

## KINETICS OF ELECTRON RECOMBINATION IN A MOLECULAR GAS EXPANDING INTO A CAVITY

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The kinetics of recombination in a diatomic or polyatomic gas dispersing into a cavity is investigated in a model gas with one ionization potential and one electron affinity.

In addition to the recombination reaction in triple collisions, which play the most important role in the case of a monatomic gas [1], dissociative recombination, ion-atom charge transfer, and reactions involving negative ions are considered. The qualitative differences in the kinetics of recombination of a molecular gas (in comparison with a monatomic gas) are due to the smallness of the relative electron concentrations at the instant of disturbance of ionization equilibrium and to the important contribution of dissociative recombination reactions and the kinetics of formation and recombination of negative ions.

In addition, owing to the greater specific heat of a polyatomic gas and the corresponding lower rate of cooling on dispersion, recombination due to collision of three charged particles is not, as distinct from the case of a monatomic gas, decisive for the asymptotic values of the adiabatic exponent and residual ionization. For this reason the values of the adiabatic exponent can be assigned irrespective of  $\alpha$  in the solution of the equations of the kinetics of recombination of diatomic and polyatomic gases. Expressions for the instant of failure of the equilibrium relationship between electrons and, respectively, positive and negative ions are obtained.

The relationship between the charged-particle concentration in a gas in ionization nonequilibrium and the time for known values of the reaction rate constants is expressed by quadratures. The values of the rate constants of some ionization processes are known only in order of magnitude. However, available data on rate constants indicate that for practically any initial data for dispersion of the products of explosion or combustion of chemical compounds ionization equilibrium is upset at a time when there is still an equilibrium ratio of concentrations of electrons and negative ions.

The kinetics of electron recombination in an expanding thermally ionized monatomic gas was considered in [1]. However, in many practically interesting cases of dispersion of a gas (emergence from a nozzle, dispersion of products of detonation of chemical explosives, etc.) the amount of atomic gas at the instant of disturbance of ionization equilibrium is relatively small and the total relative concentration of diatomic and polyatomic molecules is

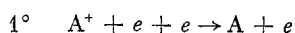
$$\alpha_m \approx 1. \quad (1)$$

The relative electron concentration is usually

$$\alpha \ll 1 \quad (2)$$

since the ionization potentials of the molecules of the bulk of the gas mixture are usually greater than their dissociation energy.

We will consider the kinetics of electron-ion recombination in a molecular gas when conditions (1) and (2) are fulfilled. In addition to the process



which is the main one [1] in the kinetics of recombination of a dispersing monatomic gas, when conditions

(1) and (2) are fulfilled we must take into account the reactions



(dissociative recombination).

The rate of dissociative recombination  $3^\circ$  is characterized at room temperatures [2-4] by a constant  $k_3 \sim 10^{-6}-10^{-7} \text{ cm}^3 \cdot \text{sec}^{-1}$  and decreases slightly with temperature [2], so that at temperatures of  $\sim 0.1 \text{ eV}$

$$k_3 \approx 10^{-8} T^{-1} \text{ cm}^3 \text{ sec}^{-1}. \quad (3)$$

We compare this value with the known [4-7] rate constants of the first two reactions

$$k_1 \approx 10^{-26} T^{-1/2} \text{ cm}^6 \cdot \text{sec}^{-1},$$

$$k_2 \approx 10^{-31} T^{-1/2} \text{ cm}^6 \cdot \text{sec}^{-1}, \quad (4)$$

if the third particle M is an atom (with atomic weight  $\sim 10-40$ ) and

$$k_2 \approx 10^{-30} T^{-1/2} \text{ cm}^6 \text{ sec}^{-1} \quad (5)$$

if M is a molecule, \* T is the temperature in eV. We find from (3), (4), and (5) that process  $3^\circ$  predominates over  $1^\circ$  if

$$\alpha \delta < 0.03 T^{1/2} \quad (6)$$

(here  $\delta$  is the density of the gas divided by its normal density) and over process  $2^\circ$ , if

$$\delta < 3 \cdot 10^2 T^{1/2}. \quad (7)$$

It follows from the Saha formula that in the case of ionization equilibrium condition (6) is fulfilled if

$$2 \cdot 10^{-3} \delta^{-1/2} I^{3/4} (T/I)^{1/4} \exp [I/2T] \gg 1. \quad (8)$$

Here I is the ionization potential (in eV) of the component making the main contribution to ionization of the gas.

