Measurement of $N_2^+ + e^-$ Dissociative Recombination in Expanding Nitrogen Flows

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The dissociative-recombination rate coefficient for the reaction $N_2^+ + e^- \xrightarrow{k_r} N + N$ has been measured in the inviscid nozzle flow of a short-duration reflected-shock tunnel and found to be given by $k_r = (1.5 \pm 0.5) \times 10^{22} T_e^{-1.5}$ cm³/mole-sec for an electron temperature range of approximately 3500–7200°K. The test gas used in these experiments was nitrogen at equilibrium reservoir conditions of 6750°K and 13.1 atm pressure and at 7200°K and 17.1 atm pressure. The electron density and the electron temperature were measured on the nozzle centerline at several axial locations using thin-wire Langmuir probes. The electron densities were simultaneously measured using microwave interferometers and found to be in good agreement with the probe data.

1. Introduction

AN important reaction governing the distribution of free electrons present in high-temperature air plasmas is

$$N + N \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2^+ + e^- \qquad (1)$$

The forward and reverse rate coefficients of this reaction are related to the local plasma conditions through the temperature, the forward rate being dependent upon the heavy-particle translational temperature while the recombination rate depends mainly on the electron temperature. It is therefore important to know these temperatures in experiments to evaluate the recombination-rate coefficient.

The available rate coefficient data for dissociative recombination of N_2^+ have generally been deduced from measurements of the electron-density decay in the afterglow of a discharge. Only in a very few cases have experiments been performed for electron temperatures in excess of 300°K. Sayers[1] obtained a data point at 3200°K, which represents the highest electron temperature at which a measurement had been made prior to this paper. He studied the electron (ion) decay of an helium (or argon)-nitrogen plasma using a Langmuir probe, from which both the electron concentration and temperature could be deduced. An rf mass spectrograph was used to identify the ions present in the plasma and to confirm that no negative ions were present.

Later, Sayers and Kerr[2] reported the preliminary results of an experiment intended to measure the two-body dissociative recombination of N_2^+ at an electron temperature of 2000°K. For this they utilized the same experimental apparatus previously described by Sayers.[1] However, the authors note the possible formation of negative ions and the subsequent electron detachment process that was absent in the previous studies. It is therefore difficult to ascertain the accuracy of this data point.

Mentzoni[3] used a microwave technique to study the electron decay of a plasma, excited by a pulsed d.c. discharge, as a function of gas temperature and pressure in the range 300–735°K and 0.5–6.0 mm Hg. He observed a pressure dependence of the reaction-rate coefficient and suggested that it may have been caused by the presence of N_3^+ and N_4^+ ions. He also notes the possibility of negative ion formation caused by impurities.

The remaining recombination rate-coefficient data have all been obtained in the temperature range of 300–400°K. Kasner et al.[4] report the results of a microwave determination of electron-density decay in the afterglow following ionization of a neon-nitrogen gas mixture. The afterglow positive ions were identified using an rf-type mass spectrometer. The results indicated that for nitrogen pressures less than 0.01 mm Hg, N_2^+ was the only significant ion present. At greater pressures, both N_3^+ and N_4^+ were also found. Later, Biondi[5] reported that the result of Ref. 4 was high by a factor of approximately 2 because of an error in the microwave electron-density calibration. Kasner and Biondi[6] reported in 1964 the same value for N_2^+ recombination in a nitrogen-helium mixture as reported in Ref. 5 for neon-nitrogen mixtures.

Faire and Champion[7] studied the electron-density decay in the afterglow of an arc discharge for nitrogen pressures greater than or equal to 0.9 mm Hg. They have corrected their results for diffusion effects, which would tend to reduce the value of the reaction-rate coefficient. They indicate that the N_2^+ recombination rate coefficient is proportional to temperature to the -0.6 power. Kasner et al.[4] claim that Faire and Champion were not observing the recombination of N_2^+ but rather the recombination of N_3^+ and N_4^+.

Biondi and Brown[8] and Faire et al.[9] have obtained the identical value of the N_2^+ dissociative-recombination rate coefficient at 300°K. Both groups used microwave techniques for diagnostic tools. Biondi and Brown worked with nitrogen pressures in the range of 2–18 mm Hg. Faire et al.[9] worked with nitrogen pressures in the range 0.01–3 mm Hg, noting that for greater pressures they found an increase in the rate coefficient probably due to the reaction $N_2^+ + e^- + N_2 \rightarrow N_2 + N_2$. A similar increase with increasing pressure was reported in Ref. 8.

Bialecke and Dougal[10] have measured the dissociative-recombination rate coefficient of N_2^+ in the temperature range 92–300°K for nitrogen pressures in the range 0.2–2.0 mm Hg. They also used a discharge tube to generate the plasma and a microwave interferometer was used to deduce the electron-density decay in the afterglow.

