ξ correspond to large wave velocities. Let us investigate the possibility of realizing the roots y_1 and y_0. Inasmuch as $y_1 = \xi = 2k_1N_0/\sigma I_0$, we have $\alpha = 2$. It is easy to verify that as $\mu \to 0$ and at $\alpha = 2$ the integral (3.10) becomes an identity. To find the solution in this case it is necessary to turn to Eq. (3.8), in which we must put $\alpha = 2$. The solution takes the form ($\mu \to 0$)

$$(|z-1|-1)/z-\ln\{[|z-1|(z+1)+1+z^2]u^2\}=C_{\pm\infty}, \tag{3.14}$$

$$C_{\pm\infty}=1-\ln 2=-1-\ln 2+2\ln y_1. \tag{3.15}$$

Relation (3.15) allows us to conclude that the root $y_1 = \xi$ is realized only in the single case when $\xi = e$, but then, as follows from the foregoing, $y_0 = e$.

In accordance with (3.14) and (3.15), the solution of Eq. (3.8) with $\xi = e$ for the regions $z \gtrless 1$ takes the form ($\mu \to 0$)

$$u=\begin{cases} z^{-1}e^{-1/z}, & z\geqslant 1\\ e^{-1}, & z\leqslant 1.\end{cases} \tag{3.16}$$

If we measure the dimensionless coordinate η from the point where $z = b_2/u = 1$, then we obtain from (3.5) in the zeroth approximation in μ, taking (3.16) into account, the following equation for the wave profile

$$\mathrm{Ei}(1)-\mathrm{Ei}(1/z)=2\eta,\quad b_2=e^{-1/z},\quad i=I/I_0=z^{-1}e^{1-1/z},\quad \eta\geqslant 0,$$
$$b_2=e^{\eta/e-1}[2-e^{\eta/e}]^{-1},\quad i=1,\quad \eta\leqslant 0, \tag{3.17}$$

where Ei is the integral exponential function. Relations (3.17), together with (3.4) and (3.7), make it possible to construct the profiles of all the variables for the case $\xi = 2k_1N_0/\sigma I_0 = e$ under consideration. For the wave velocity it is necessary to put $y = e$ in (3.13).

In the general case corresponding to the wave velocity D determined by the root $y_0 \neq e$, the zeroth approxi-

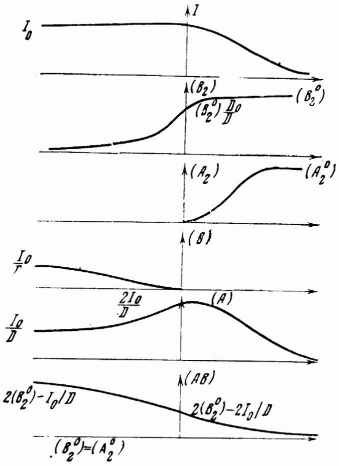


FIG. 2. Profiles of waves.

mation in μ yields for the wave profile the following relations:

$$\frac{\alpha-2}{\alpha}b_{20}^{-\alpha/2}\left\{\left(\frac{b_2}{b_{20}}\right)^{-\alpha/2}F\left(1,\frac{\alpha}{\alpha-2};\frac{2(\alpha-1)}{\alpha-2};b_2^{1-\alpha/2}\right)\right.$$
$$\left.-F\left(1,\frac{\alpha}{\alpha-2};\frac{2(\alpha-1)}{\alpha-2};b_{20}^{1-\alpha/2}\right)\right\}=\alpha\eta,$$
$$i=\frac{I}{I_0}=\frac{\alpha b_{20}^{-1}}{2-\alpha}(b_2^{\alpha/2}-b_2),\quad b=0,\quad \eta\geqslant 0; \tag{3.18}$$
$$b_2=b_{20}e^{b_{20}\eta}[2-e^{b_{20}\eta}]^{-1},\quad i=1,\ b=\frac{I_0(1-D/c)}{(B_2^0)D}-b_2,\quad \eta\leqslant 0,$$

where F is the Gauss hypergeometric function, $\alpha = \sigma D/k_1(1 - D/c) = 2y_0/\xi$, $b_{20} = y_0^{-1}$ ($y_0 \neq e$ and consequently $\alpha \neq 2$), and the origin $\eta = 0$ corresponds to $b_2/u = 1$.