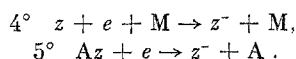
Putting  $I = 10$  in the factor in front of the exponent we have, instead of Eq. (8),

$$\sqrt{\delta} (I/T)^{3/4} \ll \exp (I/2T).$$

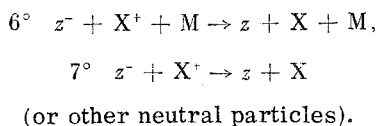
\*The specificity of the reaction  $2^\circ$  in a molecular gas is due to the rotational and vibrational transitions on collisions with electrons. At low temperatures (of the order of  $100^\circ \text{ K}$ )  $k_2 \sim T^{-1/2}$  [8].

Inequality (7) in the case of adiabatic expansion of diatomic or polyatomic gases is almost always fulfilled (an exception is the case of expansion from the initial state with temperature  $T < 0.1$  eV and  $\delta > 10^2$ , when the initial ionization is insignificant). Inequality (6) is not a restriction in such practical cases as the dispersion of products of chemical reactions (nozzle, explosion). For instance, if  $\delta < I$ , the fulfillment of Eq. (6) merely requires that  $16T \leq I$ . In the case of dispersion of a substance which initially had a density characteristic for a solid, inequality (6) is fulfilled in every case if  $23T \leq I$ . In view of what has been said we will assume in determining the time  $t = t_1$  of destruction of ionization equilibrium that reactions 1° and 2° are unimportant. Other reactions in addition to those ones considered may play an important role in recombination if negative ions can be formed in the system.

Negative ions  $z^-$  can be produced in the reactions



Possible ways of recombination of  $z^-$  with positive ions are



Processes of photorecombination of the type  $AB^+ + e \rightarrow AB$ , which are  $10^4$ – $10^5$  times slower than 3° [9], and photoattachment  $AB + e \rightarrow AB^-$  (this process can compete with 4° only at particle densities of  $\sim 10^{14}$   $\text{cm}^{-3}$  [4, 9]) will not be considered.

We will first consider recombination processes in a gas containing no negative ions (this includes the case where not all, but only the main, components of the gas mixture do not have positive electron affinity). The kinetics of ionization-recombination processes in this case is described by the equations of reactions 1°, 2°, and 3°

$$\left(\frac{d\alpha}{dt}\right)_1 = -k_1 N^2 \alpha^3 + f_1, \quad (9)$$

$$\left(\frac{d\alpha}{dt}\right)_2 = -k_2 N^2 \alpha \Sigma \alpha_+ + f_2, \quad (10)$$

$$\left(\frac{d\alpha}{dt}\right)_3 = -k_3 N \alpha \alpha_+ + f_3, \quad (11)$$

where  $N$  is the number of particles in  $1 \text{ cm}^3$ ,  $\Sigma \alpha_+$  and  $\alpha_+$  are the relative concentrations of positive ions of all particles and molecules, respectively, and  $f_1$  is the symbol for the rates of the corresponding reverse reactions.

The ionization potentials of molecules and atoms are usually comparable in value and, hence, if condition (1) holds,  $\Sigma \alpha_+ \approx \alpha_+$ . The fact that only molecular ions can combine by reaction 3° is not important in view of the rapid ion-atom charge-transfer reaction [3, 4, 9]:  $A^+ + XY \rightarrow A + XY^+$ , which has a rate constant of the order of  $10^{-3} k_3$ , but is much more rapid since  $\alpha_m \gg$

$\gg \alpha$ . The activation energies for such a reaction are usually small.

