# IONIZATION RELAXATION BEHIND THE FRONT OF A SHOCK WAVE IN ARGON WITH AIR IMPURITIES

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The results of [1–4] on ionization relaxation behind the front of shock waves in argon indicate that the mechanism and kinetics of the ionization processes change from point to point in the region. We can separate the development of the ionization process into three stages:

1) the initial stage in which the electrons to be used are formed;
2) the stage in which an electron avalanche develops during inelastic electron-atom collisions;
3) the stage in which equilibrium is approached and is characterized by the effect of recombination processes on the ionization kinetics.

Unfortunately, the published studies do not arrive at the same conclusions regarding the electron-formation mechanism in the initial stage of the process; here we can assume atom-atom collisions, atom-impurity collisions, and chemo- and photoionization are the most likely processes. Thus, Petschek and Byron [1] concluded that impurities have a considerable effect on the ionization time for the entire range of numbers they examined ($M = 10-18$). Conversely, in a study by Jones and McChesney, it was shown that the ionization-relaxation time for $M > 12$ is independent of the impruity level. Finally, in a recently published study by Wong and Bershader [3], it was noted that impurities affect the ionization time, although no corresponding experimental data are given in the study. Thus, at present, the effect of impurities on the time required for ionization equilibrium to be established is still unknown. In several studies, it was shown that for atom-atom collisions, a two-stage ionization mechanism exists; an atom is first excited and then ionized.

When the number of electrons in the relaxation region increases so much that the degree of ionization reaches a value on the order of $10^{-4}$, ionization resulting from electron-atom inelastic collisions is the most important mechanism; this is shown by the results of a theoretical analysis [1, 3]. Here the ionization rate is determined chiefly by the rate of energy exchange between electrons and ions during elastic collisions.

In the stage immediately preceding the establishment of equilibrium, recombination processes have a considerable effect on the ionization kinetics.

The appearance of continuous radiation behind the front of the shock wave is also associated with the development of recombination processes in monatomic gases. If the plasma is transparent to this continuous band of radiation, the intensity of the continuous radiation (for hydrogen-like atoms) is associated with the electron density by the familiar Uhsold-Kramer formula [5]

$$J \sim Z N_e^2 / T^{1/2}.$$

Here J is the energy radiated in all directions per cubic centimeter of gas per second directions per unit interval of frequencies, $N_e$ is the number of electrons per cubic centimeter, Z is the effective charge of the nucleus (usually taken as unity), and T is the temperature.

It is known that for the conditions of interest to us transitions between excited states and ionization of highly excited atoms, as in the corresponding reverse processes, take place much more rapidly than the excitation and ionization of atoms in the ground state and the corresponding reverse processes. We can assume, approximately, that the excited states are in Saha equilibrium with the ionized state of the atom, i.e., with free electrons.

Thus, the electron-density distribution in a shock wave can be found either by recording the intensity of the continuous spectrum or the intensity of the spectral lines corresponding to transitions between highly excited states.

This article is devoted to a study of ionization equilibrium in argon behind the front of incident and reflected shock waves. The technique using a reflected shock wave has several know advantages: assuming other conditions are the same, a higher temperature is reached and the true time of the process can be directly measured. It is, therefore, important to know whether the results obtained by the two methods agree. Moreover, it is of interest to understand that the results may be affected by the fact that the reflected shock wave propagates through a gas excited by the incident shock wave.

**Experimental Setup and Study Technique.** The study was performed in a shock tube with very precise parameters; this tube consisted of a high-pressure chamber, a diaphragm section, and a polished channel with constant internal cross section. The high-pressure chamber, which was 3.0 m long and had an internal diameter of 90 mm, was designed to operate at a maximum working pressure of 2000 atm with some reserve strength. The diaphragm section, which was adjacent to the high-pressure chamber, had a transition section 80 mm in diameter. The constant cross-section channel with diameter 80 mm and length 7 mm was intended to operate at a working pressure of 700 atm. The channel completes the working section; in this channel are three pressure-sensitive detectors made of barium titanate. The first transducer registers the direction of motion for the incident shock wave and triggers the driven sweeps of the measurement oscillographs. The other two transducers serve to measure the velocity of the incident shock wave.

