Electron density and ionization rate in thermally ionized gases produced by medium strength shock waves

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A method, based on the measurement of attenuation of microwaves, which allows the electron density and the ionization rate of shock-heated gases to be obtained, is described. Results obtained for air in the shock Mach range 8·2–10·4, and for nitrogen containing 0·25 % oxygen in the range 7·4–8·8, show that the electron density is in agreement with theoretical calculations based on thermodynamic equilibrium. Ionization time measurements in air are presented in this range and these results extend the measurements of Niblett & Blackman (1958) to a lower Mach range.

Introduction

The electrical properties of thermally ionized gases, produced by shock waves, have been studied by a number of authors. Lin (1952) and Lin, Resler & Kantrowitz (1955) measured the electrical conductivity of argon in the shock Mach range 4–16 by hydromagnetic methods. Lamb & Lin (1957) obtained data on the electrical conductivity of air in the shock Mach range 11–17 with the same type of equipment. Petschek & Byron (1957) studied the ionization mechanism of argon behind shock waves in the shock Mach range 10–18 and gathered data on the ionization times involved. Recently, Niblett & Blackman (1958) measured the ionization rate in air for shock Mach numbers 11–17 by a photographic method.

This paper presents new data on the ionization rate and electron density in air between shock Mach numbers 8·2 and 10·4 and in nitrogen, containing 0·25 % oxygen, in the shock Mach range 7·4–8·8.

The method described here (see also Low & Manheimer, 1959) is based on the interaction of microwaves with the ionized gaseous medium. The attenuation coefficient of the microwaves is related to the electrical conductivity and the dielectric coefficient of the gas. Margenau (1946) showed that these quantities may be calculated if the electron density of the gas and the collision frequency of electrons with other particles are known. Assuming thermal equilibrium it is possible (Bethe 1942; Glass, Martin & Patterson 1953; Gilmore 1955) to calculate the chemical composition of the shocked gas, and its temperature and density as functions of shock Mach number for given initial conditions.

These data enable one to calculate the electron density as well as the collision frequency of electrons with those species whose collision cross-section is known. It is, therefore, possible to obtain a theoretical curve for the attenuation coefficient of microwaves of given frequency as a function of shock Mach number for specified initial conditions.

In this work the attenuation coefficient of microwaves of 3 cm wavelength and the shock velocity are measured experimentally and compared with the results of the theoretical calculations.

By observing the attenuation as a function of time as the shock-heated gas passes through the waveguide, one can estimate the rate of ionization and obtain information about the rate of approach to thermodynamic equilibrium and the mechanisms involved.

Theory

The attenuation coefficient, α, of microwaves of circular frequency ω ($\omega = 2\pi f$, where f is the frequency in cyc/sec) which pass through a gaseous medium, assumed to be in thermal equilibrium, is given by the following relation, due to Margenau (1946):

$$\alpha^2 = \frac{\omega^2 \epsilon}{2c^2}\left\{-1 \pm \left[1 + \left(\frac{4\pi\sigma_r}{\epsilon\omega}\right)^2\right]^{\frac{1}{2}}\right\}. \tag{1}$$

For $(4\pi\sigma_r/\epsilon\omega)^2 \ll 1$ this may be approximated by

$$\alpha = \frac{2\pi\sigma_r}{c}. \tag{1a}$$

Here ϵ is the dielectric constant of the gas ($\epsilon = \epsilon_0 - 4\pi\sigma_i/\omega$), σ_r and σ_i are the real and imaginary part of the complex conductivity, and c the velocity of light in vacuum. The positive sign should be taken for $\epsilon > 0$, and the negative one for $\epsilon < 0$, since α is always real. σ_r and σ_i are given by

$$\sigma_r = \frac{4}{3\sqrt{\pi}} \frac{e^2 N_e}{m\gamma} K_2\left(\frac{\omega^2}{\gamma^2}\right) \to \frac{8}{3\sqrt{\pi}} \frac{e^2 N_e \gamma}{m\omega^2} \quad \text{as} \quad \frac{\omega^2}{\gamma^2} \to \infty, \tag{2}$$

and

$$\sigma_i = \frac{4}{3\sqrt{\pi}} \frac{e^2 N_e \omega}{m\gamma^2} K_{\frac{3}{2}}\left(\frac{\omega^2}{\gamma^2}\right) \to \frac{e^2 N_e}{m\omega} \quad \text{as} \quad \frac{\omega^2}{\gamma^2} \to \infty, \tag{3}$$

where e denotes the electron charge, m its mass, N_e the density of free electrons, and γ their mean collision frequency in the ionized mixture. $K_2(x)$ and $K_{\frac{3}{2}}(x)$ are special functions defined by Margenau (1946).