In the present experiments, both the electron temperature and number density were measured. Then the recombination rate coefficient for the dominant reaction was adjusted until the calculated number density agreed with the probe and microwave-interferometer data. The measured electron temperature history was used in calculating the variation of the

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Table 1 Chemical-kinetic model used in data correlation

No.	Reaction	Rate coefficient expression, cm^3/mole-sec or cm^6/$mole^2$-sec	Applicable Refs.
1	$N_2 + N_2 \rightarrow 2N + N_2$	$3.0 \times 10^{21 \pm 0.3} T^{-1.5} \exp(-113{,}260/T)$	25–29
2	$N_2 + N \rightarrow 2N + N$	$1.5 \times 10^{22 \pm 0.3} T^{-1.5} \exp(-113{,}260/T)$	25–28
3	$N_2^+ + N \rightarrow N_2 + N^+$	$7.8 \times 10^{10 \pm 1} T^{0.5}$	30–33
4	$N_2^+ + e^- \rightarrow 2N$	To be determined from this experiment	1–10
5	$N^+ + e^- + e^- \rightarrow N + e^-$	$8.3 \times 10^{39 \pm 2} T_e^{-4.5}$	20–24
6	$N_2^+ + N_2 + e^- \rightarrow N_2 + N_2$	$2.2 \times 10^{26 \pm 1} T_e^{-2.5}$	37
7	$N_2^+ + N + e^- \rightarrow N_2 + N$	$6.0 \times 10^{24 \pm 1} T_e^{-2.5}$	37
8	$N^+ + N_2 + e^- \rightarrow N + N_2$	$2.2 \times 10^{26 \pm 1} T_e^{-2.5}$	37
9	$N^+ + N + e^- \rightarrow N + N$	$6.0 \times 10^{24 \pm 1} T_e^{-2.5}$	37

number density along the nozzle. The relative importance of various reactions included in the reaction system was independently assessed. In Sec. 2, the experimental apparatus and procedure are briefly discussed. The method of data analysis is described in Sec. 3 and the experimental results are discussed in Sec. 4.

2. Experimental Apparatus and Technique

A pressure driven shock tube was used to produce a reservoir of high-temperature nitrogen which was subsequently expanded in a conical nozzle. The intensity of the visible and near infrared radiation and the pressure were measured in the shock tube and the electron density, electron temperature, and visible-radiation intensity were measured in the nozzle. All of these measurements were made simultaneously in each experiment. Detailed discussion of these measurements is given in Refs. 11–13.

The test gas used in these experiments was UPC nitrogen supplied by Air Products and Chemicals. A chemical analysis of the gas indicated the following: oxygen less than 0.5 ppm, total hydrocarbons less than 1 ppm, and water less than 0.15 ppm. The shock tube was purged with approximately 5.0 torr of the test gas prior to each run.

The electron number densities were measured at 11.5, 21.5, 31.5, and 41.5 in. from the nozzle throat using microwave interferometers operating at frequencies of either 35 or 17 GHz. The interferometers are discussed in more detail in Ref. 13.

The electron temperature and electron density were measured on the nozzle centerline at axial distances of 12.5, 22.5, 32.5, and 42.5 in. from the throat using thin-wire Langmuir probes. For these experiments, the probes were constructed by surrounding 0.004-in. tungsten wires with a quartz envelope, leaving a nominal 0.400-in. length of bare wire exposed. The quartz was fused to the wire at their junction. Immediately prior to each run the probe was ultrasonically cleaned in a dilute solution of sodium hydroxide to remove the tungsten oxide.

The voltage applied to the probe was swept from -6 to $+1$ v (relative to ground potential) in approximately 80 μsec, which is a sufficiently slow sweep rate[14] to avoid transient effects. The voltage sweep applied to the probe was delayed so as to be initiated at any desired time during the uniform-flow period, as illustrated on the data records presented herein. The experimental procedure used in obtaining the Langmuir probe data was described in detail in a previous paper.[15]

3. Technique Used to Determine Rate Coefficient

The reaction-rate coefficient for the two-body dissociative recombination of N_2^+ has been measured in an expanding nitrogen plasma for two experimental conditions. At the first condition the test gas was expanded from equilibrium reservoir conditions of 6750°K and 13.1 atm pressure and at the second the reservoir conditions were 7200°K and 17.1 atm pressure. In the remainder of the paper the method of data analysis is described and experimental results are presented for each of the aforementioned conditions.

