Classification: UNCLASSIFIED

Title: State of Gas Behind Front of a Strong
Shockwave

/Sostoyaniye Gaza za Frontom Sil'noy
Udarnoy Volny/

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Page(s): 18 twp

Original Language Russian

Translator: R

TRANSLATION NO.   2172

Approved by: P T.K.

Date   17 August 1966

Code 1

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 dissocation 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*.

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* 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

$$-\frac{d}{dx}(n_k v) = (n_k n_e j_{ke}^e - n_e^2 n_i j_{ek}^e) + \sum_n (n_k a_{kn} - n_n a_{nk}) +$$

$$+ P_k - a_{ek} n_e n_i + \sum_n (n_e n_n j_{nk}^e - n_e n_k j_{kn}^e) + \sum_m (n_k n_m j_{ke}^m -$$

$$- n_e n_i n_m j_{ek}^m) + \sum_{m,n} (n_k n_m j_{kn}^m - n_n n_m j_{nk}^m). \qquad (1)$$

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}^e and atoms, for example, at the mth level j_{ke}^m. The quantities j_{ek}^e and j_{ek}^m respectively account for the reverse processes; j_{kn}^e is the probability of excitation from k to n by an electron collision (k n) or by a collision of the second kind (n k); j_{kn}^m is the probability of the analogous processes upon collision with atoms in the mth state. a_{ek} is the probability of photorecombination; $a_{kn} = A_{kn}$ is the probability of spontaneous transition from k to n, $a_{kn} = 0$, if k 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 absorption of radiation from the remaining volume of gas.

Kinetic temperatures of electrons T_c, and of atoms and ions T_a are not the same. The temperatures T_c are found from the balance of energy of the electron gas* where S_{ee} is the source of energy of electrons; k_c s

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

$$\frac{d}{dx}\left(\frac{3}{2}kT_e n_e v_e\right) + kT_e n_e \frac{dv_e}{dx} = S_{ee} + \frac{d}{dx}\left(x_e \frac{dT_e}{dx}\right). \quad v_e \text{ is the velocity}$$

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.

$$\frac{d}{dx}\left(\frac{3}{2}kT_e n_e v\right) + kT_e n_e \frac{dv}{dx} = S_{ee} + \frac{d}{dx}\left(x_e \frac{dT_e}{dx}\right), \qquad (2)$$

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 conductivity, 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 $\left(\sum_m' n_m n_e Q_{me} - \right)$ 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 $\left(\sum_m' n_m n_e F_{me}\right)$ and nonelastic collisions.

$$S_{ee} = -\sum_k (U_i - U_k)(n_k n_e j_{ke}^e - n_e^2 n_i j_{ek}^e) - \frac{1}{2}\sum_{k,n} (U_n - U_k)(n_k n_e j_{kn}^e - n_n n_e j_{nk}^e) + \sum_{k,m}(\varphi_{km} n_k n_m j_{ke}^m - \varphi_{km}' n_e n_i n_m j_{ek}^m) - \sum_k \varphi_k a_{ck} n_e n_i + W_{ee} + \sum_m' n_m n_e (Q_{me} - F_{me}), \qquad (3)$$

U_i is the energy of ionization from the ground state; U_k is the energy of excitation of the kth level; $\vartheta_{km}(T_a)$ is the mean energy with which electrons are born in atom-atom collisions; $\vartheta(T_a T_e)$ and $\vartheta(T_e)$ 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

$$\rho v = \rho_1 v_1; \quad p + \rho v^2 = p_1 + \rho_1 v_1^2; \quad \frac{d}{dx}\left(H + \frac{v^2}{2} - \varkappa_e \frac{dT_e}{dx}\right) = -\frac{Q}{\rho v}. \quad (4)$$

Index 1 pertains to the gas ahead of the front. We write the expression for Q:

$$Q = \sum_{k,n}(U_n - U_k)a_{nk}n_n + \sum_k (U_i - U_k + \varphi_k)a_{ck}n_e n_i + \sum_m' n_m n_e F_{me} - \sum_{k,n}(U_k - U_n)P_{kn} - \sum_k (U_i - U_k)P_{ke} - W_{ee}. \quad (5)$$

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 $\sum (U_i - U_k)P_{ke}$, 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.

