Title: State of Gas Behind Front of a Strong Shockwave

/Sostoyaniye Gaza za Frontom Sil'noy Udarnoy Volny/

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The system of equations of kinetics and gas dynamics that determine the state of gas behind strong shock waves is recorded. A method of solution is proposed that takes into account of the presence of all excited states of the actual atoms. The relaxation in air is investigated for velocities of the shock waves \( v_1 \) 10 km/sec. The fundamental processes are clarified and the relaxation times are calculated.

Examination of the stage of the gas behind the front of a strong shock wave requires the simultaneous solution of the equations of gas dynamics and physical and chemical kinetics. Difficulties are associated with the necessity of taking into account the presence of numerous chemical species that are formed in the relaxation process, and also the multiplicity of excited states of the different atoms and molecules /1,2/.

In the present paper, an appropriate system of the equations is recorded and an approximate method of its solution is proposed that takes into account the role of the excited states.

In particular, shock waves in air at velocities \( v_1 \) 10 km/sec are examined. In spite of the approximate nature of the solution, it seems to us that substantially general results are obtained.

1. We have confirmed the estimates made earlier /3/, according to which, behind a strong shock wave (for air with \( v_1 \) 10 km/sec) dissociation occurs comparatively rapidly, and the length of the relaxation zone is determined by ionization processes. This is directly opposite to the case of small velocities, when the degree of ionization increases comparatively rapidly and arrives at equilibrium with a state of nonequilibrium dissociation and then follows the changes of the latter /4/.

2. There is a nonmonotone change of the length of the zone of ionization relaxation depending on the velocity of the shock wave. In the region \( v_1 = 9 \) to 10 km/sec, the length of the zone of ionization relaxation increases with an increase of \( v_1 \)

Basic Equations

If the velocity of the shock wave is sufficiently large, then in the equilibrium zone behind the front of the shock wave, there are practically no molecules. In an appendix applied to air, it is shown that under these conditions dissociation proceeds much more rapidly than ionization. For \( v_1 \) 10 km/sec this permits one to consider relaxation in air as relaxation in a mixture of atomic gases*.

* For other molecular gases, one obtains this same result; however, the boundary value of \( v_1 \) may be different.

We shall write the basic equations for a plane shock wave in a single component gas whose atoms may be in the ground and various excited states. The application of the results to mixtures of gases does not prevent any difficulty in principle.
If the wave is stationary, the balance of the number of particles at
the kth level of the atom has the form

\[ \frac{d}{dx} (n_k v) = (n_k n_o e^{-x} - n_o n_k e^{x}) + \sum \left( (n_k a_n - n_a n_k) + \right) \\
+ P_k - a_c n_k n + \sum \left( (n_{k,m} n_{m,k} - n_{m,k} n_{k,m}) + \sum \left( n_{k,m} / e - \right) \\
- n_{m,k} n_{k,m} / e \right) \]

The left side of (1) accounts for the transport of atoms in the flow;
\( v \) is the velocity relative to the front; \( x \) is the distance from it.
The right side accounts for collisions and radiation processes. Atoms of
the kth level are ionized by collisions with electrons with effectiveness
\( j_{ke} \) and atoms, for example, at the mth level \( j_{km} \). The quantities \( j_{ke} \)
and \( j_{km} \) respectively account for the reverse processes; \( j_{kn} \) is the
probability of excitation from k to n by an electron collision \( (k \rightarrow n) \)
or by a collision of the second kind \( (n \rightarrow k) \); \( j_{kn} \) is the probability of
the analogous processes upon collision with atoms in the mth state. \( e_k \)
is the probability of photorecombination; \( a_{kn} = a_{nk} \) is the probability
of spontaneous transition from k to n, \( a_{kn} = 0 \), if \( k \rightarrow n \) or if the level
k is metastable. The summation is carried out over all levels existing in
the plasma. \( n_e \) is the concentration of electrons; \( P_k \) is an integral term,
accounting for the formation and destruction of the kth state during ab-
sorption of radiation from the remaining volume of gas.

Kinetic temperatures of electrons \( T_e \), and of atoms and ions \( T_a \) are
not the same. The temperatures \( T_e \) are found from the balance of energy of
the electron gas where \( S_{ee} \) is the source of energy of electrons; \( k_e \) is

\*The balance of energy of the electron gas in general has the following form:

\[ \frac{d}{dx} \left( \frac{3}{2} k_e n_e v^2 \right) + k_e T_e \frac{d n_e}{dx} = S_{ee} + \frac{d}{dx} \left( n_e \frac{dT_e}{dx} \right) \]

of electrons, which may be distinguished from the velocity of the heavy
particles \( v \). However, under the conditions being investigated here the
difference between \( v_e \) and \( v \) is small.

\[ \frac{d}{dx} \left( \frac{3}{2} k_e n_e v^2 \right) + k_e T_e \frac{d n_e}{dx} = S_{ee} + \frac{d}{dx} \left( n_e \frac{dT_e}{dx} \right). \]

Coefficient of electronic thermal conductivity. As a rule, because the
gradients of the parameters of the gas are comparatively small behind the
front, transport processes are unessential. The electronic thermal con-
ductivity, as is well known, has a special place, and in a number of
cases, should be taken into account.
Under the symbol $S_{ee}$ we consider the heating of electrons during elastic collisions $\left(\sum n_m n_e Q_{me}\right)$, this sum is taken over all states of all the particles of the gas and absorption of radiation $W_{ee}$ (with free-free transitions and photo ionization), losses during free-free transitions $\left(\sum n_m n_e F_{me}\right)$ and nonelastic collisions.