The mean collision frequency γ can be defined by the gas kinetic formula

$$\gamma = v \sum_j n_j \bar{Q}_j. \tag{4}$$

n_j is the number of particles of species j per cm^3, $\bar{Q}_j$ is the average electron cross-section of particles of species j, and v is the mean velocity of the free electrons, which is related to their temperature T by (k being Boltzmann's constant):

$$\frac{mv^2}{2} = kT. \tag{5}$$

Since the temperatures reached in the experiments do not exceed 4000 °K it is justifiable to assume that the electron temperature is equal to the gas temperature. For the electron velocities obtained in this work (well below 1 eV) one should use the electron diffusion cross-section (this point is discussed at some length by Lamb & Lin 1957). The species which may contribute appreciably to the total electron collison probability $\sum_j n_j \bar{Q}j$ are, in our case: N_2, O_2, NO, N, O and A (this can be seen from figure 6 of Lamb & Lin (1957) for air and from calculations described in the Appendix for nitrogen). Data on the average electron diffusion cross-sections for all these species have been compiled by Lamb & Lin (1957). For the molecular species N_2, O_2, NO and A, their values are based on experimental data, reported by Massey & Burhop (1952). For atomic oxygen and nitrogen they used the theoretical calculations of Hammerling, Shine & Kivel (1957), which showed good agreement with their experimental results.

Since our experimental results indicate that thermodynamic equilibrium has essentially been reached in these experiments, the composition of the ionized gas (the various n_j, including the electron density N_e), its temperature and density at a given shock velocity and initial temperature and density, can be calculated from the Rankine–Hugoniot equations across the shock front, according to a method first developed by Bethe & Teller (1940) and Bethe (1942), and described in detail by Glass, Martin & Patterson (1953) and Gilmore (1955).

Techniques

The shock waves were produced in a small brass shock-tube of circular cross-section, built for this investigation (see figure 1). The internal diameter of the high-pressure section is 1 in. and that of the low-pressure section 0·5 in. This gives a higher shock strength for the same pressure ratio than a constant section shock tube (Glass *et al.* 1953).

Interchangeable sections were used so that the overall length of the tube could be varied between 80 and 130 cm. The shock velocity was measured by the ionization plug method (Birk, Erez, Manheimer & Nahmani 1954; Campbell, Malin, Boyd & Hull 1956). The metal tube incorporates a Teflon section, where the attenuation of the microwaves is measured. Teflon was chosen because of its favourable mechanical and electrical properties (good sealing properties and low losses at microwave frequencies).

Hydrogen was used as driver gas, which, owing to its low molecular weight, gives strong shock waves with reasonable pressure ratio (Glass *et al.* 1953). The gas was obtained from commercial cylinders, at a maximum pressure of 140 atm. The diaphragm, dividing the chamber from the channel, was made of several cellulose acetate sheets of 0·4 mm thickness (2–4 pieces according to desired shock strength). The channel was evacuated by a conventional vacuum system including a rotary oil pump, a 3-stage mercury diffusion pump, a cold trap filled with dry ice, and a shortened McLeod manometer. The vacuum obtained in the shock tube was better than 10μ Hg. After evacuating the system, the low-pressure section was filled with the gas under study and its flow regulated in order to obtain the

desired pressure. At a pressure of 10 mm Hg, which was used in the experiments with nitrogen, the impurity level due to leaks was 0·2 %. Experiments with air as test gas were conducted at lower pressure, between 1 and 3 mm Hg, since there were no purity limitations here while safety reasons favoured low air pressure when using hydrogen as driver gas.

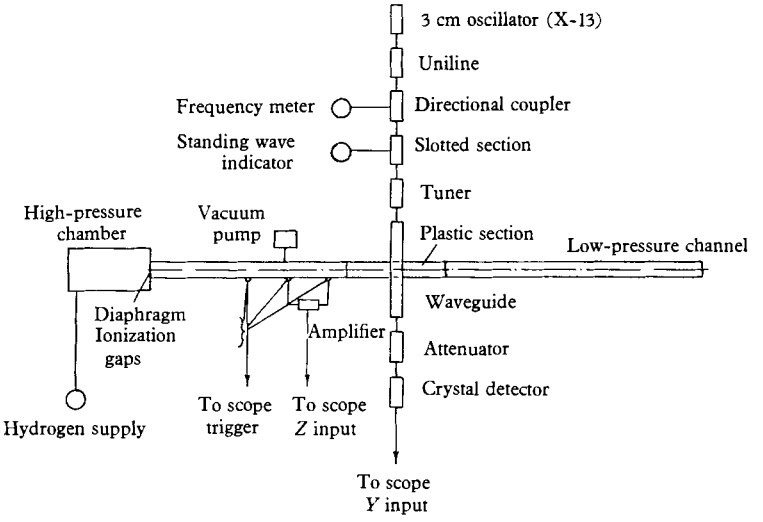

FIGURE 1. Block diagram of shock tube and microwave equipment.