In view of what has been said we will take  $\Sigma \alpha_+ = \alpha_+$  (this is also justified by the fact that  $k_2$  and  $k_3$  in the best case are known to within a factor of 2–3). Equating, as in [10, 11] the rate of change of the equilibrium electron concentration in an adiabatically expanding gas  $d\alpha^*/dt$  and  $(-k_3 N \alpha \alpha_+)$  (here and henceforth  $\alpha^*$  denotes the equilibrium value of  $\alpha$ ), we find for the time  $t_1$  of significant disturbance of ionization equilibrium that

$$-\frac{I}{2T^2} \frac{dT}{dt} = k_3 N \alpha^* \quad (12)$$

where  $I$  is the ionization potential of particles making the main contribution to the value of  $\alpha^*$ . If the rate of expansion of the gas is constant and the initial dimensions of the cloud or of the critical section of the nozzle can be neglected, then

$$-\frac{d \ln T}{d \ln t} = s(\gamma - 1), \quad \frac{I}{2T} \frac{s(\gamma - 1)}{t_1} = k_3 \alpha^*(t_1). \quad (13)$$

Here  $s$  is a number equal to three for unsteady spherical dispersion and two for unsteady cylindrical or steady spherical (nozzle) dispersion, and  $\gamma$  is the effective adiabatic exponent.

Equation (12) or (13), together with the Saha equation and the relationship  $T(t)$  for adiabatic flow, gives the time  $t_1$  of disturbance of ionization equilibrium. When  $t > t_1$  the electron concentration is given by the equation

$$\frac{d\alpha}{dt} = -[k_1 \alpha N + k_2 N + k_3] \alpha^2 N \quad (14)$$

with initial data  $\alpha(t_1) = \alpha^*(t_1)$ .

We calculate  $\alpha$  for  $t > t_1$  after noting the following. Diatomic and polyatomic gases at temperatures  $\sim 0.1$  eV are characterized by an adiabatic exponent  $\gamma \leq 1.3$  and cool much more slowly on adiabatic expansion than a monatomic gas. The relative smallness of  $\gamma$  is due to the rotational and vibrational motions of the molecules and, hence, as distinct from the case of a monatomic gas,  $\gamma$  can be assigned irrespective of the kinetics of electron recombination. It is known [1] that process 1° plays a decisive role in the kinetics of recombination of an expanding monatomic gas and leads to zero residual ionization if  $\gamma > 37/27$  for  $s = 3$  and  $\gamma > 4/3$  for  $s = 2$ . Such values of  $\gamma$  in diatomic and polyatomic gases can be attained only at late stages of dispersion, when the gas temperature becomes less than 0.1 eV. Such cooling, however, is accompanied by "freezing" of the vibrational energy. Owing to the relatively rapid transfer of vibrational energy to free electrons the cooling of the electron gas is retarded.

Thus, cooling of electrons in a molecular gas is fairly slow at all stages of dispersion and, as distinct from the case of a monatomic gas, reaction 1° does not lead to complete recombination of the electrons.

For this reason in the process of expansion of a molecular gas the ratio  $(\alpha k_1 + k_2)N/k_3$  is either almost constant, or decreases, which means that when the

initial inequalities (6) and (7) hold at time  $t_1$  we can ignore reactions 1° and 2° at  $t > t_1$  too. Hence, instead of (14) we have

$$\frac{d\alpha}{dt} = -k_3\alpha^2N, \quad (15)$$

$$\alpha = \alpha^*(t_1) \left[ 1 + \alpha^*(t_1) \int_{t_1}^t k_3 N dt \right]^{-1}$$

We find the residual ionization  $\alpha_\infty$  in the case of spherical and cylindrical dispersion. Substituting in (15) for a dispersing [10] gas\*

$$N = N_0 (t_0 / t)^s \quad (16)$$

and taking the slowly varying quantity  $k_3$  outside the integral sign at the lower limit, we find, using Eq. (13), that

$$\alpha_\infty = \alpha^*(t_1) \left[ 1 + \frac{Is(\gamma-1)}{2(s-1)T(t_1)} \right]^{-1} \quad (17)$$

We turn now to the case where the gas may contain negative ions. The vast majority of the atoms and molecules existing in nature have positive electron affinity and, hence, the considered case is very general. In gas mixtures the total relative concentrations of neutral particles  $\alpha_Z$  which form negative ions are usually close to unity. In accordance with this we consider a gas model in which  $\alpha_Z = 1$ . In addition, we assume for simplicity that all the neutral particles have a common electron affinity  $\epsilon$ .

