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Measurement of nonequilibrium effects in thermal plasmas

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Abstract - Spectroscopic measurements have been made in a 50kW RF induction plasma with argon at atmospheric pressure to assess both the importance of departures from local thermodynamic equilibrium in so-called thermal plasmas of interest to plasma processing and the significance of nonequilibrium in interpreting plasma diagnostics. In these experiments relative and absolute line intensities, continuum intensities, as well as the total radiation source strength, were separately obtained and interpreted in terms of a partial-equilibrium model. In this model the free and excited bound electrons are found to be mutually in equilibrium irrespective of departures from equilibrium with the ground state. The implications of these observations for plasma diagnostics are discussed.

INTRODUCTION

Thermal plasmas used for plasma synthesis and plasma processing at pressures near atmospheric are often described in terms of the assumption of local thermodynamic equilibrium (refs. 1,2). In this model only one temperature, and the pressure, are required to specify the thermodynamic state of the plasma and its chemical reactivity. Diagnostic techniques for thermal plasmas often assume equilibrium (refs. 3,4), and some measurements suggest that this is indeed the case (ref. 5). However, several forms of nonequilibrium can occur in such plasmas (refs. 6,7). These include depopulation of excited electronic states as a result of radiation escape, ionizational nonequilibrium associated with diffusion of free electrons, and other forms of chemical and ionizational nonequilibrium. Resulting departures from LTE can cause the "temperatures" measured by various techniques of plasma diagnostics to differ and the electron density to depart from its Saha-equilibrium value. Under such circumstances, the existence of multiple "temperatures" presents ambiguities as to the modeling of the rate of chemical reactivity. In addition, nonequilibrium discharges can cause elevated electron temperatures and densities. It has been proposed previously (refs. 8,9) that such nonequilibrium discharges can have a significant effect on chemical reactivity in plasma processing and might be used as a means of augmenting and/or controlling chemical reaction rates.

This paper discusses such nonequilibrium and possible consequences for plasma processing and plasma diagnostics. Optical measurements designed to assess the importance of nonequilibrium are described for experiments conducted with a 50 kW RF induction plasma torch at atmospheric pressure. Plasma diagnostic experiments using emission spectroscopy are discussed for an argon plasma. The data are interpreted in terms of a partial-equilibrium model in which the free and excited bound electrons are mutually equilibrated, but not necessarily in equilibrium with the ground-level density.

EXPERIMENTAL FACILITY

The measurements described here were conducted with a nominally 50 kW TAFA model 66 RF induction plasma torch, powered by a Lepel model T-50 power supply. The vertical five-coil torch has a 7.5 cm. inner diameter and an inner length of 26.5 cm. measured between the gas-injection plate and a 5 cm. exit nozzle, which is 6 cm. above the upper coil. The present experiments were conducted downstream of the nozzle using a water-cooled quartz reactor test section. The test section has an inner diameter of 5 cm. and a length of 17.5 cm. above the nozzle exit. Spectroscopic measurements reported at the "nozzle exit" were made 1 cm. downstream of the nozzle with the test section removed. (Measurements at the same location with the test section in place, made through the single quartz tube below the cooling-water passage, yielded essentially the same results as for the unconfined plasma, at least within the 4 cm. core of the plasma for which results are reported here.) Similarly, measurements at the "test-section exit" were made in the free jet 1 cm. downstream of the test-section exit. The power supply and torch, and the test section cooling-water systems, were separately instrumented with thermocouples and flow meters so as to independently obtain calorimetric energy balances for comparison with the spectroscopic measurements.