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Besides the ordinary ions n_i, there are in a plasma molecular ions n_2+. Coupling between them is accomplished by very rapid processes of recharging. Therefore, the ions are in quasiequilibrium 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

$$n_2^+ = K n_i n, \qquad (6)$$

K is the equilibrium constant of the reaction $A_2+ A^++A$. In view of (6), one can write the rate of associative ionization and dissociation recombination by means of coefficients of the type j_{ke}^m and j_{ek}^m. 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 nearlying states (to which we include also the continuous spectrum) is determined by the following system of equations: —

$$(n_k n_e j_{ke}^e - n_e^2 n_i j_{ek}^e) + \sum_n (n_k n_e j_{kn}^e - n_n n_e j_{nk}^e) +$$

$$+ \sum_m \Big[(n_k n_m j_{ke}^m - n_e n_i n_m j_{ek}^m) +$$

$$+ \sum_n (n_k n_m j_{kn}^m - n_n n_m j_{nk}^m) \Big] = 0. \qquad (7)$$

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/.

$$n_k = n_{k+1} \frac{j^e_{k,k+1}}{j^e_{k+1,k}} = \ldots = n_e n_i \frac{j^e_{ck}}{j^e_{ke}}. \tag{8}$$

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

$$\sum_m \left[(n_k n_m j_{ke}^m - n_c n_i n_m j_{ck}^m) + \right.$$

$$\left. + \sum_n (n_k n_m j_{kn}^m - n_n n_m j_{nk}^m) \right] = 0. \tag{9}$$

The difference between T_a and T_e 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

$$\frac{d}{dx}(n_1 v) = -\frac{d}{dx}\Big[v\Big(n_e + \sum_{h>1} n_h\Big)\Big] =$$

$$= -\frac{d}{dx}\Big[v\Big(n_e + n_e n_i \sum_{h>1}\frac{j_{eh}{}^c}{j_{he}{}^c}\Big)\Big] = S_1 =$$

$$= -(n_1 n_e j_{1e}{}^{c\circ} - n_e^2 n_i j_{e1}{}^{c\circ}) - (n_i^2 j_{1e}{}^{1\circ} - n_e n_i n_1 j_{e1}{}^{1\circ} - n_e^2 n_i^2 q_{e\cdot}{}^\circ) -$$

$$- (P_1 - n_e n_i a_{e1}{}^\circ),$$

где $\hspace{6cm}$ (10)

$$j_{1e}{}^{c\circ} = j_{1e}{}^c + \sum_n j_{1n}{}^c, \quad j_{e1}{}^{c\circ} + \sum_n j_{n1}{}^c \frac{j_{en}{}^c}{j_{ne}{}^c},$$

$$j_{1e}{}^{1\circ} = j_{1e}{}^1 + \sum_n j_{1n}{}^1, \quad a_{e1}{}^\circ = a_{e1} + \sum_n a_{n1}\frac{j_{en}{}^c}{j_{ne}{}^c}$$

$$j_{e1}{}^{1\circ} = j_{e1}{}^1 + \sum_{\substack{n>1 \\ m>1}} (j_{n1}{}^1 - j_{1e}{}^m - j_{1n}{}^m)\frac{j_{en}{}^c}{j_{ne}{}^c},$$

$$q_{e1}{}^\circ = \sum_{\substack{n>1 \\ m>1}} \frac{j_{en}{}^c}{j_{ne}{}^c}\Big(j_{e1}{}^n + \frac{j_{en}{}^c}{j_{me}{}^c}j_{n1}{}^m\Big),$$

$$\frac{d}{dx}\Big(\frac{3}{2}kT_e n_e v\Big) + kT_e n_e \frac{dv}{dx} = S_{ee} = \sum_m{}' n_m n_e(Q_{me} - F_{me}) +$$

$$+ W_{ee} - n_e n_1 \sum_h \varphi_h a_{eh} - U_i(n_1 n_e j_{1e}{}^{c\circ} - n_e^2 n_i j_{e1}{}^{c\circ}) + n_i^2 \varphi_{11} j_{1e}{}^1 +$$

