TRANSITION PROBABILITIES OF ARGON II

Eugene D. Tidwell
ARO, Inc.

February 1970

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FOREWORD

The research reported herein was sponsored by Headquarters, Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 64719F. The work was done by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates), contract operator of AEDC, Arnold Air Force Station, Tennessee under Contract F40600-69-C-0001. The research was done from 1967 to 1969 under ARO Projects No. BB5706 and BB5822, and the manuscript was submitted for publication on October 20, 1969.

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This technical report has been reviewed and is approved.

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ABSTRACT

With the use of two stable, highly ionized argon plasma sources, over 200 spectral lines have been measured and identified. Of these, 70 or more have been used for transition probabilities after they were found to be single, unperturbed argon ion (ArII) lines. Each line has been tested for abnormal half-widths; those with widths greater than 20 percent over normal are not used. Excitation temperatures from 1 to 8 ev ($kT_e$) have been used: (1) photographically with a 1.5-meter focal length spectrograph and (2) photoelectrically with a 0.5-meter spectrometer. As many as 33 observations have been tabulated for the stronger lines. All lines have upper state energy values between 19 and 24.5 ev and lie between 3500 and 5100 Å. The absolute intensity of the 4589 Å ArII line produced a density which agreed well with calculated local thermodynamic equilibrium conditions at $P = 340 \, \mu\text{Hg}$ and $kT_e = 1 \, \text{ev}$. All runs used at least four lines, with known transition probabilities, and as many as 12 in determining temperatures from which unknown transition probabilities were calculated. The tables and figures include wavelengths, energy states, estimated uncertainty, statistical weights, transition probabilities, and number of observations. Examples of the Maxwell-Boltzmann distributions are shown.
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NOMENCLATURE

A Transition probability, sec⁻¹
ArI Argon, neutral
ArII Argon, singly ionized
ArIII Argon, doubly ionized
E Energy, μw st⁻¹ nm⁻¹ mm⁻²

g 2J + 1 quantum number, statistical weight of electronic state, degeneracy of energy level
I  Intensity
k  Boltzmann constant
N  Number density, cm$^{-3}$
P  Pressure, microns of mercury (µHg)
Q  Partition function
T  Temperature, transmittance
$T_e$  Electron temperature
λ  Wavelength
Δ  Seidel function

SUBSCRIPTS
l  Lower state
o  Ground state
u  Upper state
SECTION I
INTRODUCTION

During the past ten years there has been increased interest in noble gas spectra in the aerospace industry. Average values of plasma properties, such as temperatures, density, and heat transfer, are no longer adequate for the updated design and testing of space vehicles. Therefore, the ability to determine precisely the flow characteristics of high-temperature gases has become increasingly important.

Because of its availability, ease of ionization, and relatively low cost, argon (Ar) gas is a natural choice for thermodynamic research of gas properties at high temperatures (Refs. 1 through 14). Argon has been used extensively in the studies of magnetohydrodynamic (MHD) flows, chemical synthesis, wind tunnel plasmas, and simulated supersonic flight. The intensities of the argon neutral (ArI) or ionized ArII spectral lines can be used to calculate flow temperatures and particle densities when correlated with their respective transition probabilities.

The purpose of this investigation was to improve the accuracy of measuring excitation temperatures by spectroscopic methods through more consistent transition probabilities of singly ionized argon (ArII) spectral lines.

Table I gives the relative (with an attempt to bring them close to absolute) transition probabilities of ArII lines spread over 5 ev in upper state energy (E_u). These results should increase the precision over those previously available. The added number of spectral lines should give greater freedom in matching line intensities. Also, when impurities overlap otherwise useful lines, other choices can be made. This in turn provides more accurate radiative heat transfer data as well as better estimates of electrical and thermal conductivity.

