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Abstract

Full Text

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On the Kinetics of Ionization Behind a Normal Shock Wave in Air

(Presented by Academician V. N. Kondrat' ev, 19 II 1962)

In the present note the results are set forth of a theoretical investigation of the kinetics of electronic processes behind a normal shock wave in air at temperatures from several thousand to approximately ten thousand degrees. Chemical and ionization phenomena in this temperature range, which is of great practical interest, are characterized by comparative simplicity, since the electron concentration under these conditions is small, so that it can be calculated on the assumption that the electronic processes do not affect the kinetics of the chemical reactions. To this it should be added that, under the indicated assumptions, the chemical processes behind the shock wave themselves admit a general investigation (1), based on the use of Ya. B. Zel' dovich' s scheme for nitrogen oxidation:

$$\mathrm{O_2 + M \underset{k'1}{\overset{k_1}{\rightleftarrows}} O + O + M}, \qquad \mathrm{O + N_2 \underset{k'4}{\overset{k_4}{\rightleftarrows}} NO + N}, \qquad \mathrm{N + O_2 \underset{k'5}{\overset{k_5}{\rightleftarrows}} NO + O}.$$

As is known, under the conditions considered the main part of the equilibrium electron concentration in the zone sufficiently far from the shock front, where chemical equilibrium has been established (hereafter denoted as the zone of chemical equilibrium—c.e.), is associated with thermal ionization of NO molecules as a result of the process

$$\mathrm{NO + M \underset{\chi i'0}{\overset{\chi_0}{\rightleftarrows}} NO^+ + e + M}. \tag{0}$$

The recombination constant χ_0' can be determined in order of magnitude on the basis of Thomson' s theory (2), according to which $\chi_0' \approx 10^{-30}$ cm^6/sec at $T = 5000$°K.

The equilibrium constant $K_p^{(0)}$ of process (0), in the temperature range considered, which exceeds the vibrational temperatures of the molecules NO and NO$^+$, may be represented by the formula

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$$K_{\mathrm{p}}^{(0)} = 2(2\pi)^{3/2}\frac{J_{\mathrm{NO}}\omega_{\mathrm{NO}^+}}{J_{\mathrm{NO}^+}\omega_{\mathrm{NO}}}\frac{\hbar^3}{(m_e kT)^{3/2}}e^{-I_{\mathrm{NO}}/kT} = 2\cdot 10^{-20}\,\vartheta^{-3/2}e^{110/\vartheta},$$

where $J_{\mathrm{NO}}, J_{\mathrm{NO}^+}, \omega_{\mathrm{NO}}, \omega_{\mathrm{NO}^+}$ are the moments of inertia and vibrational frequencies of the molecules NO and NO$^+$, $I_{\mathrm{NO}} = 9.5$ eV is the ionization energy of NO, and $\vartheta = T/1000$.

Determining the rate constant χ_0 with the aid of the principle of detailed balance from the formula $\chi_0 = \chi_0'/K_{\mathrm{p}}^{(0)}$, and the time of establishment of ionization equilibrium as a result of process (0) from the formula $\tau^{(0)} = (\chi_0\chi_0' n^3 a_{\mathrm{NO}})^{-1/2}$, where n is the total number of particles per 1 cm^3, a_{NO} is the concentration of NO molecules, it is easy to verify that $\tau^{(0)}$ considerably exceeds the time of establishment of chemical equilibrium $\tau_x \approx (k_1 n a_{\mathrm{O2}})^{-1}$ (1) (a_{O2} is the concentration of O_2 molecules). For example, at $T = 5000$°K, $n = 3\cdot 10^{17}$ cm^{-3} (i.e., at a pressure ahead of the wave front $p_1 = 1$ mm), $\tau^{(0)}/\tau_x \approx 10^5$.

Thus, we arrive at the conclusion that the process of thermal ionization of NO proceeds very slowly under the conditions considered. In other words, at the initial stage of the process of establishing chemical equilibrium, the concentration of electrons arising due to thermal ionization of NO molecules is extremely small in comparison with the equilibrium concentration of electrons attained in the c.e. zone. This conclusion, however, is in complete contradiction with the results of all available experiments ($^{3-5}$), according to which, behind a strong shock wave in air, very rapidly—over a time considerably shorter than the chemical relaxation time—high electron concentrations are reached, of the same order of magnitude as in the c.e. zone. Therefore one must assume the existence of an ionization process proceeding considerably faster than process (0).