\[
S_{ee} = -\sum (U_i - U_h) \left( n_{h}n_{e}\left( n_{a}n_{e}\right) - n_{h}n_{a}n_{e}\right) - \frac{1}{2} \sum (U_a - U_h) \left( n_{a}n_{h}n_{a}\right) - \\
- n_{a}n_{h}n_{a} + \sum (q_{km}n_{h}n_{a}n_{m} - q_{km}n_{a}n_{h}n_{m}) - \\
- \sum q_{km}n_{h}n_{a}n_{i} + W_{ee} + \sum n_m n_e (Q_{ee} - F_{me}),
\]

\(U_i\) is the energy of ionization from the ground state; \(U_k\) is the energy of excitation of the \(k\)th level; \(\phi_{km}(T_e)\) is the mean energy with which electrons are born in atom-atom collisions; \(\phi(T_e)\) and \(\phi(T_e)\) represent the average loss of energy of the electron gas per recombination act.

The equations of kinetics are solved simultaneously with the equations of conservation, considering the losses by radiation $Q$. In standard notation

\[
\rho v = \rho v_i; \quad p + \rho v^2 = p_i + \rho v_i^2; \quad \frac{d}{dx} \left( H + \frac{v^2}{2} \right) = - \frac{Q}{\rho v}.
\]

Index \(1\) pertains to the gas ahead of the front. We write the expression for $Q$

\[
Q = \sum (U_a - U_h) n_{h}n_{a} + \sum (U_i - U_h + q_{km}) n_{h}n_{a}n_{i} + \\
+ \sum n_m n_e F_{me} = \sum (U_a - U_h) P_{ha} - \sum (U_h - U_h) P_{he} - W_{ee},
\]

\(P_{kn}\) accounts for the excitation during absorption of radiation \((k n)\). Upon photoionization, part of the energy goes to strip off an electron (it is calculated as \(\sum (U_i - U_h) P_{kn}\)), and another part to impart kinetic energy to it. The latter quantity entered into (3) and is included in $W_{ee}$. We note that under certain conditions a noticeable contribution $Q$ may arise from radiation processes that are not considered in (5), in order not to make it excessively complicated. The role of these processes behind a shock wave in air will be considered further.
Besides the ordinary ions ni, there are in a plasma molecular ions n2+. Coupling between them is accomplished by very rapid processes of recharging. Therefore, the ions are in quasi-equilibrium with each other. If, in addition, it is considered that the concentration of atoms and molecules are also associated with the condition of equilibrium (with dissociation relaxation completed), then we obtain
\[ n_2^+ = K_{\text{eq}} n_1 n_2. \] (6)

K is the equilibrium constant of the reaction A2+ A4+ + A. In view of (6), one can write the rate of associative ionization and dissociation recombination by means of coefficients of the type \( j_{\text{eq}} \) and \( j_{\text{eq}} \). These processes were accounted for in the same way in (1), (3), (5).

The plasma is quasineutral; that is, \( n_e = n_i + n_2 \). Actually, there is a separation of charges, but the length of separation is small, and the diffusion is ambipolar.

Absorption of the advancing radiation brings the gas ahead of the front out of equilibrium and determines in this way the initial conditions of the relaxation /3/.

The system of equations obtained is very complicated. However, any approximate method of its solution should account for the entire totality of the excited states of an actual atom.

We note that the near lying states are very firmly bound to each other by collision processes (very large cross section, close values of energy). Therefore, all of the possible causes producing a deviation from equilibrium can more quickly change the overall population of these states than the relative distribution of particles among them. For example, the emission of radiation, significantly lowering the overall concentration of excited atoms and electrons, does not disturb the distribution of particles inside this block of states /5/. In /5/, the openness of the system was the only cause of deviation from equilibrium. Behind the shock wave, the nonequilibrium condition is principally the result of a jump of gas parameters across the front. However, for the same reason, relaxation inside the block of near excited states occurs very rapidly. The relative distribution of particles inside the block near lying states (to which we include also the continuous spectrum) is determined by the following system of equations:

\[
\begin{aligned}
\sum_{n} \left(n_{n}n_{\text{eq}} - n_{n}n_{\text{eq}}\right) + \sum_{n} \left(n_{n}n_{\text{eq}} - n_{n}n_{\text{eq}}\right) + \\
+ \sum_{n} \left(n_{n}n_{\text{eq}} - n_{n}n_{\text{eq}}\right) + \\
+ \sum_{n} \left(n_{n}n_{\text{eq}} - n_{n}n_{\text{eq}}\right)
\end{aligned}
= 0.
\] (7)

The summation over n is carried out over the collection of associated levels. In this way, all collisions that mix particles inside this block of states are accounted for.
If collisions with electrons predominate, we obtain the Boltzmann distribution (at \( T_e \)) inside the block of states /5/.

\[
\frac{n_h}{n_{h+1}} = \frac{j_{h+1}}{j_h} = \cdots = n_e \frac{j_{\text{exc}}}{j_{\text{e}}}.
\]  

(8)

If, on the other hand, atom-atom collisions predominate, then the following relations are satisfied

\[
\sum_n \left[ (n_{h_m} j_{n_h} - n_e n_{m_j} j_{\text{e}}) + \sum_m (n_{h_m} j_{n_h} - n_e n_{m_j} j_{\text{e}}) \right] = 0.
\]  

(9)

The difference between \( T_a \) and \( T \) makes the distribution of particles in the block complicated even in this case.

