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TECHNICAL REPORT

MEASUREMENT OF $NO^{+} + e^{-}$ DISSOCIATIVE RECOMBINATION IN EXPANDING AIR FLOWS

By: Michael G. Dunn and John A. Lordi

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Prepared For:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

TECHNICAL REPORT
CONTRACT NO. NAS-5-9978
SEPTEMBER 1968

CORNELL AERONAUTICAL LABORATORY, INC.
OF CORNELL UNIVERSITY, BUFFALO, N. Y. 14221

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FOREWORD

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ABSTRACT

The dissociative-recombination rate coefficient for the reaction $NO^+ + e^- \xrightarrow[k_r]{} N + O$ has been measured in the inviscid nozzle flow of a short-duration reflected-shock tunnel and found to be given by $k_r = (5.4 \pm 0.9) \times 10^{21}\ T_e^{-1.5}\ cm^3/mole\ sec$ for an electron temperature range of approximately 2000°K to 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 distributions of free electrons present in high-temperature air plasmas is

$$N + O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} NO^+ + e^- \tag{1}$$

The forward and reverse rate coefficients of this reaction are related to the local plasma conditions through the temperature. Since the forward rate coefficient of Eq. (1) depends on the heavy-particle temperature while the recombination rate coefficient depends also upon the electron temperature, it is important to know the variation of the latter rate coefficient with the electron temperature. A body of experimental data, including the present data, suggests that for the flow about an entry body, the electron temperature will not be in equilibrium with the heavy-particle temperature.

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 $NO^+ + e^- \xrightarrow[k_r]{} N + O$ in a nonequilibrium expansion of air. The rate-coefficient measurements were made in the electron-temperature range of approximately 2000°K to 7000°K by fitting calculated and measured values of electron number density. The experiments were performed in the inviscid flow of the 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°K to 5100°K. Lin and Teare[2] later used these data to infer the value of the reverse data 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 $k_r = 1.8 \times 10^{21}\ T^{-1.5}\ cm^3/mole\ sec$. 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 to 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 result in some difficulty in the data interpretation. With these reservations in mind, several investigators[11-17] have measured the recombination rate coefficient for NO^+ in an afterglow plasma.

The temperature dependence of the reverse rate coefficient has recently been discussed by Hansen[18] who argued that the temperature dependence for the reaction $NO^+ + e^- \longrightarrow N + O$ varies from $T^{-1/2}$ to $T^{-1.5}$ as the temperature increases. It is demonstrated that if constant transition probability at the N + O and NO^+ potential crossing is assumed then the above 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. In the following sections, the shock tunnel and the type of instrumentation utilized to make the above measurements are briefly described.

2.1 Shock-Tunnel Design and Operation

The shock tube utilized in this work (see Fig. 1) has a 3.0-inch I.D. driver tube which is 9.0-ft. long. Provision is included for heating the driver gas (hydrogen in these experiments) to a maximum temperature of 680°K. The driven tube is 98-ft. long with an inside diameter of 6 inches. Flow is initiated by rupturing the double diaphragms which initially separate the driver and driven gases. The last two feet of the driven tube comprise an instrumentation section which has several observation ports within 5-3/4 inches from the end wall.

The shock-wave velocity is measured over the last 18.6 feet of driven tube using thin-film temperature gauges which are mounted flush with the wall. The first four intervals are approximately 4 feet each and the last interval is approximately 2.6 feet. Electronic counters, started and stopped by signals from the thin-film gauges, are used to measure the elapsed time for shock-wave passage between stations. The last thin-film gauge is located 5-3/4 inches from the driven-tube end wall.

The entrance to the nozzle throat is less than one throat diameter in length. Downstream of the throat the passage diverges rather slowly and becomes tangent to the nozzle wall at a location 2-3/4 inches downstream. A 0.002-inch-thick mylar diaphragm is used to separate the driven tube from the nozzle, thus permitting evacuation of the nozzle while the driven tube is loaded.

The conical nozzle used in these experiments has a half-angle of 13° and is constructed of Fiberglas. Instrumentation ports are located at axial intervals of 10.0 inches with the first set at 11.5 inches from the throat. These ports are sufficiently large to contain the microwave-interferometer horns. The nozzle is initially evacuated to a pressure of approximately 10^{-3} torr and the leak rate is such that at the time the driven-tube diaphragm ruptures, the pressure in the nozzle is in the range 10^{-3} to 10^{-2} torr.

2.2 Instrumentation

Measurements of the radiation intensity in the spectral range 0.35 to 1.13 microns were made in the reflected-shock region looking normal to the tube axis. These measurements were taken at 3-1/4 and 3/4 inches from the end wall using silicon photodiodes (EGG model SD-100).

The reflected-shock pressure was measured using shock-mounted Kistler 603-A transducers. Pressure measurements were made at the sidewall stations located 3/4 and 3-1/4 inches from the end wall.

The electron number densities were measured in the nozzle at 11.5, 21.5, 31.5, and 41.5 inches 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. Crystal detectors having a rise time much less than the available test time were used to make these measurements.

A thin-wire Langmuir probe, aligned so that the flow velocity was parallel to the cylindrical axis, was used on the centerline of the nozzle to measure the inviscid-flow electron density and electron temperature. A detailed discussion of the development of these probes for measurement of electron temperatures and number density in shock-tunnel flows is presented in Ref. 19. The probes were constructed by surrounding 0.004-inch tungsten wires with a quartz envelope, leaving a nominal 0.200-inch or 0.400-inch length of bare wire exposed (ℓ/d of 50 or 100). The quartz was fused to the wire at their junction. Immediately prior to each run the probe was ultrasonically cleaned in a sodium-nitrite solution to remove the tungsten oxide and placed in the nozzle which was then evacuated to approximately 10^{-3} torr. A probe was used for only a single experiment and then discarded.

The voltage applied to the probe was swept through voltage excursions as large as -10 to +10 volts, in a period of time significantly less than the duration of uniform flow but long enough to avoid electronic transient effects. However, a voltage sweep of 20 volts was seldom necessary to obtain the probe characteristic. 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.

Radiation-intensity measurements were made in the nozzle at 11.5, 21.5, and 31.5 inches from the throat using RCA 1P28 photomultiplier tubes. These measurements were used to monitor the qualitative behavior of the nozzle starting process and to ascertain the duration and uniformity of the test flow.

2.3 Experimental Procedure

The thin-wire Langmuir probes discussed in Sec. 2.2 were held in a flat plate-wedge model which was then 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-inch station (in some experiments the 25.5-inch station was used) and simultaneously measure the electron density at the 11.5- and 21.5-inch stations with the 35 and 17 GHz microwave interferometers, respectively. The probe was then moved to the 33-inch location, the 35 GHz interferometer moved to the 21.5-inch location, the 17 GHz interferometer to the 31.5-inch location and the experiment was repeated. The above procedure was repeated for the 43-inch location. At the 11.5- and 13-inch 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-inch 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 above conditions and the method of data analysis is described.

3.1 Langmuir-Probe and Microwave-Interferometer Measurements

The experimental conditions discussed above 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[20] 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.[21] The data reduction procedure is thoroughly discussed in Ref. 19 and will not be repeated here.