One of the processes of this type, which is taken as the basis for the subsequent analysis, is reaction (^{2})

$$\mathrm{N} + \mathrm{O} \underset{\chi_1'}{\overset{\chi_1}{\rightleftarrows}} \mathrm{NO}^+ + e, \tag{1}$$

which proceeds with an expenditure of energy Δ, equal to the difference between I_{NO} and the dissociation energy of the NO molecule (6.5 eV), i.e. only 3 eV. The constant of dissociative recombination χ_1' may be taken equal to 10^{-6} cm^3/sec (as in works (^{5,6})) and constant, since it follows from theoretical considerations (^{7}) that it depends only very weakly on temperature.

The equilibrium constant $K_{\mathrm{p}}^{(1)}$ of process (1) can be calculated on the basis of the general theory (see (^{8})). If it is assumed that the particles N, O, NO$^+$ are in their ground electronic states (neglect of excited electronic states at the comparatively low temperatures considered will not introduce a substantial error), then $K_{\mathrm{p}}^{(1)}$ is given by the formula

$$K_{\mathrm{p}}^{(1)} = \frac{1}{2} g_0 g_N \left(\frac{m_0 m_N}{m_e m_{\mathrm{NO}}^{+}} \right)^{3/2} \frac{\Delta E_k \Delta E_{\mathrm{B}}}{(kT)^2} e^{\Delta/kT} = 0.25 \cdot 10^6\, \vartheta^{-2} e^{35/\vartheta}, \tag{2}$$

where $g_0 = 9$, $g_N = 4$, $\Delta E_k = \hbar \omega_{\mathrm{NO}^+}$, $\Delta E_{\mathrm{B}} = \hbar^2 / 2J_{\mathrm{NO}^+}$. The constant χ_1 can now be determined from the principle of detailed balance, i.e.

$$\chi_1 = \chi_1' / K_{\mathrm{p}}^{(1)} = 4 \cdot 10^{-12}\, \vartheta^2 e^{-35/\vartheta}.$$

The equation describing the change in the electron concentration α_e along a streamline can be written in the form

$$\frac{d\alpha_e}{dt} = \chi_1 n \alpha_0 \alpha_N - \chi_1' n \alpha_e^2 = \chi_1' n \left(\alpha_e^{(1)2} - \alpha_e^2 \right), \tag{3}$$

where

$$\alpha_e^{(1)} = \sqrt{\frac{\alpha_0 \alpha_N}{K_{\mathrm{p}}^{(1)}}} = 2 \cdot 10^{-3} \vartheta e^{-17.5/\vartheta} \sqrt{\alpha_0 \alpha_N} \tag{4}$$

is the equilibrium electron concentration corresponding to chemically nonequilibrium values $\alpha_0, \alpha_N, \vartheta$; $t = \int_0^s ds/v$ is the time measured along the streamline (coordinate s) from the wave front (v is the gas velocity behind the front). The relation of the quantities $\alpha_0, \alpha_N, \vartheta$ to the time t is given by formulas derived in (^{1}) on the basis of the assumption of a quasi-stationary character of the change in the concentration of N atoms, which agree with the results of numerical integration in (^{9}).

$$\frac{\alpha_N}{\alpha_0} = \frac{k_4 \alpha_{\mathrm{N2}}}{k_5 \alpha_{\mathrm{O2}} + k_4' \alpha_{\mathrm{NO}}}, \qquad t = \frac{1}{2 k_1 n \alpha_{\mathrm{O2}} b}, \tag{5}$$

where $k_1 = 10^{-8} e^{-59/\vartheta}$, $\vartheta = \vartheta_2 - 6.5 a_0$, $b = 380/\vartheta_2^2$, $\vartheta_2 = T_2/1000$, $\alpha_{\mathrm{O2}} = \alpha_{\mathrm{O2}}^0 - \frac{1}{2}\alpha_0$, $\alpha_{\mathrm{O2}}^0 = 0.21$. The temperature behind the jump (T_2) is related to the temperature ahead of the jump (T_1) by the relation $T_2/T_1 = 0.14 M^2$. Using formulas (4), (5), one can, in principle, determine the profile α_e by numerical integration of equation (3).

