Partition Function Cutoff and Lowering of the Ionization Potential in an Argon Plasma

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A comparative value for the lowering of the ionization potential in an argon plasma has been determined from values of the series limits for recombination of free plasma electrons into the $1s$ and $2p$ states of the argon atom obtained from the measured frequency dependence of the electron continuum. The results have been used to compare existing theories which relate the ionization potential lowering to the electron density and temperature.

I. INTRODUCTION

When computing the composition of a plasma using the Saha equation, one must not overlook the fact that the equation is derived for an equilibrium system with negligible interaction energy. Equilibrium conditions are enhanced at higher densities and temperatures due to the increased collision rates. As both density and temperature are increased, however, the effects of particle interactions must be considered. These interactions manifest themselves in the form of two important corrections which must be considered when computing the composition of an atmospheric pressure plasma, i.e., cutoff of the partition function and lowering of the ionization potential.

Several methods for treating the partition function cutoff have been described in the literature. Bond,[1] using a method originally suggested by Bethe,[2] has terminated the sum at the principal quantum number of the circular orbit whose radius is equal to one-half the mean distance between particles. Unsöld[3] has derived an expression for the lowering of the potential energy distribution of an atom due to the microfield of the neighboring ion which he has employed to determine both the partition function cutoff and the ionization potential lowering. Elste and Jugaku[4] have calculated partition functions employing a probability function derived from the Unsöld relation which in effect adjusts the statistical weights of the states to assure convergence of the series at the higher levels; the cutoff was based on the principal quantum number of hydrogen-like states. Ecker and Weizel[5] have derived an approximate expression relating the cutoff principal quantum number to electron density and temperature by introducing into the Schrödinger equation a screening potential according to the Debye-Hueckel theory for strong electrolytes. Again the method is applicable only to hydrogen-like states.

Due to the complex nature of the argon atom's energy level structure the above methods cannot be directly applied here. The approach taken has been to determine as accurately as possible the extent of the lowering of the ionization potential which is then used to determine the highest state which must be included in the partition function sum. The detailed effect of interactions on the energy level structure of the atom has not been taken into consideration.

For theoretical determination of the lowering of the ionization potential several approximate expressions are available. Most widely used is the Unsöld[3] relation, which considers only the microfield effect. Weizel and Rompe,[6] using Debye-Hückel theory, give an expression which considers only the polarization effect. Ecker and Weizel[5] have improved upon the theory by considering contributions of the electrical interaction energy (microfield and polarization) to the total internal energy of the gas. This energy was then used in the derivation of the Saha equation, yielding a theoretical expression for the total lowering of the ionization potential. More recently Brunner[7] has treated the microfield effect in a more sophisticated manner than Unsöld and proceeded to add it to the combined "lattice interaction" and "polarization" terms of Ecker and Weizel, thereby making what appears to be a double correction for the microfield effect. Duclos and Cambel[8] have pointed out that there is a critical electron density below which only the effect of Debye polarization is expected to contribute to the lowering of the ionization potential.

The present work covers an estimate of the lowering of the ionization potential in an atmospheric pressure argon plasma from experimental observations, its comparison with the above theories and the effect of their corrections on the computed plasma composition.

II. EXPERIMENTAL

A. Plasma Source

The plasma was that of a 5-mm, 400-amp, direct-current thermal arc in argon at a pressure of 1.1 atm burning between a $\frac{1}{8}$-in. diam, 1% thoriated tungsten cathode ground to a 60° conical tip and a copper plate anode. Linde cylinder argon with <50 parts/million

[1] J. W. Bond, Los Alamos Scientific Laboratory of the University of California Report LA-1693, 1954 (unpublished).
[2] H. A. Bethe, Office of Scientific Research and Development Report No. 369, PB #27307, 1942 (unpublished).
[3] A. Unsöld, Z. Astrophys. **24**, 355 (1948).
[4] G. Elste and J. Jugaku, Astrophys. J. **125**, 742 (1957).
[5] G. Ecker and W. Weizel, Ann. Physik **17**, 126 (1956).
[6] R. Rompe and W. Weizel, *Theorie Elektrischer Lichtbogen und Funken* (J. A. Barth, Verlag, Leipzig, 1949).
[7] J. Brunner, Z. Physik **159**, 288 (1960).
[8] D. P. Duclos and A. B. Cambel, Z. Naturforch. **16a**, 711 (1961).