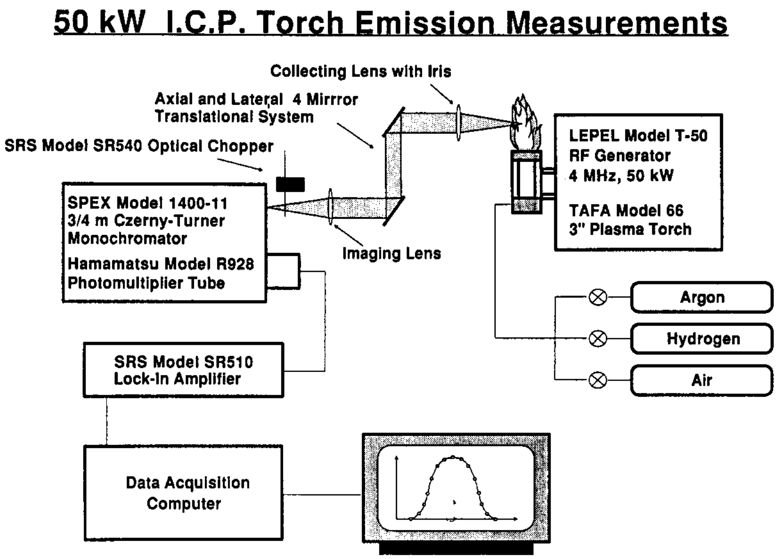

Figure 1

Plasma emission measurements were made using a Spex 3/4 meter scanning monochromator fitted with a Hamamatsu model R928 photomultiplier tube. Absolute-intensity calibrations were obtained by means of a tungsten strip lamp, with a calibration traceable to NBS standards. The optical arrangement for lateral and axial scanning of the plasma is shown in Fig. 1. Total radiation measurements in the wavelength range 250nm to 2500nm were made with a self-calibrating Scientech model 36-0001 pyroelectric detector, using a traversing arrangement similar to that shown in Fig. 1. Lateral traverses of emission and total radiation data were transformed to radial variations within the plasma using an Abel-inversion technique (ref. 10).

TEMPERATURE AND ELECTRON DENSITY NONEQUILIBRIUM

Several approaches have been used for temperature determination in thermal plasmas, including measurement of absolute line intensities, comparison of relative line intensities, and interpretation of continuum intensities from recombination radiation by use of the Saha equation (ref. 11). If, and only if, the plasma is in local thermodynamic equilibrium these techniques will be equivalent, in principle, but with differing sensitivities and accuracies. On the other hand, departures from LTE could produce unknown errors in the inferred temperature. Such errors would occur, for example, if recombination radiation were used to infer the temperature under circumstances where the electron density is not in Saha equilibrium with the ground-level density. In the present measurements, radial distributions of the absolute and relative intensities of eight lines of neutral argon and the recombination continuum at 553 nm. were measured using an experimental facility described in the preceding section, and interpreted separately to assess the significance of departures from LTE.

A typical Boltzmann plot of relative line intensities is shown in Fig. 2, for a torch power of 46.7 kW and argon flow rate of 160 slpm. Boltzmann temperatures, denoted by T_B, calculated from the slopes of plots such as that of Fig. 2 are compared with the temperatures based on the absolute intensity of the ArI line at 430 nm. in Figs. 3 and 4, for the torch nozzle exit and the test-section exit, respectively. Torch conditions for these figures are the same as for Fig. 2.

Here the absolute line-intensity temperatures are denoted by T_{LTE} and are calculated from the relation

$$\frac{n_j}{g_j} = \frac{1}{g_1} \frac{p}{kT_{LTE_j}} e^{-\varepsilon_j/kT_{LTE_j}} \qquad (1)$$

where n_j is the number density and ε_j the energy of the jth excited level. For convenience and clarity, p/kT has been substituted for the ground-level density n_1; this follows from the fact that for all experimental conditions reported here the

