Measurement of Electron Temperature and Number Density in Shock-Tunnel Flows. Part II: $NO^+ + e^-$ Dissociative Recombination Rate in Air

Michael G. Dunn* and John A. Lordi†
Cornell Aeronautical Laboratory Inc., Buffalo, N. Y.

The dissociative-recombination rate coefficient for the reaction $NO^+ + e^- \rightarrow_{k_r} N + O$ has been measured in the inviscid nozzle flow of a short-duration reflected shock tunnel and found to be given by $k_r = (6.7 \pm 2.3) \times 10^{21}\ T_e^{-1.5}$ cm³/mole sec for an electron temperature range of approximately 2000–7000°K. These experiments were performed in air at equilibrium reservoir conditions of 6850°K and 22 atm pressure and at 7200°K and 25 atm pressure. Thin wire Langmuir probes were used to measure the electron temperature and electron density on the nozzle centerline. The electron densities were simultaneously measured using microwave interferometers and found to be in good agreement with the values obtained from the Langmuir probe data. The measured electron temperatures, which were considerably greater than the calculated heavy particle translational temperature, were used in determining k_r from the number density data.

1. Introduction

One of the most important reactions governing the distribution of free electrons present in high-temperature air plasmas is

$$N + O \underset{k_r}{\overset{k_f}{\rightleftarrows}} NO^+ + e^- \qquad (1)$$

The forward and reverse rate coefficients of this reaction are related to the local plasma conditions through the temperature. The forward rate coefficient of Eq. (1) depends on the heavy particle translational temperature whereas the recombination rate coefficient is principally dependent upon the electron temperature. In order to obtain the rate coefficient from experimental measurements, it is important to know both of these temperatures.

Measurements of the NO^+ deionization rate coefficient in which the electron temperature and electron density were simultaneously obtained have not been reported in the literature for an air plasma undergoing an expansion from a high-temperature reservoir. This lack of data motivated the present experiments to determine the reaction rate coefficient for the electron depletion reaction

$$NO^+ + e^- \underset{k_r}{\rightarrow} N + O$$

in a nonequilibrium expansion of air. The rate coefficient measurements were made in the electron temperature range of approximately 2000–7000°K by fitting calculated and measured values of electron number density. The experiments were performed in the inviscid flow of a conical nozzle of a short-duration, reflected-shock tunnel.

The forward rate coefficient for the formation of NO^+ was first measured by Lin[1] in shock-tube flows. His measurements were obtained for heavy particle translational temperatures ranging from 4400 to 5100°K. Lin and Teare[2] later used these data to infer the value of the reverse rate coefficient through the equilibrium constant after applying a correction factor of about 5 to the lower bound estimate of Lin[1] to account for the effect of finite dissociation rate. Because these data were obtained in shock-tube flows, they made the assumption that the electron temperature was equal to the heavy particle translational temperature and proposed a coefficient given by $k_r = 1.8 \times 10^{21} T^{-1.5}$ cm³/mole sec. It is noted in Ref. 2 that if this value of k_r were increased by a factor of 2, then better agreement would be achieved between calculated and observed electron density distributions behind the incident shock. However, the authors did not feel that such an adjustment was justified in view of other existing uncertainties in dissociation rate coefficients.

Frohn and DeBoer[3] and Thompson[4] have also made shock-tube measurements of ion density profiles behind incident shocks in air. In Ref. 3 it is reported that in order to correlate their data the reverse rate proposed in Ref. 2 had to be increased by a factor of 2. It is also noted in Ref. 3 that the data of Ref. 4 were best correlated by increasing the Lin and Teare[2] rate by a factor of 3 (Ref. 4 does not report the magnitude of the rate coefficient used in the data analysis). In addition to these measurements, several others[5–8] have been performed in a shock-tube facility in which the gas processed by the reflected shock is allowed to flow down a quartz tube in which the dissociative recombination of NO^+ takes place. The value of the rate coefficient for the dissociative recombination of NO^+ has also been inferred by Eckerman and Stern[9] and by Eschenroeder and Chen[10] using electron density measurements obtained in the near wake of small projectiles fired in ballistic ranges. The electron temperatures were not measured in these experiments.