A typical swept-voltage probe characteristic obtained for a reservoir condition of 6850°K and 22 atm pressure is shown in Fig. 2. The oscilloscope sensitivity for the data record of Fig. 2(a) was set so as to emphasize the electron-retarding and electron-current regions of the probe characteristic. The applied probe voltage was simultaneously recorded and is shown as the lower trace in Fig. 2(a). In these experiments the probe voltage was swept from -5 to +2 volts. Figure 2(b) was obtained simultaneously on a different oscilloscope with the sensitivity adjusted so as to emphasize the ion-current region and the location of the floating potential, V_f . Again the applied probe voltage was simultaneously recorded. Figure 2(c) shows the microwave-interferometer data record obtained just upstream of the Langmuir probe in which the upper trace is attenuation and lower trace is phase-shift relative to the incident signal. The time at which the probe voltage sweep was initiated is indicated on the interferometer phase-shift trace. The magnitude of the electron density measured at the interferometer station was 1.8×10^{10} e^-/cm^3 during the uniform flow period.

The probe data shown in Figs. 2(a) and (b) were reduced using an optical comparator. Figure 3 illustrates the reduced probe characteristic for the electron-retarding and electron-current regions. The collected current data in the electron-retarding region are seen to fall on a straight line on the semilogarithmic plot suggesting that the electron velocity distribution was Maxwellian. At the conditions of this experiment, the value of e/kT_e was 6.90 eV^{-1} corresponding to an electron temperature of 1685°K.

The electron density was obtained from the Langmuir-probe data, assuming NO^+ to be the dominant positive ion, within the framework of Laframboise' theoretical results.[21] It suffices to note that several authors have found experimentally[22-24] 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. $\chi_p < -10$ where

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

and V_p is the voltage applied to the probe and V_∞ is the plasma potential. This region of the experimentally obtained characteristic and Laframboise' theory for $T_i/T_e = 0$ were used to obtain the electron number densities from the Langmuir-probe data presented here (see Ref. 19 for detailed discussion). The Langmuir-probe and microwave-interferometer data records obtained for the second experimental condition (reflected-shock temperature of 7200°K at 25 atm) were very similar to those shown on Fig. 2.

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 and number-density data has been described in detail in Ref. 25. 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 air species in the present calculations are given in Ref. 25. 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[23, 26] have also observed electron temperatures greater than the heavy-particle temperature in high-temperature nozzle expansions. Several authors[27-31] 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 involves several unknown inelastic cross sections. 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 while the remaining species production rates were evaluated at the heavy-particle temperature.

For the purposes of computing the electron recombination rate the electron temperature was assumed equal to the heavy-particle translational temperature until a specified point in the expansion. Downstream of this point the electron temperature was assumed to remain at a constant value, the final level being adjusted within the range indicated by the probe measurements. It should also be noted that the forward rate of Eq. (1) is negligible at the point where the electron temperature is assumed to depart from the heavy-particle temperature.

In the nozzle-flow calculations discussed below, the actual variation of the nozzle cross-sectional area with axial distance was used to obtain the electron number density as a function of area ratio. Previous measurements[20] of the nozzle-wall boundary-layer growth were then used to obtain the cross-sectional area of the inviscid core at each nozzle station. This latter 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 and degree of expansion of the present study, the boundary-layer correction was not sufficient to warrant repeating the nozzle-flow calculation specifying the area-ratio variation of the inviscid core.

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 4 presents electron temperature measurements performed using the thin-wire Langmuir probes at 13, 23, 33, and 43 inches ($A/A_* = 81, 248, 480$, 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-inch locations.

The previous section noted that the correlation procedure assumed that the electron temperature was in equilibrium with the heavy-particle translational temperature until a value was reached that was representative of the experimentally determined electron temperatures. For this experimental condition, the electron temperatures selected were 3000, 2500, and 2000°K as illustrated by the dashed lines on Fig. 4.

The electron-temperature measurements are seen to scatter approximately ± 10 percent 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. 5 was approximately ± 15 percent about an average value which was typical of these experiments which were performed at an incident-shock Mach number of $11.6 \pm .05$. The corresponding variation in reservoir electron density was ± 9 percent, 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. 5 as a function of inviscid area ratio. The probe measurements obtained at 13 and 23 inches 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-inch 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-inch station were slightly less than the probe diameter. At the 23- to 25-inch locations these mean free paths were approximately equal to the probe diameter but at 33 inches and beyond they were significantly greater than the probe diameter. It is therefore probable that at the 13-inch 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 influence of electron temperature on the predicted electron-density distribution for a nonequilibrium expansion is illustrated by Fig. 5 on which the results of four 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, 18] The rate coefficient suggested by Lin and Teare[2] ($1.8 \times 10^{21}\ T_e^{-1.5}\ cm^3$/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. If the measured electron temperature is utilized and if 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. 5. In the previous paragraphs it was noted that the three values of electron temperature considered to be representative of the expansion were $2500 \pm 500°K$. This variation in electron temperature is of the same order as the scatter in the number density data.

It is also important to evaluate the influence of variations in the pretemperature coefficient on the data correlation. Figure 6 presents the results obtained by evaluating the rate coefficient at an electron temperature of 2500°K and pretemperature factors of $(3 \pm 0.5)\, 1.8 \times 10^{21}$ cm^3/mole sec. This variation in the pretemperature factor predicts the number density history with the scatter of the experimental data. Thus for this experimental condition the rate coefficient for the two-body dissociative recombination of NO^+ is given by $k_r = (5.4 \pm 0.9) \times 10^{21} T_e^{-1.5}$ cm^3/mole sec.

The electron-concentration distributions calculated for the nonequilibrium expansion from this reservoir condition are shown on Fig. 7. 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 percent. 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 inches from the throat and again found to be considerably greater than the translational temperature.

The measured electron densities are compared in Fig. 8 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 inches from the throat and the microwave interferometer at 21.5 inches are shown to be in good agreement. However, the Langmuir-probe number densities at 15.5 inches are about 35 to 40 percent below the trend of the microwave-interferometer and downstream Langmuir-probe data due to collisional effects as discussed in Sec. 3.1.1. With the exception of these measurements, the experimental data are well correlated by a rate coefficient approximately three times that of Ref. 2.

The rate coefficient was evaluated at an electron temperature of 2200 ± 500°K on the basis of the measured electron temperatures. 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 data obtained at 7200°K and 25 atm 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. 18 on Fig. 9. 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.

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[18] in which it is demonstrated that the temperature dependence varies from $T^{-1.5}$ to $T^{-.5}$ 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 $k_r = (5.4 \pm 0.9) \times 10^{21}\ T_e^{-1.5}\ cm^3/\text{mole sec}$ for a temperature range of approximately 2000 to 7000°K.

REFERENCES

1. Lin, S. C., "Ionization Phenomenon of Shock Waves in Oxygen-Nitrogen Mixtures," Research Rept. 33, June 1958, Avco Everett Research Lab., Everett, Mass.

2. Lin, S. C., and Teare, J. D., "Rate of Ionization behind Shock Waves in Air II. Theoretical Interpretations," The Physics of Fluids, Vol. 6, March 1963, pp. 355-375.

3. Frohn, A., and de Boer, P. C. T., "Ion Density Profiles behind Shock Waves in Air," AIAA Journal, Vol. 5, Feb. 1967, pp. 261-264.

4. Thompson, W. P., "Ionization and NO Production in Air at 3000 - 5000°K," Bulletin of the American Physical Society, Vol. 10, Sept. 1965, p. 727.

