Ionization behind Shock Waves in Nitrogen-Oxygen Mixtures

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It is shown theoretically and experimentally that the initial oxygen concentration has a strong influence on the ionization rate in nitrogen-oxygen mixtures. The theoretical results are obtained by solving the chemical rate equations together with the hydrodynamical conservation equations. Ion density profiles are measured in a shock tube using various electrostatic probes. The impurity level in the test gas due to outgassing of the shock tube walls is estimated to be less than 1 ppm.

I. Introduction

IN the present paper ionization rates in binary gas mixtures of nitrogen and oxygen are studied for shock Mach numbers between $M_s = 7$ and $M_s = 17$. Various recent papers on ionization rates in air[1,2] have shown that the predominant carrier of positive charges in the Mach number range considered here is the NO^+ ion which is obtained mainly from the reaction

$$N + O \leftrightharpoons NO^+ + e$$

The purpose of the present paper is to investigate the influence of the initial oxygen concentration on the ionization relaxation time and on the equilibrium values of the ion density, the temperature and the mass density. Theoretical ion density profiles for the Mach number range of $M_s = 7$ to $M_s = 20$ are compared with shock tube measurements for various nitrogen-oxygen mixtures.

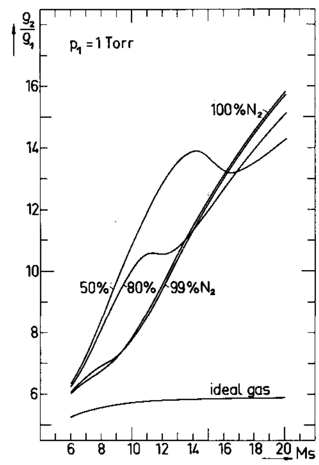

Fig. 2 Density ratio across normal shock wave as a function of shock Mach number for different N_2/O_2 mixtures.

II. Theory

Previous work on the ionization of air has shown that the dominant species are O_2, N_2, O, N, NO, O^+, N^+, O_2^+, N_2^+, NO^+, e.

Numerical results for the equilibrium data are shown in Figs. 1–4. From Fig. 1 it is seen that the effect of the oxygen concentration is to increase the deviation from the ideal gas behaviour. The curves for nitrogen-oxygen mixtures with 20 vol% O_2 coincide with the results of Lewis and Burgess[3] for air. In Figs. 3 and 4 the temperature and number density of the charged particles are shown as a function of the oxygen concentration for the shock Mach number $M_s = 10$ and the initial pressure $p_1 = 1$ torr. It is seen that a small amount of oxygen has a pronounced effect on the density of charged particles.

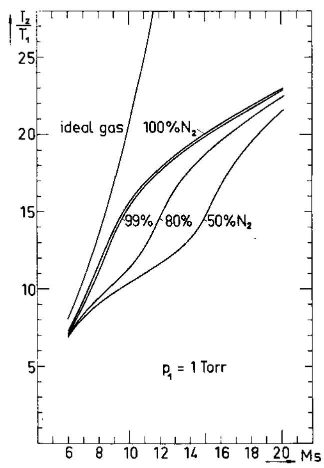

Fig. 1 Temperature ratio across normal shock waves as a function of shock Mach number for different N_2/O_2 mixtures.

In order to get an impression of the influence of the atomic ions O^+ and N^+ on the equilibrium data all calculations have been repeated with the reduced set of species O_2, N_2, O, N, NO, O_2^+, N_2^+, NO^+, e. The results deviate no more than 3% from the first calculations. Thus the following set of chemical reactions has been used for the evaluation of the ionization relaxation times:

