Kinetics of Ar-He Atmospheric Pressure Surface Wave Discharges

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Abstract. An atmospheric pressure surface wave discharge generated using several Ar-He mixtures has been studied with emission spectroscopy techniques. Deviations in the excitation (Boltzmann) and ionization (Saha) equilibriums respect to the case of pure Ar discharges have been found for He concentrations as low as 10%. The relevance of these deviations grows as the concentration of He in the discharge does. While no exact equilibrium can be stated without knowledge of the electron temperature, departure of the discharge respect to pLTE is clear and consequently alternative diagnostic methods that do not require LTE must be employed.

1. Introduction
The thermodynamic equilibrium (TE) of plasmas, which is related to the detailed balance principle and so to the proper balance of kinetics processes taking place within a discharge, is a general issue in plasma physics to which special attention must be paid. Although it does not seem relevant for practical applications of discharges, that usually imply far from equilibrium systems except for some cases such as arc discharges and thermonuclear plasmas, it is very important when dealing with plasma diagnosis since some methods, particularly spectroscopic ones, require of the existence of, at least, partial local thermodynamic equilibrium (pLTE).

2. Experimental Setup
Figure 1 shows a schematic block diagram of the plasma source and the optical detection and data acquisition systems for emission spectroscopy measurements.

Microwave power was provided to the plasma by a SAIREM 12kT/t microwave generator of 2000 W maximum power in continuous mode, equipped with a water cooled circulator to avoid power reflection damage. The power was coupled to the plasma by a surfaguide device and two impedance matching means of the wave launcher make the power reflected from the applicator back to the generator lower than 5% of the incident power.

The discharge was contained in quartz tubes of several inner (2, 4 and 5 mm) and outer (3, 5 and 6 mm) radii. Since the quartz tubes containing the discharge suffer a great damage for powers over 300 W [1], the discharge tube was coaxially surrounded by another quartz tube of 8.5 mm internal radius in order to avoid this problem. This external tube made up a jacket through which a dielectric liquid (1–Tetradecene) or air circulated. In our experiments, the plasma column is extended to both sides of the
wave launcher and direct and inverse columns appear. The direct column is considered that one where the gas flux and the propagation of the wave takes place in the same sense contrarily to what happens in the inverse.

![Experimental Setup](image)

Figure 1. Experimental Setup.

Several gas mixtures of high purity (99.999 %) Ar and He, were used as plasma gases keeping the same total flow equal to 1 slm (standard litre per minute). The flows for Ar, He and mixtures were controlled by HI-TEC flow controllers (IB 31) with different maximum flow limits (0.25 and 5 slm). Several He concentrations were used, ranging 0 – 99 %.

An optical fiber was used to pick up the light emitted from the discharge at \( z = 2 \) cm from the plasma end and, also, to drive it to the entrance slit of a Jobin-Yvon-Horiba monochromator previously calibrated and equipped with a 2400 grooves/mm holographic grating. A Hamamatsu R928P photomultiplier and a Symphony CCD were used as radiation detectors. In each measure, spectrums from \( H_\beta \) line were taken for electron density measurement, as well as those of some ArI lines. Hydrogen atoms were present as impurities in the plasma gas.

3. Results

3.1 Excitation temperatures of the Ar atomic system.

Since no atomic lines of He or ionic lines of Ar could be detected, only excitation temperature of the ArI system could be calculated. Two different temperatures were calculated for each experimental data set from the slopes of the Boltzmann-Plots: one from the linear fit connecting the 4p and the 5p states (lower levels) \( T_1 \), and another from the linear fit connecting the levels above 5p (upper levels) \( T_2 \).