$$+ n_e n_i n_1\Big[\sum_{h>1}\frac{j_{eh}{}^c}{j_{he}{}^c}(\varphi_{h1}j_{he}{}^1 + \varphi_{1h}j_{1e}{}^h) - \sum_h \varphi_{h1}{}' j_{eh}{}^1\Big] +$$

$$+ n_e^2 n_i^2 \sum_{m>1}\frac{j_{en}{}^c}{j_{me}{}^c}\Big[\sum_{h>1}\varphi_{hm}\frac{j_{eh}{}^c}{j_{he}{}^c}j_{he}{}^m -$$

$$- \sum_h \varphi_{hm}{}' j_{eh}{}^m\Big] + \sum_{h>1}(U_i - U_h)s_h, \hspace{2cm} (11)$$

$$\frac{d}{dx}\Big[\Big(\frac{5}{2}kT_e + \frac{m_e v^2}{2}\Big)\Big(n_i + \sum_h n_h\Big)v\Big] + v\frac{d(kT_e n_e)}{dx} = -Q - S_{ee} + U_i S_1 +$$

$$+ \sum_{h>1}(U_i - U_h)\frac{d}{dx}\Big(n_e n_i \frac{j_{eh}{}^c}{j_{he}{}^c}v\Big). \hspace{2cm} (12)$$

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_1 depend only upon the temperatures T_a, 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 $\sum_{k>1} (U_i - U_k) s_k$ — is a small quantity.

Using hydrogen-like upper excited states, one can evaluate, $\sum_{k>1} n_k$, where $\bar{k}$ is the last of the discrete states existing in the plasma

$$\frac{1}{n_e^2} \sum_{k=k'}^{\bar{k}} n_k \approx \frac{(Ry \cdot kT_e)^2 \cdot h^3}{2(2\pi m_e kT_e)^{3/2}} \int_{(U_i - U_{\bar{k}})/kT_e}^{(U_i - U_{k'})/kT_e} x^{-1/4} e^x dx. \qquad (13)$$

If T_e is not very small, then $\sum_{k>1} n_k \ll n_e$, 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, $j_{1e}^e \ll \sum_k j_{1k}^e$. If $\sum_{k>1} n_k \ll n_e$, then almost all of the newly formed excited atoms 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:

$$\frac{d\alpha}{dx} = \frac{1}{nv} S_e,$$

$$S_{ee} - \frac{3}{2} kT_e S_e = 0. \qquad (14)$$

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

$$nv \frac{d}{dx}\left(\frac{5}{2} kT_a + akT_e\right) = -Q - S_{ee} - U_i S_e.$$

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?

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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 ridigly 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 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. As a result of various collisions, there are formed the ions N^+, O^+, NO^+, N_2^+, O_2^+. Since ions are

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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_N^+, n_0^+; their sum is n_i^*. The degree of

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*The concentrations of molecular ions may be found as a small increment with the help of the relations $(n_0 + n_0 + n_{N}o^+ + 2n_{0_2}+)/n_N + n_N + n_{NO}^+ + 2n_{N_2}) = 0.21/0.79$ and equations of the type equation (6): $n_{NO}^+ = n_N^+ n_0 K_i = n_N n_0^+ K2$, $n_{N_2}^+ = n_N n_N^+ K4$, $n_0^+ n_0 K3$.

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is $a = N_e /n$, $n = n_0 + n_N + n_i$.

The condition $= const$ reduces to $nv = const$.   Then

$$\frac{d(n_e v)}{dx} = S_e = -\frac{d}{dx} \sum_k (n_{N_k} + n_{0_k})v \approx$$

$$\approx -\frac{d}{dx} \sum_{k=1}^{3} (n_{N_k} + n_{0_k})v. \tag{15}$$

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

$$S_e \approx \sum_{k=1}^{3} \{(n_{N_k} n_e j_{ke}^e - n_e^2 n_N^+ j_{ek}^e) + (n_{0_k} n_e i_{ke}^e - n_e^2 n_0^+ i_{ek}^e) +$$