5. Stein, R. P., Scheibe, M., and Gunton, R. C., "Volume Recombination Coefficient of Electrons with NO^+ Ions in Shock Heated Air," Paper 64-57, 1964, AIAA.

6. Laurmann, J. A., "Non-Equilibrium Effects in Slightly Ionized Gases," Proceedings of the 5th U.S. Navy Symposium on Aeroballistics, Oct. 1961.

7. Syverson, M. W., Stein, R. P., Shaw, T. M., Scheibe, M., and Gunton, R. C., "Electron-NO^+ Recombination in Shock-Heated Air," Paper presented at the American Physical Society Meeting, Nov. 20-22, 1961, Berkeley, Calif.; Bulletin of the American Physical Society, Vol. 7, April 1962, p. 378.

8. Stein, R. P., Scheibe, M., Syverson, M. W., Shaw, T. M., and Gunton, R. C., "Recombination Coefficient of Electrons with NO^+ Ions in Shock-Heated Air," The Physics of Fluids, Vol. 7, Oct. 1964, p. 1641; also LMSC Rept. 2-60-63-3, Dec. 1963.

9. Eckerman, J., and Stern, R. G., "Electron-Ion Recombination in High Temperature Air," Paper 63-445, 1963, AIAA.

10. Eschenroeder, A. Q., and Chen, T., "Near-Wake Ionization behind a Sphere in Hypersonic Flight I. Reaction Kinetics," Tech. Rept. TR 65-01H, Sept. 1965, General Motors Defense Research Labs., Goleta, Calif.

11. Biondi, M. A., "Electron-Ion and Ion-Ion Recombination," APP No. 4, Tech. Rept. No. 2, Sept. 1963, Atomic and Plasma Physics Lab., Physics Dept., Univ. of Pittsburgh, Pittsburgh, Pa.

12. Gunton, R. C., and Shaw, T. M., "Electron-Ion Recombination in Nitric Oxide in the Temperature Range 196 to 358°K," The Physical Review, Vol. 140, No. 3A, Nov. 1965, pp. A756-763; see also "Ambipolar Diffusion and Electron Attachment in Nitric Oxide in the Temperature Range 196 to 358°K," The Physical Review, Vol. 140, Nov. 1965, pp. A748-755.

13. Gunton, R. C., and Inn, E. C. Y., "Rates of Electron Removal by Recombination, Attachment and Ambipolar Diffusion in Nitric Oxide Plasmas," The Journal of Chemical Physics, Vol. 35, Nov. 1961, p. 1896.

14. van Lint, V. A. J., Parez, J., Wyatt, M. E., and Nichols, D. K., "Recombination and Attachment in Ionized Gases," RTD TDR-63-3076, Dec. 1963.

15. Doering, J. P. and Mahan, B. H., "Photoionization of Nitric Oxide," The Journal of Chemical Physics, Vol. 36, Feb. 1962, pp. 669-674.

16. Bortner, M. H., "An Experimental Study of the Deionization of NO^+," Scientific Rept. No. 1, April 1965, General Electric Missile and Space Division.

17. Weller, C. S., and Biondi, M. A., "Temperature Dependence of Recombination of NO^+ Ions and Electrons," Bulletin of the American Physical Society, Feb. 1968, p. 199.

18. Hansen, C. F., "Temperature Dependence of the $NO^+ + e^-$ Dissociative-Recombination-Rate Coefficient," The Physics of Fluids, April 1968, pp. 904-906.

19. Dunn, M. G., and Lordi, J. A., "Development of Free-Molecular Langmuir Probes for Measurement of Electron Temperature and Number Density in Shock-Tunnel Flows," submitted to the AIAA Journal for publication.

20. Dunn, M. G., "Experimental Study of the Starting Process, Flow Duration, and Nozzle Boundary Layer in a High Enthalpy Shock Tunnel," Rept. No. AI-2187-A-6, Nov. 1967, Cornell Aeronautical Lab., Buffalo, New York.

21. Laframboise, J. G., "Theory of Spherical and Cylindrical Langmuir Probes in a Collisionless, Maxwellian Plasma at Rest," UTIAS Rept. No. 100, March 1966, Institute for Aerospace Studies, Univ. of Toronto, Toronto, Canada.

22. Graf, K. A., and de Leeuw, J. H., "Comparison of Langmuir Probe and Microwave Diagnostic Techniques," Journal of Applied Physics, Vol. 38, Oct. 1967, pp. 4466-4472.

23. Sonin, A. A., "Free-Molecule Langmuir Probe and Its Use in Flow-field Studies," AIAA Journal, Vol. 4, Sept. 1966, pp. 1588-1596.

24. Sonin, A. A., "The Behavior of Free Molecule Cylindrical Langmuir Probes in Supersonic Flows, and Their Application to the Study of the Blunt Body Stagnation Layer," UTIAS Rept. No. 109, Aug. 1965, Institute for Aerospace Studies, Univ. of Toronto, Toronto, Canada.

25. Lordi, J. A., Mates, R. E., and Moselle, J. R., "Computer Program for the Numerical Solution of Nonequilibrium Expansions of Reacting Gas Mixtures," Rept. AD-1689-A-6, June 1965, Cornell Aeronautical Lab., Buffalo, New York.

26. Talbot, L., Chou, Y. S., and Robben, F., "Expansion of a Partially-Ionized Gas through a Supersonic Nozzle," Rept. No. AS-65-14, Aug. 1965, Univ. of Calif., Berkeley, Calif.

27. Hurle, I. R., and Russo, A. L., "Spectrum-Line Reversal Measurements of Free-Electron and Coupled N_2 Vibrational Temperature in Expansion Flows," The Journal of Chemical Physics, Vol. 43, 1965, pp. 4434-4443.

28. Appleton, J. P., and Bray, K. N. C., "The Conservation Equations for a Nonequilibrium Plasma," The Journal of Fluid Mechanics, Vol. 20, 1964, pp. 659-672.

29. Bray, K. N. C., and Pratt, N. H., "Effects of Certain Energy Transfer Process on Population Distributions in Expanding Gas Flows," AGARD Conference on Recent Advances in Aerothermochemistry, Vol. 1, 1967, pp. 59-110.

30. Hurle, I. R., "On the Thermal Energy Transfer between Free Electrons and Molecular Vibration," The Journal of Chemical Physics, Vol. 41, 1964, pp. 3592-3603.

31. Hurle, I. R., Russo, A. L., and Hall, J. G., "Spectroscopic Studies of Vibrational Nonequilibrium in Supersonic Nozzle Flows," The Journal of Chemical Physics, Vol. 40, 1964, p. 2076.