3.1 Procedure for Calculating Electron-Density Distribution

The technique used to determine the rate coefficient for the dissociative-recombination of N_2^+ was to vary the rate coefficient in order to match calculated and measured nozzle electron densities. The calculations were performed with the nozzle-flow computer program described in Ref. 16. This program computes the solution for the gasdynamic properties and chemical composition in the expansion of an arbitrary gas mixture from an equilibrium reservoir state through a given nozzle geometry. The vibrational and electronic degrees of freedom of the species are assumed to maintain thermodynamic equilibrium, but the chemical reactions are allowed to proceed at finite rates. In the calculations performed here the following species were included: N_2, N, N_2^+, N^+, and e^-. The thermodynamic properties employed for these species are given in Ref. 16. The chemical kinetic model is shown in Table 1. The impurities in the gas supply and those due to any leakage are negligible sources of electrons in these experiments.

In applying the nozzle-flow program to the flow of weakly ionized gases, the electrons are treated as a separate chemical element and the gas is assumed to be an electrically neutral, ideal mixture. In the standard version of this program, transport processes are neglected and the electron temperature is assumed equal to the heavy-particle translational temperature. However, in the present nozzle experiments, the electron temperature was measured and found to be appreciably greater than the heavy-particle temperature. Since the electron recombination rate in the nozzle depends on the electron temperature, this disparity between the temperatures could have a significant effect on the inferred rate coefficient. For this reason the computer program was modified to include the dependence of the electron recombination rate on the electron temperature.

Several authors[17–19] have discussed the possible mechanisms for electron heating in such flows and have formulated a general electron-energy conservation equation. However, the solution of this equation is quite difficult and so the approach taken here to calculate the nozzle-flow electron density was of a semiempirical nature. Rather than attempting a solution of the electron energy equation, the variation of the electron temperature was prescribed on the basis of the Langmuir probe measurements.

For the flow situation of interest here, a nozzle expansion from a high-temperature equilibrium reservoir, reactions 6–9 (Table 1) are negligible compared with the other deionization paths. The reaction rates are several orders of magnitude lower because of the small collision frequencies. Although it is not included in the table, clearly the reaction $N_2^+ + e^- + e^- \rightarrow N_2 + e^-$ will also be negligible compared with the dissociative-recombination reaction at the ionization levels en-

countered here. The number of collisions of two electrons with N_2^+ will be far less frequent than two-body collisions of an electron and N_2^+.

The concentration of N^+ along the nozzle is governed by the charge exchange process (reaction 3) and the three-body electron recombination reaction (reaction 5). Several authors[20–23] have reported measurements of the reaction of two electrons with an atomic ion. In addition, Makin and Keck have made a theoretical study of this reaction.[24] In correlating the number-density data, the rate coefficient for reaction 5 was varied between two orders of magnitude less than and two orders of magnitude greater than the theoretical value. The effect of including this reaction on the charged species concentrations was found to be negligible.

At this point the chemical kinetic model can be reduced to four important reactions, the neutral dissociation-recombination reactions (reactions 1 and 2), the charge-exchange reaction (reaction 3), and the dissociative-recombination of N_2^+ (reaction 4). The neutral chemistry is coupled to the charged particle chemistry through the N_2 and N concentrations. The rate coefficients for reactions 1 and/or 2 have been measured by several authors.[25–29] The uncertainty quoted in Table 1 amounts to a factor of 2. However, in the calculations performed here, even a considerably larger variation was found to have little effect on the charged species concentrations.

The rate coefficient for reaction 3 is not nearly so well known as those for reactions 1 and 2. Wray et al.[30] suggested that the cross section for this reaction is the same as that for the $O_2^+ + O$ reaction and, on the basis of a communication with Sayers (see Ref. 31 and 32 for room temperature values) recommended a rate coefficient given by $7.8 \times 10^{11} T^{0.5}$. More recently, Fite[33] (in Chap. 13) suggested that, on the basis of atmospheric observations, the rate coefficient is no larger than approximately 6×10^{12}. He did not feel that a temperature dependence could be assigned. Also in Ref. 33, Bortner and Kummler suggest a constant value of approximately 6×10^{11}, which is also based on atmospheric observations. The value given in Table 1 of $7.8 \times 10^{10\pm1} T^{0.5}$ more than covers this range of uncertainty.

Typical results for the variation of the species concentrations along the nozzle are shown in Figs. 1a and b. This solution was obtained for a reservoir temperature of 6750°K and a reservoir pressure of 13.1 atm. The mean values of the rate coefficient expressions listed in Table 1 were used and the reverse rate coefficients were computed from the equilibrium constants. The results for the neutral species concentrations, shown in Fig. 1a, indicate the reason that the charged species concentrations are fairly insensitive to the rate coefficients for the neutral chemistry. The N_2 and N concentrations become frozen at nearly the reservoir values because the three-body recombination reactions become unimportant at an earlier point in the expansion than the bimolecular charged-particle reactions.