$$+ (P_{N_k} - n_e n_N^+ u_{ek}^e) + (P_{0_k} - n_e n_0^+ \beta_{ek}^e) +$$

$$+ (n_{N_k} n_{N_i} j_{ke}^{i*} - n_e n_{N_i} n_N^+ j_{ek}^{i*}) + (n_{0_k} n_{0_i} i_{ke}^{i*} - n_e n_{0_i} n_0^+ i_{ek}^{i*}) +$$

$$+ (n_{N_k} n_{0_i} g_{ke}^{i*} - n_{N_i} n_e n_0^+ g_{ek}^{i*})\}. \tag{16}$$

In contrast to (10) the summations in j_{ch}^{e*}, j_{he}^{e*}, a_{ch}^{*} are carried out for $n \geqslant 3$. Further $j_{he}^{i*} = \frac{1}{2} \sum_{n=1}^{3} \frac{j_{hn}^{e}}{j_{n1}^{e}} j_{he}^{n}$, $j_{ch}^{i*} = \frac{K_{4}}{2} \sum_{n=1}^{3} j_{ch}^{n}$. The designations

j_{he}^{e}, j_{he}^{i}, j_{ch}^{n}, a_{ch} и т. д. are reserved for the atom N. For the atom O we introduce i_{he}^{e}, i_{he}^{i}, i_{ch}^{n}, β_{ch} analogously. For example' $i_{ch}^{i*} = \frac{1}{2} \sum_{n=1}^{3} \frac{i_{hn}^{e}}{i_{n1}^{e}} i_{ch}^{n}$.

For the process of formation of NO^{+} we introduce the coefficient

$g_{he}^{n}:g_{he}^{i*} = \sum_{n=1}^{3} \frac{i_{hn}^{e}}{i_{n1}^{e}} g_{he}^{n}$, $g_{ch}^{i*} = K_{4} \sum_{n=1}^{3} g_{ch}^{n}$. $p_{N_{h}}$ and $p_{O_{h}}$ account for the absorption of radiation.

The source of energy of electrons is

$$S_{ce} \approx \sum_{m}' n_{e} n_{m} Q_{me} - \sum_{h=1}^{3} \Bigg[U_{N}(n_{e} n_{x_{h}} j_{he}^{e} - n_{e}^{2} n_{N}^{+} j_{ch}^{e*}) +$$

$$+ U_{O}(n_{e} n_{O_{h}} i_{he}^{e} - n_{e}^{2} n_{O}^{+} i_{ch}^{e*}) - \Bigg(\frac{1}{2} n_{N_{h}}^{2} \sum_{n=1}^{3} \frac{j_{hn}^{e}}{j_{nh}^{e}} j_{he}^{n} \varphi_{hn}^{N} -$$

$$- n_{e} n_{N}^{+} n_{N_{h}} \frac{K_{4}}{2} \sum_{n=1}^{3} j_{ch}^{n} \varphi_{nh}^{\prime N} \Bigg) - \Bigg(\frac{1}{2} n_{O_{h}}^{2} \sum_{n=1}^{3} \frac{i_{hn}^{e}}{i_{nh}^{e}} i_{he}^{n} \varphi_{hn}^{O} -$$

$$- n_{e} n_{O}^{+} n_{O_{h}} \frac{K_{3}}{2} \sum_{n=1}^{3} i_{ch}^{n} \varphi_{nh}^{\prime O} \Bigg) - \Bigg(n_{O_{h}} n_{N_{h}} \sum_{n=1}^{3} \frac{i_{hn}^{e}}{i_{nh}^{e}} g_{he}^{n} \varphi_{hn}^{NO} -$$

$$- n_{e} n_{O}^{+} n_{N_{h}} K_{4} \sum_{n=1}^{3} g_{ch}^{n} \varphi_{nh}^{\prime NO} \Bigg) + n_{e} n_{N}^{+} \varphi_{h}^{N} a_{ch} + n_{e} n_{O}^{+} \varphi_{h}^{O} \beta_{ch} \Bigg], \quad (17)$$