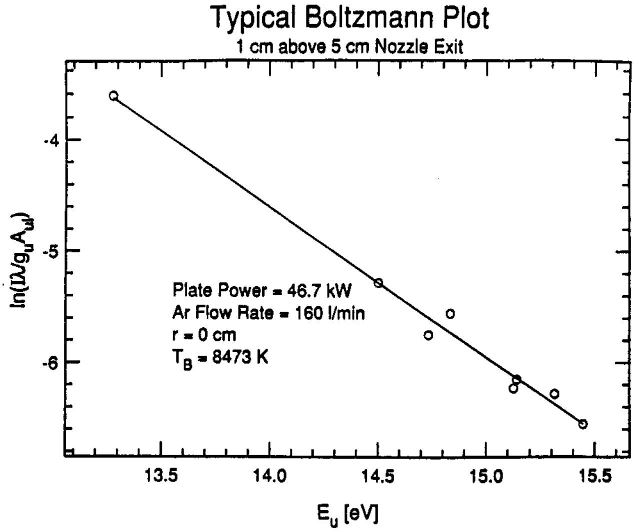

Figure 2

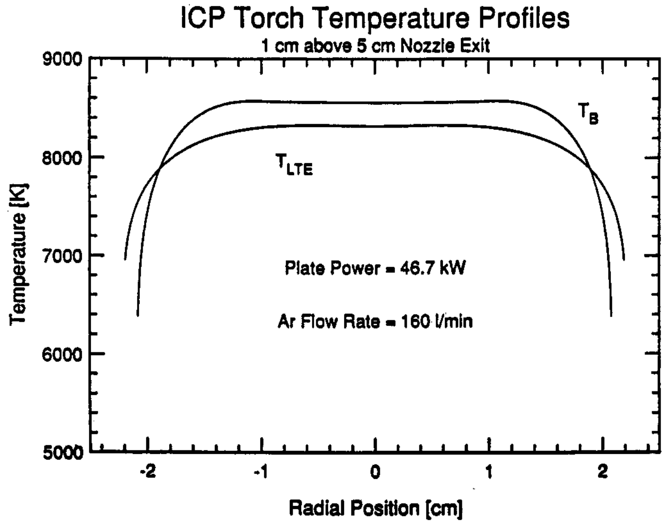

Figure 3

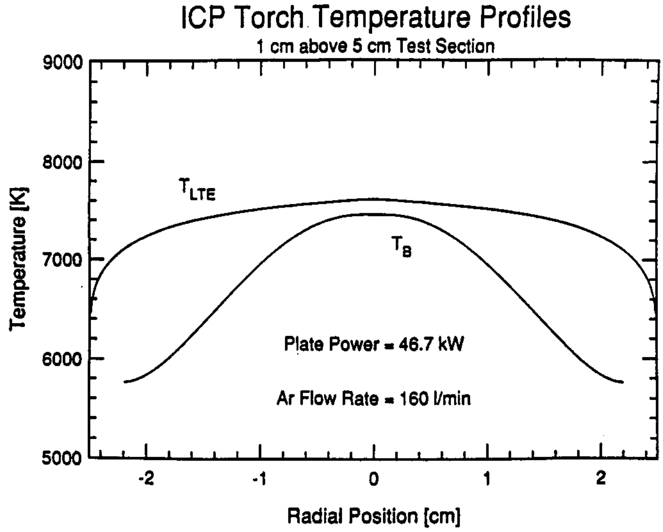

Figure 4

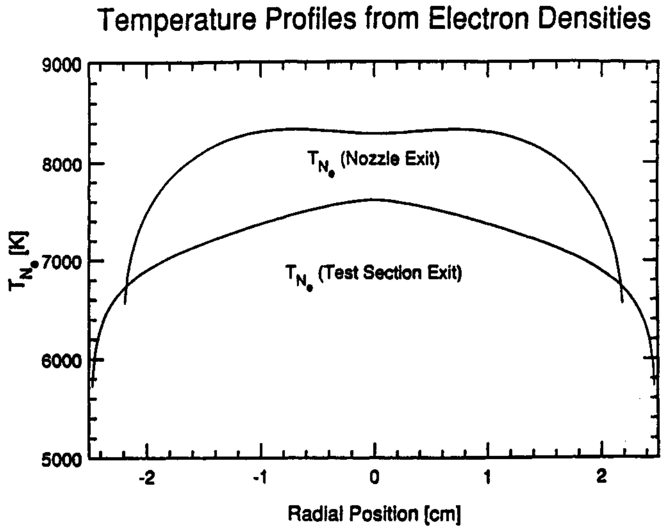

Figure 5

electron number density is small compared to the total argon number density, and the electronic partition function is essentially the ground-level degeneracy g_1. Similar results are obtained when T_{LTE} is based on other lines with relatively well-known Einstein coefficients. If the measured profiles of recombination radiation at 533 nm. are interpreted following Bott (ref. 11) using the Saha equation to infer temperatures T_{ne}, the results shown in Fig. 5 are closer to the absolute line-intensity temperatures T_{LTE} than to the Boltzmann relative-intensity temperatures T_B. (The measured values of electron density themselves can easily be obtained from Fig. 5 and the ground-level Saha equation.)

These results show that for the nozzle exit in the central region of the plasma, the Boltzmann temperature T_B is approximately 250K above T_{LTE}. This difference is consistent with depopulation of bound electronic states as a result of radiation escape. On the other hand, at both the nozzle and the test-section exits (Figs. 3 and 4), T_{LTE} is greater than T_B in the outer regions of the plasma, consistent with diffusion of free electrons toward the cool walls, and finite electron recombination rates (ref. 6). Although this nonequilibrium is small at the nozzle exit, it is pronounced for the recombining plasma at the test-section exit.

A detailed review of all the data show that they can be interpreted in terms of a *partial equilibrium model* in which the bound and free electrons are mutually in partial equilibrium at the Boltzmann temperature T_B, as given by the excited-state Saha equation

$$\frac{n_e^2}{n_j} = \frac{2\,g_i}{g_j}\left(\frac{2\pi m_e k T_B}{h^2}\right)^{3/2} e^{-\varepsilon_{j\lambda}/KT_B} \qquad (2)$$

where $\varepsilon_{j\lambda}$ is the ionization energy of the jth excited level, g_i represents the ion partition function, and the other symbols have their usual meaning. An approximate collisional-radiative model indicates that as a result of trapping of the ultraviolet resonance radiation the population of the first excited level (j=2) should be nearly in equilibrium with the ground-level (j=1). Thus, the partial equilibrium model is defined by Equation 2, with j > 2.