The remaining data on the two-body dissociative recombination of NO^+ have been obtained in the temperature range of approximately 200–400°K by studying the afterglow of a gas discharge. One of the difficulties with discharge tube studies has been to determine whether the ion undergoing recombination is in fact the one of interest. In addition, the problems of ambipolar diffusion and attachment of electrons can cause some difficulty in the data interpretation. With these reservations in mind, several investigators[11–14] have measured the recombination rate coefficient for NO^+ in an afterglow plasma. Young and St. John[15] produced NO^+ using chemionization and by monitoring the time history of

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* Principal Engineer, Aerodynamic Research Department. Member AIAA.

† Research Aerodynamicist, Aerodynamic Research Department. Member AIAA.

the ion current they were able to obtain a recombination rate coefficient.

The temperature dependence of the reverse rate coefficient has recently been discussed by Hansen[16] who argued that the temperature dependence for the reaction $NO^+ + e^- \rightarrow N + O$ varies from $T^{-0.5}$ to $T^{-1.5}$ as the temperature increases. It is demonstrated that if a constant transition probability at the N + O and NO^+ potential crossing is assumed then the aforementioned temperature dependence can be derived.

In the present experiments, both the electron temperature and number density were measured. The measured nozzle flow electron temperature was used in calculating the variation of the number density along the nozzle. The recombination rate coefficient was then adjusted until the calculated number density agreed with the probe and microwave data. In Sec. 2, the experimental apparatus and diagnostic techniques are discussed. The method of data analysis and the experimental results are discussed in Sec. 3.

2. Experimental Apparatus and Technique

A pressure driven shock tube was used to produce a reservoir of high-temperature air 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. A description of the shock tunnel, the Langmuir probe construction, and supplementary diagnostic measurements routinely performed in this facility are described in Refs. 17 and 18. Therefore, this section will be confined to a brief discussion of the microwave interferometers and thin wire probes used to obtain the measurements described here.

The electron number densities were measured in the nozzle at 11.5, 21.5, 31.5, and 41.5 in. from the throat using microwave interferometers operating at frequencies of either 35 or 17 GHz. Thin quartz windows were used at the horn, nozzle wall interface to separate the plasma from the microwave waveguide. Use of the interferometers in this manner resulted in an integrated measurement of the propagation path electron number density, including any possible effects of boundary-layer gradients. The phase shift and attenuation of the received signal were measured separately as were the incident and reflected power. A typical microwave interferometer data record is presented in Ref. 17.

The voltage applied to the probe was swept through a voltage range of −5 to +2 v, in a period of time significantly less than the duration of uniform flow but long enough to avoid electronic transient effects. Reference 17 includes a typical Langmuir probe data record from which the current-voltage characteristics were obtained. The voltage sweep applied to the probe was delayed so as to be initiated at any desired time during the uniform flow period.

The thin wire Langmuir probes were held in a flat plate wedge model which was mounted so that the probe was aligned with the flow on the nozzle centerline. It was therefore not possible to obtain Langmuir probe data at more than one axial location for a given run. The procedure used was, for example, to perform an experiment with the tip of the probe located at the 23-in. station (in some experiments the 25.5-in. station was used) and simultaneously measure the electron density at the 11.5- and 21.5-in. stations with the 35 and 17 GHz microwave interferometers, respectively. The probe was then moved to the 33-in. location, the 35 GHz interferometer moved to the 21.5-in. location, the 17 GHz interferometer to the 31.5-in. location and the experiment was repeated. This procedure was repeated for the 43-in. location. At the 11.5- and 13-in. locations only the 35 GHz interferometer and the Langmuir probe were utilized. By using this technique, the electron number density was measured independently at the 21.5- and 31.5-in. locations using both microwave interferometers. The resulting electron densities were in good agreement with each other.