Heretofore, several authors have measured or calculated transition probabilities for the strongest of the ArII lines under moderate temperatures and pressures with disagreements as high as a factor of 100. Choosing 12 single lines of nearly equal intensities and comparing the Maxwell-Boltzmann temperature plots from previously available transition probabilities measured by several authors (Refs. 6, 10, 11, 12, and 13) clearly suggest that the 1963 measurements by Olsen (Ref. 6) are the best to use for a linear, consistent set.

Because of the problems encountered in calculating the exact coupling parameters for argon, as shown by the spread in the A_u values in Fig. 1 for Garstang, and to gain a greater confidence in the base values, it was advisable to measure the absolute value of at least one ArII line. This was done for the 4589 Å line using the temperature determined from Olsen's other transition probabilities and a carefully calibrated system. The 4589 Å line was chosen because its singularly high E_u bares extra weight in projecting the Boltzmann plot to unknown gA at higher E_u (Fig. 1).
### TABLE I

<table>
<thead>
<tr>
<th>λ, Å</th>
<th>E_u, cm⁻¹</th>
<th>E_u, ev</th>
<th>Δ/Eu, 10⁻⁶ sec⁻¹</th>
<th>Δ/ΔA/Å, percent</th>
<th>Number of Determinations</th>
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<td>187589.62</td>
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<td>22.80</td>
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<td>4</td>
<td>41.80</td>
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</tbody>
</table>

*Δ/ΔA/Å percent = estimated uncertainty calculated by dividing the mean deviation by the mean value.*
Fig. 1 Comparison of Boltzmann Temperature Plots

![Boltzmann Temperature Plots](image)

**Fig. 1** Comparison of Boltzmann Temperature Plots

\[ \text{log } \lambda / \text{sec}^{-1} \]

\[ E_v, \text{ ev} \]

**TABLE II**

**PRESENT ArII TRANSITION PROBABILITIES COMPARED WITH OTHER DATA**

<table>
<thead>
<tr>
<th>( \lambda, \text{ A} )</th>
<th>( A_{ul} \times 10^{-7} \text{ sec}^{-1} )</th>
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<tr>
<td>3729.29</td>
<td>2.56</td>
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<td>5062.07</td>
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</table>

*Olsen [10] 1959
Olsen [16] 1963

Underlined wavelengths indicate six lines used to set absolute value

"Calculated value."
The Olsen transition probabilities of the six lines underlined in Table II gave a very smooth straight line with the present measured intensities. Using these six lines and the new calculated value for 4589 Å, which agrees with Garstang (Ref. 11) and Griem (Ref. 13), it was felt that an adequate base has been chosen for the rest of the 70 ArII lines listed in Table I.

**SECTION II
EXPERIMENTAL PROCEDURE**

2.1 APPARATUS

Two steady-state, highly ionized Ar plasma sources have been used to produce the ArII spectra.

2.1.1 Low Pressure, Magnetically Confined Ar Plasma; Hollow Cathode

The system is shown in Fig. 2, and a detached drawing of the anode-cathode region is given in Fig. 3. This is a hollow tantalum cathode discharge using Ar as the ionizing medium (Ref. 1). The vacuum chamber is 30 cm long and 20 cm in diameter made of stainless steel. The pumping system comprises a Freon® baffled 6-in. oil diffusion pump with a net speed of 400 liters/sec. This is backed by a Freon baffled 50-ft³/min roughing and finishing pump. The baffles minimized the oil backstreaming into the discharge chamber and helped establish the 10⁻⁷ torr base pressure. TaII lines were emitted during the first 20 seconds of each run due to cathode sputtering; consequently, temperature runs were made only after this stabilization period was complete.
The Ar supplying the discharge was bled from a high pressure, bone-dry Ar bottle through the hollow cathode. At a pressure of from 300 to 400 μHg the discharge became thermionically emitting under the influence of the longitudinal magnetic field. The pressure then was reduced to the 10⁻⁴ torr operating range.