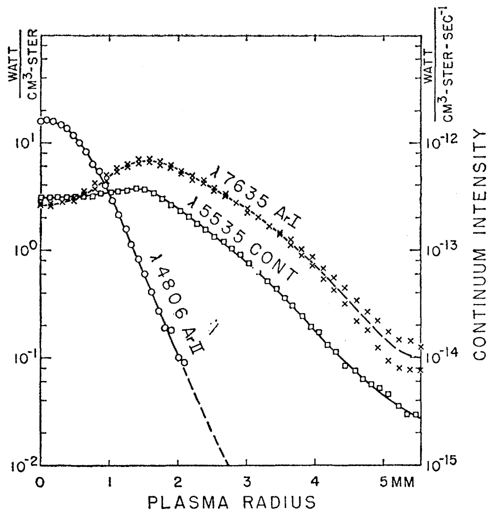

FIG. 1. Radial intensity distributions measured in a 400-amp, 1.1-atm, 5-mm, argon arc plasma.

impurity was passed over a titanium getter heated to about 800°C and bled through the chamber at a flow rate of 3 to 5 ft^3/hr. Under these conditions the arc has been operated continuously for periods up to 100 hr with <10 mg total weight loss from the cathode and no measurable change in the anode surface. The stability of the arc was such that absolute radiation intensities measured during this period of operation were reproducible to $\pm 3\%$. Electrical and thermal properties of the plasma were described in detail in earlier papers.[9,10]

B. Measurements

The principal experimental measurement was the radial intensity distribution of the total (free-free +free-bound) electron continuum at fixed wavelengths over the spectral range $3000<\lambda<12\,000$ A. Integrated intensities were measured on an absolute intensity scale using the crater of the pure graphite positive electrode of a low-current carbon arc in air as a radiation standard. An Ebert-type plane grating spectrograph was used having a first order dispersion of 8.4 A/mm. Detection was made at $\lambda<6000$ A with an RCA 1P28 photomultiplier and at $\lambda>6000$ A with a Dumont 6911 infrared photomultiplier. Intensities were recorded directly on a strip-chart recorder as a function of position along a projected diameter. Variations in depth of the plasma as a function of position along its diameter made it necessary to correct the observed integrated intensity distributions to true radial distributions, which amounts to a numerical evaluation of the inverted Abel integral equation. The method used has been described in detail by Nestor and Olsen.[11] In addition to the electron continuum, radial distributions of the λ4806 Ar II and λ7635 Ar I spectral line intensities were measured on the absolute scale at the same position along the axis of the plasma so as to provide independent measurements of the radial temperature distribution. Because of the low intensity of the continuum in the infrared region of the spectrum, it was necessary to use a 3-mm wide exit slit on the spectrograph which meant measurement over a band width $\Delta\lambda=25$ A. In the visible and ultraviolet regions the band width was reduced to 0.4 A to avoid interference by neighboring spectral lines. In all measurements the wavelength region under consideration was first scanned in wavelength with a narrow exit slit to determine the optimum wavelength at which the radial continuum intensity distribution could subsequently be measured with the broad exit slit.

C. Results

Direct experimental results consist of radial intensity distributions of the electron continuum measured at fixed wavelengths from 3000 to 12 000 A. A sample radial intensity distribution of the measured continuum is plotted along with similar distributions for the atom and ion lines in Fig. 1, and the corresponding radial temperature distributions determined from each of these radial intensity distributions are shown in Fig. 2. The two sets of points indicated on the radial intensity distribution of the λ7635 Ar I line on Fig. 1 were measured at the beginning and end of a 48-hr period of continuous arc operation using independent intensity calibrations. The results are indicative of the accuracy and reproducibility of experimental data. The Kramers-Unsöld theory [Eq. (1) of Sec. III-A] was used to compute the theoretical ϵ_ν vs T curve for the continuum shown in Fig. 3. Particle densities and partition functions were obtained from the plasma composition calculations described in Sec. IV. For calculation of the theoretical temperature dependence of the line intensities shown on Fig. 3, transition probabilities given in (10) were used. Numerical values for these are also given on Fig. 3.