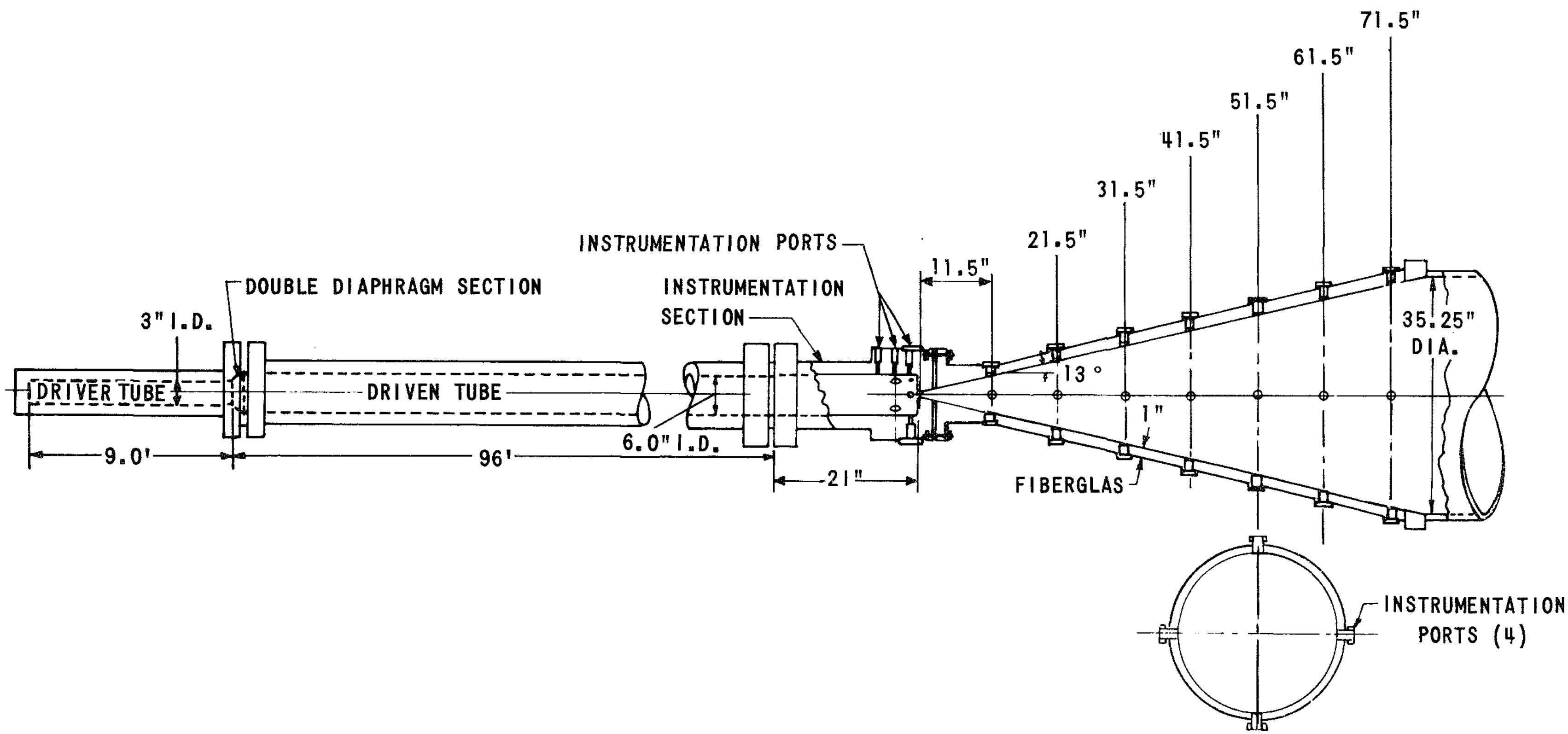
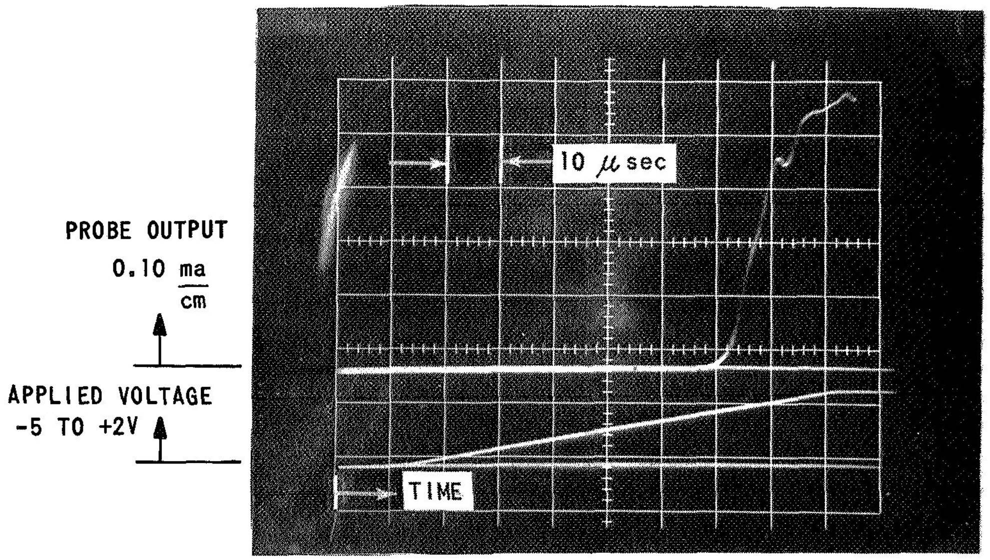


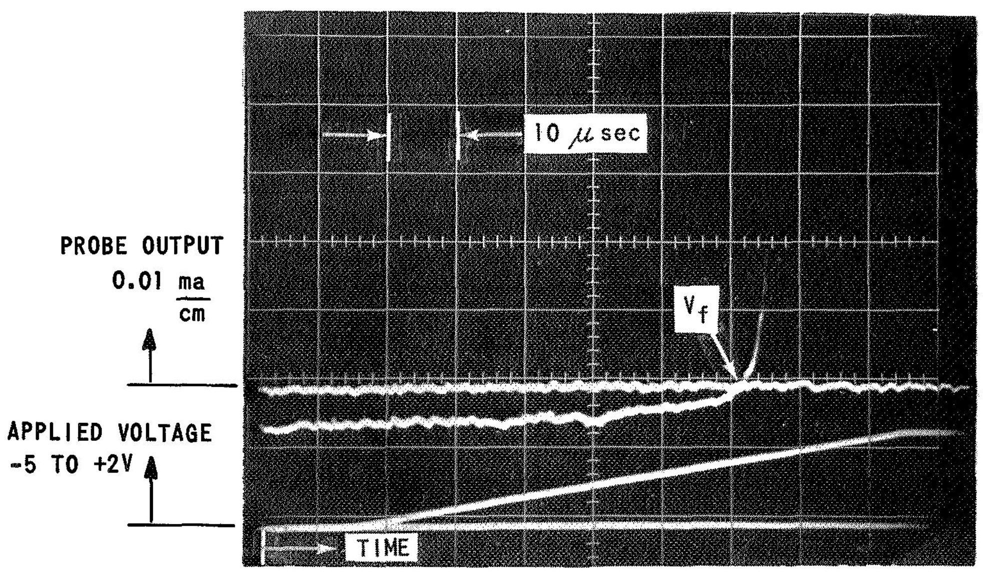
Figure I SCHEMATIC OF EXPERIMENTAL APPARATUS

REFLECTED-SHOCK PRESSURE: 22 atm
REFLECTED-SHOCK TEMPERATURE: 6850°K
DRIVEN: 10 torr AIR

NOTE: LANGMUIR PROBE LOCATED AT 25.5 INCHES FROM NOZZLE THROAT AND MICROWAVE INTERFEROMETER LOCATED AT 21.5 INCHES FROM THROAT.