2.1.2 High Enthalpy, MHD Ar Arc Accelerator

The second system used as a plasma source of ArII is shown in Fig. 4. This 4- x 4- x 8-ft vacuum chamber houses a magnetohydrodynamic (MHD) arc accelerator which utilizes its self-induced magnetic field to accelerate a plasma. A 1600-cfm booster pump system was capable of maintaining a base pressure of 1 to 10 μHg and typical run pressures of 300 μ for an Ar mass flow rate of 0.15 gm/sec. Three 32-in. diffusion pumps were capable of maintaining a 5-μ pressure with the same Ar mass flow rate of 0.15 gm/sec.
Steady-state arc power capabilities are more than 400 kw provided by eight commercial welding units. The highest current used during the temperature investigation was 1400 amp at 75 v or nearly one-fourth the maximum capability. The arc operating under moderate conditions is shown in Fig. 5.

2.1.3 Spectroscopic

a. A 1.5-meter focal length Jarrell-Ash spectrograph (Fig. 4).

b. A 0.5-meter focal length Jarrell-Ash Ebert spectrometer and table mount with x-y-z manual control.

c. A Jarrell-Ash recording microdensitometer.

d. Optics; i.e., lens, beam splitters, mirrors, photomultipliers, glass filters, camera, and standard tungsten-strip lamp.

e. An alignment laser and power meter.

The spectrograph and spectrometer systems were designed to give maximum response at 4000 Å with reasonably flat response up to 5000 Å. The gratings had 30,000 lines/in. and were normally used in the first order except in the case where it was used to identify the strongly overlapped region of 3500-3600 Å at higher resolution using higher orders. In the second source (MHD) the 3545 and 3588-Å ArII lines were occasionally
overlapped and seldom could be used. However, in the first source (hollow cathode) these lines were well separated from nearby lines and were used to a distinct advantage since these two lines had the highest upper state energy values for which the transition probabilities (Ref. 2) were known at that time.

2.2 CALIBRATION

Photomultiplier calibration was established by direct comparison with a tungsten-strip lamp at the wavelengths of the ArII lines in question. This secondary standard lamp was calibrated by comparison with an NBS standard lamp. Three-standard lamp calibration curves are shown in Fig. 6.

![Fig. 6 Calibration of Secondary Standard Lamp, 6v](image-url)
The photographic plates were then calibrated at three to four lamp currents using the optical setup in which the ArII spectra were to be taken. Figure 7 shows the Ar spectrum with three calibration continua produced in this way. The plates must go through an additional calibration because of the logarithmic sensitivity of the emulsions. This is called the “three point” H&D curve calibration, modified by the Seidel function which extends the linear portion of the typical “S” curve to linearize a greater range of transmittance values. The Seidel formula is

\[ \Delta = \log \left( \frac{1}{T} \right) - 1 \]  

where \( T \) is the transmittance. From the three calibration points (continuum portions of Fig. 7) at each wavelength the \( \Delta \) or Seidel function is plotted against \( E \) in Fig. 8. It should be noted that two consecutive plates taken from the same carton may have different calibration slopes. This indicates that each plate should be calibrated instead of depending on a single calibration for all emulsions of the same sensitivity class and batch number.

2.3 METHOD

The intensity, \( I \), of the light emitted from a homogeneous, optically thin gas at wavelength \( \lambda_{ul} \), produced by a transition between an upper energy level, \( E_u \), and a lower level, \( E_l \), is given by

\[ I = C \, A_{ul} \, N_u / \lambda_{ul} \]  

\( C \) represents a constant.
where \( C \) is an experimentally determined constant, \( A_{ul} \) is the Einstein emission coefficient or the number of transitions per second from state \( u \) to \( l \), and \( N_u \) is the population of state \( u \).