$$O_2 + M + 5{,}1\ \text{ev} \leftrightharpoons 2O + M \quad (1)$$

$$N_2 + M + 9{,}8\ \text{ev} \leftrightharpoons 2N + M \quad (2)$$

$$NO + M + 6{,}5\ \text{ev} \leftrightharpoons O + N + M \quad (3)$$

$$N_2 + O + 3{,}3\ \text{ev} \leftrightharpoons NO + N \quad (4)$$

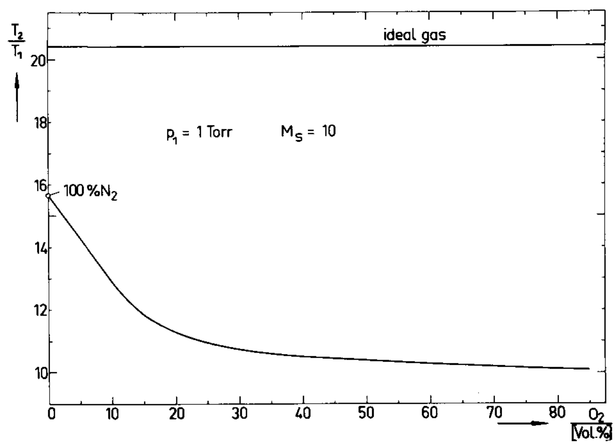

Fig. 3 Temperature ratio across normal shock wave as a function of initial oxygen concentration for shock Mach number $M_s = 10$ and initial pressure $p_1 = 1$ torr.

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Index categories: Thermochemistry and Chemical Kinetics; Shock Waves and Detonations.

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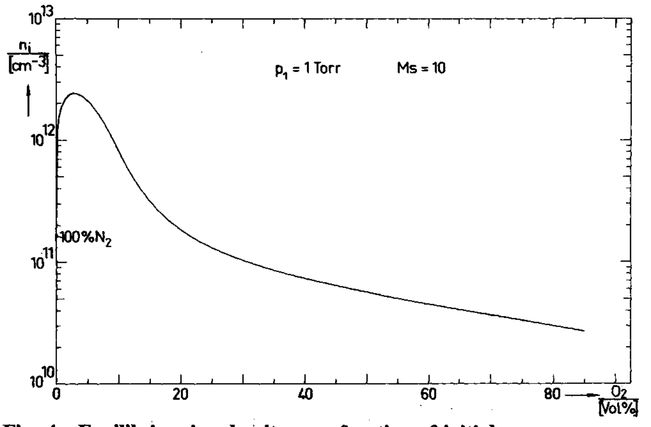

Fig. 4 Equilibrium ion density as a function of initial oxygen concentration for shock Mach number $M_s = 10$ and initial pressure $p_1 = 1$ torr.

$$NO + O + 1{,}4\,ev \leftrightarrows O_2 + N \quad (5)$$
$$O_2 + N_2 + 1{,}9\,ev \leftrightarrows 2NO \quad (6)$$
$$N + O + 2{,}8\,ev \leftrightarrows NO^+ + e \quad (7)$$
$$O + O + 6{,}9\,ev \leftrightarrows O_2^+ + e \quad (8)$$
$$N + N + 5{,}8\,ev \leftrightarrows N_2^+ + e \quad (9)$$

The ionization relaxation time τ is defined as usual by the relation

$$\tau = n_{io}/(dn_i/dt)_{max} \quad (10)$$

where $(dn_i/dt)_{max}$ is the maximum ion density gradient and n_{io} is the maximum value of the ion density. For ion profiles which show an overshoot the first maximum is chosen. For reaction (7)

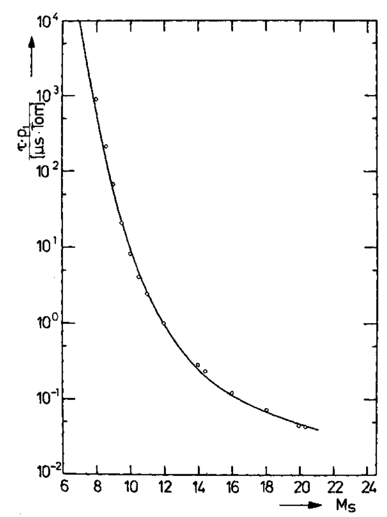

Fig. 5 Comparison of ionization relaxation time for air as a function of shock Mach number computed in the present paper (open circles) with Thompson's theoretical result[2,5] (solid line).

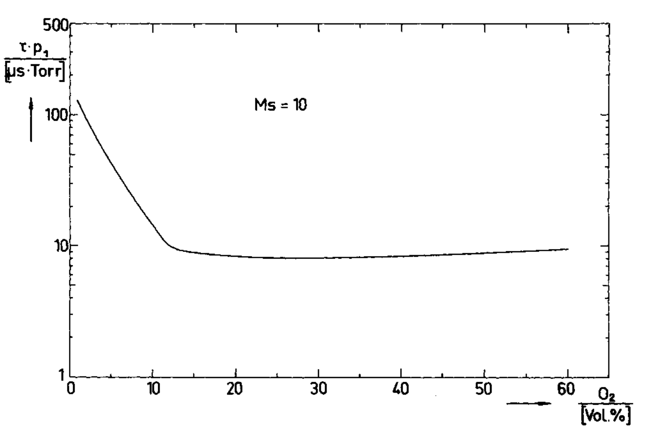

Fig. 6 Ionization relaxation time as a function of initial oxygen concentration for shock Mach number $M_s = 10$.