U_{O} and U_{N} - 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, $n_N \approx 0,79n(1-\alpha)$, $n_O \approx 0,21n(1-\alpha)$. Then we have

$$\frac{S_e}{n^2} = \alpha(1-\alpha)(0,79j_{te}^{e\cdot\cdot} + 0,21i_{te}^{e\cdot\cdot}) + (1-\alpha)^2(0,79^2 j_{te}^{1\cdot\cdot} +$$

$$+ 0,79\cdot0,21g_{te}^{1\cdot\cdot} + 0,21^2 i_{te}^{1\cdot\cdot}) + \sum_{k=1}^{3}\left[\left(P_{N_k} - \alpha^2\frac{n_N^+}{n_e}\alpha_{e1}^{\cdot\cdot}\right) + \right.$$

$$\left. + \left(P_{O_k} - \alpha^2\frac{n_O^+}{n_e}\beta_{e1}^{\cdot\cdot}\right)\right], \tag{18}$$

$$\frac{S_{ee}}{n^2} = \alpha^2 Q_{te} + \alpha(1-\alpha)(0,79Q_{Ne} + 0,21Q_{Oe}) - \alpha(1-\alpha)(U_N\cdot0,79j_{te}^{e\cdot\cdot} +$$

$$+ U_O\cdot0,21i_{te}^{e\cdot\cdot}) + (1-\alpha)^2(\overline{\varphi}^N\cdot0,79j_{te}^{1\cdot\cdot} + \overline{\varphi}^{NO}\cdot0,79\cdot0,21g_{te}^{1\cdot\cdot} +$$

$$+ \overline{\varphi}^O\cdot0,21^2 i_{te}^{1\cdot\cdot}). \tag{19}$$

Here the following notation has been used:

$$j_{te}^{e\cdot\cdot} = \left(1 + \frac{j_{21}^e}{j_{12}^e} + \frac{j_{31}^e}{j_{13}^e}\right)^{-1}\sum_{k=1}^{3}\frac{j_{1k}^e}{j_{k1}^e}j_{ke}^e,$$

$$j_{te}^{1\cdot\cdot} = \left(1 + \frac{j_{21}^e}{j_{12}^e} + \frac{j_{31}^e}{j_{13}^e}\right)^{-2}\sum_{k=1}^{3}\frac{j_{1k}^e}{j_{k1}^e}j_{ke}^1,$$

$$\alpha_{e1}^{\cdot\cdot} = \sum_{k=1}^{3}\alpha_{ek}^{\cdot},$$

$$\overline{\varphi}^N j_{te}^{1\cdot\cdot} = \frac{1}{2}\left(1 + \frac{j_{21}^e}{j_{12}^e} + \frac{j_{31}^e}{j_{13}^e}\right)^{-2}\sum_{k,n=1}^{3}\frac{j_{1n}^e j_{1k}^e}{j_{n1}^e j_{k1}^e}j_{ke}^n\varphi_{kn}^N.$$

The remaining notation is introduced analogously.

It can be shown that under our conditions for $\alpha \leqslant 0,3\alpha_{eq}$ (the index eq pertains to equilirbium 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 10 km/sec relaxation is determined by the following processes. At first associative ionization predominates
$$N + O \rightleftharpoons NO^+ + e, \quad N + N \rightleftharpoons N_2^+ + e, \quad O + O \rightleftharpoons O_2^+ + e.$$ 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.

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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 magnitide 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:

$$j_{ri}^1 = 6 \cdot 10^{-3} T^{-\frac{1}{2}}, \quad i_{ri}^1 = 4 \cdot 10^{-3} T^{-\frac{1}{2}}, \quad g_{ei}^1 = 3 \cdot 10^{-3} T^{-\frac{1}{2}} \ cm^3/cek. \quad (20)$$

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 N 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_a. The indeterminancy of is unessential since at the beginning of relaxation, the electron temperature does not affect the ionization rate.