We simplify the system of equations obtained earlier using (8), that is, assuming the coupling between excited and ionized states is essentially by electron collisions. We include in the block of combined states all the excited levels and the continuous spectrum. This is possible if there are no excited states near the ground state. Then we obtain
\[
\frac{d}{dx}(n_1\nu) = -\frac{d}{dx}\left[\nu\left(n_0 + \sum_{k>1} n_k\right)\right] = \\
= -\frac{d}{dx}\left[\nu\left(n_0 + n_{1s} + \sum_{k>1} \frac{j^s_k}{j^s_0}\right)\right] = S_1 = \\
= -(n_0 j_{1s}^s - n_0^2 \alpha_{1s} j_{1s}^s) - n_{1s}^2 j_{1s}^s - n_{1s}^2 \gamma_{1s} - \\
- (P_1 - n_{1s} \alpha_{1s} - \dot{\alpha}_{1s}) ,
\]
(10)

\[
\dot{j} = j + \sum_n j_n, \quad \dot{\alpha} = \alpha + \sum_n \alpha_n, \quad \alpha_{1s} = \alpha + \sum_n \alpha_n.
\]

\[
\dot{\alpha}_{1s} = \alpha + \sum_n \left(\dot{\alpha}_n - \dot{\alpha}_s - \dot{\alpha}_m\right) \frac{j^s_n}{j^s_0},
\]

\[
g_{1s} = \sum_{n \neq 1s} \frac{j^s_n}{j^s_0} \left(\dot{j}_n + \frac{j^s_n}{j^s_0} j^s_m\right).
\]

\[
\frac{d}{dx}\left(\frac{3}{2} kT_0 n_0 \nu + kT_0 \nu \frac{dv}{dx}\right) = S_0 = \sum_n n_0 (Q_{1m} - P_{1m}) + \\
+ W_{1s} - n_{1s} \sum_h \phi_{1s} - U_1 (n_0 j_{1s}^s - n_{1s} j_{1s}^s) + n_{1s} \phi_{1s} + \\
+ n_{1s} \left[\sum_{h \neq 1s} \frac{j_{1s}^s}{j_{1s}^s} \left(\phi_{1s} j_{1s}^s + \phi_{1s} j_{1s}^s\right) - \sum_{h} \phi_{1s} j_{1s}^s\right] + \\
+ n_{1s} \sum_{h \neq 1s} \left[\sum_{h} \frac{j_{1s}^s}{j_{1s}^s} \left(\phi_{1s} j_{1s}^s + \phi_{1s} j_{1s}^s\right) - \sum_{h} \phi_{1s} j_{1s}^s\right] - \\
- \sum_{h} \phi_{1s} j_{1s}^s + \sum_{h} (U_t - U_h) s_h,
\]
(11)

\[
\frac{d}{dx}\left[\left(\frac{5}{2} kT_0 + \frac{m_{1s}^2}{2}\right)(n_1 + \sum_n n_k)\nu + \nu \frac{d(kT_0 n_0)}{dx}\right] = -Q - S_0 + U_1 S_1 + \\
+ \sum_{h>1} (U_t - U_h) \frac{d}{dx}(n_{1s} \frac{j^s_1}{j^s_0} \nu).
\]
(12)
Equation (10) is not much more complicated than each of the equations of the initial system (1). In it, as in (11)-(12), all coefficients attached to $n_e$, $n_i$, $n_i$ depend only upon the temperatures $T_0$, $T_e$ and can be calculated. In equations (11) $s_k$ is the algebraic sum of the number of transitions at level $k$ as a result of collisions with electrons. As a rule $\sum_{k=1}^7 (U_t - U_k) s_k$ is a small quantity.

Using hydrogen-like upper excited states, one can evaluate $\sum n_h$, is the last of the discrete states existing in the plasma

$$\sum_{k=1}^7 n_k \approx \frac{\hbar y iT_e}{2(2\pi m_e kT_e)^{3/2}} \int_{(U_t - U_k)/kT_e}^{U_t} e^{-x} x^3 \, dx.$$  \hspace{1cm} (13)

If $T_e$ is not very small, then $\sum n_h \ll n_e$, which reflects the predominance of the statistical weight of the continuous spectrum over the statistical weight of the discrete states. We assume that ionization and excitation is basically accomplished by electron collisions, in which case, $j_{ue} \ll \sum_{k=1}^7 j_{uk}$. If $\sum n_h \ll n_e$ then almost all of the newly formed excited states should be ionized, which also corresponds to the approximation of "slow ionization" adopted in /1,2/. In the regimes examined in /1,2/ the conditions of "slow ionization" were satisfied.

Behind the front of the shock wave, equation (11) rapidly becomes quasistationary: in the left side one can neglect the terms with the products $dT_e/dx$ and $dv/dx$. In addition, under certain frequently occurring conditions, the derivatives $dn_k/dx$ are small, when $k \neq 1$. Then the equations are simplified:

$$\frac{da}{dx} = -\frac{1}{nu} S_e, \quad S_e - \frac{3}{2} kT_e S_e = 0.$$ \hspace{1cm} (14)

Here, we have introduced the degree of ionization $a = n_e/n$ and have considered the condition of conservation $nu = \text{const}$; $n = n_i + \sum n_k$ - is the total number of heavy particles. As a rule, equation (12) is also simplified.

$$nu \frac{d}{dx} \left( \frac{5}{2} kT_e + akT_e \right) = -Q - S_e - U_i S_e.$$

Combination of the levels up to the limit have simplified the problem by rendering it unnecessary to examine the kinetics of formation and destruction of individual excited states. What reasons can prevent this?
The coupling of states in the block is accomplished by collisions. If the frequency of the radiation processes is much less than the frequency of these collisions, luminescence (deexcitation) does not disturb the equilibrium of particles in the block. We note that this condition does not appear to be necessary /5/.