It follows therefore from the foregoing that at a fixed value of ξ there is realized in the system a wave whose velocity and profile are determined in a unique manner (it is necessary to put $y = y_0$ in (3.13)).

In the particular case when the rate of the chain reaction, which coincides with double the rate of its slow link (1.2) is equal to the photodissociation rate of the reagent A_2, i.e., $\xi = 2k_1N_0/\sigma I_0 = 1$, the wave profile is described by the following analytic relations:

$$\frac{1}{b_2}+\ln\left(\frac{1-b_2}{b_2}\right)-2=-4\eta,\quad i=4b_2(1-b_2),\quad \eta\geqslant 0,$$
$$b_2={}^1\!/_2e^{\eta/2}(2-e^{\eta/2})^{-1},\quad i=1,\quad \eta\leqslant 0. \tag{3.19}$$

Thus, the obtained velocity and profile describe the wave completely. It follows from the analysis that allowance for the chain transformations leads to an increase in the velocity and to a broadening of the profile of the photodissociation wave (see Fig. 2).

4. CASE OF UNEQUAL BINARY-GAS COMPONENT DENSITIES, $\Delta \neq 0$

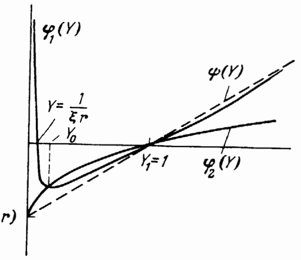
In this case we choose the origin at the point $\eta = 0$, where the following equation is satisfied

$$u|_0-\Delta=b_2|_0.$$

In the zeroth approximation in μ we then obtain from (9) for the density of the active centers B

$$b=0\ \text{if}\ b_2-u+\Delta>0,\ \eta\geqslant 0,$$
$$b=-b_2+u-\Delta\ \text{if}\ b_2-u+\Delta<0,\ \eta\leqslant 0. \tag{4.1}$$

FIG. 3. Graphical determination of the root of Eq. (4.7): $\varphi_1(Y) = (1-Y).\ln(1/\xi Y + 1-r)$, $\varphi_2(Y) = \ln(rY + 1-r)$, $\psi(Y) = (1-Y)\ln(1-r)$, $1/\xi r < 1$, $r < 1$.



For the region $\eta \geq 0$ the system (3.5) reduces to

$$\frac{du}{d\eta}=-\alpha u(b_2-u+\Delta),\quad \frac{db_2}{d\eta}=2ub_2, \tag{4.2}$$

from which we get

$$\frac{du}{db_2}=\frac{\alpha}{2}\frac{u}{b_2}-\frac{\alpha\Delta}{2b_2}-\frac{\alpha}{2}. \tag{4.3}$$

We write the solution of the linear equation (4.3) in the form

$$b_2^{-\alpha/2}(u-\Delta)+\frac{\alpha}{2-\alpha}b_2^{-\alpha/2+1}=C. \tag{4.4}$$

The constant C is determined from the conditions for $\eta \rightarrow \infty$, where $u = 0$ and $b = 1$, and for $\eta = 0$, where $u = u_0 = I_0(1 - D)/c)/(B_2^0)D$ and $b_2 = b_{20} = u_0 - \Delta$:

$$C=\frac{\alpha}{2-\alpha}-\Delta=\frac{2}{2-\alpha}(u_0-\Delta)^{(2-\alpha)/\alpha}. \tag{4.5}$$

Relation (4.5) is the equation for the wave velocity. It is convenient to rewrite this equation in the form

$$\left(\frac{r}{y}+1-r\right)^{1-y/\xi r}=\frac{y}{\xi}+1-r,$$
$$r=\frac{(A_2^0)}{(B_2^0)},\quad y=\frac{D(A_2^0)}{I_0(1-D/c)},\quad \xi=\frac{2k_1(B_2^0)}{\sigma I_0}. \tag{4.6}$$