The cross sections for calculation of $j_{ie}^\circ, j_{2e}^\circ, i_{ie}^\circ$ 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 $18,000°K$

$$j_{ie}^{\circ\circ} = 3 \cdot 10^{-10} \gamma \overline{T_e} e^{-110\,600/T_e}, \quad i_{ie}^{\circ\circ} = 1.8 \cdot 10^{-10} \gamma \overline{T_e} e^{-130\,600/T_e} \ cm^3/cek. \quad (21)$$

The precision of these coefficients is sufficient i. 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:

$$Q_{ie} = \frac{2e^4 \gamma \overline{2\pi m_e}}{m_i} \frac{kT_e - kT_e}{(kT_e)^{\frac{3}{2}}} \left[\ln \frac{9(kT_e)^3}{8\pi e^6 n_e} + 1 \right].$$

For atom-electron equations it has been found that

$$Q_{ae} = \frac{4m_e}{m_a} \sqrt{\frac{8kT_e}{\pi m_e}} \sigma(kT_a - kT_e)[1 - (1 + T_e/T_v)^{-3}]$$

$= 6 \cdot 10^{-16}$ cm^2 for N and $5.5 \cdot 10^{-16}$ for O. Correspondingly, $T_v = 3.1 \cdot 10^4$ and $1.2 \cdot 10^4 \,°K$. 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.

$_{ek}$ and $_{ek}$ are found with the help of transition proababilities attained by the quantum defect method. In the range $T_c = 8$ to $20) \cdot 10^3 \,°K$.

$$\alpha_{ei}^{\bullet\bullet} = 5{,}0 \cdot 10^{-8} e^{-8{,}0 \cdot 10^{-4} T_e} + 1{,}2 \cdot 10^{-11} e^{-1{,}6 \cdot 10^{-4} T_e}, \, cm^3/cek. \qquad (22)$$

The quantity of $\beta_{ei}^{\bullet\bullet}$ 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 argone 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 coll. Independently of whether we find the cross section from the method of Milford /6/, or use the quaziclassical expressions /9/, it turns out that in the interesting range of n_e and for p_i 10^{-5} atm/ 1. 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

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necessary values of alpha, the electron-atom cross sections are large enough /10/ 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_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 $\cdot = 0.5$ $_{eq}$. 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 $_{ek}^{*}$ and $_{ck}^{*}$ instead of the life time of isolated atoms, the effective life times /11/ It turns out that such effective values $_{ek}$ and $_{ck}$ 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 $\cdot = 0.5$ $_{eq}$ the relaxation in air proceeds according to a binary scheme*.

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*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 $p_1 x$. (We recall that $_{eq}$ depends on p_1. The solution obtained above is justified for $\cdot - 0.5^q$. Consequently, the profiles constructed as functions of $p_1 x$ for different p_1 are correct in different intervals $p_1 x$). As an example, figure 1 shows the profiles of alpha, T_a and T_e 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 leads to an indeterminancy in T_c. Calculations with various did not give noticeably different results, although for a small x, T_e underwent strong changes (figure 1 shows the case $= 0$). For the same reason, it is also unimportant that the electronic conductivity tends to increase T_c in the region of small x.

The dependence of T_a and T_c on x was discussed by us earlier /2/.

Figure 2 shows the dependence of $P_1 t$ 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 km/sec*. For v_1 7 km/sec, the length of the

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*Relaxation behind the front of strong shock waves in air were consider-
ed by V.A. Bronshten /16/. It was assumed that ionization is accomplished by
collisions with electrons (atom-atom collisions were not considered). It
was assumed that in the entire unequilibrium region, the relation of the con-
centration of atoms in excited and ground states was determined by the Boltzmann
Law. It was assumed that such a high concentration of excited states is
created by absorption of radiation. Excitation by collisions was not con-
sidered. An elementary calculation shows that the energy being radiated by
the shock wave is clearly insufficient for maintaining the Boltzmann distri-
bution in the conditions of the nonequilibrium zone of the shock wave. In
addition, thermo-dynamically contradictory expressions were used for the
coefficients of triple recombination and ionization by electron collisions.
Since the elementary processes of ionization considered in /6/ are not re-
liable, it is hard to imagine that the characteristics of the nonequilibrium
zone obtained by V.A. Bronshten are reliable in order of magnitude.