Moving behind the front of the shock wave, an element of gas gets into different conditions. It is necessary that the relaxation time corresponding to the mixing of particles in the block should be much less than the total relaxation time. This is fulfilled in the combination of energetically near levels.

If radiation transitions to the ground state are neglected, then any scheme of combining levels that rigidly couples excited atoms and electrons permits at the beginning of the relaxation the consideration only of the entrance of particles into the block. The population of the excited levels turns out to be small in comparison with the Boltzmann population calculated with respect to the ground state. Therefore, collisions of the second kind, bringing particles out of the block of states, as well as recombination, can be neglected up to a degree of ionization very close to equilibrium. At this stage, the block of levels represents a passive reservoir since the atoms getting into it cannot leave.

One cannot make a priori such a general conclusion concerning luminescence, since the corresponding process - absorption of radiation from the remaining volume of gas - is not always sufficiently intense. But since the concentration of excited atoms is small, there are a number of cases in which the first stage luminescence can be neglected in comparison with ionization and excitation by collisions.

Behind strong shock waves the degree of ionization in the region close to equilibrium is large, and the relations (8) are justified. Directly behind the front, on the other hand, atom-atom collisions may predominate. As a rule, the cross sections of these collisions are unknown. However, it has already been noted that in a number of cases at the beginning of relaxation, an assumption concerning the nature of the distribution of particles inside the block of levels, from the point of view of development of the relaxation process, is not essential. This significantly simplifies the problem.

Sometimes it is expedient to separate two blocks of levels. Thus, if there are low-lying excited levels near the ground state, they can be combined with it.

Concluding the remarks relative to the method of solution of the equations of kinetics, we emphasize the necessity of carefully checking the possibility of combining the levels into a block.

Relaxation Behind Strong Waves in Air

For \( v_1 = 10 \text{ km/sec} \), molecules dissociate very rapidly (see appendix), after which their concentration becomes negligibly small. Therefore, we are concerned with relaxation in a mixture of \( O \) and \( N_2 \). As a result of various collisions, there are formed the ions \( N^+, O^+, NO^+, N_2^+, O_2^+ \). Since ions are
found in quasiequilibrium with each other, it turns out that the concentration of molecular ions is negligibly small.

Let us introduce some notation. The concentration of atoms is denoted by \( n_0 \), \( n_N \). If we are concerned with a definite th state: \( n_{0k} \), \( n_{Nk} \). The concentrations of ions are \( n_{+X} \), \( n_{+X} \); their sum is \( n_{+X} \). The degree of

\[ n_{+X} \]

The concentrations of molecular ions may be found as a small increment with the help of the relations \( n_0 + n_0 + n_{+X} + 2n_{+X} + n_{+X} + 2n_{+X} / n_X + n_{+X} + n_{+X} + 2n_{+X} = 0.21/0.79 \) and equations of the type equation (6): \( n_{+X} = n_{+X} + n_{+X} = n_{+X} + n_{+X} \).

is \( a = \frac{n_e}{n} = n_0 + n_X + n_{+X} \).

The condition \( n_Y = \text{const} \) reduces to \( n_Y = \text{const} \). Then

\[
\frac{d(n_0, n_X)}{dx} = S_e = -\frac{d}{dx} \sum (n_{+X} + n_{+X}) n_X \approx \frac{d}{dx} \sum (n_{+X} + n_{+X}) n_X. \tag{15}
\]

In the solution of actual problems, an insufficiency of information concerning atom-atom collisions frequently makes it impossible to evaluate the kinetics of the excited states in the first stage of relaxation. In the case of air, this difficulty can be avoided since the atom-atom excitation cannot compete with associative ionization. Therefore, electrons arise, omitting the upper excited states. The distribution of atoms among the excited states, from the point of view of the development of ionization, is of no interest at this stage.

With a larger \( n_e \), the ionization becomes stepwise. But then, it can already be shown that atoms are distributed over two blocks of states, internal equilibrium of which is maintained by electron collisions. The ground state and two neighboring ones enter into the first, and the remaining levels and continuous spectrum into the second.

Let us write the system of equations for this scheme of combination of levels. We take account of electronic processes and associative ionization. The source of electrons is

\[
S_e \approx \sum_{h=1}^{3} \left\{ \left( n_{+X} h_{\alpha h} - n_{+X} h_{\alpha h} \right) + \left( n_0 h_{\alpha h} - n_0 h_{\alpha h} \right) + \left( h_{\alpha h} - h_{\alpha h} \right) + \left( n_0 h_{\alpha h} - n_0 h_{\alpha h} \right) + \left( n_0 h_{\alpha h} - n_0 h_{\alpha h} \right) + \left( n_0 h_{\alpha h} - n_0 h_{\alpha h} \right) \right\}. \tag{16}
\]
In contrast to (10) the summations in $j_{e}^{m}$, $j_{a}^{m}$, $\alpha_{e}^{m}$ are carried out for $n \geq 3$. Further

$$j_{e}^{m} = \frac{1}{2} \sum_{n=1}^{m} j_{e}^{n} j_{a}^{n}, j_{a}^{m} = \frac{3}{2} \sum_{n=1}^{m} j_{a}^{n}.$$  

The designations $j_{e}^{m}$, $j_{a}^{m}$, $\alpha_{e}^{m}$ are reserved for the atom $X$. For the atom $O$ we introduce $j_{o}^{m}$, $l_{o}^{m}$, $\beta_{o}^{m}$ analogously. For example $l_{o}^{m} = \frac{1}{2} \sum_{n=1}^{m} j_{o}^{n} j_{o}^{n}$.