| [He] (%) | \( T_1 \) (K) | \( T_2 \) (K) |
|----------|------------|------------|
| 0 (\( r_i = 2 \) mm) | 5400 ± 400 | 4500 ± 300 |
| 30 (\( r_i = 2 \) mm) | 6100 ± 140 | 5500 ± 400 |
| 50 (\( r_i = 4 \) mm) | 5800 ± 140 | 4900 ± 300 |
| 70 (\( r_i = 4 \) mm) | 6100 ± 140 | 4700 ± 250 |
| 90 (\( r_i = 5 \) mm) | 5900 ± 140 | 3500 ± 200 |
| 99 (\( r_i = 5 \) mm) | 6100 ± 180 | 3400 ± 210 |
In Table 1 it is clear that two very different temperatures are needed to describe the atomic state distribution function for He proportions above 50% in the discharge, showing variations in the excitation/ionization scheme of the ArI system.

A relative depopulation of the higher levels of the ArI system at high He concentrations can be clearly observed in Figure 2. This can be attributed to the differences in the frequency for electron-atom collisions for effective momentum transfer between argon and helium [1] and so a larger number of collisions between electrons and He atoms are expected. This induces a lower population on the upper levels of ArI provided that in the stepwise excitation scheme the upper levels of ArI are mainly populated by collisions with electrons of the bulk of the electron energy distribution function.

3.2 Griem’s Criterion applied to an Ar-He discharge.

For a given excited atomic state, the effective quantum number \( p \) can be derived from the following expression

\[
p = z \left( \frac{E_{HH}}{E_{i,n}} \right)^{\frac{1}{2}}
\]  

(1)

where \( z \) is the effective charge of the nucleus, \( E_{HH} \) is the ionization energy of the hydrogen atom and \( E_{i,n} \) is the ionization energy of the \( n \)-th excited atomic state.

Griem’s criterion [3] is the most simple way typically used to identify deviations from local thermodynamic equilibrium. According to this criterion a critical level \( p_{cr} \) can be calculated as a function of the electron density \( n_e \) and temperature \( T_e \) of the discharge.

\[
p_{cr} = 62 \left( \frac{T_e}{n_e^2} \right)^{\frac{1}{17}}
\]  

(2)

According to Griem’s criterion, those levels with quantum effective numbers above \( p_{cr} \) are considered in saturation, being its population and depopulation processes carried out mainly by electron collisions. Levels whose \( p \) falls under \( p_{cr} \) are in capture radiative cascade or corona balances, and are populated by electron collisions and depopulated by radiative processes.

In Figure 2, \( p_{cr} \) values have been calculated for discharges with different Ar/He proportions. Electron density values have been calculated from the Stark broadening of the Balmer series \( H_\beta \) line [4]. Electron temperatures where estimated from the values of \( T_1 \), considered as a lower limit to \( T_e \) [5] and the behaviour of theoretical available data [6] of similar discharges at reduced pressure. Though this does not provide exact values of the electron temperature, the influence of this parameter on Griem’s criterion has been proved to be less important as compared to electron density [3].
As can be seen, even at a low concentration of He in the discharge, 4p levels enter in the capture radiative cascade zone. As the He concentration increases, these levels completely exit the saturation zone and other levels (3d) start being affected.

4. Conclusions.
The need for two excitation temperatures to properly describe the ArI atomic state distribution function as the He concentration grows up over 50%, related to a relative depopulation of the higher levels (above 5d), indicates that the higher levels start to separate from Saha equilibrium.

On the other hand, the departure from equilibrium pointed out by Griem’s criterion indicates the lower lying excited levels (4s, 4p, 3d) of the ArI system are populated by electron collisions and depopulated by radiative processes ($p < p_{cr}$) and so the Boltzmann equilibrium is not verified for this levels.

This information, together with an increase of the discharge radius (reduction of the radial contraction) point to a decrease of the influence of processes involving molecular ions such as associative ionization and dissociative recombination, while the influence of molecular dimmers such as He metastable molecules can not be neglected.

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Figure 3. Gotrian diagram of Ar atomic system. The different lines represent critical $p$ values calculated according to Griem’s criterion from the experimental data.