The positive ion histories are shown in Fig. 1b. Measurements were performed at area ratios greater than 70 beyond which the N_2^+ concentration is so low that the electron concentration is essentially equal to the N^+ concentration. Nozzle calculations have demonstrated that the dissociative-recombination of N_2^+ is in fact the reaction which controls the level of the N^+ concentration, providing the charge exchange reaction (reaction 3 of Table 1) is fast enough. It was found that if the rate coefficient value of reaction 3 is greater than or equal to 1×10^{12}, then this reaction remains close to equilibrium in the initial part of the expansion. At small area ratios, reaction 3 consumes N^+ to produce N_2^+. If the value of the coefficient at elevated temperatures is 6×10^{11} or less then reaction 3 as well as reaction 4 becomes a rate-limiting step. The influence of reaction 3 on the rate coefficient deduced for the reaction $N_2^+ + e^- \rightarrow 2N$ will be discussed in more detail in the following section.

The reaction rates remaining in the chemical-kinetic model that depend on the electron temperature are the forward rate

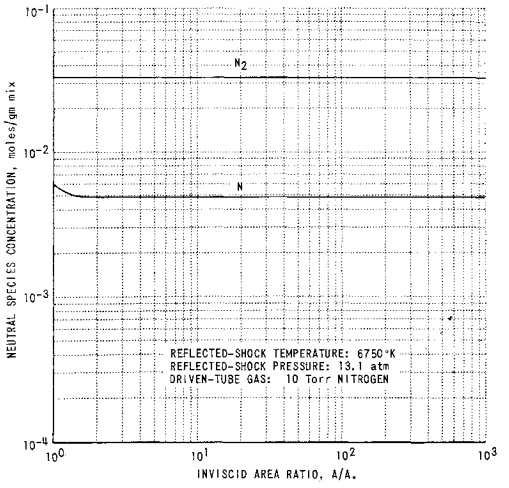

Fig. 1a Neutral species distribution in nozzle flow.

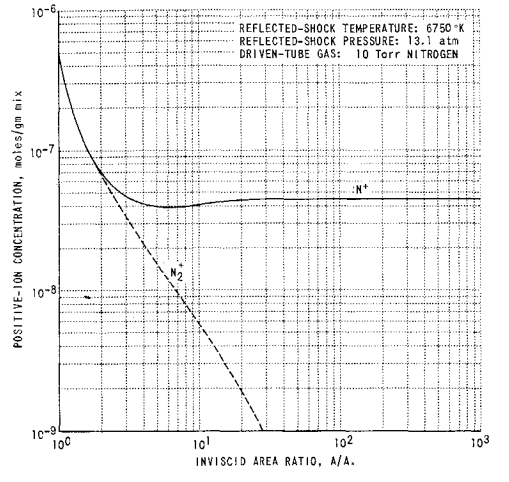

Fig. 1b Positive-ion distribution in nozzle flow.

of the dissociative recombination and both the forward and reverse rates of the three-body, two-electron recombination reactions. As discussed previously these reaction-rate coefficients are evaluated at the electron temperature prescribed on the basis of the measured values. The specified variations for the electron temperature are discussed in Sec. 4. For some of the prescribed temperature histories, the reverse rate of reaction 4 is small but not negligible at the point where the electron and heavy-particle temperatures begin to differ. The reverse rate of reaction 5 was always negligible at this point. The reverse rate coefficient of reaction 4 was calculated from the ratio of the forward rate coefficient to the equilibrium constant, evaluated at the heavy-particle temperature.

In all of the nozzle flow calculations performed in this study the prescribed nozzle cross-sectional area was that of the inviscid core. The boundary-layer displacement thickness was computed using the method of Ref. 34. This method has previously been verified experimentally for air expansions from comparable reservoir conditions.[12] For the conditions of these experiments the boundary-layer correction is small.

3.2 Langmuir Probe and Microwave-Interferometer Measurements

A typical swept-voltage probe characteristic obtained on the nozzle centerline for a reservoir condition of 7200°K and 17.1 atm is shown in Figs. 2a and b. These oscilloscope records were recorded simultaneously using two oscilloscopes with the vertical sensitivities adjusted to emphasize the

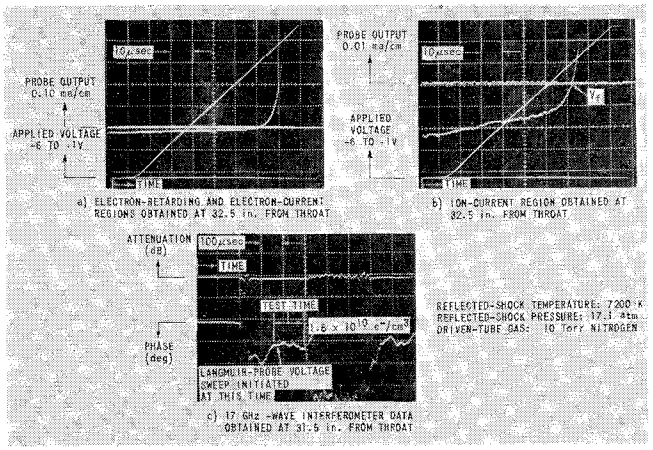

Fig. 2 Typical probe characteristic and microwave-interferometer data in nitrogen plasma.