The Mach numbers obtained experimentally were 20–25 % lower than those expected for an ideal shock tube. This is caused by imperfect rupture of the diaphragm, heat losses to the walls, and boundary layer effects. These perturbations are pronounced owing to the small bore of the tube (Lin 1952), for example, observed a difference of 12 % between ideal and actual Mach number even with a shock tube of internal diameter 1·5 in.). The velocity of the shock during its downward travel was measured between three stations immediately before the test section. No attenuation was detected within the accuracy of our shock velocity measurements ($\pm$ 1 %).

The microwave equipment used was in the 3 cm range (exploratory experiments in the 1 and 10 cm ranges showed that the method may be used successfully with these wavelengths too). A Varian X-13 oscillator was our power source; the line included conventional components for the measurement of standing wave ratio, as indicated in figure 1. The standing wave ratio was minimized (about 1·05) before each experiment. The microwave output was displayed on the Y input of a Du Mont 329 oscilloscope and photographed by a Du Mont Oscillorecord camera. The scope was triggered by a signal coming from an ionization plug through a video amplifier. Two further ionization plugs were connected, through a second channel of the same amplifier, to the Z input of the scope and darkened the trace at the passage of the shock front.

A typical oscillogram is shown in figure 2. M is here 9·8 (the speed of sound in air is 340 m/sec). We can distinguish (from left to right) the arrival of the shock front at the first plug (onset of the trace, point A), its passage over the second and

third plug (darkening of the trace, points B and C). As the shock front arrives at the waveguide we see a decrease in microwave power, the maximum attenuation (0·03 V), point D, being reached after about 9 μsec. The undisturbed output is 0·3 V. From the voltage ratio V_0/V_1 the attenuation coefficient, α, is calculated by the relation

$$\alpha\,(\text{db/cm}) = \frac{8{\cdot}7}{2l_{\text{eff}}} \ln \frac{V_0}{V_1}. \tag{6}$$

Here l_{eff} is the effective path of the microwaves through the attenuating medium. This quantity, which depends on the microwave field and the geometrical configuration, was determined experimentally to be 0·73 cm.

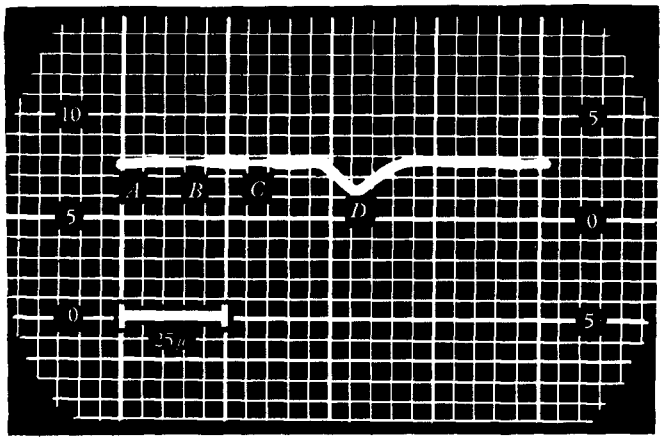

FIGURE 2. Oscillogram of microwave attenuation as a function of time. Shock wave in air, at pressure 1 mm Hg, M = 9·8. Time base 5 microseconds per scale division. Amplification 20 mV per scale division. The first spark plug triggers the trace. The passage of the shock wave over the second and third spark plugs are indicated by a darkened trace at B and C. The maximum attenuation at point D is about 0·03 V and is reached after 9 μsec.

Calibration experiment

The attenuation caused by a gas discharge in our microwave system was compared with results of Udelson, Creedon & French (1957). Instead of the shock tube, a discharge tube of the same diameter was passed through the waveguide and a d.c. discharge in hydrogen was produced using a power supply of variable voltage (0–5000 V), which enabled us to raise the discharge current to a maximum of 7·5 mA. The ratio of the microwave power without discharge and during discharge was measured by the current in the crystal detector and a sensitive galvanometer. The crystal was operated in the square law region and the attenuation constant, α', is therefore given by a relation analogous to (1):

$$\alpha\,(\text{db/cm}) = \frac{8{\cdot}7}{2l_{\text{nom}}} \ln \frac{i_0}{i_1}, \tag{7}$$

taking a nominal path l of 1 cm (i_0 is the current without discharge, i_1 the current during discharge). This was compared with the attentuation constant, α, calcu-

lated from Udelson's data and Margenau's theory; the ratio α/α' was found to be approximately constant ($1{\cdot}37 \pm 0{\cdot}09$) for different discharge currents and hydrogen pressures; the mean value of the effective path l_{eff} was therefore 0·73 cm.