For the process of formation of $XO^{+}$ we introduce the coefficient

$$g_{o}^{m} g_{o}^{m} = \sum_{n=1}^{m} j_{o}^{m} j_{o}^{m}, g_{o}^{m} = K_{1} \sum_{n=1}^{m} g_{o}^{m}, P_{X_{k}} and \rho_{X_{o}}$$

account for the absorption of radiation.

The source of energy of electrons is

$$S_{m} \approx \sum_{n} n_{m} n_{m} Q_{m} = \sum_{n=1}^{m} \left[ U_{m}(n_{m} n_{m} j_{e}^{m} - n_{m}^{2} n_{m}^{2} j_{e}^{m}) + U_{o}(n_{m} n_{m} l_{o}^{m} - n_{m}^{2} n_{m}^{2} l_{o}^{m}) - \left( \frac{1}{2} n_{o}^{2} \sum_{n=1}^{m} j_{o}^{m} j_{o}^{m} q_{o}^{m} - n_{o} n_{o} q_{o}^{m} \right) - \left( \frac{1}{2} n_{o}^{2} \sum_{n=1}^{m} l_{o}^{m} l_{o}^{m} q_{o}^{m} - n_{o} n_{o} q_{o}^{m} \right) \right]$$

$$- n_{o} n_{o}^{2} n_{k}^{2} \left( \frac{3}{2} \sum_{n=1}^{m} j_{o}^{m} q_{o}^{m} \right) - n_{o} n_{o}^{2} n_{k}^{2} \left( \frac{3}{2} \sum_{n=1}^{m} l_{o}^{m} q_{o}^{m} \right) + n_{e} n_{e}^{2} \alpha_{e}^{m} + n_{o} n_{o}^{2} \beta_{o}^{m} \right]$$

(17)

$U_{m}$ and $U_{o}$ - are the ionization energies of atoms of oxygen and nitrogen.

This system of equations of kinetics (to it should be added the equation for $T_{a}$) is an integrodifferential system. For its solution it is necessary to overcome significant difficulties of calculation. However, in a number of cases, the system can be simplified.
At the beginning of relaxation certain processes are unessential. In addition, \( n_X \approx 0.79n(1-u) \), \( n_0 \approx 0.21n(1-u) \). Then we have

\[
\frac{S_x}{n^3} = \alpha(1 - u)(0.79j_{x^{**}} + 0.21i_{x^{**}}) + (1 - u)^2(0.79j_{x^{**}} + 0.21i_{x^{**}}) + \sum_{k=1}^3 \left[ \left( P_k z - \alpha^2 \frac{n_{x^{**}}}{n_x} \beta_{x^{**}} \right) + \left( P_{n_x} - \alpha^2 \frac{n_{x^{**}}}{n_x} \beta_{x^{**}} \right) \right].
\]

(19)

\[
\frac{S_{x^{**}}}{n^3} = \alpha^2 Q_{x^{**}} + \alpha(1 - u)(0.79Q_{x^{**}} + 0.21Q_{x^{**}}) - \alpha(1 - u)(0.79j_{x^{**}} + 0.21i_{x^{**}}) + U_0(1 - u)^2(0.79j_{x^{**}} + 0.21i_{x^{**}}) + \sum_{k=1}^3 \left[ \left( P_k z - \alpha^2 \frac{n_{z^{**}}}{n_z} \beta_{z^{**}} \right) + \left( P_{n_z} - \alpha^2 \frac{n_{z^{**}}}{n_z} \beta_{z^{**}} \right) \right].
\]

(18)

The following notation has been used:

\[
j_{x^{**}} = \left( 1 + \frac{j_{x^*} + j_{x^*}}{j_{x^*}} \right)^2 \sum_{k=1}^3 \frac{j_{x^*}}{j_{x^*}} j_{x^*},
\]

\[
j_{x^{**}} = \left( 1 + \frac{j_{x^*} + j_{x^*}}{j_{x^*}} \right)^2 \sum_{k=1}^3 \frac{j_{x^*}}{j_{x^*}} j_{x^*},
\]

\[
a_{x^{**}} = \sum_{k=1}^3 a_{x^{**}},
\]

\[
\tilde{\bar{\varphi}}_{j_{x^{**}}} = \frac{1}{2} \left( 1 + \frac{j_{x^*} + j_{x^*}}{j_{x^*}} \right)^2 \sum_{k=1}^3 \frac{j_{x^*}}{j_{x^*}} j_{x^*} a_{x^{**}}.
\]

The remaining notation is introduced analogously.

It can be shown that under our conditions for \( \alpha \leq 0.3a_e \) (the index eq pertains to equilibrium parameters attained in the absence of loss) one can neglect collisions of the second kind and recombination carrying particles out of the upper block into the lower, and also radiation processes both in the kinetics and in the balance of energy. The equations of conservation are correspondingly simplified.