All observed continuum intensity distributions exhibit an off-axis peak which appears at the radius where the plasma temperature, determined from the atom and ion line intensities, is 16 000°K. This temperature corresponds exactly with the location of the maximum of the theoretical temperature distribution of the continuum and is defined as the continuum normal temperature. Although the radial position of this peak is affected by changes in plasma geometry, its maximum intensity for a given wavelength and ambient pressure remains constant. The measured off-axis peak intensities at any given frequency are reproducible to $\pm 3\%$ except for the extreme red region of the spectrum where both the intensity of radiation (on λ scale) and sensitivity of the detection system are low. The frequency dependence of the continuum observed at its normal temperature is shown on the semilogarithmic plot of

[9] H. N. Olsen, Phys. Fluids 2, 614 (1959).
[10] H. N. Olsen, Fourth Symposium on Temperature, Columbus, Ohio, Paper B 8-4, March 27, 1961 (unpublished).
[11] O. H. Nestor and H. N. Olsen, Soc. Ind. and Appl. Math. Rev. 2, 200 (1960).

Fig. 4. Each experimental point represents the average off-axis peak intensity of three radial intensity distributions measured at the given frequency.

III. INTERPRETATION OF RESULTS

A. Absolute Intensity of the Continuum

The total continuum emitted by the plasma is due to a combination of two types of radiative transition of "free" plasma electrons. Electrons deflected by Coulomb interactions with positive ions are slowed down, transforming kinetic energy into radiation. This is the well-known bremsstrahlung continuum which results from radiative transitions between positive-energy states (hyperbolic orbits). Added to this radiation is that due to radiative recombinations of electrons with positive ions into elliptical or capture orbits. The two types of radiation are superimposed to the extent that it is not possible to separate them experimentally.

Unsöld,[12] using the classical Kramers theory, has developed a theoretical expression for the sum of the two types of radiation. In this treatment he has assumed recombinations into hydrogen-like states which are sufficiently dense to permit the sum over discrete states to be replaced by an integral. The theory leads to a continuum which is frequency independent up to a cutoff frequency ν_g defined by the interval between the effective ionization potential and the energy level above which the assumption of dense states is valid. The theoretical total continuum emission coefficient expressed in w/cm^3-sr-sec^{-1} is given by

$$\epsilon_\nu = 5.41\times 10^{-46} Z^2 n_i n_e / T^{\frac{1}{2}}, \tag{1}$$

where Z is the effective charge of the perturbing ion, n_e and n_i the electron and ion densities in cm^{-3}, and T the plasma temperature in °K.

For comparison with experimental results the theoretical continuum intensity corresponding to $T = 16\,000$°K is plotted as the dashed curve in Fig. 4. The observed discrepancy between theory and experiment may be attributed to the assumption of dense, hydrogen-like states which is, of course, not valid for the argon atom. Also, the contribution from extremely

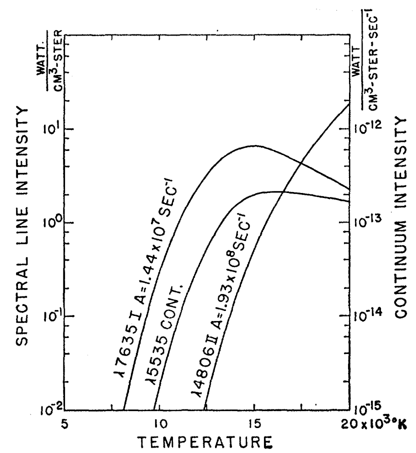

FIG. 3. Theoretical intensity-temperature curves for atomic and ionic spectral lines and the electron continuum of a 1.1-atm argon plasma.

broadened spectral lines in some regions as well as an increase in the effective charge of the ion due to a penetration of the free electrons into the outer electron shells, which have not been taken into consideration, are in the direction to help account for this discrepancy. Because of the lower atom densities at this temperature and pressure, the atom bremsstrahlung is not expected to contribute appreciably to the total continuum.

The discrepancy between measured and calculated continuum intensities may be further explained by the fact that the classical theory requires a quantum-mechanical correction. Greene[13] and Karzas and Latter[14] have shown that this correction (Gaunt factor) is in the direction to increase the bremsstrahlung radiation by a factor of at most 1.3 in the visible region of the spectrum. Again, these correction factors are based on hydrogenic, screened Coulomb wave functions which probably do not hold for argon. A correction of about a

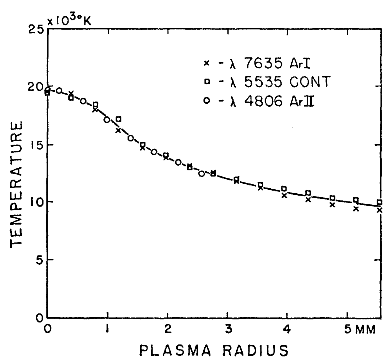

FIG. 2. Radial temperature distributions determined from the radial intensity distribution of Fig. 1 using the theoretical intensity-temperature curves of Fig. 3.