Results

(*a*) *Experiments in air*

The experiments in air were performed with two different lengths of the channel in the shock tube (65 and 80 cm); the initial pressure of air in the channel being varied between 1 and 3 mm Hg in order to obtain different Mach numbers. Hydrogen from a commercial container at pressures between 80 and 120 atm. was the driver gas. The shock Mach numbers obtained ranged from 8·2 to 10·4. The frequency of the microwaves employed was 10,000 Mc/sec.

Mach number	Collision frequency (sec^{-1})	Electron density (cm^{-3})	Real part of electrical conductivity (c.g.s.)	Imaginary part of electrical conductivity (c.g.s.)	Dielectric coeff. (c.g.s.)	Attenuation coeff. (db/cm)
8	$5{\cdot}5 \times 10^{9}$	$1{\cdot}3 \times 10^{10}$	$6{\cdot}75 \times 10^{8}$	$5{\cdot}1 \times 10^{7}$	0·99	0·012
8·4	6·3	2·25	$1{\cdot}30 \times 10^{7}$	8·75	0·98	0·024
8·9	7·35	4·7	3·20	$1{\cdot}8 \times 10^{8}$	0·96	0·059
9·5	8·8	$1{\cdot}1 \times 10^{11}$	8·70	4·2	0·92	0·17
9·8	9·75	1·7	$1{\cdot}50 \times 10^{8}$	6·4	0·87	0·29
10·15	$1{\cdot}1 \times 10^{10}$	2·8	2·65	$1{\cdot}05 \times 10^{9}$	0·79	0·55
10·4	1·15	4·0	4·00	1·45	0·70	0·87
11	1·25	9·5	$1{\cdot}00 \times 10^{9}$	3·8	0·24	3·50

TABLE 1. Data on high-frequency (10,000 Mc/sec) electric properties of shock-heated air. Initial pressure: 1 mm Hg. Initial temperature: 293 °K.

The theoretical attenuation coefficient, α, for an initial pressure of 1 mm Hg and an initial temperature of 293 °K, was calculated for a shock Mach range 8–11 from equations (1), (2) and (3). The data required for the computations (electron density, composition, density and temperature of the shock-heated air and electron diffusion cross-sections) were all taken from Lamb & Lin (1957). The results are tabulated in Table 1, which includes the attenuation coefficient, α, in db/cm, the real and imaginary parts of the complex conductivity, σ_r and σ_i, and the dielectric coefficient, ϵ (all in c.g.s. units).

Table 2, in which the experimental results are presented, includes the measured Mach number, M; the ratio of the microwave output before passage of the shock wave, V_0, to the output at maximum attenuation, V_1; the attenuation coefficient, α, which is obtained from V_0/V_1 by means of equation (6); the initial air pressure, p_1, and the time, τ, between ionization onset and the moment when its maximum value is reached.

In addition, a normalized coefficient of attenuation, for an initial pressure of 1 mm Hg, has been calculated in order to make comparison possible with the data of Table 1. Normalization was achieved by dividing the experimental attenuation coefficient by the square of the initial pressure. For the low conductivity values

obtained in these experiments one may use equation (1*a*) and the asymptotic form of equation (2), getting for α the relation:

$$\alpha = \frac{16\sqrt{\pi}}{3}\frac{e^2 N_e \gamma}{m\omega^2}. \tag{8}$$

Use of this approximation, instead of the exact equations (1), (2) and (3), introduces for $M = 10{\cdot}4$, the maximum experimental value, an error less than 0·5 %. Equation (8) shows that α is proportional to the product $N_e\gamma$ and both these quantities increase linearly with the initial pressure p_1.