Since the partial equilibrium described by this model is maintained by collisions between excited electronic states and free electrons, the Boltzmann temperature T_B should agree with the free-electron translational temperature T_e. This is supported by detailed collisional-radiative calculations (refs. 12-15), such as those of Bates, Kingston and McWhirter, which show equilibration, at sufficient electron densities, between the electron temperature T_e and the Boltzmann slope temperature T_B of high- lying bound electronic states. In the absence of plasma currents in the region under study, the electron energy equation (refs. 16,6) shows relatively small differences between the electron temperature T_e and the heavy-particle gas temperature T_g for the conditions of our experiments, except near the test-section wall.

Although the present approach has similarities to the methodology of Eddy (refs. 17,18), who has also discussed departures from LTE, there are significant differences, particularly as to the determination of the electron temperature. A direct measurement of T_e, perhaps through the relative wavelength dependence of the recombination radiation, would be helpful in furthering our understanding of partial equilibrium in thermal plasmas. In the present experiments, calorimetric energy-balance measurements including the measured radiation loss support the foregoing partial-equilibrium description. If, on the other hand, the electron temperature (and indirectly the gas temperature) at the test section exit is evaluated according to the prescription of reference 18, the energy balance does not close, by a significant margin.

Since T_{ne} is calculated from the ground-level Saha equation (2), with $j = 1$, discrepancies between T_B and T_{ne} indicate departures from ionizational equilibrium. Thus, the measured electron density, based on the recombination continuum, is significantly greater than the equilibrium electron density, based on the ground-level Saha equation and T_B, at the test-section exit, where the discrepancy is the largest. However, at both the nozzle and test-section exits, the measured values of the electron density agree to within experimental uncertainty with the values predicted by the excited-state Saha equation (2) for $j > 2$ when based on the Boltzmann temperature T_B (but not when T_{LTE} is used), as shown in Fig. 6, in support of the partial-equilibrium description.

The radiation source strength of argon was measured at the nozzle exit, test-section exit, and several other locations along the test-section using the pyroelectric detector described under Experimental Facility. To interpret these results as a function of temperature, corrections were made for the nonequilibrium discussed in the preceding section. These corrections are small at the nozzle exit, however, and our principal observations with regard to the radiation source strength could have been obtained from these measurements alone. Indeed, the agreement between radiation source strength of the nozzle and test-section exits, as interpreted, provides additional support for the partial-equilibrium model. Measured values of the source strength from 5000 to 8500K agree with theoretical predictions, but are well over an order of magnitude lower than those reported by Emmons (ref. 3) at temperatures below 7500K. Emmons used T_{ne} to set his temperature scale and made other equilibrium assumptions in interpreting his data. Analysis (ref. 6) of his data, however, indicates that ionizational nonequilibrium similar to that observed here at the test-section exit was significant in the earlier experiments at the temperatures for which we have obtained new measurements. Thus we believe that nonequilibrium in the only previous measurements of radiation source strength below 10,000K accounts for the discrepancy from the values we have obtained, thus underscoring the importance of considering possible departures from local thermodynamic equilibrium. In particular, we suggest that "temperature" measurements, such as T_{LTE} and T_{ne}, which implicitly rely on equilibrium with the ground state be used with caution. In spite of the sensitivity associated with large energy differences, the resulting accuracy implied by this sensitivity may be illusionary.

These results show that for our conditions different measurement techniques can lead to "temperatures" differing by as much as a thousand degrees as the result of departures from local thermodynamic equilibrium. This ambiguity can be resolved, at least in the present situation, in terms of a partial equilibrium model in which the state of the plasma is characterized by three parameters; the pressure, the Boltzmann temperature T_B, and the electron density. For the free-flowing plasma, departures of the electron