Calculation of Relaxation in Air

For shock waves with velocities \( v_1 \leq 10 \text{ km/sec} \) relaxation is determined by the following processes. At first associative ionization predominates

\( \bar{N} + \bar{O} = \bar{N}^+ + \bar{e}, \ N + \bar{N} = \bar{N}^+ + \bar{e}, \ 0 + \bar{O} = \bar{O}^+ + \bar{e}. \) With an increase of \( n_e \) the effect of stepwise ionization by electrons increases and the rate of ionization is determined principally by elastic electron-ion collisions. At the beginning of the relaxation, the electrons, which already appeared "hard" to a significant degree, are heated by elastic collisions with atoms.
Let us evaluate the rate of the various processes that we have chosen for calculation. Using experimental data on the dissociative recombination, one can find the rate of associative ionization. The recombination coefficients of the ions \(N_2^+\), \(NO^+\), \(O_2^+\), measured at low temperatures, are close in magnitude and large. This means that in each case the potential curves of the recombination products and the molecular ion intersect near the fundamental vibrational level of the ion, \(K = 0\), (for \(N_2^+\) such a point of intersection is still unknown, which, apparently, is a manifestation of the general shortage of information concerning unstable states). With such a character of the intersection, the coefficients of recombination ordinarily depend on \(T\) as \(T^{-3/2}\). Making use of this fact for extrapolation to larger \(T\), we have:

\[
\begin{align*}
\lambda_1 &= 6 \cdot 10^{-5} T^{-3/2}, \\
\lambda_2 &= 4 \cdot 10^{-3} T^{-3/2}, \\
\lambda_3 &= 3 \cdot 10^{-3} T^{-3/2} \exp[\text{c.c.}] \quad (20)
\end{align*}
\]

These numbers are taken from [4], where similar arguments are given. In view of the impossibility of exactly establishing the recombination products (for example, one of the atoms of \(X\) may be weakly excited) it has been assumed in (20) that the atoms are in the ground states. For large \(T\), this assumption does not too greatly affect the ionization.

Apparently, the following effects produce the greatest error with increasing \(T\). First, the \(T^{-3/2}\) does not consider the changes of population of the lower vibrational levels, which reduces the recombination coefficient. Second, the reaction passes also through others, lying above the point of intersection. This increases the recombination coefficient.

As a light particle, the electron attains the entire excess energy over the threshold. With an intersection of the potential curves near \(K = 0\) the crosssection of the process rapidly falls off with an increase of energy. In view of this is small. Under other circumstances the cross section may depend on the energy, a problem which is complicated by that fact that the ion may form at different levels \(K\). A rough evaluation shows that does not exceed \(kT_3\). The indeterminacy of is unessential since at the beginning of relaxation, the electron temperature does not affect the ionization rate.

The cross sections for calculation of \(j_{e^+}, j_{e^-}, i_{e^+}, i_{e^-}\) are found from the method proposed in [6,7]. In it, the peculiarities of the exact behavior of the cross section near the threshold and for large energies was more completely taken into account. In the range \(T_e = 8000\) to \(18,000\)K

\[
\begin{align*}
\lambda_{e^+} &= 3 \cdot 10^{-10} (kT_e)^{1/2} \exp[108 600kT_e] \\
\lambda_{e^-} &= 1.8 \cdot 10^{-16} (kT_e)^{1/2} \exp[1/cck] \quad (21)
\end{align*}
\]

The precision of these coefficients is sufficient it is considered that the rate of excitation by electrons is to a significant degree determined by the transfer to them of energy from the heavy particles [7].

The transfer of energy from ions to electrons is found in the ordinary way:

\[
Q_e = \frac{2e^2 \gamma_2 m_e}{m_i} \frac{kT_e - kT_i}{(kT_e)^{1/4}} \left[ \ln \frac{Q(kT_e)^{1/4}}{8 \pi^2 n_e} + 1 \right].
\]
For atom-electron equations it has been found that

\[ Q_{ee} = \frac{4m_e}{m_i} \sqrt{\frac{8kT_e}{\pi m_e}} \sigma(kT_e - kT_i)[1 - \left(1 + \frac{T_e}{T_i}\right)^{-1}]. \]

= 6 · 10^{-16} cm² for N and 5.5 · 10^{-16} for O. Correspondingly, \( T_e = 3.1 \cdot 10^6 \)
and 1.2 · 10^6 K. These constants came from approximations of the cross sections measured in /8/.

The distribution of electrons over velocities was assumed Maxwellian. Estimates have shown that for those \( n_e \) for which excitation and ionization by electrons becomes essential, the Maxwellian distribution occurs.

\( v_k \) and \( v_k \) are found with the help of transition probabilities attained by the quantum defect method. In the range \( T_c = 8 \) to 20 \( \cdot 10^3 \) K.

\[ \sigma_{ee} = 5.0 \cdot 10^{-4} e^{-5.54e^{-T_e}} + 1.2 \cdot 10^{-11} e^{-1.54e^{-T_e}}, \text{cm}^2/\text{sec}. \quad (22) \]

The quantity of \( \beta_{ee} \) has a similar value.

Associative ionization is such a powerful mechanism for initial ionization that in the zone of relaxation one may disregard the absorption of radiation from the remaining volume of gas. An upper estimate of the effect of radiation can be made by assuming that all photons that are radiated in the direction of the front and that correspond to transitions onto the lower three levels, are effectively absorbed. In argon the associative ionization proceeds slowly and radiation processes were substantial /2/.

The equations of kinetics are written for the case in which equilibrium inside the two blocks of levels is maintained by electron collisions. We show that the nature of the distribution inside the blocks begins to have an effect only when the adopted assumption turns out to be justified.