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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*. Up to v_1 = 9 km/sec the length of the relaxation is determined

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

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by the kinetic decomposition of molecules. Figure 2 shows the results of
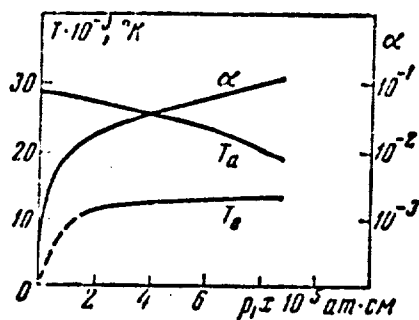these papers.

Fig. 1: Profile of the parameters
of a nonequilibrium gas behind a
shock wave. v_1=12 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 indeter-
minancy of T_e for small x (see text)
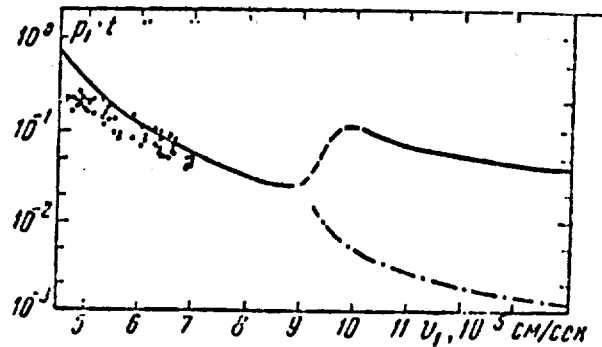this portion is given in Figure 1
by dashes.

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=0.02mm Hg.
Ionization relaxation: calculation (for
v_1 9,/4/, for v_1 10,present work); --,
experimental data /4/. Dissociation relax-
ation: __.__ is evaluation carried out in
appendix.

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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

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*In fact, in the interval $v_1 = 9$ to 10 km/sec, $_{eq}$ changed by a factor of 10 (in the range from 10-11 km/sec by a factor of 2) and the energy of ionization made a noticeable contribution to the enthalpy.

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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 satisifed better the large 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_{N2^+} 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 undissociated 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 noticeable cooled owing to the emission of radiation. If ρ 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.

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In a subsequent paper we hope to examine the entire region of relaxation using the general equations written above.

The authors thank Yu. P. Ragzer for valuable comments.

Appendix

Dissocation 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 N_2. We introduce

$$\beta = n_N / (n_N + 2n_{N_2}), \quad m' = 2m_N + \xi m_O, \quad \xi = 0.21/0.79.$$

then

$$\partial\beta / \partial x = m'(2\rho_1 v_1)^{-1} S_N(x). \tag{23}$$

With the notation S_N for the source of atoms of nitrogen we consider

$$N_2 + M \rightleftharpoons 2N + M, \quad M = O, N, N_2. \tag{24}$$
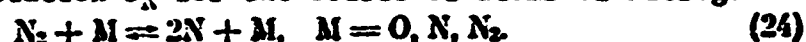
Introducing for their rates the notation $k^{(O)}, k^{(N)}, k^{(N_2)}$ we obtain

$$S_N = [(n_N + n_O + n_{N_2}) / (1 + 2\xi + \beta)]^2 (1 - \beta) \times$$
$$\times [2\beta k^{(N)} + 2\xi k^{(O)} + (1 - \beta) k^{(N_2)}]. \tag{25}$$

Equation (23) is integrated considering the conditions of conservation

$$kT = (H_0 m' - \xi D_{O_2} - \beta D_{N_2}) \left/ \left(\frac{9}{2} + 5\xi + \frac{\beta}{2}\right)\right., \quad p \approx p_0 \tag{26}$$

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 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 /4/. We calculate the degree of ionization attained in the course of dissociation:

$$\alpha(x) = m' [\rho_1 v_1 (1 + 2\xi + \beta)]^{-1} \int_0^x S_e \, dx. \tag{27}$$

For $v_1 = 10$ km/sec, during the time t_{dis} there is attained $1.7 \cdot 10^{-3}$. This quantity is small and does not affect the subsequent course of the relaxation.

The case $v_1 = 9$ 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 characterisitcs 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, 95, 1965) in which the times of relaxation were measured. For shock waves with $v_1 = 10.9$ and 11.25 km/sec and $p_1 = 0.1$ mn Hg, the time of ionization relaxation is t 1 sec. This is good confirmation of our conclusions.