3. Discussion of Results

The reaction rate coefficient for the two-body dissociative recombination of NO^+ has been measured in an expanding air plasma for two experimental conditions. At the first of these the gas was expanded from equilibrium reservoir conditions of 6850°K and 22 atm pressure and at the second the reservoir conditions were 7200°K and 25 atm pressure. In order to obtain the rate coefficient, the electron temperatures and number densities were both measured in the expansion.

In the remainder of the paper the experimental results are presented for each of the previously described conditions and the method of data analysis is also described.

3.1 Langmuir-Probe and Microwave Interferometer Measurements

The experimental conditions discussed previously were selected because they represented relatively high-enthalpy expansions and because a detailed study of the nozzle starting process, flow uniformity, and wall boundary-layer growth had been previously conducted[18] for the 7200°K and 25 atm condition. The appropriate time after shock reflection at which uniform nozzle flow could be expected was thus known as was the uniformity of the inviscid nozzle flow. It was then relatively simple to select nozzle locations for which the flow was free molecular with respect to the diameter of the Langmuir probe, making it possible to interpret the probe data within the framework of existing theory.[19] The data reduction procedure is thoroughly discussed in Ref. 17 and will not be repeated here.

The electron density was obtained from the Langmuir probe data, assuming NO^+ to be the dominant positive ion, within the framework of Laframboise's theoretical results.[19] It suffices to note that several authors have found experimentally[20–22] that the number density can be most reliably obtained from that region of the probe characteristic where the net current is essentially equal to the ion current, i.e., where the dimensionless probe potential $\chi_p < -10$;

$$\chi_p = (e/kT_e)(V_p - V_\infty) \tag{2}$$

In Eq. (2), V_p is the voltage applied to the probe and V_∞ is the plasma potential. For $\chi_p < 0$ the slope of the $\ln j_e$ vs V_p curve yields the electron temperature from the relation

$$d \ln j_e / dV_p = e/kT_e \tag{3}$$

where j_e is the electron current density.

The experimentally obtained characteristic in the region $\chi_p < -10$ and Laframboise's theory for $T_i/T_e = 0$ were used to obtain the electron number densities from the Langmuir probe data presented here (see Ref. 17 for detailed discussion). For the values of R_p/λ_D appropriate for these experiments his theoretical results for $T_i/T_e = 1.0$ are nearly equal to those for $T_i/T_e = 0$. Consequently, use of the $T_i/T_e = 0$ results for the present experiments has a negligible effect on the inferred electron densities.

3.2 Technique Used to Determine Rate Coefficient from Experimental Data

The nozzle flow computer program used to infer a value for the reaction rate coefficient from the electron temperature data and number density data has been described in detail in Ref. 23. This computer program can generate 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. The thermodynamic and chemical kinetic data used for the neutral

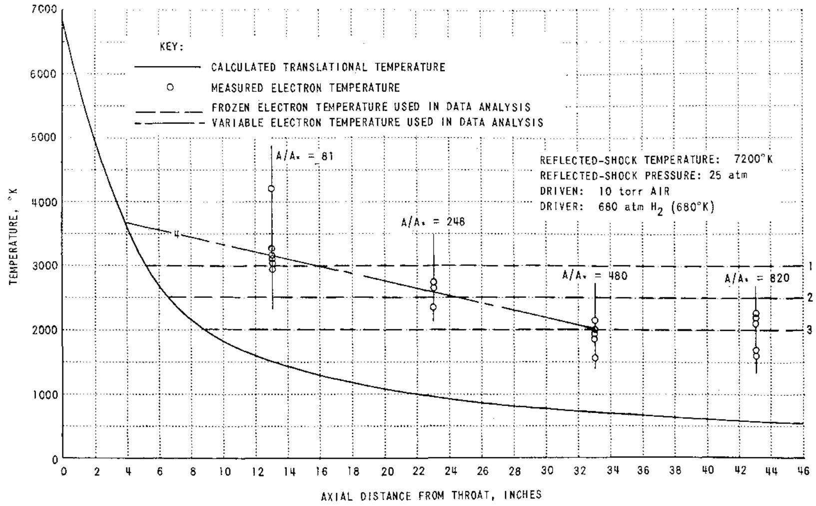

Fig. 1 Measured electron temperature in expanding air plasma.

air species in the present calculations are given in Ref. 23. The chemical reactions include the dissociation of N_2, O_2, and NO, and the bimolecular NO exchange reactions. For the conditions of the present experiments NO^+ is the dominant ion in air and the dissociative-recombination path is the major deionization path. Hence this reaction was the only one involving the charged species included in the calculations.