Mach number	Output ratio	Initial pressure (mm Hg)	Attenuation coefficient (db/cm)	Ionization time (μsec)	Normalized atten. coeff. (db/cm)
8·2	1·025	2·9	0·15	10	0·018
8·45	1·03	2·5	0·175	11	0·028
8·5	1·065	3	0·38	9	0·042
8·9	1·045	2	0·26	9	0·065
9·1	1·035	1·5	0·205	8	0·091
9·2	1·075	1·8	0·45	9	0·14
9·3	1·04	1·4	0·25	12	0·13
9·5	1·065	1·4	0·38	9	0·19
9·5	1·05	1·2	0·29	10	0·20
9·5	1·05	1·2	0·29	10	0·20
9·5	1·11	1·6	0·62	8	0·24
9·8	1·085	1·2	0·48	8	0·34
9·8	1·06	1·0	0·35	8	0·35
9·8	1·075	1·1	0·45	7	0·35
9·8	1·095	1·2	0·54	8	0·37
9·8	1·10	1·2	0·565	9	0·39
9·8	1·12	1·3	0·67	8	0·40
9·8	1·11	1·2	0·62	10	0·43
10·0	1·11	1·1	0·62	10	0·51
10·4	1·175	1·0	0·96	10	0·96

TABLE 2. Results of experiments in air.

A comparison between the calculated attenuation coefficient and the experimental results is given in figure 3. The agreement is seen to be good; the slight tendency to higher values shown by the experiments may be explained by assuming that the effective path l_{eff} is somewhat longer than the one used. No difference was observed between results obtained with different lengths of the channel in the shock tube. This is to be expected, since the duration of the uniform flow is longer than the ionization time in all experiments (the shortest duration of uniform flow was 14μsec, while the largest ionization time measured reached only 12μsec). This fact shows that thermodynamic equilibrium has indeed been reached in the heated air. (Experiments performed in argon, where the ionization time is known to be longer than the duration of uniform flow in our tube (Petschek & Byron 1957), showed indeed larger attenuation for a longer shock tube.)

The time elapsed between ionization onset and the attainment of its maximum value (where thermodynamic equilibrium is reached) varies between 7 and 12 μsec.* The product of this ionization time, τ, by the initial pressure, p_1, is plotted as function of Mach number, M, in figure 4, where the results of Niblett &

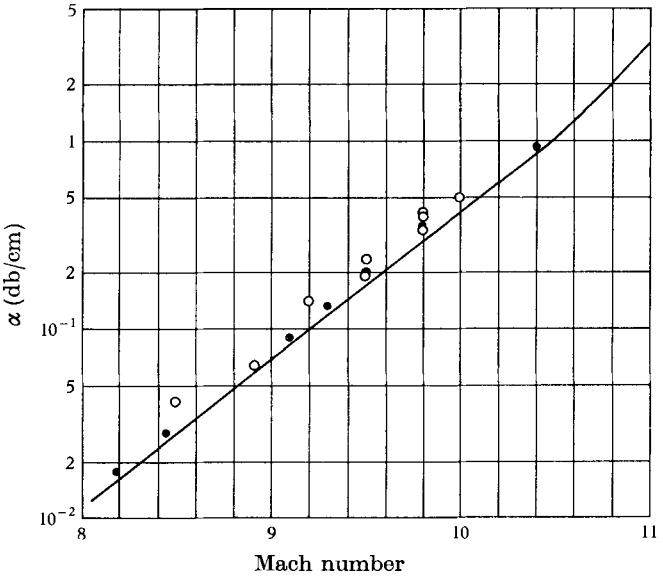

FIGURE 3. Attenuation coefficient for air in db/cm *vs* Mach number. Initial pressure 1 mm Hg, initial temperature 293 °K. The theoretical curve is shown as the heavy line. ○, Short shock tube; ●, long shock tube.

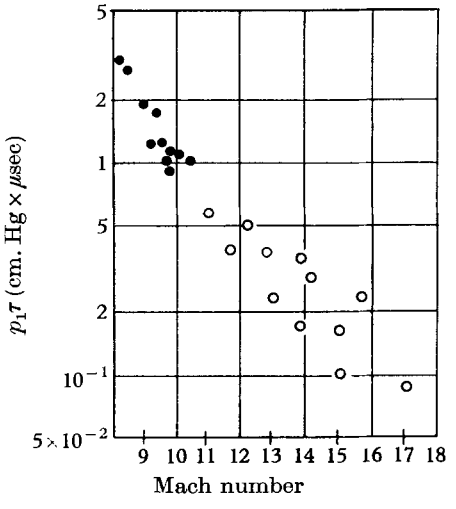

FIGURE 4. Experimental values of ionization time in air *vs* Mach number. ○, Niblett & Blackman; ● present work.

* It might be objected that the ionization time cannot be measured with any accuracy with a microwave waveguide whose cross-section is of the order of 1 in. × ½ in. We therefore performed several experiments with a specially constructed waveguide with cross-section 1 in. × 0·1 in. The results were approximately the same.