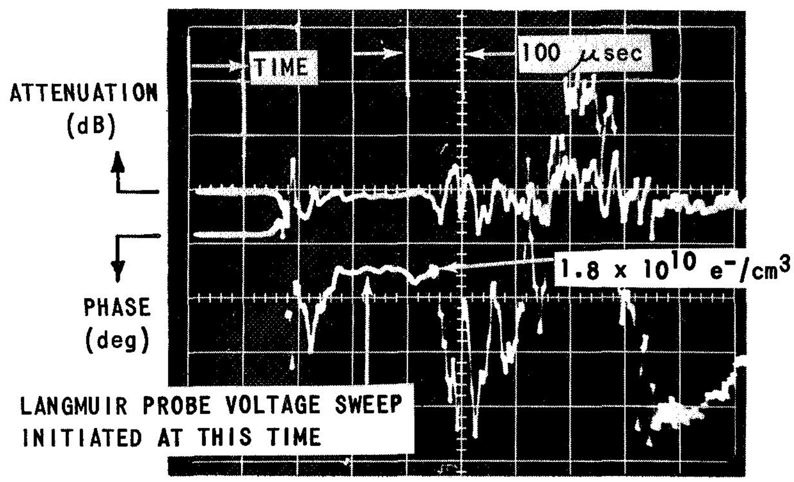


(a) ELECTRON-RETARDING AND ELECTRON-CURRENT REGIONS



(b) ION-CURRENT REGION

Figure 2 TYPICAL PROBE CHARACTERISTIC AND MICROWAVE-INTERFEROMETER DATA IN AN AIR PLASMA



(c) 17 GHz μ-WAVE INTERFEROMETER DATA