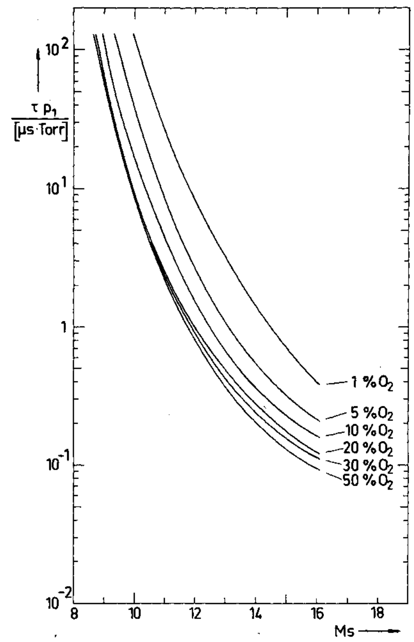

Fig. 7 Ionization relaxation time as a function of shock Mach number for different initial oxygen concentrations.

the following values for the rate constant and for the constant of the law of mass action have been used[4]:

$$\overleftarrow{k}_7 = 4.8 \cdot 10^{-8} \cdot (kT)^{-1/2} \cdot (1 - e^{-0.27/kT})\, cm^3/sec$$
$$K_7 = 1.4 \cdot 10^{-4} \cdot (kT) \cdot (1 - e^{-0.27/kT})^{-1} \cdot e^{-2.8/kT}$$

where kT is in electron volts. For the remaining reactions Lin and Teare's reaction constants[1] have been used. Numerical results for the relaxation time in air obtained from reactions (1–9) are shown in Fig. 5 together with the result of Thompson's[2] calculation. It has been shown in various recent papers that Thompson's curve is in good agreement with the experimental results.[5–7] In Figs. 6 and 7 the relaxation time is shown as a function of the oxygen concentration and of the shock Mach number, respectively. It can be seen that the relaxation time is changed by an order of magnitude when the oxygen concentration varies between 1 vol% and 10 vol%. This seems to be similar to the behavior of a gas with a small amount of rate increasing impurities.

III. Experiments

Measurements of the ionization relaxation time in various nitrogen-oxygen mixtures have been performed in a pressure driven stainless steel shock tube for oxygen concentrations between 1 vol% and 30 vol%. The low pressure section had a length of 10 m and an inner diameter of 90 mm. The entire shock tube including the thin film heat-transfer gages and ion probes, valves and connections could be baked at 400°C. After a baking period of 8 hr a vacuum of $2 \cdot 10^{-8}$ torr could be obtained with a pumping station which consisted mainly of a two-stage mechanical pump, two oil diffusion pumps in series, two baffles and a high vacuum zeolite molecular sieve. Gold rings have been used as sealing gaskets for the pumping station and for the shock tube. The main disadvantage of metal sealing gaskets, that they can be used only once, has been overcome in the present paper with the reusable metal-sealing-gasket of Ref. 8. Aluminium sheet of 1–3 mm thickness has been used for the diaphragms. The sea between diaphragm and shock tube was provided by circula knife edges at the ends of the low-pressure and the high-pressur section. Either hydrogen or helium were used as the driver gas It is estimated that in this shock tube the impurity level due to outgassing of the walls could be reduced to 0.2 ppm at an inita pressure of 1 torr. This precaution is found essential for obtain ing reproducable results in mixtures with low oxygen concen tration and low Mach number.