In applying the nozzle flow program to the flow of weakly ionized gases, in the absence of applied fields, 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 constant. For this reason the computer program was modified to evaluate the electron recombination rate as a function of the electron temperature.

Previous experimenters[21,24] have also observed electron temperatures greater than the heavy-particle temperature in high-temperature nozzle expansions. Several authors[25–29] have discussed the possible mechanisms for electron heating in such flows and have formulated a general electron energy conservation equation. Since the solution of this equation is quite difficult, 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. In the nozzle flow calculations, the electron recombination rate coefficient was evaluated at the electron temperature whereas the remaining species production rates were evaluated at the heavy particle temperature.

The electron temperature histories used in reducing the data are given in the ensuing section. At the point where the electron and heavy particle temperature begin to differ, the ionization rate is small but not negligible compared to the recombination rate. In the nozzle flow calculations, the ionization rate coefficient was computed from the ratio of the recombination rate coefficient to the equilibrium constant, evaluated at the heavy particle temperature.

In the nozzle flow calculations discussed below, the prescribed nozzle cross-sectional area was that of the inviscid core. Previous measurements[18] of the nozzle wall boundary-layer growth were used to determine the appropriate displacement thickness history so that the inviscid area ratio could be calculated from the known geometry. This area ratio distribution was then used together with the computer solution to obtain the number density as a function of distance along the nozzle centerline. For the reservoir conditions of the present study, the boundary-layer correction was relatively small.

3.3 Determination of Rate Coefficient

As previously noted, the rate coefficient for the deionization of NO^+ was measured for two separate reflected-shock conditions, 6850°K at 22 atm pressure and 7200°K at 25 atm pressure, respectively. The latter condition was investigated in considerably more detail than was the former and therefore will be discussed first in the following pages.

3.3.1 Experiments at 7200°K and 25 atm pressure

Figure 1 presents electron temperature measurements obtained using the thin wire Langmuir probes at 13, 23, 33, and 43 in. ($A/A_* = 81$, 248, 480, and 820, respectively) from the nozzle throat. The calculated heavy particle translational temperature is also presented for comparison purposes and shown to be significantly lower than the electron temperature. The electron temperature is shown to decrease with increasing axial distance until a relatively constant value is reached at the 33- and 43-in. locations. The electron temperature distributions used in the data correlation are shown in Fig. 1. For curves 1, 2, and 3 the electron temperature is in equilibrium with the heavy particle translational temperature until a value is reached that is representative of the experimentally determined electron temperatures. For this experimental condition, the electron temperatures selected were 3000, 2500, and 2000°K as illustrated. Curve 4 represents an electron temperature history that also approximates the data but allows for a more gradual departure from the translational temperature.

The electron temperature measurements are seen to scatter approximately ±10% about an average value. This scatter in the electron temperature measurements is typical of all the results presented, and is in part due to the lack of complete reproducibility of the shock-tube conditions and in part to the accuracy with which the slope of the current-voltage characteristic can be determined in the electron retarding region. The scatter in the corresponding electron density measurements presented in Fig. 2 was approximately ±15% about an average value which was typical of these experiments, performed at an incident shock Mach number of 11.6 ± 0.05. The corresponding variation in reservoir electron density was ±9%, which accounts for a large part of the observed data scatter. The remaining scatter is due to the accuracy with which the data records can be read.