Figure 2 (Continued) TYPICAL PROBE CHARACTERISTIC AND MICROWAVE-INTERFEROMETER DATA IN AN AIR PLASMA

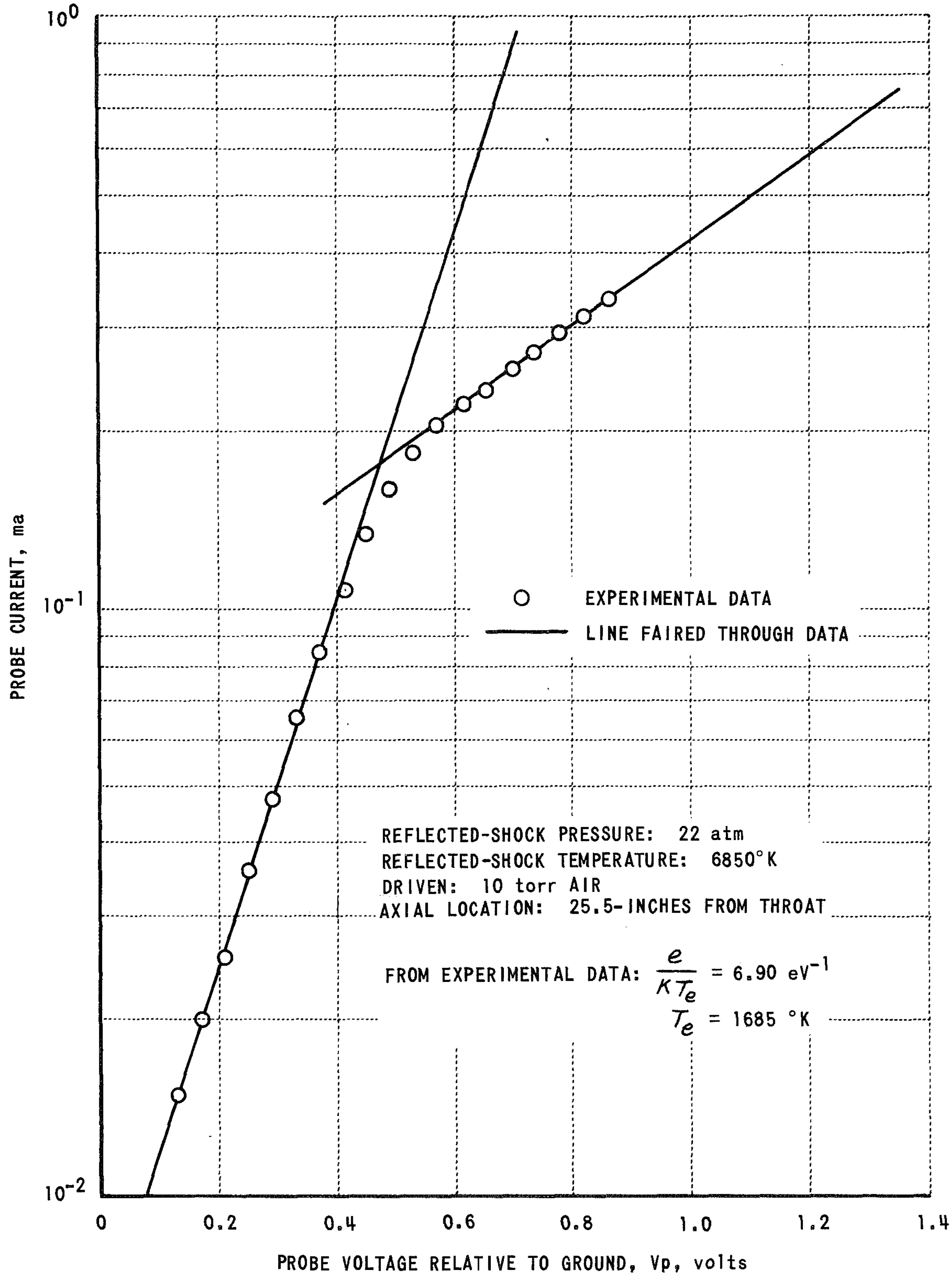


Figure 3 ELECTRON-RETARDING AND ELECTRON-CURRENT REGIONS OF EXPERIMENTAL PROBE CHARACTERISTIC IN AIR

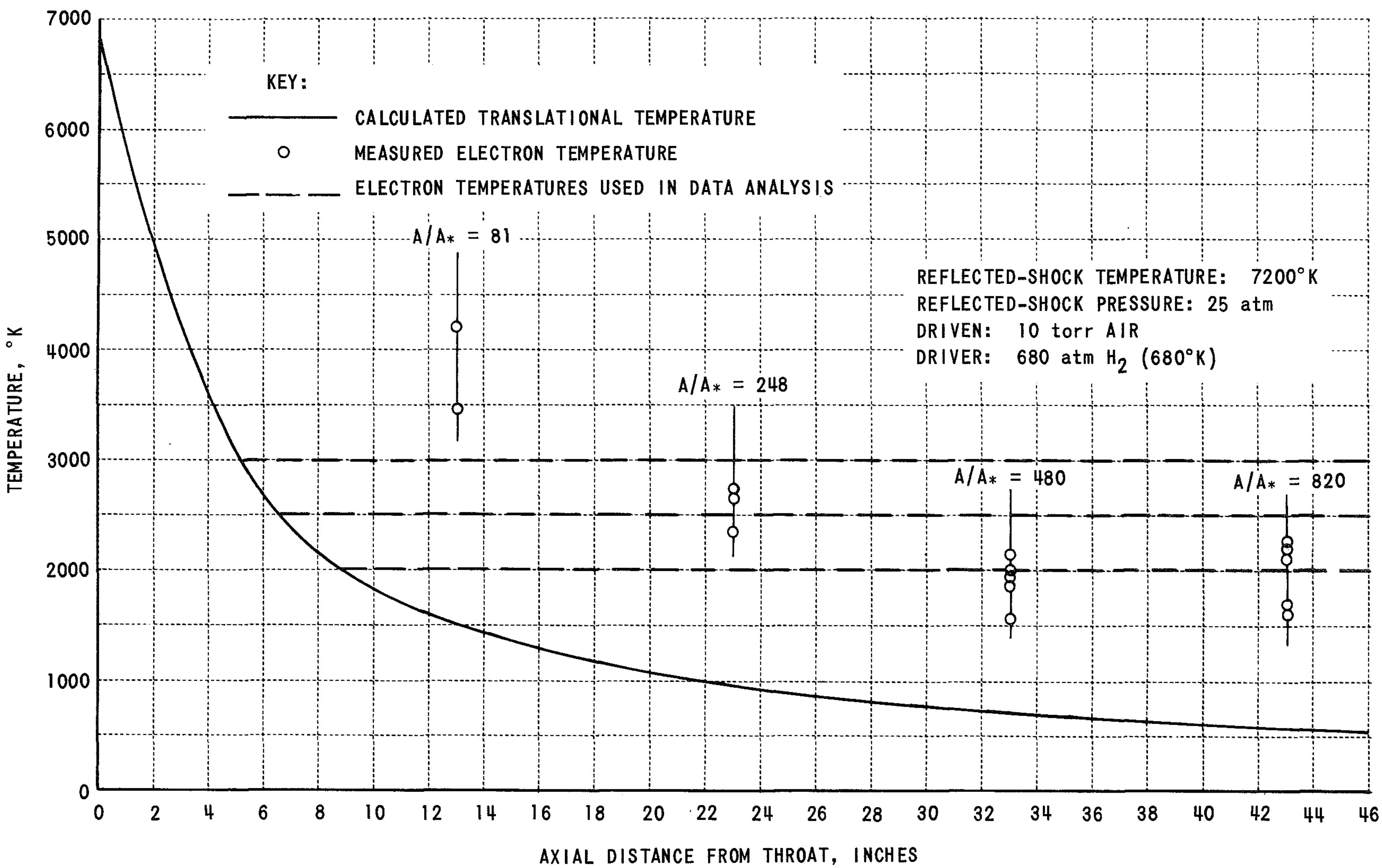


Figure 4 MEASURED ELECTRON TEMPERATURE IN EXPANDING AIR PLASMA