The kinetics of recombination is described by equation (11) and the equations of reactions 4°–7°. Reaction 5° is usually highly endothermic\*\* and, hence, proceeds at a low rate. In an adiabatically expanding gas the direction of reaction 5° may be reversed, depending on the kinetics of recombination of atoms or radicals of A. If the reverse reaction to 5°, with a rate constant of the order  $10^{-10}$  cm<sup>3</sup>/sec [3, 4, 9], is to be largely neutralized by reaction 4°, then  $\alpha_A \alpha_- \gg \alpha\delta$ , where  $\alpha_A$  and  $\alpha_-$  are the relative concentrations of

particles of A and negative ions. This is a fairly rigid condition, since it follows from the Saha formula that  $\alpha_- \ll \alpha\delta$  at very low temperatures  $T < \frac{1}{3} \epsilon$ , at which the concentrations of atoms or radicals of A capable of reaction 5°, if any are present in the system, are usually much less than unity. For this reason process 5° will be neglected from now on.

We present, like Eq. (9)–(11), the equations of the kinetics of reactions 4°, 6°, and 7° in the form

$$\left( \frac{d\alpha}{dt} \right)_4 = -k_4\alpha N^2 + f_4, \quad \left( \frac{d\alpha_-}{dt} \right)_6 = -k_6\alpha_+ \alpha_- N^2 + f_6,$$

$$\left( \frac{d\alpha_+}{dt} \right)_7 = -k_7\alpha_+ \alpha_- N + f_7.$$

The constant  $k_6$  and the typical (in order of magnitude) values of the constants  $k_4$  and  $k_7$  are

$$k_6 \approx 3 \cdot 10^{-28} (T)^{-3/2} \text{ cm}^6 \cdot \text{sec}^{-1},$$

$$k_4 \approx 5 \cdot 10^{-31} (T)^{-1/2} \text{ cm}^6 \cdot \text{sec}^{-1},$$

$$k_7 \approx 2 \cdot 10^{-8} (T)^{-1/2} \text{ cm}^6 \cdot \text{sec}^{-1}. \quad (18)$$

The second formula of Eq. (18) at temperatures  $\sim 0.1$  eV satisfactorily reproduce the data of [13] for O<sub>2</sub>. The rate of process 4° in the case of O<sub>2</sub> depends on the effectiveness of stabilization [4] of the excited state of the negative ion O<sub>2</sub><sup>-</sup>. In a complex mixture of gases the rate of reaction 4° will presumably be comparable with that of reactions (18). We note that the application of the principle of detailed balance to the data of [4] for the reverse reaction 4° in the case of collision of negative oxygen ions and atoms of inert gases when the colliding particles have energies of  $\sim 10$  eV, or more, leads to the relationship  $k_4 \approx \approx 10^{-31}/T$ . Approximately the same relationship is obtained for the corresponding reactions with the negative hydrogen ion [4].

At normal temperature  $k_7 \approx 10^{-7}$  cm<sup>3</sup>·sec<sup>-1</sup> [9]. An analysis of calculations [14] shows that  $k_7$  decreases with increase in temperature approximately as  $T^{-1/2}$ . This leads to expression (18) for  $k_7$ .\*

When negative ions are present ionization equilibrium in the considered gas model is characterized not by one, but by two, relationships between  $\alpha_+$ ,  $\alpha_-$ , and  $\alpha$ , depending on the temperature and gas density, e.g., by two Saha equations

$$\alpha_+ \alpha = \varphi(T, \delta), \quad (19)$$

$$\alpha_- = \alpha \chi(T, \delta). \quad (20)$$

Ionization equilibrium during the dispersion of the gas will be upset at time  $t_1$  when at least one of these relationships fails to hold. To find out which of them fails first, we compare the expressions for the time  $t_1$  in the two cases. We write the Saha formulas and the condition of quasi-neutrality of the plasma in the form

\*The data of [15] cannot be regarded as very reliable, but the orders of magnitude are probably correct [9].

\*The parameter  $t_0$  is equal to the initial radius  $r_0$  of the cloud divided by the velocity of inertial dispersion  $u$ . If the flared part of the nozzle is conical  $r_0$  is equivalent to the radius of the critical section multiplied by the cotangent of half the apical angle of the cone.