Fig. 1
Fig. 1

Fig. 2
Fig. 2

Since, however, the rate constants χ_0, χ_0' are very large, it should be expected that equilibrium (1) is established rapidly, i.e., during the main stage of the process there is an approach to chemical equilibrium $\alpha_e = \alpha_e^{(1)}$. To verify this, let us put $\alpha_e = \alpha_e^{(1)} + x$ and take $x \ll \alpha_e^{(1)}$. Then from equation (3) there follows the equation* for the correction x

$$\frac{d\alpha_e}{dt} \approx \frac{d\alpha_e^{(1)}}{dt} \approx -\chi_1' n \alpha_e^{(1)} x, \tag{6}$$

i.e.

$$\alpha_e \approx \alpha_e^{(1)} \left(1 - \tau^{(1)} \frac{d \ln \alpha_e^{(1)}}{dt}\right),$$

where $\tau^{(1)} = 1/2\chi_1' \alpha_e^{(1)} n$ is the time of approach to equilibrium for process (1). As is easy to see, the quantity $\tau^{(1)} d \ln \alpha_e^{(1)}/dt \sim \tau^{(1)}/\tau_x$ under the conditions considered is indeed small and lies within the range 0.1–0.01. Therefore, for calculating α_e one may use formula (4) in combination with formula (5).

An example of such a calculation at a pressure ahead of the front $p_1 = 1$ mm and $T = 5000$°K is given in Fig. 1. (In these and the subsequent calculations the constant $k_5 = 2 \cdot 10^{-10} e^{-3.1/\vartheta}$ was used with a pre-exponential factor one order of magnitude larger than that adopted in (1) and (9) (see (10))). There, for comparison, a plot is also given of the electron concentration $\alpha_e^{(0)} = \sqrt{\alpha_{\mathrm{NO}}/nK_p^{(0)}}$, calculated according to equilibrium (0). It is seen from Fig. 1 that $\alpha_e^{(1)}$, as a function of t, has a maximum reached in a time $t \sim 10^{-4}$ sec., several tens of times smaller than the time for establishment of chemical equilibrium (see (1), Fig. 1), and moreover the value of $\alpha_e^{(1)}$ at the maximum, in order of magnitude ($\alpha_e \sim 10^{-7}$), coincides with the electron concentration in the c.e. zone. These regularities (also observed for other values of the parameters p_1, T_2) are in complete qualitative and reasonable quantitative agreement with the results of the experiments described in (3-5).

It is natural to define the time during which the electron concentration appreciable in experiment is reached as the time τ, corresponding–

corresponding to its maximum, $\alpha_e^{(1)} = \alpha_{\max}^{(1)}$. According to (5),

$$\tau = \frac{1}{2k_1^{(m)} n^{(m)} \alpha_{\mathrm{O2}}^{(m)} b}, \tag{7}$$

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* In equation (6) the term dx/dt has been discarded; as is easy to show, it is of a higher order of smallness in comparison with $d\alpha_e^{(1)}/dt$ and $2\chi_1' n \alpha_e^{(1)} x$.

where the quantities $k_1^{(m)}$, $\alpha_{O2}^{(m)}$, $n^{(m)}$ correspond to the values of t, α_{O2}, ϑ for which $\alpha_e^{(1)} = \alpha_{\max}^{(1)}$.

Figure 2 gives the graph, found from formula (7), of the dependence of the quantity tp_1 ($p_1 = 1$ cm Hg, τ in microseconds) in semilogarithmic scale on the Mach number M, as well as the experimental points from work $^{(3)}$. Taking into account the roughness of both the theory and the experiment, the agreement should be considered satisfactory.

If in formula (5) the term $k_4'\alpha_{NO}$ is neglected in comparison with $k_5\alpha_{O2}$, then for τ and $\alpha_{\max}^{(1)}$ we obtain simple formulas which, like (7), are valid in order of magnitude:

$$\alpha_{\max}^{(1)} = 10^{-3}\vartheta_2 e^{-35/\vartheta_2 - \vartheta_2^2/230}, \tag{8}$$

$$\tau = \frac{2.6\, e^{59/\vartheta_2}}{n_2\,(0.21 - \vartheta_2^2/460)}\,\frac{\vartheta_2^2}{380}. \tag{9}$$

It is interesting to note that, according to (8), $\alpha_{\max}^{(1)}$ does not depend on p_1, but only on T_2. In contrast, the quantity $\alpha_e^{(0)}$, determined from equilibrium (0), always depends substantially on the pressure p_1.

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