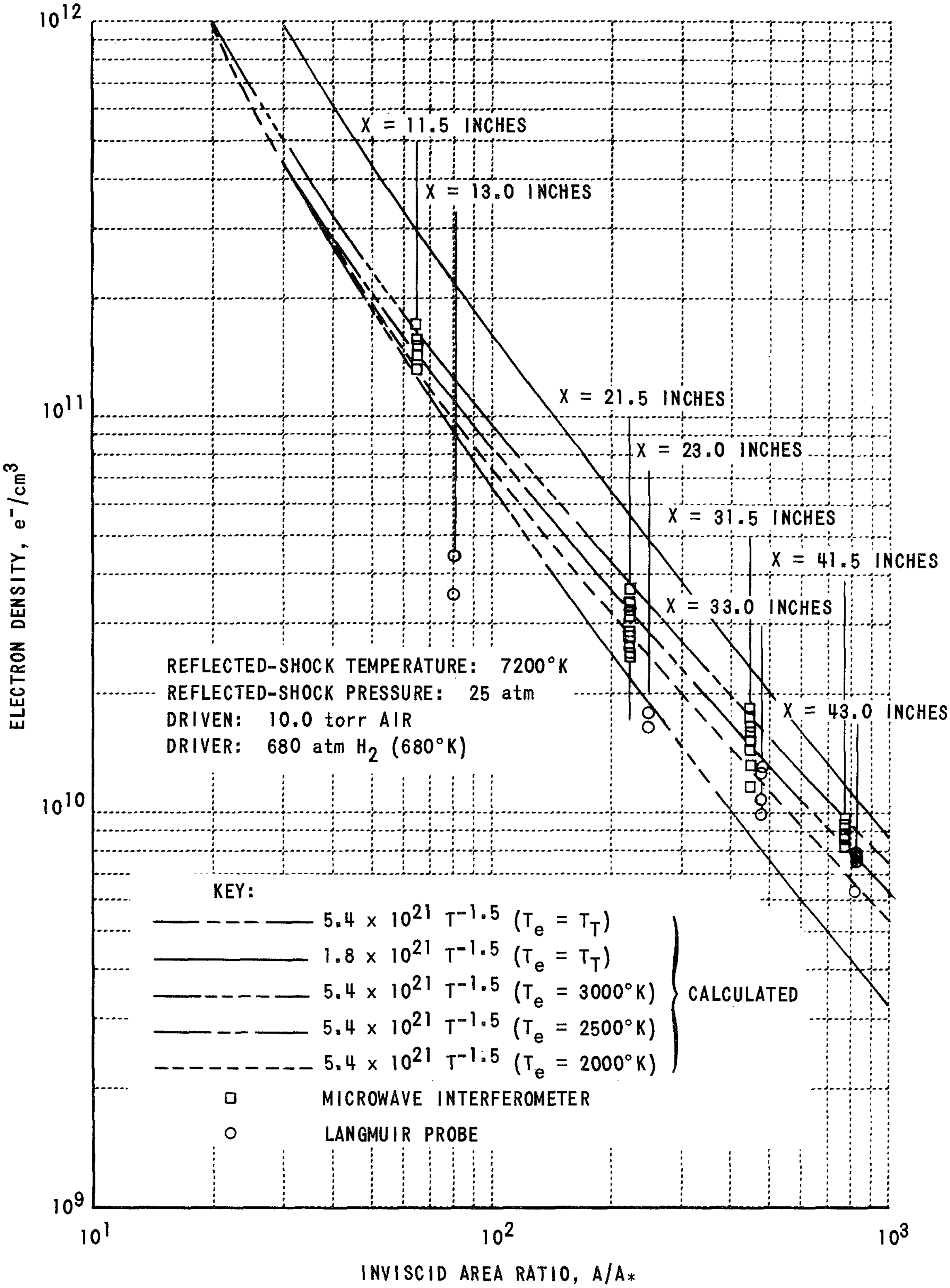


Figure 5 MEASURED ELECTRON DENSITY IN EXPANDING AIR PLASMA

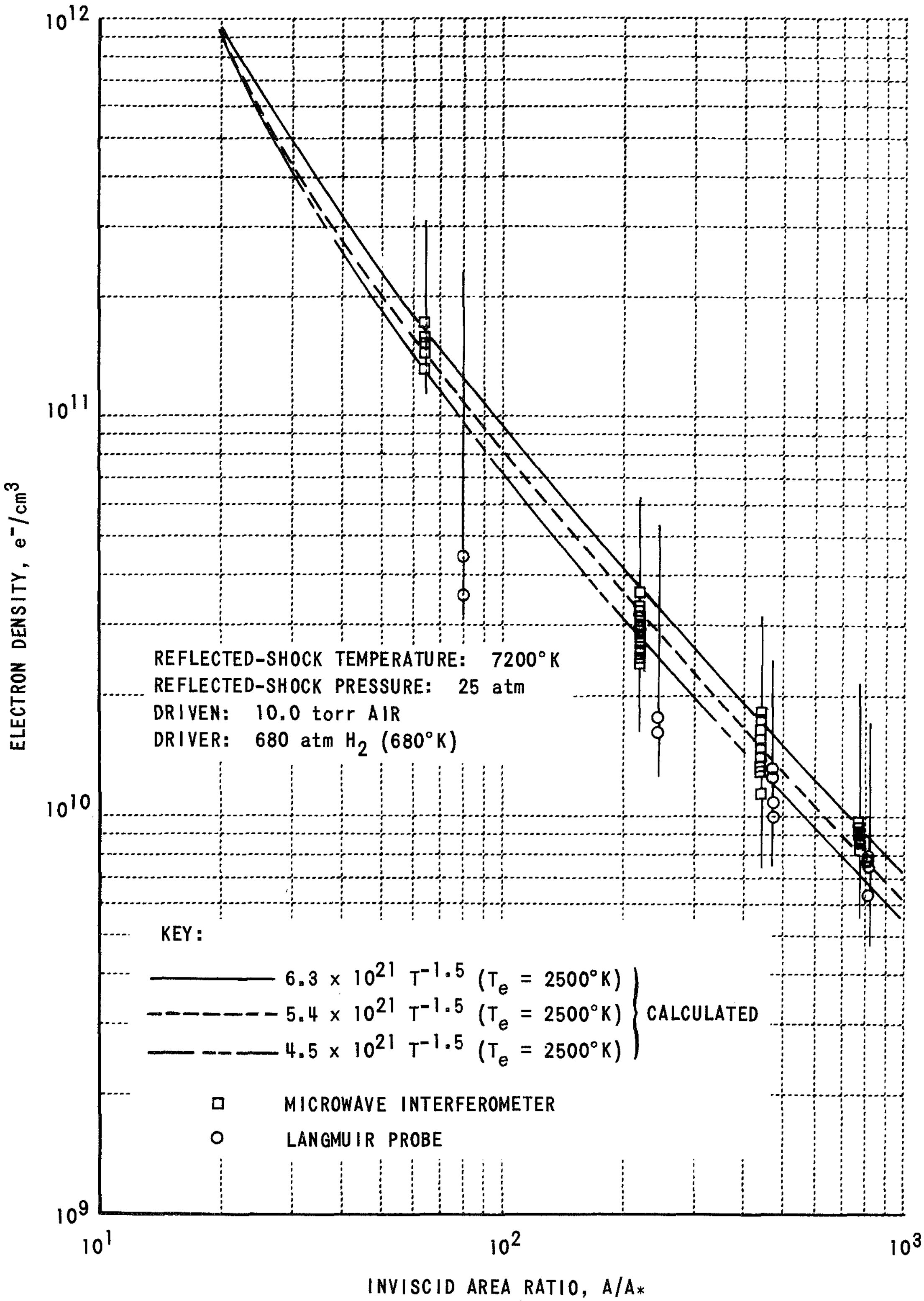


Figure 6 INFLUENCE OF PRE-TEMPERATURE FACTOR ON ELECTRON-DENSITY DISTRIBUTION

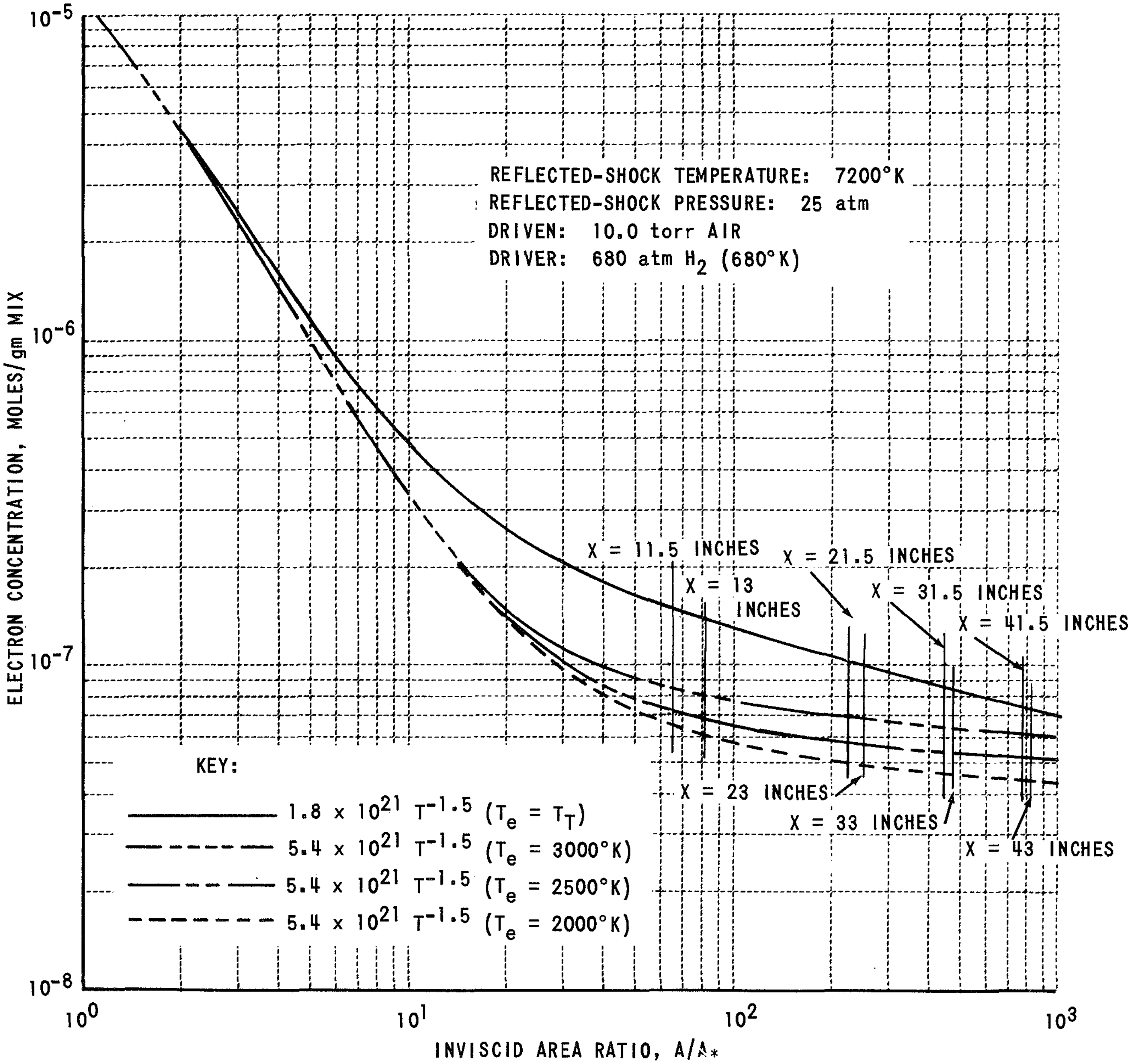