It is easy to verify that Eq. (4.6) admits of the solution $y_1 = \xi r$. If we introduce the substitution $Y = y/\xi r$ and take logarithms at both sides of (4.6), then we obtain the equivalent equation:

$$(1-Y)\ln(1/\xi Y+1-r)=\ln(rY+1-r). \tag{4.7}$$

Equation (4.7) was investigated graphically. Figure 3 shows plots of $\varphi_1(Y) = (1 - Y) \ln(1/\xi Y + 1 - r)$ and $\varphi_2(Y) = \ln(rY + 1 - r)$. These curves intersect at the points $Y_1 = 1$ and Y_0 ($Y_1 = 1$ corresponds obviously to the root $y_1 = \xi r$). The value of Y_0 is determined numerically. In the case when the φ_1 and φ_2 curves are tangent, the roots coincide, $Y_1 = Y_0 = 1$, and this case corresponds to the relation $\xi^{-1} = e^{-r} + r - 1$; when $r = 1$ this relation goes over in the previously obtained $\xi = e$. In analogy with the case of equal concentrations, it can be shown that the photodissociation wave corresponds only to the root Y_0, which determines the wave velocity in a unique manner.

With the aid of (4.2), (4.4), and (4.5) we obtain for the wave profile

$$2\eta=\int_{b_{20}}^{b_2}b_2^{-1}\left(\Delta+Cb_2^{\alpha/2}-\frac{\alpha}{2-\alpha}b_2\right)^{-1}db_2,\quad u=\Delta+Cb_2^{\alpha/2}-\frac{\alpha}{2-\alpha}b_2,\quad \eta\geqslant 0,$$
$$b_2=(b_{20}+2\Delta)e^{(b_{20}+2\Delta)\eta}\left[2\left(\frac{\Delta}{b_{20}}+1\right)-e^{(b_{20}+2\Delta)\eta}\right]^{-1},\quad u=u_0,\quad \eta\leqslant 0. \tag{4.8}$$

It must be emphasized that the form of the analysis is valid, but not for any ratio of the component densities of the initial binary gas. The reason is that the condition for $\eta \rightarrow -\infty$ and the conservation conditions (3.4) impose definite limitations on this relation. Since the rates of change of the dynamic variables vanish when $\eta \rightarrow -\infty$, it follows from physical considerations that the boundary conditions have the form $I = A_0$ that the boundary conditions take the form $I = I_0$ and $(A_2)_{-\infty} = 0$ and (1) either $(A)_{-\infty} = 0$ $((B_2)_{-\infty} \neq 0)$, or else (2) $(B_2)_{-\infty} = 0$ $((A)_{-\infty} \neq 0)$. Case (1) corresponds to an excess of B_2 molecules, so that all the produced active centers A are consumed in the formation of the product; case (2) corresponds to an excess of the A_2 molecules. The foregoing analysis corresponds to case (2). It follows from (3.4) that the condition $(A)_{-\infty} > 0$ is equivalent to the inequality

$$\frac{(B_2{}^0)}{(A_2{}^0)} < 1 + \frac{I_0}{(A_2{}^0)D}\left(1 - \frac{D}{c}\right). \qquad (4.9)$$

5. ALLOWANCE FOR THE CHAIN-BREAKING PROCESSES

The foregoing analysis was made under the assumption that the chain breaking has little influence on the photodissociation-wave propagation in the initial binary gas. At sufficiently high pressures, the breaking of the chain (1.4) is due mainly to recombination processes. The recombination of the active centers leads to a decrease of the photon beam free path and consequently decreases the wave velocity. To eliminate the influence of this factor it is necessary to satisfy the condition[2] $l \lesssim D\tau_{\mathrm{rec}}/2$, where l is the thickness of the gas layer ($\sigma(A_2^0)l \gg 1$) and τ_{rec} is the recombination time.