Special ports for registering the gas radiation behind theshock-wave front are placed near the second and third pressure pickups; in this case, a special two - rayoptical system is needed. This device consist of a lens with focal length 94 mm which focuses the center of the shock tube on a slit 0.1 mm wide; in this case, the magnification is 1 : 1. The space resolution of this system is 1.0 mm. With a second lens, this slit is projected onto a semitransparent screenwherethe light beam is separated into two rays each of which then strikes the input slit of LSP-51 spectrographs wit FEP-1 cameras. Signals from the FEU-17 are fed to the OK-17M oscillograph through cathode repeaters. Here the load on the photomultiplier is 4.7 Ω for an input capacitance of 50 $\mu\mu$F for the cathode repeaters. One optical channel is used to record the continuous spectrum intensity near 5000 Å. This region of the spectrum is free from argon and impurity lines. The second channel is used to register the radiation intensity of the 4300 Å spectral line of argon; this corresponds to the 4S2°- 5p3 transition.

To generate the shock waves, hydrogen was used as the accelerating as. However, in order to excite strong shock waves in the high-pressure chamber, a hydrogen-oxygen mixture was burned; in this case, the initial molar ratio of oxygen to hydrogen was about 0.12 which corresponded to an optimum sound velocity in the combustion products. In order to ensure that combustion was uniform, special measures were taken to ensure that the components mixed well and the mixture burned uniformly within the entire high-pressure chamber. Thorough mixing was ensured by simultaneously filling the chamber through 60 inputs; in this case, the gas entered the channel tangentially. Over the entire length of channel, uniform ignition which took place simultaneously, was realized by exploding a thin conductor stretched along the axis of the channel and across which a capacitor discharged. The experiments could be repeated for each mode with sufficiently good results. The device made it possible to obtain shock waves in argon and air with Mach numbers as large as 40.

Experiments on determining the time required for ionization equilibrium to be established were performed both behind incident and reflected shock waves. Here the moment at which the incident and reflected shock waves pass the window slit is recorderd by the pressure transducer. The value used for the relaxation time is the time elapsed between the passage of a shock wave and the realization of a uniform radiation region identical to the equilibrium region. In experiments with incident shock waves, the end was placed 10 cm from the slit; in experiments with reflected shock waves, the end was moved 1.2 cm closer to the slit in order to reduce the time between the arrival of the incident and reflected shock waves and to minimize the effect of processes resulting in the formation of the "seeding" electrons behind the incident shock wave.

**Results.** All experiments were performed for an initial argon pressure of 5 mm Hg. The low-pressure chamber in this case was evacuated to $4.0 \cdot 10^{-2}$ mm Hg so that the impurity level in these experiments was $8 \cdot 10^{-3}$. Figure 1 shows a typical oscillogram of the increase in background intensity and the 4300 Å line behind the front of a shock wave. The experimental results indicate that for the Ar lines and for a continuous spectrum roughly the same relationship is observed for the increase in intensity with time (in this case, both processes have the same relaxation times). This result confirms the assumption that equilibrium between the highly excited and ionized states of the argon atom is rapidly established.

The results obtained from measuring the ionization-relaxation time in these experiments are shown by lines 1 and 4 in Fig. 2 which shows $p_1\tau$ as a function of $1/T_A$, here p is the initial pressure, $\tau$ is the relaxation time, and $T_A$ is the unrelaxed temperature. In contrast to experiments with a reflected shock in which the theoretical value for the pressure was taken as $p_1$ (this must occur ahead of the incident shock wave in order that the pressure behind it be equal to the pressure behind the reflected shock wave), we took $p_1 = 5$ mm Hg as initial pressure in our experiments. We should first note that the ionization-relaxation times obtained in experiments with reflected shock waves do not agree either with the corresponding values obtained behind an incident wave or with those values calculated in the laboratory for the true particle time in accordance with idea shock—wave theory. Line 3 in Fig. 2 shows this relationship. As follows from this figure, the points obtained from experiments with a reflected shock wave lie above this curve and the relaxation time behind the reflected shock wave is approximately two or three times greater than the relaxation time behind an incident shock wave (for the same temperatures).

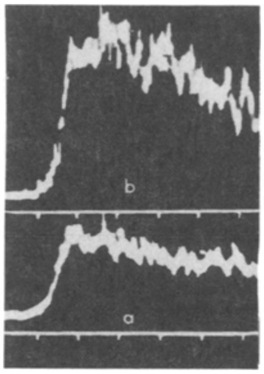

Fig. 1. Oscillogram of the change in intensity of continuous spectrum (a) and 4300 Å line (b) behind the front of an incident shock wave. The sweep is in 10 μsec divisions.

This result is not expected since it is logical to assume that if processes leading to the formation of seeding electrons take place behind the incident shock wave the only possible result is a decrease in relaxation time for measurements performed behind the front of a reflected shock wave. The experimentally obtained increase in ionization time, in our opinion, is due either to the fact that the process is not ideal or that radiation affects the ionization process.