Figure 7 CALCULATED ELECTRON CONCENTRATIONS

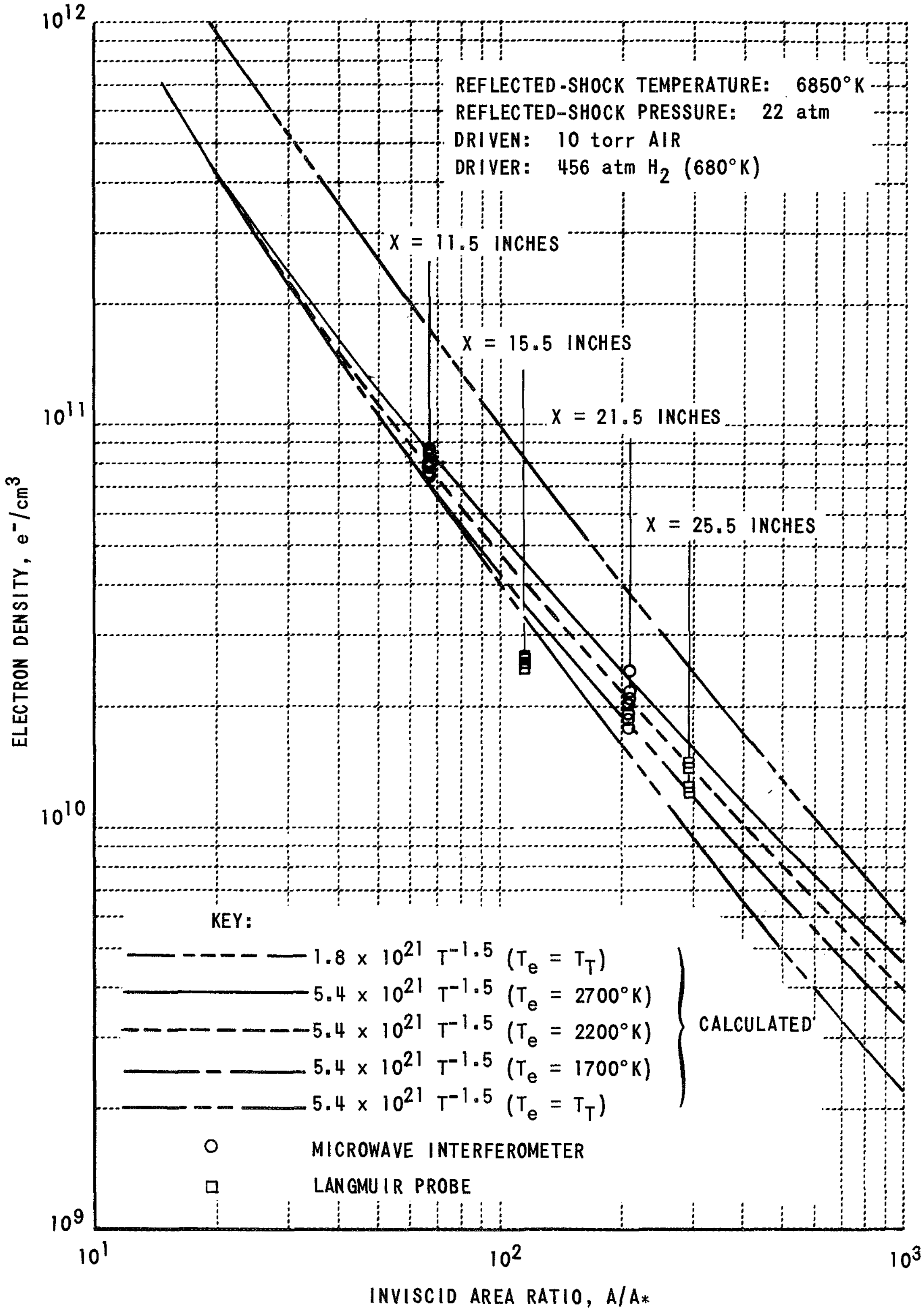


Figure 8 COMPARISON OF MEASURED AND CALCULATED ELECTRON DENSITY IN NOZZLE FLOW

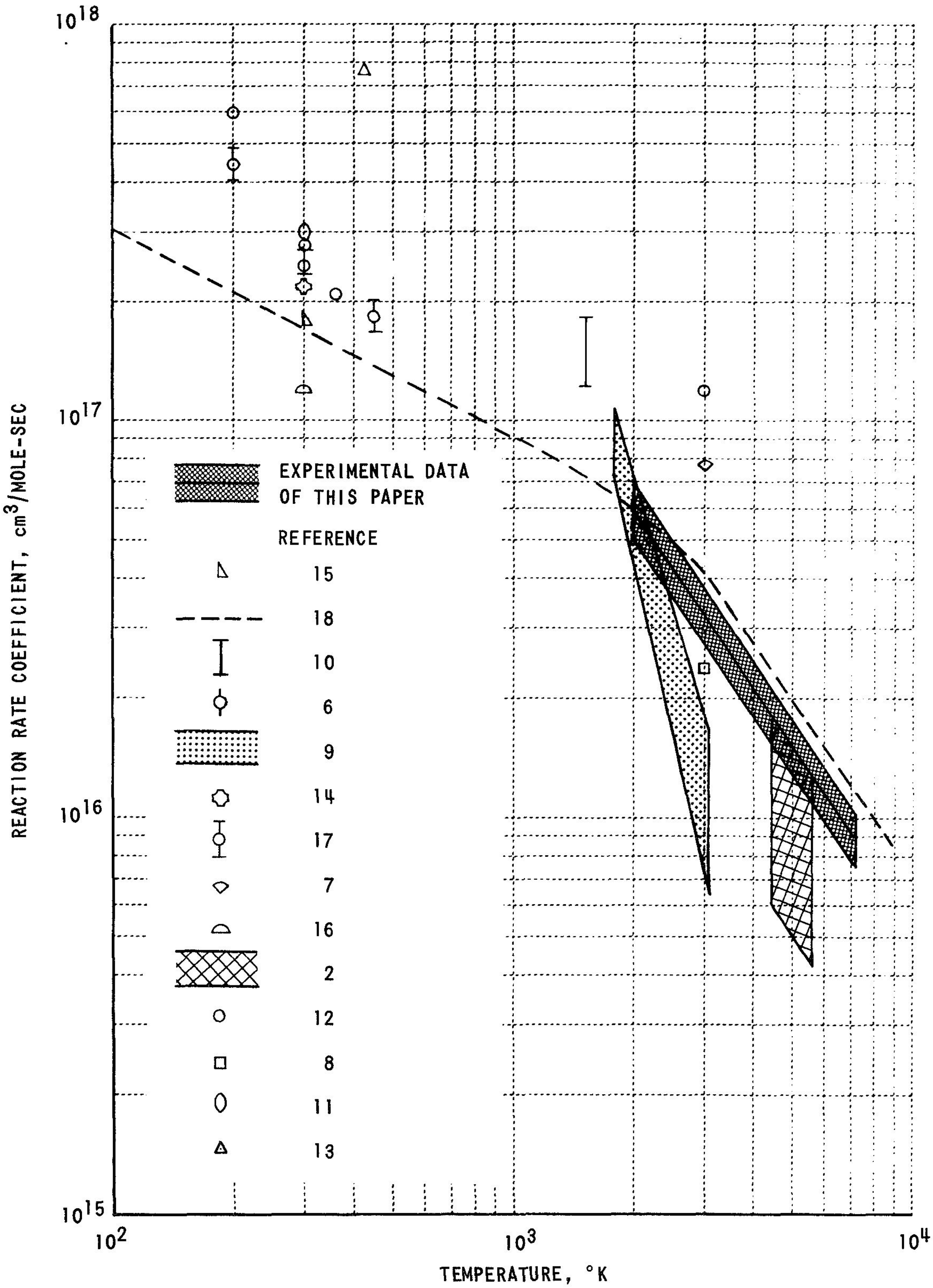


Figure 9 REACTION-RATE COEFFICIENT DATA FOR THE REACTON $NO^+ + e^- \xrightarrow[k_r]{} N + O$

CAL