Blackman (1958) for higher Mach range are also reproduced. Our experimental points give an extension of their results and their scatter is of the same order of magnitude.

The good agreement obtained for the electron density between experiment and theory confirms the fact that the principal contribution to ionization in air in the shock Mach range 8–10·5, corresponding to equilibrium temperatures of 2800–3500 °K, is due to nitric oxide, NO, whose ionization potential is the lowest of all abundant species. The same conclusion was reached by Lamb & Lin (1957) for the shock Mach range 11–17.

The short ionization times measured agree with the hypothesis put forward by Glick, Klein & Squire (1957) that nitric oxide is formed by reaction of atomic oxygen with molecular nitrogen, since the relaxation times involved are all very short.

(*b*) *Experiments in nitrogen*

The nitrogen used in our experiments was obtained from commercial containers of low purity (containing 2 % of oxygen); the gas was purified by passing through a column of heated colloidal copper and its oxygen content reduced to about 0·2 %. At the pressure of 10 mm Hg used, the impurity level (air) due to leaks was 0·2 %. The total oxygen content of the gas was, therefore, of the order of 0·25 %. The driver gas was again hydrogen at pressures between 80 and 140 atm. The shock Mach numbers obtained ranged from 7·45 to 8·8.

The theoretical attenuation coefficient, α, for an initial pressure of 10 mm Hg and an initial temperature of 300 °K has been calculated for a shock Mach range of 7·4–9, according to equations (1), (2) and (3).

The temperature and density of the shocked gas as a function of Mach number were taken from Waldron (1958). Although his data were computed for pure nitrogen, a numerical check showed that the inclusion of 0·25 % O_2 changed the results by less than 0·5 % and this could be neglected at the accuracy level used in the computations. The composition of the gas was calculated from the chemical equilibrium, conservation of matter, and conservation of charge equations. Details of the computational method are given in the Appendix. Data on the electron diffusion cross-sections were taken again from Lamb & Lin (1957). Results of the calculations are tabulated in table 3.

Theoretical computations of the equilibrium composition for pure N_2 in the same temperature range were also performed. They show that the addition of a small amount of O_2 causes a very marked increased in the electron density, N_e. For pure nitrogen N_e is $4{\cdot}75 \times 10^6$ cm^{-3} at $M = 7{\cdot}4$, while the value for the mixture containing 0·25 % O_2 is $1{\cdot}45 \times 10^{10}$; the figures for $M = 9$ are $1{\cdot}65 \times 10^{10}$ and $1{\cdot}05 \times 10^{12}$, respectively. It appears, therefore, that the dominating factor in the ionization process in the mixture is nitric oxide, NO, whose ionization potential, 9·25 eV, is the lowest of all species present.

The experimental results are gathered in table 4, which includes the measured Mach number, the ratio of microwave outputs and the coefficient of attenuation.

Figure 5 shows comparison between the experimental data and the calculated values. The agreement is fair. The fact that some of the experimental values are

somewhat higher than the theoretical curve may be caused by some slight increase in the oxygen content of the gas, possibly due to poor purification by the copper column.

Mach number	Collision frequency (sec^{-1})	Electron density (cm^{-3})	Real part of electrical conductivity (c.g.s.)	Imaginary part of electrical conductivity (c.g.s.)	Dielectric coeff. (c.g.s.)	Attenuation coeff. (db/cm)
7·4	$4{\cdot}35 \times 10^{10}$	$1{\cdot}45 \times 10^{10}$	$2{\cdot}80 \times 10^{7}$	$2{\cdot}95 \times 10^{7}$	0·994	0·05
7·9	4·9	7·20	$1{\cdot}35 \times 10^{8}$	$1{\cdot}25 \times 10^{8}$	0·975	0·25
8·2	5·25	$1{\cdot}65 \times 10^{11}$	3·05	2·60	0·948	0·57
8·35	5·45	2·45	4·55	3·95	0·921	0·86
8·8	5·9	6·85	$1{\cdot}25 \times 10^{9}$	$1{\cdot}0 \times 10^{9}$	0·798	2·57
9	6·2	$1{\cdot}05 \times 10^{12}$	1·95	1·30	0·742	4·14

TABLE 3. Data on high-frequency (20,000 Mc/sec) electrical properties of shock-heated nitrogen, containing 0·25 % O_2. Initial pressure: 10 mm Hg. Initial temp.: 300 °K.