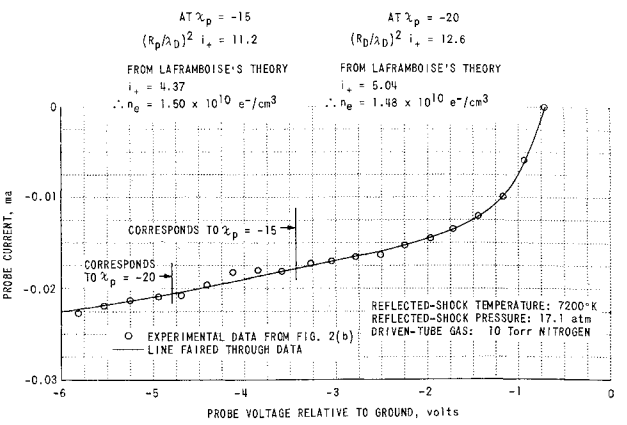

Fig. 4 Ion-current region of experimental probe characteristic.

electron-retarding and electron-current regions in Fig. 2a and the ion-current region and the location of the floating potential, V_f, on Fig. 2b. The voltage applied to the probe was recorded on the lower channel of each oscilloscope. In these experiments the probe voltage was swept from -6 to $+1$ v relative to ground potential. Figure 2c shows the phase shift and attenuation of the incident energy obtained from a microwave interferometer at a location just upstream of the Langmuir probe. The time at which the probe voltage sweep was initiated is indicated on this figure.

The current-voltage characteristics were obtained from oscilloscope records using an optical comparator. Figures 3 and 4 illustrate the electron-retarding and ion-current regions obtained from the oscilloscope records presented in Fig. 2a and b. For a Maxwellian distribution of electron velocity, the current collected in the electron-retarding region should fall on a straight line on the semilogarithmic plot when the current exceeds approximately 2–3 times the ion saturation value. Thus the straight-line portion should be expected to begin at about 6×10^{-2} ma which is consistent with the measurement as illustrated on Fig. 3. It is reasonable to conclude that the electron velocity distribution was Maxwellian in these experiments.

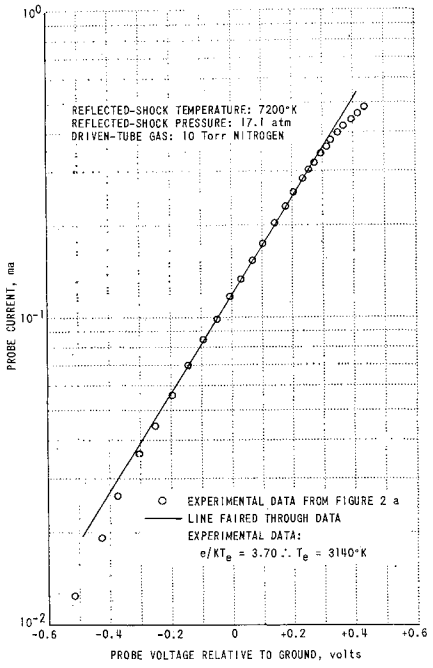

Fig. 3 Electron-retarding and electron-current regions of experimental probe characteristic in nitrogen plasma.

The electron density was obtained from the Langmuir probe data, assuming N^+ to be dominant ion within the framework of Laframboise's theoretical results.[35] The procedure used here in reducing the data is discussed in Refs. 13 and 15. The electron number density obtained from Fig. 4 at $\chi_p = -15$ and $\chi_p = -20$ were 1.50×10^{10} and 1.48×10^{10} e^-/cm^3, respectively, as compared with the electron-density value of 1.8×10^{10} e^-/cm^3 measured just upstream of the probe with the 17 GHz microwave interferometer.

4. Determination of Rate Coefficient

It was previously mentioned that the rate coefficient for the deionization of N_2^+ by the reaction $N_2^+ + e^-$ was measured at two separate reflected-shock conditions, 6750°K at 13.1 atm pressure and 7200°K at 17.1 atm pressure, respectively. Detailed number-density and electron-temperature measurements were performed at both of these conditions and are discussed in this section.