\*\*An exception is the case where the gas contains molecules with a dissociation potential  $D$  less than their electron affinity  $\epsilon$  or the difference between  $D$  and  $\epsilon$  is insignificant. Halogens are among the relatively simple molecules which have this property. In this case  $k_4$  in all the following formulas must be replaced by  $k_4 N + \alpha_h k_5$ , where  $\alpha_h$  is the relative concentration of halogens and  $k_5 \approx 10^{-9}$  m<sup>3</sup>·sec<sup>-1</sup>. This value of  $k_5$  is derived from the relationship between the cross section of the process  $I_2 + e \rightarrow I^- + I$  and the electron energy [12].

$$(\alpha_+^*)^2 = 240 \alpha_0 T^{3/2} \frac{g_+}{g_0 \delta} \exp \frac{-I}{T} (1 + \kappa), \quad (21)$$

$$\alpha_-^* = \frac{\kappa \alpha_+^*}{1 + \kappa}, \quad \alpha^* = \frac{\alpha_+^*}{1 + \kappa}, \quad (22)$$

where, as in Eq. (20)

$$\kappa = \frac{\alpha_-^*}{\alpha^*} = \frac{\delta g_-}{240 g_0 T^{3/2}} \exp \frac{\epsilon}{T}. \quad (23)$$

Here  $\alpha_0$  is the concentration of the components undergoing ionization, and  $g_0$ ,  $g_+$ , and  $g_-$  are the electronic statistical sums of neutral particles, positive ions, and negative ions.

The main temperature dependence of  $(\alpha_+^*)^2$  is given by the factor  $\exp(-I/T)$  and, hence, the time  $t_1$  of significant failure of equality (19) without failure of Eq. (20) is given, like Eqs. (12) and (13), by the relationships

$$\begin{aligned} & [k_3 + \kappa(k_6 N + k_7)] N \alpha^* = \\ & = - \frac{d\alpha_+^*}{\alpha_+^* dt} = - \frac{I}{2T^2} \frac{dT}{dt} = \frac{I}{2T} \frac{s(\gamma-1)}{t_1}. \end{aligned} \quad (24)$$

If equality (20) fails without alteration of the equilibrium between  $\alpha$  and  $\alpha_+$ , then, using Eqs. (21), (22), and (23)

$$\begin{aligned} & [k_4^- + (k_6 N + k_7) \alpha_+^*] N = \\ & = - \frac{d\alpha_-^*}{\alpha_-^* dt} = \frac{2\epsilon - I}{2T^2} \frac{dT}{dt} = \frac{I - 2\epsilon}{T} \frac{s(\gamma-1)}{t_1}. \end{aligned} \quad (25)$$

The rate constant  $k_4^-$  of the reverse reaction 4° is connected with  $k_4$  by the relationship

$$k_4^- = k_4 \delta / \kappa. \quad (26)$$

Substituting Eq. (26) into Eq. (25) and expressing  $\alpha$  in terms of  $\alpha_+$  in Eq. (24) by means of relationship (22) we find that the failure of equality (19) occurs before that of equality (20), if

$$L \equiv \frac{[k_4 N + \kappa(k_6 N + k_7) \alpha_+^*] (1 + \kappa) I}{[k_3 + \kappa(k_6 N + k_7)] \alpha_+^* \kappa (I - 2\epsilon)} > 1. \quad (27)$$

It can easily be shown that in view of the equality of the orders of magnitude of  $k_3$  and  $k_7$  [see (3) and (18)]

$$L \cong 1 \quad (28)$$

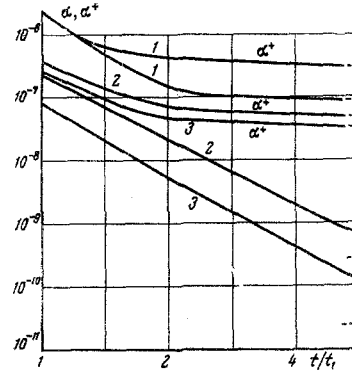
irrespective of the values of  $\kappa$ ,  $\delta$ , and all  $k_i$ . So, when  $k_3 = k_7$

$$L = \left\{ \frac{k_4 N (1 + \kappa) + k_6 N \kappa \alpha_+^*}{[k_3 + \kappa(k_6 N + k_7)] \alpha_+^* \kappa} + 1 \right\} \frac{I}{I - 2\epsilon} > 1.$$

According to Eq. (28), ionization equilibrium (19) is disturbed either earlier than, or almost at the same time as, the disturbance of the "equilibrium" ratio of electrons and negative ions in Eq. (20). Thus, the time  $t_1$  is given by relationship Eq. (24).