Mach number	Output ratio	Attenuation coefficient (db/cm)
7·45	1·01	0·06
7·95	1·07	0·40
8·1	1·075	0·43
8·15	1·08	0·46
8·25	1·15	0·83
8·35	1·16	0·89
8·35	1·17	0·94
8·4	1·19	1·03
8·4	1·20	1·09
8·4	1·22	1·19
8·45	1·22	1·19
8·45	1·23	1·23
8·45	1·27	1·42
8·55	1·32	1·65
8·55	1·32	1·65
8·6	1·34	1·75
8·65	1·39	1·96
8·65	1·43	2·13
8·65	1·43	2·13
8·8	1·54	2·57
8·8	1·58	2·67

TABLE 4. Results of experiments in nitrogen.

The maximum electron density, calculated from the experimental data, was reached in about 15 μsec, a somewhat longer time than in air, probably due to the lower oxygen content.

A rough estimate of the dissociative recombination coefficient of nitric oxide can be obtained from the experimental ionization rate and the general principle of detailed balancing. This calculation is in order of magnitude agreement with recombination coefficients of typical diatomic molecular ions (Loeb 1955).

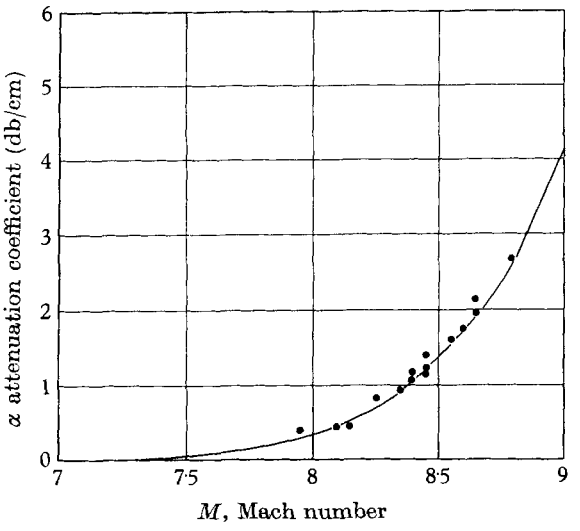

FIGURE 5. Attenuation coefficient for nitrogen with 0·25 % oxygen. Initial temperature: 300 °K. Initial pressure: 10 mm Hg.

Discussion

The attenuation range in which this method can be used most efficiently, giving results comparable in their precision to other techniques, is between 0·1 and 10 db. For attenuation smaller than 0·1 db special precautions for stabilizing the klystron's output are required, since otherwise the high amplification required will result in unfavourable signal-to-noise ratio.

This attentuation range covers a variety of conditions of the gas under test, in which a number of parameters can be varied:

(*a*) The microwave path in the ionizing medium, which determines the value of the attenuation coefficient, may be varied between wide limits by appropriate planning of the apparatus and therefore $p_1\tau$ may be measured for large and small values.

(*b*) The microwave frequency may be varied from millimetre to 10 cm waves, and therefore N_e can be measured for values between 10^{10} and 10^{14} electrons per cm^3 (this includes high Mach numbers for small gas pressures). It would at any rate be best to perform such measurements at a number of frequencies. In this case one could obtain the collision frequency, as well as the electron density from the experimental data.

(*c*) Shock strength and initial pressure.

A wide range of temperatures and pressures in different gases may therefore be covered; in particular, relatively low Mach numbers, where other known methods give unsatisfactory results, may be studied.

Appendix

Composition calculations for nitrogen, containing 0·25 % *oxygen*

Our problem is to calculate the equilibrium composition of a gas mixture, containing initially 99·75 % N_2 and 0·25 % O_2 at a pressure of 10 mm Hg and a

temperature of 300 °K, for shock Mach numbers 7·4–9. Assuming only single ionization occurs, the reactions involved are:

$N_2 \rightleftarrows 2N + 9{\cdot}7592$ eV/molecule	Dissociation of N_2
$O_2 \rightleftarrows 2O + 5{\cdot}1155$ eV/molecule	Dissociation of O_2
$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftarrows NO + 0{\cdot}9313$ eV/molecule	Formation of NO
$N_2 \rightleftarrows N_2^+ + e^- + 15{\cdot}58$ eV/molecule	Ionization of N_2
$N \rightleftarrows N^+ + e^- + 14{\cdot}5482$ eV/molecule	Ionization of N
$O_2 \rightleftarrows O_2^+ + e^- + 12{\cdot}05$ eV/molecule	Ionization of O_2
$O \rightleftarrows O^+ + e^- + 13{\cdot}6173$ eV/molecule	Ionization of O
$NO \rightleftarrows NO^+ + e^- + 9{\cdot}25$ eV/molecule	Ionization of NO

From these we derive the following system of eleven simultaneous algebraic equations (concentrations of the various species, in terms of number of particles per original gas mixture molecule, are indicated by square brackets):