The electron density measurements obtained with the Langmuir probes and the microwave interferometers are presented in Fig. 2 as a function of inviscid area ratio. The

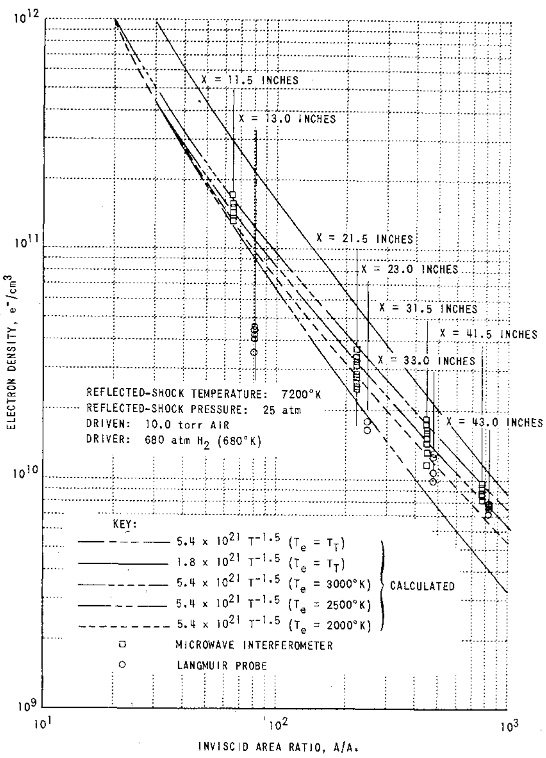

Fig. 2 Measured electron density in expanding air plasma.

probe measurements obtained at 13 and 23 in. are shown to be lower than the interferometer measurements. This result was anticipated because of the relatively small value of the ion-neutral and neutral-neutral mean free paths at these locations. These small mean free paths have a particularly important influence on the electron density measurements because the ion current region of the probe characteristic was used to obtain the magnitude of the number density. At the 33- and 43-in. locations, the number densities obtained with the two measuring techniques are in good agreement.

In using the free molecular theory to interpret the probe data, the magnitude of the various mean free paths relative to the probe diameter is an important consideration. For both of the experimental conditions discussed here, the ion-ion, electron-electron, electron-ion, and electron-neutral mean free paths were all more than one order of magnitude greater than the probe diameter at all measuring stations. However, the neutral-neutral and the ion-neutral mean free paths at the 13-in. station were slightly less than the probe diameter but at 33 in. and beyond they were significantly greater than the probe diameter. It is therefore probable that at the 13-in. location the current collection by the probe was inhibited by the relatively small ion-neutral mean free path. However, since all of the electron mean free paths were large, the electron temperatures deduced from the probe characteristic at this nozzle location are reasonable because of the insensitivity of electron collection to the magnitude of the neutral-neutral or the ion-neutral mean free paths.

The manner in which the electron temperature history influences the electron density distribution for a nonequilibrium expansion is illustrated by Fig. 2 on which the results of five separate calculations are plotted. The temperature coefficient of the NO^+ recombination rate coefficient was selected to be -1.5 on the basis of previous experimental and theoretical work.[2,16] The rate coefficient suggested by Lin and Teare[2] ($1.8 \times 10^{21}\ T_e^{-1.5}$ cm³/mole sec) was evaluated at the heavy particle translational temperature and found to overestimate the measured number densities. Obviously, if the measured electron temperature were used in this calculation, then the predicted number density at a given area ratio would be increased, thus amplifying the disagreement. When the measured electron temperature is utilized and the rate coefficient of Ref. 1 is increased from $1.8 \times 10^{21}T_e^{-1.5}$ to $5.4 \times 10^{21}T_e^{-1.5}$, then it is possible to correlate the measured electron density data as shown on Fig. 2. The three curves obtained with the rate coefficient evaluated at the electron temperature correspond to curves 1, 2, and 3 of Fig. 1. The result obtained using a rate coefficient of $5.4 \times 10^{21}T_e^{-1.5}$, evaluated at the heavy particle temperature, is shown for comparison.