In the general case, it is rather difficult to take the chain-breaking processes into account. In a number of cases the molecules of the impurity gas, say oxygen, take part in the chain-breaking reaction. If one of the active centers is a hydrogen atom, then the chain-breaking reaction is of the form[4] $H + O_2 + M \rightarrow HO_2 + M$; the reaction produces the low-activity free radical HO_2. Assuming a reaction of similar kind and that the process of chain breaking is sufficiently slow, and also that the molecules A_2 are the most effective third particles in the recombination of the active centers B and the impurity molecules, it is possible to take formal account of the chain breaking by introducing in the right-hand side of the last equation of the system (3.2) the term $+\Gamma(B)(A_2)$. This equation then takes the form

$$D(B)' = -k_1(A)(B_2) + k_2(B)(A_2) + \Gamma(B)(A_2). \qquad (5.1)$$

In real cases the inequality $\Gamma/\max(k_1, k_2) \ll 1$ is usually satisfied. It is then easy to obtain in this case from the initial system of equations the two integrals

$$(A) = \frac{2I}{D} + \frac{\Gamma}{(k_2+\Gamma)}[(B_2) - (B_2{}^0)] - \frac{k_2}{(k_2+\Gamma)}(B),$$

$$(A_2) = (A_2{}^0) + \frac{k_2}{(k_2+\Gamma)}[(B_2) - (B_2{}^0)] + \frac{k_2}{(k_2+\Gamma)}(B) - \frac{I}{D}. \qquad (5.2)$$

Taking (5.2) into account and using the same dimensionless quantities as before, we transform the initial system into the following one:

$$u' = -\alpha u\left[\Delta + \frac{\gamma}{1+\gamma} + \frac{1}{(1+\gamma)}b_2 - u + \frac{b}{1+\gamma}\right],$$

$$b_2' = b_2\left[2u + \frac{\gamma}{(1+\gamma)}(b_2 - 1) - \frac{b}{1+\gamma}\right],$$

$$\mu b' = -\mu b_2\left[2u + \frac{\gamma}{(1+\gamma)}(b_2 - 1) - \frac{b}{1+\gamma}\right]$$

$$+ (1+\gamma)b\left[\Delta + \frac{\gamma}{1+\gamma} + \frac{1}{1+\gamma}b_2 - u + \frac{b}{1+\gamma}\right], \qquad (5.3)$$

where $\gamma = \Gamma/k_2 \ll 1$.

For simplicity, let us investigate the case of equal concentrations, $\Delta = (A_2^0)(B_2^0) - 1 = 0$. Just as before, assuming the variable b to follow in a quasistationary manner the variation of the variables u and b_2, we get in the zeroth approximation in μ

$$b = 0, \quad \eta \geqslant 0,$$

$$b = u(1+\gamma) - b_2 - \gamma, \quad \eta \leqslant 0,$$

where the origin ($\eta = 0$) corresponds to the equations

$$b_{20} = u_0(1+\gamma) - \gamma, \qquad u_0 = \frac{I_0(1 - D/c)}{(B_2{}^0)D}. \qquad (5.4)$$

Neglecting the second term in the second equation of (5.3), we can obtain for the region $\eta \geq 0$ the integral

$$\beta_2^{-\alpha/2}\left(u - \frac{\gamma}{1+\gamma}\right) + \frac{\alpha}{2-\alpha}\beta_2^{-\alpha/2+1} = C,$$

$$\beta_2 = b_2/(1+\gamma). \qquad (5.5)$$

The constant C in (5.5) is determined from the conditions at $\eta \rightarrow +\infty$, where u = 0 and $b_2 = 1$, and at $\eta = 0$, where (5.4) is satisfied:

$$C = (1+\gamma)^{\alpha/2-1}\left[\frac{\alpha}{2-\alpha} - \gamma\right] = \frac{2}{2-\alpha}\left[u_0 - \frac{\gamma}{1+\gamma}\right]^{-\alpha/2+1}. \qquad (5.6)$$

The equation for the wave velocity (5.6) is conveniently written in the form

$$\left[\frac{1+\gamma}{y} - \gamma\right]^{1-y/\xi} = \frac{y}{\xi}(1+\gamma) - \gamma. \qquad (5.7)$$