(*a*) $[N_2] + \frac{1}{2}[NO] + \frac{1}{2}[N] = 0{\cdot}9975$

(*b*) $[O_2] + \frac{1}{2}[NO] + \frac{1}{2}[O] = 0{\cdot}0025$

(*c*) $K_1 = [N]^2/[N_2]$

(*d*) $K_2 = [O]^2/[O_2]$

(*e*) $K_3 = [NO]/([N_2].[O_2])^{\frac{1}{2}}$

(*f*) $K_4 = [N_2^+].[e^-]/[N_2]$

(*g*) $K_5 = [N^+].[e^-]/[N]$

(*h*) $K_6 = [O_2^+].[e^-]/[O_2]$

(*i*) $K_7 = [O^+].[e^-]/[O]$

(*j*) $K_8 = [NO^+].[e^-]/[NO]$

(*k*) $[N_2^+] + [N^+] + [O_2^+] + [O^+] + [NO^+] = [e^-]$

(*a*) and (*b*) are conservation of matter equations, (*c*) to (*j*) chemical equilibrium equations, and (*k*) is the conservation of charge. The K_n are equilibrium constants, given in terms of concentrations and may be calculated according to the following relation (Gilmore 1955):

$$K_n = \left(\frac{\rho_0 T_0}{\rho T}\right)^{\Delta n} \exp\left[\frac{\Delta E_0^0}{RT} - \Delta\left(\frac{F^0 - E_0^0}{RT}\right)\right],$$

where Δn is an integer, indicating the change in the number of particles in the reaction, ΔE_0^0 the energy of reaction at 0 °K, $\Delta(F^0 - E_0^0)$ the change in the standard free energy caused by the reaction, R the universal gas constant, ρ_0 and T_0 standard reference density and temperature (1 atm. and 0 °C).

Since we showed that it is permissible to employ Waldron's (1958) data for the temperature and density of the shocked gas, ρ and T, it is possible to calculate all equilibrium constants using free energy and reaction energy data tabulated by Gilmore (1955).* These computations were performed for six values of M in the range of interest.

One can now solve the equation system (*a*)–(*k*), but its non-linearity makes this a rather laborious task. Preliminary calculations indicate that the degree of ionization is small (less than 10^{-6}) and it is therefore permissible to perform the calculations in two steps. In the first step ionization is neglected and a system consisting of equations (*a*)–(*e*) is solved by an iterative method. In the second

* For N and N_2 more detailed tables by Woolley (1956) were used.

step we are interested in finding the electron density N_e; for this purpose we need only to know the electron concentration $[e^-]$. From equations (f)–(k) we obtain:

$$[e^-] = \sqrt{(K_4[N_2] + K_5[N] + K_6[O_2] + K_7[O] + K_8[NO])}. \quad (A\,1)$$

An order of magnitude check of the equilibrium constants and concentrations involved shows that in the range of interest all terms of the sum under the square root in equation (A 1) can be neglected in comparision with $K_8[NO]$. This is a consequence of the fact that the ionization potential of nitric oxide is much lower than that of the other components.

Results of the computations, including concentrations of all non-ionized particles and electron concentration and number density are tabulated in table 5.

Mach number	$[N_2]$	$[N]$	$[NO]$	$[O_2]$	$[O]$	$[e^-]$	N_e (cm^{-3})
7·4	0·9964	$1{\cdot}4 \times 10^{-5}$	$2{\cdot}3 \times 10^{-3}$	$3{\cdot}2 \times 10^{-4}$	$2{\cdot}1 \times 10^{-3}$	$6{\cdot}9 \times 10^{-9}$	$1{\cdot}45 \times 10^{10}$
7·9	0·9966	7·7	1·75	1·2	3·05	$3{\cdot}3 \times 10^{-8}$	7·20
8·2	0·9967	$3{\cdot}95 \times 10^{-4}$	1·35	$5{\cdot}8 \times 10^{-5}$	3·5	7·3	$1{\cdot}65 \times 10^{11}$
8·35	0·9967	3·15	1·2	4·1	3·65	$1{\cdot}1 \times 10^{-7}$	2·45
8·8	0·9966	$1{\cdot}05 \times 10^{-3}$	$8{\cdot}3 \times 10^{-4}$	1·6	4·15	2·95	6·85
9	0·9964	1·75	6·8	1·0	4·3	4·5	$1{\cdot}05 \times 10^{12}$

TABLE 5. Gas composition and electron density for nitrogen with 0·25 % oxygen in shock Mach range 7·4–9. Initial pressure: 10 mm Hg. Initial temperature: 300 °K.

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