4.1 Measurements Performed for 6750 °K at 13.1 atm Pressure

The electron-temperature measurements performed in the expanding plasma are presented in Fig. 5 and are compared with the calculated heavy-particle translational temperature. The thin-wire probes were used to obtain electron temperatures at 12.5, 22.5, 32.5, and 42.5 in. ($A/A^* = 78$, 238, 470, and 770) from the nozzle throat. The electron temperature

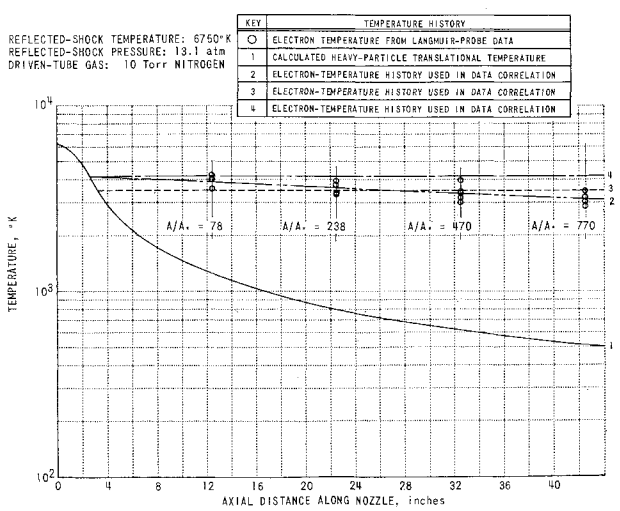

Fig. 5 Measured electron-temperature in expanding nitrogen plasma.

was found to decrease in a slow but nearly linear manner, from the first to the last measuring station. The electron-temperature measurements are seen to scatter approximately ±10% about an average value. This scatter in the electron-temperature is typical of all the results presented here and in our previous work.[13,15]

The electron-density measurements obtained with the Langmuir probes and the microwave interferometers are presented in Fig. 6 as a function of inviscid area ratio. The electron-density measurements scatter by approximately ±20% about an average value. The degree of reproducibility of the incident-shock Mach number was such that ±10% of this scatter could be attributed to scatter in shock strength. The probe measurements of electron density obtained at 12.5 and 22.5 in. fall below the microwave-interferometer measurements. This result was anticipated[13] because of the relatively small value of the ion-neutral and neutral-neutral mean free paths at these locations. At the 32.5- and 42.5-in. locations, where the flow is free-molecular with respect to the probe diameter, the two measuring techniques are in good agreement. It is noted, however, that the electron temperatures measured at 12.5 and 22.5 are not influenced by these collisional effects. An experiment was performed with a 0.002-in.-diam × 0.200-in.-long probe and the electron density deduced from the probe was found to approach the microwave-interferometer value while the electron temperature remained unchanged.

The semiempirical technique discussed in Sec. 3.1 was used to obtain the dissociative recombination reaction-rate coefficient from the electron-density and electron-temperature data. The temperature dependence for the dissociative-recombination reaction was selected to be −1.5 by applying to the nitrogen system the same theoretical argument previously presented by Hansen[36] for the reaction $NO^+ + e^- \rightarrow N + O$. The remaining variables were the constant factor of reaction 4 and the rate coefficient of reaction 3. Lines C, D, and A on Fig. 6 were obtained for the rate coefficient of reaction 4 given by $(1.5 \pm 0.5) \times 10^{22} T_e^{-1.5}$ and the rate coefficient for reaction 3 equal to or greater than $7.8 \times 10^{11} T^{0.5}$. Decreasing the rate coefficient of this latter reaction to $7.8 \times 10^{10} T^{0.5}$ resulted in approximately a 3% increase in the predicted number density. However, decreasing the rate to

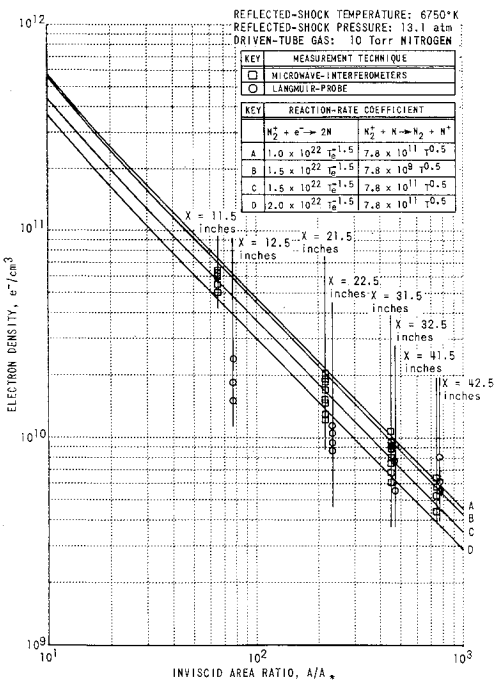

Fig. 6 Measured electron density in expanding nitrogen plasma.