The temperature enters the formula through its role of populating the upper level depicted by the Maxwell-Boltzmann law

\[
N_u = N_0 \frac{g_u}{g_0} e^{-E_u/kT}
\]  

(3)

\( N_0 \) is the population of the ground state and \( g_0 \) is the degeneracy or statistical weight of the ground state.
Equation (2) becomes

\[ I = \frac{C_1 \epsilon_u A_u \ell}{\lambda_u \ell} e^{-E_u/kT} \]  

(4)

where

\[ C_1 = \frac{C N_o}{g_o} \]

Transcribing to logarithmic form,

\[ \log_{10} \frac{I \lambda_u \ell}{\epsilon_u A_u \ell} = \log_{10} C_1 - \frac{0.434 E_u}{kT} \]  

(5)

Introducing a value for \( k \) of \( 0.8624 \times 10^{-4} \) ev/deg,

\[ T = -\frac{5040E}{\log_{10} \frac{I \lambda}{gA} - C_2} \]  

(6)

where \( T \) is in °K, \( gA = g_u A_u g_u \), and \( E \) is \( E_u \) in electron volts (ev). The value of \( T \) is most readily obtained from a plot of \( \log I \lambda/gA \) versus \( E \) as far as the relative \( gA \) for each spectral line is known. The slope of the line is \( - (5,040/T) \), and the value of \( C \) will not change the slope. As for the computer, since the logarithms normally have a base \( e \), the slope is \( - (11,600/T) \).

A typical Boltzmann plot by computer is shown in Fig. 9. The six solid points were used as standard lines. They correspond to the six lines underlined in Table II from which the absolute values of all lines in Table I were calculated.

SECTION III
RESULTS

More than 90 percent of all the observed spectral lines were ArII. Occasional ArI and ArIII lines were seen, depending on arc current, magnetic field, mass flow rate, and field of view within the arc column. Molecular bands were orders of magnitude weaker than ArII, if they were seen at all.

Operating conditions for the hollow cathode arc were pressures of \( 10^{-4} \) torr, magnetic fields of 580 to 1600 gauss, and temperatures of 2 to 8 ev (\( kT_e \)) determined by radial inversion of the 1/2-in.-diameter flow field (Ref. 2).

The MHD arc shown in Fig. 4 operated at pressures of \( 10^{-1} \) to \( 10^{-3} \) torr, Ar mass flow rates 0.05 to 0.15 gm/sec, electron densities of \( 10^{14} \) cm\(^{-3} \), and temperatures of 1 to 2.5 ev (\( kT_e \)).

Steady-state operation was limited to currents less than 1400 amp at \( 10^{-1} \) torr, although runs of 20 sec duration were made at 2500 amp and 70 v. No temperature runs were made at these higher currents.
According to the straight Boltzmann plots, both sources exhibited local thermodynamic equilibrium wherever these measurements were taken. Two spectral lines, 4579 and 4589 Å, were observed with and without a reflecting mirror behind the arc as a test for self-absorption. Both lines showed less than five percent reduction in energy according to calculated intensity. Line profiles were observed with the 1.5-m spectrograph with a reduced slit to minimize instrumental broadening; asymmetric or abnormally broadened lines were not used in this project.

REFERENCES


With the use of two stable, highly ionized argon plasma sources, over 200 spectral lines have been measured and identified. Of these, 70 or more have been used for transition probabilities after they were found to be single, unperturbed argon ion (ArII) lines. Each line has been tested for abnormal half-widths; those with widths greater than 20 percent over normal are not used. Excitation temperatures from 1 to 8 ev (kT_e) have been used: (1) photographically with a 1.5-m focal length spectrograph and (2) photoelectrically with a 0.5-m spectrometer. As many as 33 observations have been tabulated for the stronger lines. All lines have upper state energy values between 19 and 24.5 ev and lie between 3500 and 5100 Å. The absolute intensity of the 4589 Å ArII line produced a density which agreed well with calculated local thermodynamic equilibrium conditions at P = 340 μHg and kT_e = 1 ev. All runs used at least four lines, with known transition probabilities, and as many as 12 in determining temperatures from which unknown transition probabilities were calculated. The tables and figures include wavelengths, energy states, estimated uncertainty, statistical weights, transition probabilities, and number of observations. Examples of the Maxwell-Boltzmann distributions are shown.
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