The first effect is associated with the formation of a nonstationary boundary layer behind the front of the moving shock wave; this leads to the experimentally—observed acceleration of the contact surface. As shown by Roshko and Mirels [4, 6] when the true time rather than the laboratory time is used, in addition to the usual factor $\rho_2/\rho_1$ it is necessary to introduce an additional factor associated with the formation of a boundary layer behind the shock-wave front. The magnitude of this factor which is equal to the ratio of the true time to the time defined by ideal theory is shown in Fig. 3 as a function of the dimensionless distance $l/l_m$. Here $l$ is the distance from the shock-wave front and $l_m$ is the maximum length of gas heated by the shock wave; this maximum value occurs at the point where the total gas flow through the boundary layer is equal to the gas flow through the shock-wave front.

In accordance with [5], we can write

$$\frac{l}{l_m} = \frac{16\beta^2}{d^2}\left(\frac{T_2}{T_1}\right)\frac{\mu_1}{\rho_1}\left(\frac{\rho_2}{\rho_1} - 1\right)\tau .$$

Here $\beta$ is a parameter roughly equal to 3; d is the diameter of the shock-tube channel, $\mu$ and $\rho_1$, are the velocity and density ahead of the shock wave; $T_1$, $T_2$, $\rho_1$ and $\rho_2$ are, respectively, the temperatures and densities ahead of and behind the shock-wave front; $\tau$ is the time in the laboratory coordinate system.

Estimates show that under our experimental conditions this correction is about 10–15%for experiments with M on the order of 11. As M increases and the ionization—relaxation time decreases, this correction can be ignored.

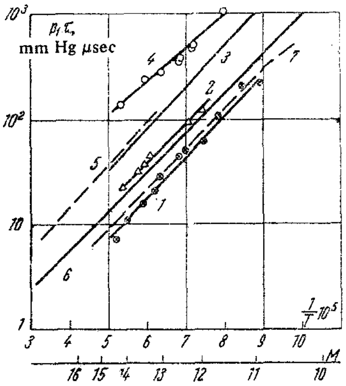

Fig. 2. Temperature dependence of the relaxation times on initial pressure. Data for lines: 1(crosses) $p_1 = 5$ mm Hg, impurity content $8 \cdot 10^{-3}$, laboratory time; 2(triangles), $p_1 =$ $= 5$ mm Hg, impurity content $3 \cdot 10^{-4}$, laboratory time; 3, curve 1 scaled to particle time; 4 (circles). reflected shock wave, $p_1 = 5$ mm Hg, impurity content $8 \cdot 10^{-3}$, particle time; 5, data of [3], $p_1 = 5$ mm Hg, impurity content $10^{-5}$, laboratory time; 6, data of [1], impurity content $5 \cdot 10^{-5}$, laboratory time; 7, data of [12], $p_1 =$ $= 5$ mm Hg, impurity content $10^{-2}$ and $3 \cdot 10^{-3}$, laboratory time.

The correction associated with the increase in density owing to ionization is even smaller. Thus, the increases in density owing to ionization is even smaller, Thus, the increase inionization-relaxation time behind a reflected shock wave is evidently associated with the effect of radiation. In fact, in experiments with an incident shock wave the heated-gas region is fairly extended whereas in experiments with a reflected shock wave the dimension of the "plug" is not very large near the end of the chamber.

It was noted above that the effect of impurities on the ionization time is still not understood at present. Actually, Petschek and Byron are the only ones to consider this problem; however, despite the conclusion that impurities play a very important role over the entire range of change in M it is not difficult to verify that the ionization time obtained in [1] for an impurity level of $10^{-3}$ in argon are identical with the results obtained for impurity level of $5 \cdot 10^{-5}$ . Hones and McChesney concluded that impurities have no effect on the time required for ionization equilibrium to be established for impurity levels of $10^{-2}$ and $3.5 \cdot 10^{-3}$ and for M greater than 12; in their study it was shown that a three-fold change in the experimental impurity level led to an insignificant change in the ionization time which was certainly an insufficient for solving this important problem.

To understand the effect of air impurities on the ionization time a series of experiments was performed for an impurity content of $3 \cdot 10^{-4}$. Curve 2 in Fig. 2 shows these experimental results and indicates that the impurities affect the time required for ionization equilibrium to be established. The discrepancy between the experimental data obtained for the two impurity levels $8 \cdot 10^{-3}$ and $3 \cdot 10^{-4}$ becomes even greater if the drop in temperature due to impurity dissociation is allowed for. This correction must be introduced since at temperatures of 10, 000-8, 000 °K the vibrational and dissociative relaxation times for oxygen and nitrogen are much less than the ionization times. For experiments with an impurity content of $8 \cdot 10^{-3}$ the temperature correction is about 850° K while in experiments with an impurity level of $3 \cdot 10^{-4}$ this correction can be ignored. A similar temperature correction must also be introduced into the data of Jones and McChesney; then their conclusion that the ionization time is not sensitive to the impurity level for M greater than 12 is no longer conclusive.