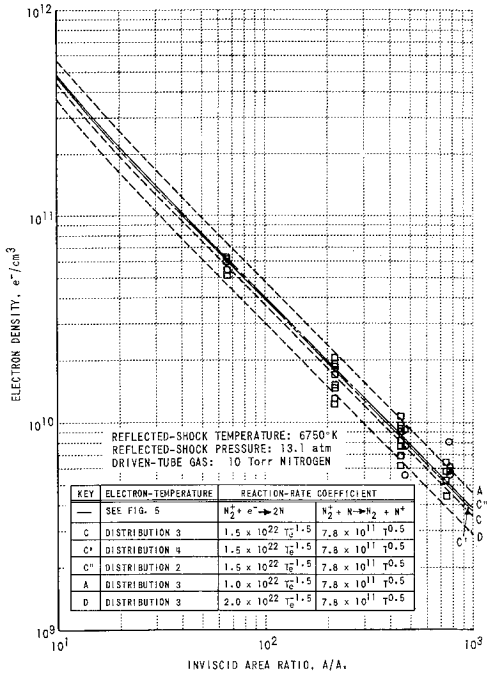

Fig. 7 Influence of electron-temperature history of reaction-rate coefficient determination.

$7.8 \times 10^9 T^{0.5}$ resulted in the prediction of line B. This result is still within the uncertainty of $(1.5 \pm 0.5) \times 10^{22} T_e^{-1.5}$ for reaction 4. All of the preceding calculations were performed for the electron-temperature distribution given by line 3 in Fig. 5. That is, the electron temperature was assumed to be in equilibrium with the translational temperature down to 3500°K at which it was frozen.

The influence of the selected electron-temperature distribution on the accuracy of the reported reaction-rate coefficient is an important consideration. Figure 7 illustrates the influence of electron-temperature distribution on the predicted electron-density history. Freezing the electron temperature at 4200°K instead of 3500°K results in an 8% increase in local electron density, while the linear fit to the electron-temperature measurements results in a 5% number-density increase. Both of these results are well within the uncertainty band described by lines A and D.

4.2 Measurements Performed for 7200°K at 17.1 atm Pressure

The Langmuir probe and microwave-interferometer measurements discussed previously were repeated in detail for a reservoir condition of 7200°K at 17.1 atm pressure. Measurements were again obtained at the same axial locations. Since the boundary-layer growth on the nozzle wall for this second condition was essentially unchanged from the previous experimental condition, the inviscid area ratios at which data were obtained also remained unchanged.

Figure 8 presents the measured electron temperatures and compares them to the calculated heavy-particle translational temperature. Lines 2–4 represent electron-temperature distributions that were considered in correlating the electron-density data in order to deduce the rate coefficient. The influence of the electron-temperature history on the data correlation was similar to that reported here for the previous experimental condition. Therefore, in order to simplify the data correlation, the electron temperature was assumed to be in equilibrium with the translational temperature from the reservoir to 3700°K at which it was frozen (distribution 3 on Fig. 8).

The measured electron densities are compared on Fig. 9 with number-density distributions calculated using the same

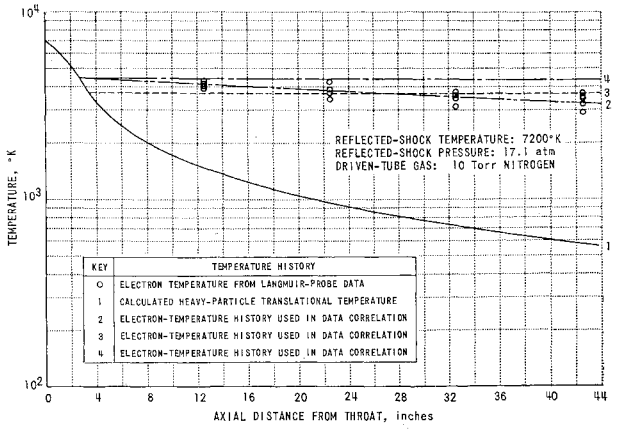

Fig. 8 Measured electron temperature in expanding nitrogen plasma.

rate coefficients that were used to correlate the data of the previous experimental condition. Once again, the Langmuir probe electron-density data at the two upstream stations were somewhat below the microwave data because of collisional effects and thus have not been included on the plot. Lines C, A, and D represent the results obtained for rate coefficients of $(1.5 \pm 0.5) \times 10^{22} T_e^{-1.5}$ for reaction 4 and $7.8 \times 10^{11} T^{0.5}$ for reaction 3. Increasing the rate coefficient of reaction 3 had no influence on the calculated distributions. Decreasing the rate to $7.8 \times 10^{10} T^{0.5}$ increased the calculated number density for line C by approximately 10% but still was within the uncertainty bounds, i.e., lines A and D. Decreasing this rate even further to $7.8 \times 10^{9} T^{0.5}$ resulted in line B which is clearly outside the data scatter. In the data correlation of the previous experimental condition (see Fig. 6) line D was within the data scatter. In order to correlate the data from both experimental conditions with the same set of rate coefficients it is necessary for the rate coefficient of reaction 3 to be greater than $7.8 \times 10^{9} T^{0.5}$ as suggested by Refs. 30 and 33.