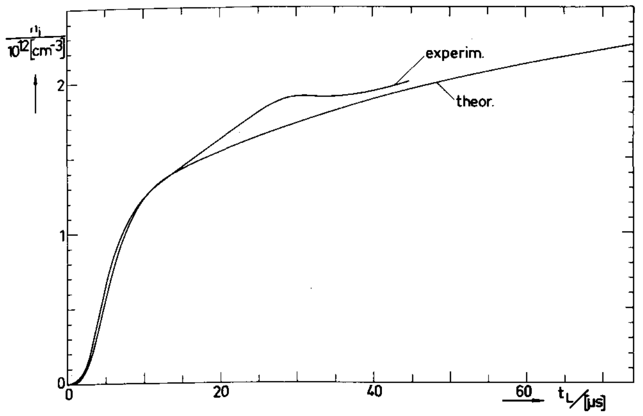

Fig. 8 Comparison of theoretical and experimental ion density profiles for shock Mach number $M_s = 10.7$, initial pressure $p_1 = 0.7$ torr and initial oxygen concentration of 5%. The ion density is plotted as a function of laboratory time t_L.

The nitrogen-oxygen mixtures were provided by Deutsche Edelgas GmbH. The impurity levels of nitrogen and oxygen were ...2 ppm H_2O, ...0.1 ppm H_2, ...5 ppm (Ar + He + Ne) and ...5 ppm H_2O, ...8 ppm Ar, ...2 ppm (Kr + Xe + C_nH_m), respectively. The pressure in the test section was measured on a bakable capacitance manometer which was calibrated periodically against a McLeod gage. The shock speed has been measured with three thin film heat-transfer gages. The amplified and differentiated signals were used to trigger two electronic counters. Measurements were taken at initial pressures between 0.05 torr and 40 torr. The variation of the ion density behind the shock wave was detected with a hollow total collector probe[5,9] and with Langmuir probes[10] of diameters between 0.05 mm and 0.2 mm. Ion densities have been evaluated using a relation between probe current i_s and ion density n_i which has been given by McLaren and Hobson[10]

$$i_s = K\tfrac{1}{4}n_i C_{th}\, e\, 2\pi r_s l_s$$

where $C_{th} = (8kT_+/\pi m_+)^{1/2}$ is the freestream thermal velocity of the ions, e the charge of a positive ion, r_s the probe radius and l_s the probe length. The quantity K is given approximately by the equation

$$K = 4M_2C_2/(1 + Re)^{0,5}$$

where M_2 is the flow Mach number, Re is the Reynolds number. The constant C_2 which depends on the gas properties is not known. This means that absolute measurements of ion densities are not possible. The values for C_2 giving the best agreement between theoretical and experimental ion density profiles are

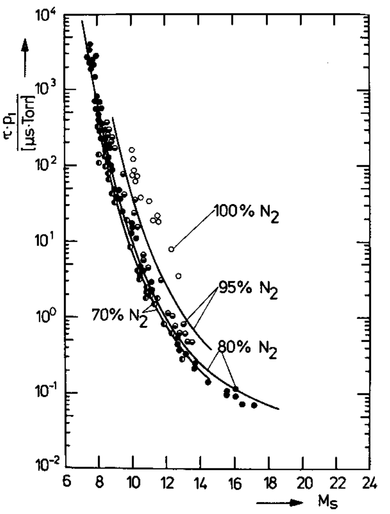

Fig. 9 Comparison of experimental and theoretical results for ionization relaxation time for initial oxygen concentrations of 30%, 20%, 5%, and pure nitrogen.

Table 1 Constant C_2 used for different oxygen nitrogen mixtures

C_2	N_2/O_2
2,5	99/1
3	95/5
50	80/20
60	70/30

listed in Table 1. In Fig. 8 a theoretical ion density profile is compared with a measured profile evaluated with $C_2 = 3$. The ion density profile and hence the relaxation time do not depend on C_2. In Fig. 9 experimental results are shown for the product $p_1 \cdot \tau$ as a function of the shock Mach number M_s with the initial oxygen concentration as a parameter.

Approximately 20% of the measurements, especially those at low Mach numbers, have been obtained with a hollow total collector probe.[5,9] In ten experiments density profiles have been obtained with the Langmuir probe and the hollow total collector probe at practically the same Mach number. The shape of the profile was the same within the experimental error. Absolute values for the equilibrium density which could be evaluated from the signal of the hollow total collector probe were usually by a factor of two lower than the theoretical values.

IV. Conclusions

In the present paper the ionization mechanism for oxygen-nitrogen mixtures is investigated theoretically using nine chemical reactions. The numerical solution of this problem shows that the relaxation time depends strongly on the initial oxygen concentration. Varying the oxygen concentration from 0% to 10% results in a change of the relaxation time of an order of magnitude. These theoretical results are confirmed by shock tube experiments.

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