Making the substitutions $\gamma \rightarrow r' - 1$ and $\xi \rightarrow (1+\gamma)\xi'$ we can easily verify that the equation for the wave velocity coincides fully with the equation (4.6) investigated above. Equation (5.7) is transcendental and its solution can be obtained by numerical methods. In the case when the rate of the chain reaction greatly exceeds the photodissociation rate, this equation admits of an approximate analytic solution

$$y_0 \approx \sqrt{\xi}\left[1 - \frac{1}{2}\left(\frac{1}{\sqrt{\xi}} - \gamma\right)\ln\left(\frac{1}{\sqrt{\xi}} - \gamma\right)\right]. \qquad (5.8)$$

Relation (5.8) corresponds to the inequalities

$$\gamma < \frac{1}{\sqrt{\xi}} \ll 1, \qquad \left|\ln\left(\frac{1}{\sqrt{\xi}} - \gamma\right)\right| \ll \sqrt{\xi}. \qquad (5.9)$$

From (5.8) we get the physically understandable deduction that the chain-breaking processes decrease the propagation velocity of the photodissociation wave.

Taking the chain breaking into account we obtain in this case for the wave profile

$$2\eta = \int_{b_{20}}^{b_2} b_2^{-1}\left[\frac{\gamma}{1+\gamma} + C\left(\frac{b_2}{1+\gamma}\right)^{\alpha/2} - \frac{\alpha}{(2-\alpha)}\frac{b_2}{(1+\gamma)}\right]^{-1} db_2,$$

$$(5.10)$$

$$u = \frac{\gamma}{1+\gamma} + C\left(\frac{b_2}{1+\gamma}\right)^{\alpha/2} - \frac{\alpha}{(2-\alpha)}\frac{b_2}{(1+\gamma)}, \quad b = 0, \quad \eta \geqslant 0;$$

$$b_2 = b_{20}e^{b_{20}\eta}[2 - e^{b_{20}\eta}]^{-1}, \quad u = u_0, \quad b = u(1+\gamma) - b_2 - \gamma, \eta \leqslant 0.$$

The obtained velocity and profile describe the wave completely. It follows from the analysis that allowance for the chain transformations leads to an increase in the velocity and to a broadening of the profile of the photodissociation wave.

Let us consider the particular case of the binary mixture H_2-Cl_2. The absorption cross section for Cl_2 is σ (λ_{max} = 3300 Å) = 2.6×10^{-19} cm², and at $T \approx 300°$ K we have $k_1 = 1.45 \times 10^{-13}$ cm³/sec and $k_2 = 3.1 \times 10^{-11}$ cm³/sec ($k_1 \ll k_2$). At $(Cl_2^0) = (H_2^0) = 2 \times 10^{18}$ cm⁻³ and $I_0 = 10^{24}$ cm⁻² sec⁻¹ we have $\xi = 2.25$, so that we obtain for the velocity $D \approx 1.2 \times 10^6$ cm/sec, and the front width at the e^{-1} level amounts to $\Delta x \approx 3$ cm.

6. CONCLUSION

In conclusion let us determine the conditions for the applicability of the performed analysis. It is obvious that the pump radiation should be sufficiently monochromatic, so as to neglect the effect of the "wings" of the absorption contour.

In the investigation of the kinetics of the photodissociation wave, with allowance for the chain transformations, it was implicitly assumed that the reactions occur under isothermal conditions, which in general is valid for "cold" chemical reactions. Yet for a number of binary mixtures the reactions (1.1) and (1.2) are accompanied by release of heat. To eliminate the thermal effect in such cases it is necessary to employ rather intensive heat dissipation, which is perfectly feasible in practice (external cooling, addition of inert gas). The thermal effect can lead, in principle, to the formation of a detonation wave (the velocity of the latter at $Q \lesssim 50$ kcal/mole is of the order of $v_{det} \lesssim 10^5$ cm/sec); in order for the photodissociation wave profile not to be distorted when allowance is made for the chemical reactions, it is necessary to satisfy the inequality $D \gg v_{det}$; estimates have shown that this condition is satisfied for a number of concrete cases.

The limitations connected with the recombination and diffusion effects, and also those connected with the possible formation of a weak shock wave due to the pressure drop on the photodissociation wave front, as was indicated in [2], remain in force, naturally, also in the case under consideration.

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