Thus, the data shaown in Fig. 2 indicates that air impurities affect the time required for ionization equilibrium to be established, but this effect only appears upon a significant change in impurity level. Thus, one order change in impurity level leads to an increase inionization time by a factor of two or three.

**Formation Mechanism of Initial Electrons.** In several articles, various assumptions were put forward as to the ionization mechanism in the initial stage. An analysis of some of these mechanisms is given in an article by L. M. Biberman and I. T. Yakubov [10], who arrived at the conclusion that the excitation of atoms by resonant radiation leaving the equilibrium zone is the primary reason for the formation of initial electrons. This results in a significant increase in concentration of the excited atoms which are then easily ionized by electron collision. In our opinion, it would seem that if this process was to be of primary importance the impurity level should not affect the ionization-relaxation time if the impurities themselves did not participate in the process).

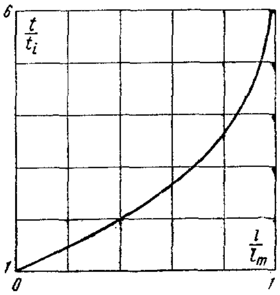

Fig. 3. The ratio of the true time t to the time $t_i$ determined from idea theory, as a function of the distance to the shock-wave front.

In view of the data obtained by Jones and McChesney [2], there is some doubt as to the validity of the conclusions drawn and to their interpretation. Our data confirm the conclusions of Petschek and Byron [1], i.e., impurities have an important effect on the ionization-relaxation time. However, their estimates showed that neither thermal ionization of the impurities nor photoionization provide an explanation of the experimentally observed rapid increase in ionization in the initial stage behind the shock wave front. In order to describe the ionization kinetics in the initial stage, they assumed that the "seeding" electrons form as a result of argon-impurity atom collisions; after processing their experimental data, the following equation was obtained:

$$\frac{d\alpha}{dt} = (1-\alpha)^2 A N_+ \exp\left(\frac{-E}{kT}\right). \tag{1}$$

Here $\alpha$ is the degree of ionization, $N_+$ is the impurity-particle density, T is the relaxation temperature, k is Boltzmann's constant, A and E are constants respectively equal to $8 \cdot 10^{-8}$ cm$^3$/sec and 11.5 eV (the excitation potential of argon).

However, the value obtained by Petschek and Byron for A is not generally accepted since this value corresponds to an unrealistically high value for the cross section of inelastic atom-atom collisions. In fact, from the kinetic equation it is known that

$$\frac{d\alpha}{dt} = (1-\alpha)^2 N_+ \left(\frac{2kT}{\pi\mu}\right)^{1/2} Q\left(1+\frac{E}{kT}\right)\exp\left(\frac{-E}{kT}\right). \tag{2}$$

Here $\mu$ is the reduced mass of the colliding particles and Q is the process cross section. Upon substituting the value for A obtained by Petschek and Byron into (2) we obtain $Q = 4 \cdot 10^{-14}$ cm$^2$ which is approximately $10^6$ times greater than the cross section for excitation and ionization by collision with atoms having the considered range of energies.

Moreover, from Eq. (1) it follows that the ionization-relaxation time must be proportional to the impurity concentration since the time taken up by the initial stage is roughly equal to the buildup time of the electron avalanche; the time corresponding to the recombination stage is relatively small and can be ignored. However, this relationship has not been experimentally confirmed and indicates that the formation mechanism for seeding electrons in the presence of impurities is complex and sufficient data is still not available at present for understanding this process.

To determine the kinetic laws governing argon ionization it is necessary to perform experiments with pure argon. For this reason, we consider the study of Wong and Bershader [3] in which the impurity content is $10^{-5}$. In this case, we can assume that the initial electrons form as a result of a two-stage process:

$$\mathrm{Ar} + \mathrm{Ar} \rightarrow \mathrm{Ar}^* + \mathrm{Ar}, \tag{3}$$

$$\mathrm{Ar}^* + \mathrm{Ar} \rightarrow \mathrm{Ar}^+ + e + \mathrm{Ar}. \tag{4}$$

Under this assumption, their experimental results can be described if we use the expression

$$k_3 = 8.9 \cdot 10^{-12}\left(\frac{kT}{E}\right)^2 \exp\left(\frac{-E}{kT}\right) \qquad \left[\frac{\mathrm{cm}^3}{\mathrm{sec}}\right] \tag{5}$$

for the rate constant of Eq. (3).