We compare the life time of the state with the interval of time between collisions that bring an atom from one of the neighboring levels to the upper level. Independently of whether we find the cross section from the method of Milford /6/ or use the quasiclassical expressions /9/, it turns out that in the interesting range of \( n_e \) and for \( P_i = 10^{-5} \text{ atm} \), in addition, it is necessary to compare the effectiveness of electron-atom and atom-atom collisions that mix particles between the upper levels. Estimates have shown that for those \( n_e \) when the nature of the combination of levels in the block is essential, the atom-atom collisions can be neglected.

The excited states of the basic configuration are metastable. With the
necessary values of alpha, the electron-atom cross sections are large enough to maintain equilibrium inside the lower blocks of levels.

The relaxation in argon has been studied earlier /2/. It began with a certain final degree of ionization. The large values of p\textsubscript{1} permitted combining the upper levels already for these values of alpha; that is, the assumption of ionization of the excited states was justified.

The equations of kinetics were solved up to \( t = 0.5 \) eq. It was possible to disregard luminescence, collisions of the second kind, and recombination. The effect of luminescence in (14), evaluated with the help of (24), attained a maximum of 30%. Actually, the lines that provide the main contribution to (22) are strongly reabsorbed, that is, it is necessary to consider not only radiation from the given elementary volume of gas, but also the absorption by it of radiation from the remaining gas. This can be done approximately by introducing into the determination \( e_k^* \) and \( e_k^* \) instead of the life time of isolated atoms, the effective life times /11/.

It turns out that such effective values are an order of magnitude smaller than (22). Radiation cooling in this part of the relaxation may also be neglected; \( Q = 0 \).

Discussion of the Results.

The analysis of elementary processes carried out above shows that up to \( t = 0.5 \) eq the relaxation in arc proceeds according to a binary scheme.*

*In references /4,2,13/ where the nonequilibrium was investigated behind shock waves in air for \( v_1 = 9 \) km/sec, the binary nature of the relaxation was also noted. However, in argon /2/, the relaxation process was not binary as a result of the essential effect on the relaxation of radiation issuing from the equilibrium zone.

For a given \( v_1 \) this permits one to construct a universal profile of the nonequilibrium parameters as functions of \( p_1x \). (We recall that \( \alpha_{eq} \) depends on \( p_1 \). The solution obtained above is justified for \( t = 0.5 \).

Consequently, the profiles constructed as functions of \( p_1x \) for different \( p_1 \) are correct in different intervals \( p_1x \). As an example, figure 1 shows the profiles of alpha, Ta and Te for \( v_1 = 12 \) km/sec.

The region of small x in figure 1 should not be given great significance. Naturally, there is a small overlapping (unessential for the development of relaxation) of the regions of ionization and dissociation. In addition, the lack of precision of determination of \( T_e \) leads to an indeterminacy in \( T_e \). Calculations with various did not give noticeably different results, although for a small x, \( T_e \) underwent strong changes (figure 1 shows the case \( t = 0 \). For the same reason, it is also unimportant that the electronic conductivity tends to increase \( T_e \) in the region of small x.

The dependence of \( T_a \) and \( T_e \) on x was discussed by us earlier /2/.

Figure 2 shows the dependence of \( P_1t \) on the velocity \( v_1 \) (t is the relaxation time in the laboratory system of coordinates).

Investigations of relaxation in air were carried out earlier for shock
waves with velocities $v_1 = 9 \text{ km/sec}$. For $v_1 = 7 \text{ km/sec}$, the length of the

zone of relaxation of ionization was measured - the distance at which the concentration of electrons, sharply increasing, arrives at quasiequilibrium with the state of the gas that is slowly changing in process of dissociation relaxation*. $v_1$ to $v_1 = 9 \text{ km/sec}$ the length of the relaxation is determined by the kinetic decomposition of molecules. Figure 2 shows the results of these papers.

---

We note that at such velocities this quasiequilibrium value of $n_e$ exceeds its equilibrium value. A calculation carried out for $v_1 = 9 \text{ km/sec}$ showed that for large $v_1$ this excess disappears /4/.

---

Fig. 1: Profile of the parameters of a nonequilibrium gas behind a shock wave. $v_1=12 \text{ km/sec}$. The result does not depend on the pressure ahead of the front $p_1$ (up to $-0.5$; $-eq(p_1)$). In view of the indeterminancy of $T_e$ for small $x$ (see text) this portion is given in Figure 1 by dashes.

Fig. 2: Dependence on the velocity of the shock wave of the product of the relaxation time $t$ (in the laboratory system) and the pressure ahead of the front $p_1$ (in units of microsecond millimeters Hg). $p_1=0.02 \text{ mm Hg}$. Ionization relaxation: calculation (for $v_1 9/4$, for $v_1 10$, present work); --, experimental data /4/. Dissociation relaxation: --- is evaluation carried out in appendix.
It follows from figure 2 that in the range $v_1 = 9$ to $10$ km/sec, the character of the relaxation sharply changes.* For $v_1$ 10 km/sec the total relaxation time is determined by the kinetics of ionization. In the range $v_1 = 9$ to $10$ km/sec the calculation of relaxation is complicated. However, it is clear that the time of ionization relaxation should increase with increasing $v_1$. This result is not associated with the precision of determining the rates of associative ionization. Use of other values of these quantities changes the absolute values of the time of ionization relaxation but preserves the nonmonotonicity. Meanwhile, we assume that more precise values of reaction rates should not lead to a sharp change of the quantitative results.