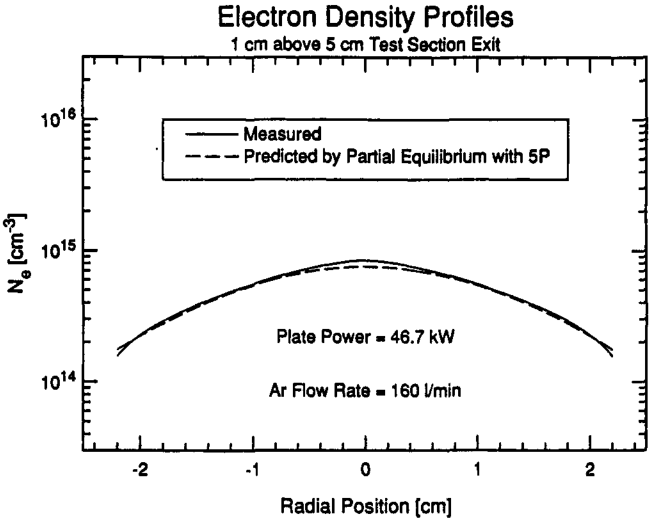

Figure 6

density from its LTE value by greater than an order of magnitude are observed. The measurements show, however, that partial equilibrium is maintained between the free electrons and excited electronic states. Realization of the former and use of the latter may prove helpful in planning diagnostic strategies for plasma processing.

CHEMICAL NONEQUILIBRIUM

It has been proposed (refs. 8,9) that elevated electron temperatures and densities can affect chemical reaction rates in thermal plasmas. Such nonequilibrium could occur in the plasma torch itself or be imposed by means of an auxiliary discharge to enhance or control chemical reactivity. To test this hypothesis we have placed a water-cooled molybdenum electrode at mid-height in the test section and obtained a nonequilibrium auxiliary discharge by loading the electrode through a low-inductance resistor bank. Since the resulting configuration derives its power from the RF supply, the auxiliary discharge can be thought of as an inductively transferred arc. Currents of up to 10 amps through the 3.4 cm^2. electrode cause electron temperature increases of more than 1000K above the gas temperature and corresponding nonequilibrium increases in electron density. Preliminary experiments have been conducted with H_2 and N_2 added to the argon plasma. Diagnostics include the strengths of Ar, H, and N lines, the recombination continuum, and the rotational temperature of N_2^+ from the band at 391 nm. Under these conditions the predictions of references 8 and 9 would suggest that collisions with relatively energetic free electrons could drive the dissociation of molecular species above the equilibrium value at the gas temperature. Our measurements to date are in accord with these predictions. For example, for 5% N_2 in argon at a gas temperature of about 5000K, as determined from the rotational temperature, the N atom population and hence the degree of dissociation of N_2 is found to be significantly greater than its equilibrium value (at the gas temperature) when the electron temperature is raised to approximately 6500K. In terms of the power dissipated in the plasma, the energy cost to dissociate the molecular species is notably less than if the entire plasma, rather than only the free electrons, were increased in temperature. Experiments are currently underway to explore the effects of such nonequilibrium on chemical reactivity over a range of conditions.

REFERENCES

1. M. Boulos, Pure and Applied Chemistry, 57, 1321 (1985).
2. P. N. Estey, 7th International Symposium on Plasma Chemistry (1985); also available as EPRI Report EM-4336 (1985).
3. H. W. Emmons, Phys. Fluids, 10, 1125 (1967).
4. M. Boulos, P. Fauchais and E. Pfender, Diagnostic Techniques in Thermal Plasma Processing, U.S. Department of Energy (1986).
5. P. D. Scholz and T. P. Anderson, J. Quant. Spectr. and Rad. Transfer, 8, 1411 (1968).
6. C. H. Kruger, Phys. Fluids, 13, 1737-1746 (1970).
7. E. Pfender, 8th International Symposium on Plasma Chemistry. Tokyo, Japan, 2 (1987).
8. C. H. Kruger, 8th International Symposium on Plasma Chemistry. Tokyo, Japan, 19-25 (1987).
9. C. H. Kruger, Plasma Chemistry and Plasma Processing, 9, 435-441 (1989).
10. C. J. Cremers and R. C. Birkebak, Applied Optics, 5, 1057-1064 (1966).
11. J. F. Bott, Phys. Fluids 9, 1540-1547 (1966).
12. D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. A, 270, 155, 297 (1962).
13. D. R. Bates and A. E. Kingston, Planet. Space Sci., 11, 1 (1963).
14. D. R. Bates and A. E. Kingston, Proc. Phys. Soc., 83, 43 (1964).
15. J. F. Shaw, M. Mitchner, and C. H. Kruger, Phys. Fluids, 13, 325, 32 (1970).
16. M. Mitchner & C. H. Kruger "Partially Ionized Gases", Wiley (1973).
17. T. L. Eddy, J. Quant. Spectrosc. Radiat. Transfer, 33, 197-211 (1985).
18. T. L. Eddy, AIAA Paper 89-2830, 25th Joint Propulsion Conference, Monterey, CA (1989).