Unfortunately, the cross section for the excitation process of atom-atom collisions in the range of energies of interest is not known; therefore, it is not possible to calculate the rate of process (3). We only note that Eq. (5) applies for reasonable values of the cross section for excitation by collision with atoms (roughly $10^{-20}$ cm$^2$).

When air impurities are present in argon associative ionization can play a very important role in the formation mechanism of seeding electrons. It is known that at ahigh temperatures we can ignore the contribution of molecular ions to equilibrium ionization. However, these ions can play a very important role in the kinetics of ionization equilibrium. Since air is the main impurity in both our experiments and the experiments of other authors we can assume that the initial electrons form as a result of the following associative-ionization reaction:

$$\mathrm{N} + \mathrm{O} \rightarrow \mathrm{NO}^{+} + e - 2.8\ \mathrm{eV}, \tag{6}$$

$$\mathrm{N} + \mathrm{N} \rightarrow \mathrm{N}^{+}_{2} + e - 5.8\ \mathrm{eV}, \tag{7}$$

$$\mathrm{O} + \mathrm{O} \rightarrow \mathrm{O}^{+}_{2} + e - 6.9\ \mathrm{eV}. \tag{8}$$

The first of these processes is, probably, the most important. It is of interest to compare the rate of processes (3) and (6). The rate constant of reaction for (6) was determined by Lin and Teare [7]:

$$k_6 = 5 \cdot 10^{-11}\, T^{-1/2} \exp \frac{-32500}{T}, \qquad \frac{\mathrm{cm}^3}{\mathrm{sec}}\ . \tag{9}$$

We give the ratio of the velocity $\varkappa = k_6 N_0 N_{\mathrm{N}} / k_3 N_{\mathrm{Ar}}^{2}$. of processes (3) and (6) as a function of the number M of a shock wave for an air impurity level of $10^{-2}$:

$$\begin{array}{rcccc} M = & 10.3 & 11.3 & 12.7 & 14.6 \\ T,\ ^{\circ}\mathrm{K} = & 10\,000 & 12\,000 & 15\,000 & 20\,000 \\ \varkappa = & 25 & 3.3 & 0.3 & 2.6 \cdot 10^{-3}\ . \end{array}$$

It follows from these data that an air impurity content on the order of $10^{-2}$ (which occurs in our experiments and the experiments of Jones and McChesney) can affect the time required for ionization equilibrium to be established when $M < 12$. However, for an impurity content less than $10^{-3}$, its effect on the ionization time will probably be insignificant.

In this case, initial electrons can form as a result of reactions (3) and (4). In principle, we can assume that associative ionization occurs for argon:

$$\mathrm{Ar} + \mathrm{Ar} \rightarrow \mathrm{Ar}^{+}_{2} + e\ , \tag{10}$$

since it is well known that molecular argon ions exist. However, it is hardly likely that this process takes place at a rate noticeably greater than excitation or ionization by atom-atom collisions. In fact, according to the data in [8], the bound energy of the $\mathrm{AR}_2^+$ molecular ion corresponding to its decay into Ar and $\mathrm{Ar}^+$ is very low (1.05 eV). Therefore, the activation energy for the reaction of (10) is $15.76 - 1.05 = 14.71$ eV (15.76 is the argon ionization potential). Process (10), allowing for the contribution of unexcited atoms, i.e., including the energy due to the translational motion of the atoms, is just as adiabatic as excitation reaction of (3) or atom-atom ionization and takes place no more rapidly than (3). If, however, an excited atom

$$\mathrm{Ar} + \mathrm{Ar}^{*} \rightarrow \mathrm{Ar}^{+}_{2} + e \tag{11}$$

contributes to a reaction of type (10) the ionization rate will be determined not by the rate of (11) but by the rate at which argon atoms are excited; this is similar to the case which exists for the two-stage process of (3) and (4). It is interesting to note that the cross section of process (1), which includes the participation of an excited argon atom with excitation energy 14.71 eV (sufficient for activation) is close to the gas-kinetic cross section. This can be estimated from the equilibrium constant and the known rate of the reverse reaction (defined in [9]).

Note that when the rate of the forward process (10) is calculated from the rate of dissociative recombination and the equilibrium constant for (10) a very large value is obtained in comparison with (3). However, this procedure is not to be recommended since in the experimentally studied process of dissociative recombination the energy liberated goes into exciting the argon rather than into the translational energy of the atoms.

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