It is also important to evaluate the influence of variations in the pretemperature coefficient on the data correlation. Figure 3 presents the results obtained by evaluating the rate coefficient at an electron temperature of 2500°K and pretemperature factors of $(3 \pm 0.5)\ 1.8 \times 10^{21}$ cm³/mole sec. This variation in the pretemperature factor predicts the number density history within the scatter of the experimental data. Thus for these electron temperature distributions the rate coefficient for the two-body dissociative recombination of NO^+ is given by $k_r = (5.4 \pm 0.9) \times 10^{21}\ T_e^{-1.5}$ cm³/mole sec.

The sensitivity of the predicted number density to the assumed form of the electron-temperature variation has also been investigated.‡ The electron temperature history denoted as curve 4 on Fig. 1 was also used to calculate the number density variation along the nozzle. As shown on Fig. 4, values of the recombination rate coefficient between $5.4 \times 10^{21}\ T_e^{-1.5}$ and $9.0 \times 10^{21}\ T_e^{-1.5}$ fit the data in this case. These values of the rate coefficient do not differ appreciably from those obtained using the electron temperature histories given by curves 1, 2, and 3 in Fig. 1. Hence, a value of the rate coefficient of $(6.7 \pm 2.3) \times 10^{21}T_e^{-1.5}$ is suggested on the basis of these experiments. The uncertainty given for the rate coefficient reflects the accuracy to which the electron temperature could be determined, the influence of the different elec-

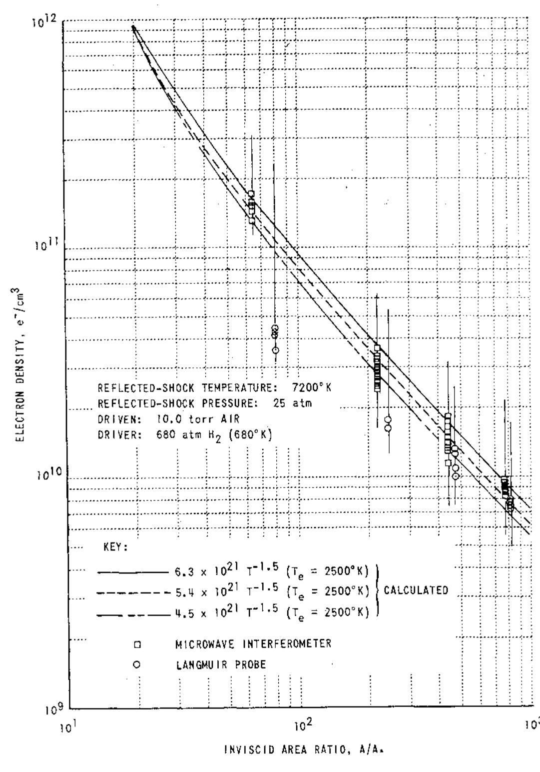

Fig. 3 Influence of pretemperature factor on electron density distribution.

‡ In Ref. 30 only curves 1, 2, and 3 on Fig. 1 were used for the electron temperature and the reported value of k_r was $(5.4 \pm 0.9) \times 10^{21}T_e^{-1.5}$. Since then additional data were obtained at the 13-in. station and are included here. These additional data permit a better determination of the electron temperature at lower area ratios.

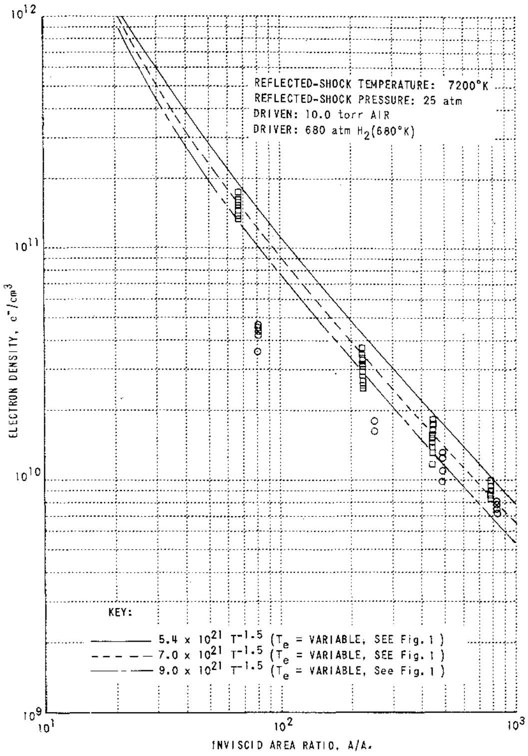

Fig. 4 Influence of variable electron temperature on data correlation.

tron temperature distributions, and the scatter in the number density data.