It should be noted that the assumptions lying at the base of our considerations are satisfied better the larger $v_1$. For this reason, the case, $v_1$ 10 km/sec is more subject to the effect of various unfavorable factors, such as incompleteness of dissociation relaxation and inexactness in the effectiveness of dissociative ionization.

In this paper, questions connected with luminescence of the gas behind the shock wave are not considered. One should keep in mind that frequently the role of some component in the kinetics and in the radiation from the shock wave are completely different. A small concentration of some intensely radiating component of the gas may not have any effect on the kinetics. For example, if the processes of recharging are insufficiently rapid, then $n_{e^2}$ may be comparatively large; it can exceed its value in equilibrium while remaining substantially less than the concentration of atomic ions. Therefore, in spite of the strong connection over the major portion of the relaxation length, of the concentration of excited atoms and electrons, the problem of the concentration of radiating particles cannot be considered solved. Moreover, during the first part of the relaxation the concentrated part of the excited atoms is sufficiently known and there is a definite number of still undisassociated molecules. Without having any effect on the kinetics, the two latter circumstances can be very important from the point of view of luminescence behind the shock wave. However, with an increase of $v_1$ their effect should be reduced.

We have considered the region of ionization relaxation in which one can neglect reverse processes. The region in which the gas passes through a state very close to equilibrium is very complicated. In this region, reverse processes are very important. In addition, the last stage of relaxation takes place in a gas which may be noticeably cooled owing to the emission of radiation. If $\gamma$ is large, then the gas can achieve equilibrium before radiation cooling substantially lowers its internal energy. Later, equilibrium will be preserved but with a general lowering of the temperature /15/. It is possible, however, that the emission of radiation will have a substantial effect already in the last stage of relaxation. In this case, equilibrium is generally not attained as a consequence of continuous uncompensated combination of excited and ionized states /5/. If, however, the effectiveness of collision processes is sufficiently large, then the gas arrives at a state of local equilibrium but with a temperature lower than that calculated in the assumed absence of radiation losses.
In a subsequent paper we hope to examine the entire region of relaxation using the general equations written above.

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Appendix

Dissociation relaxation for large \( v_1 \).

It has been noted /3/ that the length of the zone of dissociation relaxation behind a strong shock wave is very small. The molecules dissociate directly in collisions with atoms and with one another. We make the following equation.

Under our conditions the molecules of \( O_2 \) dissociate practically simultaneously. Let us examine the kinetics of dissociations of \( K_2 \). We introduce

\[
\beta = m_0 / (m_0 + 2m), \quad m' = 2m + 2m_0, \quad \xi = 0.21 / 0.79.
\]

then

\[
\frac{\partial \beta}{\partial x} = m'( \omega \rho _0 n_0 - \rho \rho ' \rho _0 ) - S_N (x). \tag{23}
\]

With the notation \( S_N \) for the source of atoms of nitrogen we consider

\[
N_2 + M = 2N + M, \quad M = 0, N, N_2. \tag{24}
\]

Introducing for their rates the notation \( \lambda^{(0)}, \lambda^{(N)}, \lambda^{(N_2)} \) we obtain

\[
S_N = \left[ \frac{m_0 + m_0 + m_N}{(1 + 2 \beta + \beta)} \right] (1 - \beta) \times
\]

\[
\times [2 \beta \lambda^{(0)} + 2 \beta \lambda^{(N)} + (1 - \beta) \lambda^{(N_2)}]. \tag{25}
\]

Equation (23) is integrated considering the conditions of conservation

\[
kT = (h \omega ' m' - \xi \rho _0 - \beta \rho _0 ) \left( \frac{9}{2} + 5 \xi + \beta \right), \quad \rho \approx \rho _0. \tag{26}
\]

We have assumed that the vibrational relaxation of \( N_2 \) has finished. This assumption does not affect the result.

The given calculation, carried out with rates of dissociation taken from the review /13/, are presented in Figure 2. The time \( t_{dis} \) corresponds to the point at which the fraction of molecules is 0.08 of the entire number of particles. At velocities \( v_1 \) \( 10 \text{ km/sec} \) \( t_{dis} \) is comparatively small.

Associative ionization occurs simultaneously with dissociation. But the degree of ionization attained in the time \( t_{dis} \) is small and does not affect the parameters of the gas, as occurs also for \( v_1 \) \( 9 \text{ /sec/} \). We calculate the degree of ionization attained in the course of dissociation:

\[
a(x) = m'( \omega \rho _0 (1 + 2 \xi + \beta) ) \int_0^x S_N dx. \tag{27}
\]
For $v_1 = 10 \text{ km/sec}$, during the time $t_{44}$ there is attained $1.7 \times 10^{-3}$. This quantity is small and does not affect the subsequent course of the relaxation.

The case $v_1 = 9 \text{ km/sec}$ was also examined. Here the dissociation of $N_2$ through the formation of $NO$ plays as large a role as in (24). Ionization relaxation proceeds simultaneously with dissociation. As expected, the obtained characteristics of ionization relaxation agreed with that presented in /4/.

**NOTE ADDED IN PROOF.** After the present paper was submitted for publication a paper appeared by R.A. Allen, A. Tekstoris and John Wilson (J. Quantit. Spectr. Radiat. Transf. 5, 55, 1965) in which the times of relaxation were measured. For shock waves with $v_1 = 10.9$ and $11.25 \text{ km/sec}$ and $p_1 = 0.1 \text{ mm Hg}$, the time of ionization relaxation is $t = 1 \text{ sec}$. This is good confirmation of our conclusions.

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