The results obtained in this paper are compared with those of previous investigators in Fig. 10. Whenever the electron temperature was reported, it was used in compiling the data plot. Our value is approximately 10 times greater than the

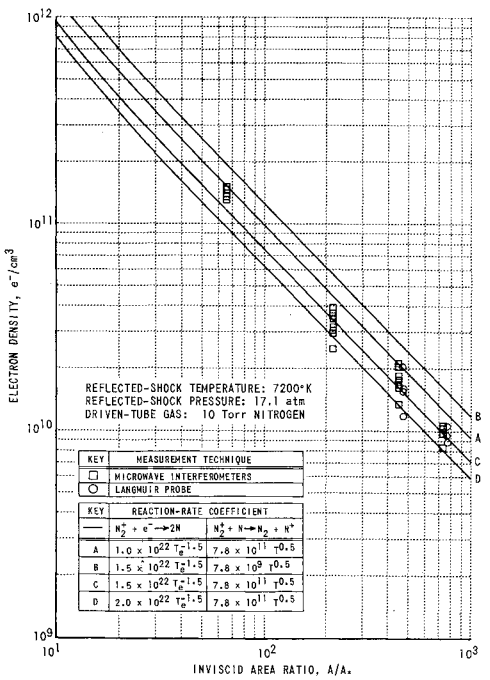

Fig. 9 Electron-density measurements in expanding nitrogen plasma.

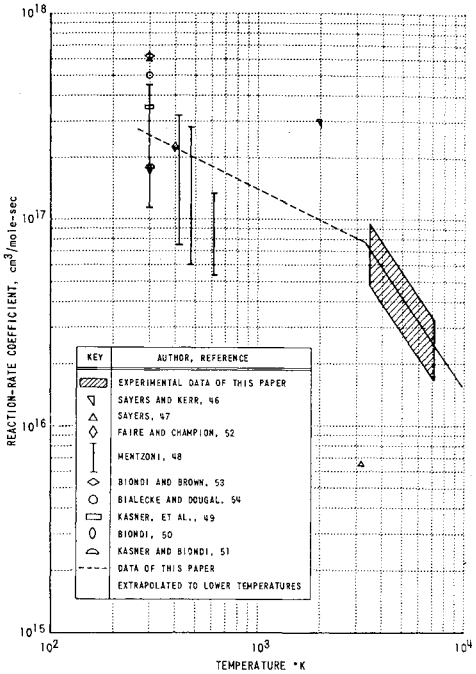

Fig. 10 Reaction-rate coefficient data for the reaction $N_2^+ + e^- \rightarrow N + N$.

value initially reported by Sayers[1] and approximately one-third the value later reported by Sayers and Kerr.[2]

The data reported here do not extend below 3500°K. However, an estimate of the low-temperature rate coefficient can be obtained and is illustrated on Fig. 10 by the dotted line. Faire and Champion[7] suggested that on the basis of their low-temperature experimental data the rate coefficient should have a -0.6 temperature dependence. An estimate of the temperature dependence can be obtained by applying the technique used by Hansen[36] (in his $NO^+ + e^-$ study) to the reaction $N_2^+ + e^- \rightarrow N + N$. If it is assumed that constant transition probability exists at the $N + N$ and N_2^+ potential crossing, then the temperature dependence of this reaction should be the same as for the $NO^+ + e^- \rightarrow N + O$ reaction. In this technique, the temperature dependence of the rate coefficient is proportional to that of the rotational and vibrational partition functions. At low temperatures, the rate coefficient is inversely proportional to the square root of the temperature, while at high temperature it becomes proportional to temperature to the -1.5 power. The procedure used here to obtain the dashed line on Fig. 10 was to match the $T^{-0.5}$ temperature dependence to our data at the characteristic vibrational temperature of N_2^+ ($\theta_v = 3130$°K). This extrapolation to low temperature agrees reasonably well with the available experimental data.

5. Conclusions

The $N_2^+ + e^-$ recombination rate coefficient was measured in a nitrogen plasma that had expanded from equilibrium reservoir conditions of 6750°K at 13.5 atm pressure and 7200°K at 17.1 atm pressure. The resulting reaction-rate coefficient for the recombination of N_2^+ is given by $k_r = (1.5 \pm 0.5) \times 10^{22} T_e^{-1.5}$ cm³/mole sec for an electron temperature range of approximately 3500–7200°K.

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