The electron concentration distributions calculated for the nonequilibrium expansion from this reservoir condition are shown on Fig. 5. This plot illustrates that the electron concentration has decreased by more than two orders of magnitude from the throat value prior to the first measuring station. Between the first and last stations the electron concentration decreases by about 50%. Notice that the electron concentration is independent of the local gas density and therefore the electron depletion is due entirely to recombination.

3.3.2 Experiments at 6850°K and 22 atm pressure

The Langmuir probe and microwave interferometer measurements reported in Sec. 3.3.1 were repeated in considerably less detail for a reservoir condition of 6850°K at 22 atm pressure. Electron temperature measurements were obtained at 15.5 and 25.5 in. from the throat and again found to be considerably greater than the translational temperature.

The measured electron densities are compared in Fig. 6 with number density distributions calculated using several different rate coefficients for the recombination of NO^+. The electron number densities obtained from the Langmuir probe at 25.5 in. from the throat and the microwave interferometer at 21.5 in. are shown to be in good agreement. However, the Langmuir probe number densities at 15.5 in. are about 35 to 40% below the trend of the microwave interferometer and downstream Langmuir probe data due to collisional effects as discussed in Sec. 3.3.1. Since less data were obtained for this condition, electron temperature histories similar to curves 1, 2, and 3 on Fig. 1 were used to obtain the predicted number densities. The final levels chosen for the electron temperature were 2200 ± 500°K on the basis of the measured values. The pretemperature factor was again varied through the range $(5.4 \pm 0.9)10^{21}$ and the predicted electron density histories bounded all of the measurements with the exception of the upstream Langmuir probe data. It was therefore concluded that the NO^+ recombination rate coefficient that correlated the electron density obtained at 7200°K and 25

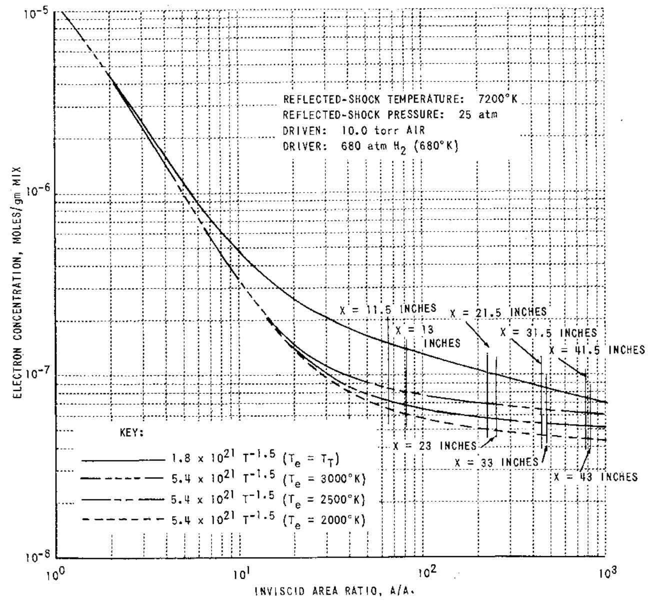

Fig. 5 Calculated electron concentrations.

pressure also correlates the data for this experimental condition.

4. Summary

The $NO^+ + e^-$ recombination rate coefficient was measured in an air plasma that had expanded from a reservoir temperature of approximately 7000°K and reservoir pressure of approximately 25 atm. The electron temperature at the final measuring station in the nozzle was approximately 2000°K. These results are compared with previous measurements and the prediction of Ref. 16 on Fig. 7. Whenever the electron temperature was reported, it was used in compiling the data plot. However, in many cases the electron temperature was unknown and thus it was necessary to use the inferred gas translational temperature.