Beginning at time  $t_1$ , the rate of reduction of  $\alpha$  (exponential up to this time) becomes much less than that of  $\alpha^*$  [compare Eqs. (14) and (22)]. The direction of reaction 4° is altered and the formation of negative ions can be (depending on the initial data, see below) an ef-

fective trap for free electrons. All the remaining processes at  $t > t_1$  have little effect. Let  $t_2 \geq t_1$ . We note also that condition (20) in any case is fulfilled accurately



at the moment when reaction 4° is reversed. When  $t < t_2$ , according to Eq. (20) and the condition of quasi-neutrality of the plasma,

$$\alpha = \frac{\alpha_+}{1 + \kappa}, \quad \alpha_- = \kappa \alpha. \quad (29)$$

The concentration  $\alpha_+$  satisfies the equation

$$\begin{aligned} \frac{d\alpha_+}{dt} & = \frac{-N [k_3 + \kappa(k_6 N + k_7)] \alpha_+^2}{1 + \kappa} \\ & \equiv P(t) \alpha_+^2 \quad \text{for } t < t_2 \end{aligned} \quad (30)$$

and, hence,

$$\alpha_+ = \alpha_+^*(t_1) \left[ 1 + \alpha_+^*(t_1) \int_{t_1}^t P(t) dt \right]^{-1}.$$

At the time  $t_2$  of failure of quasi-equilibrium of reaction 4° [or, what is the same thing, of relationship (20)] and when  $t > t_2$

$$\frac{d \ln \alpha}{dt} = -k_3 \alpha_+ N - k_4 N^2. \quad (31)$$

On the other hand, when  $t_1 < t \leq t_2$ , using (29) and (30) we obtain

$$\frac{d \ln \alpha}{dt} = P(t) \alpha_+ - \frac{d \ln (1 + \kappa)}{dt}. \quad (32)$$

Equating (31) and (32), we find for the time  $t_2$

$$k_3 \alpha_+ N + k_4 N^2 = \frac{d \ln (1 + \kappa)}{dt} - P(t) \alpha_+. \quad (33)$$

This equation, together with Eqs. (23), (29), (13), and (16), gives  $t_2$ , the temperature, density, and charged-particle concentration at  $t = t_2$ . Integrating Eq. (31), using Eq. (16), and taking the weakly varying factor out from under the integral sign at the lower limit (including the factor  $\alpha_+$ ), we find

$$\begin{aligned} \alpha & = \alpha(t_2) \exp \left\{ \frac{k_4 N^2 (t_2) t_2}{2s-1} \left[ \left( \frac{t_2}{t} \right)^{2s-1} - 1 \right] \right\} + \\ & + \frac{k_3 \alpha_+(t_2) N (t_2) t_2}{s+1} \left[ \left( \frac{t_2}{t_1} \right)^{s-1} - 1 \right], \end{aligned} \quad (34)$$

Set	$t_1$ , sec	$\delta(t_1)$	$1/T(t_1)$	$\kappa(t_1)$	$t_2$ , sec	$\delta(t_2)$	$1/T(t_2)$	$\kappa(t_2)$
1	$25 \cdot 10^{-4}$	$16 \cdot 10^{-4}$	36.4	0.04	$29 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	38.9	0.06
2	$35 \cdot 10^{-4}$	$8 \cdot 10^{-3}$	41.2	0.54	$14 \cdot 10^{-3}$	$69 \cdot 10^{-5}$	68	27
3	$52 \cdot 10^{-5}$	$37 \cdot 10^{-3}$	38.6	1.9	$26 \cdot 10^{-4}$	$15 \cdot 10^{-4}$	73.5	203

$$\alpha_{\infty} = \alpha(t_2) \exp \left[ -\frac{k_4 N^2(t_2) t_2}{2s-1} - \frac{k_3 N(t_2) t_2}{s-1} \right]. \quad (35)$$