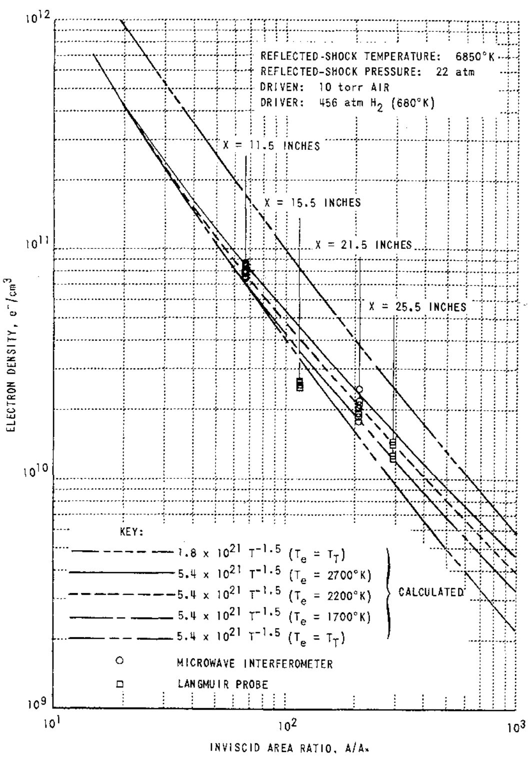

Fig. 6 Comparison of measured and calculated electron density in nozzle flow.

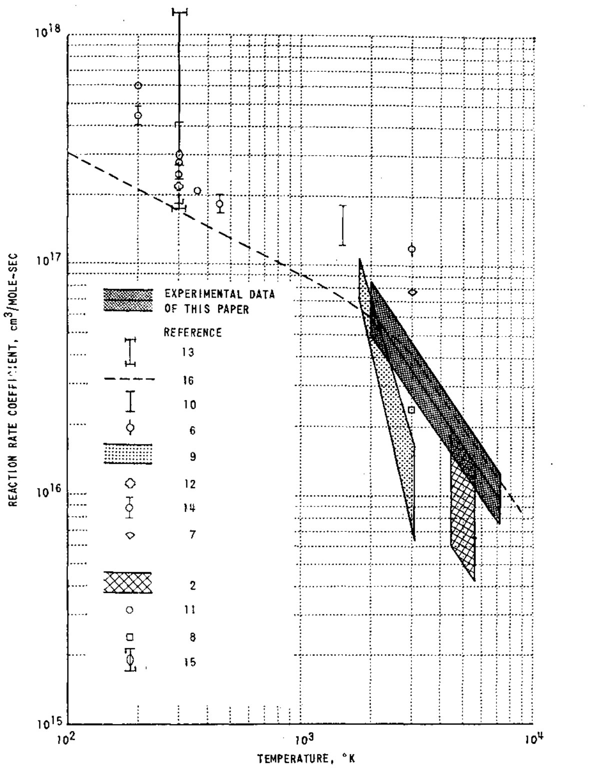

Fig. 7 Reaction rate coefficient data for the reaction $NO^+ + e \xrightarrow[k_r]{} N + O$.

If the rate coefficient obtained in this study were extrapolated to temperatures below 500°K the resulting values would be in disagreement with existing low-temperature data. However, this result is as expected on the basis of the recent theoretical work of Hansen[16] in which it is demonstrated that the temperature dependence varies from $T^{-1.5}$ to $T^{-0.5}$ as the temperature decreases.

The measurements presented in this paper are the first obtained in a shock-tunnel environment for which both the electron temperature and number density were measured. The reaction rate coefficient for the two-body dissociative recombination of NO^+ is given by

$$k_r = (6.7 \pm 2.3) \times 10^{21} \, T_e^{-1.5} \text{ cm}^3/\text{mole sec}$$

for a temperature range of approximately 2000–7000°K.

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