The concentration  $\alpha_+$  at  $t > t_2$  can be found by numerical integration of Eq. (30), where  $\kappa$  must be replaced by  $\alpha_+/\alpha - 1$ , and  $\alpha$  is replaced by the explicit expression (34). Equations (33), (34), and (35) and the equation for  $\alpha_+$  are greatly simplified if  $\kappa(t_2) \gg 1$  and

$$k_4 N(t_2) \gg (k_6 N + k_7 - k_3) \alpha_+(t_2).$$

In this case, instead of Eqs. (33), (34), and (35), referring to Eq. (23), we have

$$\begin{aligned} k_4 N^2(t_2) &= -\frac{\varepsilon}{T^2} \frac{dT}{dt} = \frac{\varepsilon}{T(t_2)} \frac{s(\gamma-1)}{t_2}, \\ \alpha &= \alpha(t_2) \times \\ &\times \exp \left\{ \frac{s(\gamma-1)}{(2s-1)} \frac{\varepsilon}{T(t_2)} \left[ \left( \frac{t_2}{t} \right)^{2s-1} - 1 \right] \right\}, \\ \alpha_{\infty} &= \alpha(t_2) \exp \left[ -\frac{s(\gamma-1)\varepsilon}{(2s-1)T(t_2)} \right], \\ \frac{d\alpha_+}{dt} &= -N(k_6 N + k_7) \alpha_+^2 \equiv Q(t) \alpha_+^2, \\ \alpha_+ &\approx \alpha_+ = \alpha_+(t_2) \left[ 1 + \alpha_+(t_2) \int_{t_2}^t Q(t) dt \right]^{-1}. \end{aligned}$$

We note also that when  $t \geq t_1$ , usually  $k_6 N \ll k_3$  [for this  $\delta$  must be  $\ll 3 \cdot 10^2 (T)^{5/2}$ ]. If this condition is satisfied and in view of the approximate relationships (3) and (18) we take  $k_3 = k_7$ , then Eq. (30) is independent of  $\kappa$  and its integration gives

$$\alpha_+ = \alpha_+^*(t_1) \left[ 1 + \frac{\alpha_+^*(t_1) N_1(t_1) k_3 t_1}{s-1} \left( 1 - \frac{t_1^{s-1}}{t^{s-1}} \right) \right]^{-1},$$

or, in view of Eqs. (24) and (29)

$$\alpha_+ = \alpha_+^*(t_1) \left[ 1 + \frac{I_s(\gamma-1)}{2T_1(s-1)} \left( 1 - \frac{t_1^{s-1}}{t^{s-1}} \right) \right]^{-1} \quad (t > t_1).$$

The figure shows the values of  $\alpha(t/t_1)$  and  $\alpha_+(t/t_1)$  for three sets of initial data for  $s = 2$ . The gas is characterized by the values  $\gamma = 1.2$  and  $\varepsilon/I = 0.2$ . The first set corresponds to the initial data:  $I/T_0 = 10$ ,  $\delta_0 = 1$ ,  $t_0 = r_0/u = 10^{-4}$  sec; the second set to;  $I/T_0 = 10$ ,  $\delta_0 = 10$ ,  $t_0 = 10^{-4}$  sec; and the third set to;  $I/T_0 = 20$ ,  $\delta_0 = 1$ ,  $t_0 = 10^{-4}$  sec.

The values of  $t_1$ ,  $t_2$ ,  $\delta$ ,  $1/T$  and  $\kappa$  at  $t = t_1$  and  $t = t_2$  are given in the table.

We recall that the density and temperature at  $s = 2$  and  $\gamma = 1.2$  are connected with  $t$  in the following way:

$$\delta = \delta(t_1) \left( \frac{t_1}{t} \right)^2, \quad T = T(t_1) \left( \frac{t_1}{t} \right)^{0.4}.$$

The values of the ratio  $t = t_2/t_1$  are indicated on the  $\kappa$  axis of the figure.

The figure shows that the formation of negative ions leads to a considerable reduction of  $\alpha$  when  $t_1 < t < t_2$ . After  $t_2$  the reduction of  $\alpha$  is relatively slight. A great difference between  $\alpha$  and  $\alpha_+$  is observed in the second and third sets, where the values of  $\kappa(t_2)$  are large.

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