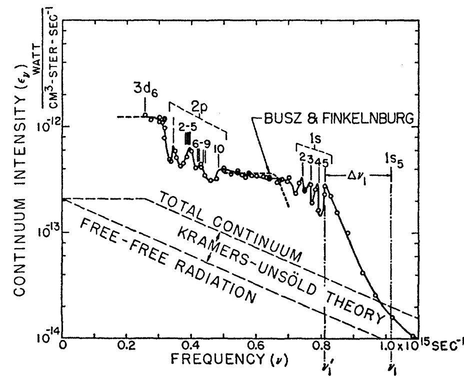

FIG. 4. Frequency dependence of the absolute intensity of the total electron continuum measured at $T = 16\,000$°K in a 400-amp, 1.1-atm, argon arc plasma.

[12] A. Unsöld, Ann. Physik **33**, 607 (1938).

[13] J. Greene, Astrophys. J. **130**, 693 (1959).

[14] W. J. Karzas and R. Latter, Rand Corporation Report No. RM-2010-AEC, ASTIA #AD156046, 1957 (unpublished).

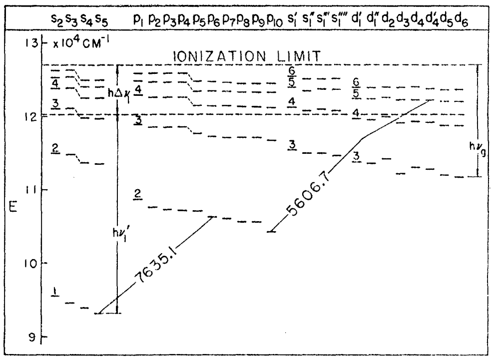

FIG. 5. Energy level diagram for argon I.

factor of 5 is actually required to bring theory and experiment into agreement.

It is interesting to note that despite this discrepancy between experimental and theoretical values of the continuum intensity, the temperature and density dependence appears to be correct as evidenced by the fact that measured temperatures in the region of the normal temperature obtained by the Fowler-Milne method using normalized relative intensities of the continuum measured at fixed frequencies, agree well with those obtained in the same manner from spectral line intensities as shown on Fig. 2. The existence of an off-axis peak which appears at the same radius for all intensity distributions measured over the entire wavelength range with a stable plasma geometry further supports this conclusion.

B. Frequency Dependence of the Continuum

Although the frequency dependence of the measured continuum cannot be explained in detail by the Kramers-Unsöld theory, the theory does serve as a guide for interpreting the experimental results. The theory predicts a frequency-independent continuum up to the cutoff frequency, ν_g, as defined above. Referring to the energy level diagram in Fig. 5, one would expect the cutoff frequency for the unperturbed atom, which corresponds with the interval between the ionization limit and the $3d_6$ term, to appear at 4.6×10^{14} sec^{-1}. A lowering of the ionization limit is in a direction to shift this cutoff frequency to a lower value. However, all that one can conclude about ν_g from the experimental results of Fig. 4 is that it is $<3.0\times10^{14}$ sec^{-1}. This means that the ionization potential lowering, ΔV_R, required to explain the observed radiation must be greater than 0.65 v. The subscript R is introduced to distinguish the ΔV determined from the radiation characteristic from that required by the Saha equation. This differentiation will be discussed further in Sec. IV.

A more accurate determination of ΔV_R can be made by associating the sharp discontinuity in the continuum appearing at $\nu_1'=8.1\times10^{14}$ sec^{-1} with the effective series limit for recombination into the $1s_5$ state of the atom. This leads to an experimental value for ΔV_R of 0.85 v. This association seems justified since the locations of series limits corresponding with all of the $1s$ and $2p$ states and the cutoff limit defined by the $3d_6$ term agree well with the observed continuum when determined from this value of ΔV_R, as indicated by the short vertical lines on Fig. 4.

For frequencies above the cutoff, the continuum should fall off according to $e^{-h\nu/kT}$, and the slope of the $\ln \epsilon$ vs ν curve should yield the plasma temperature. In moving from the cutoff frequency to higher frequencies, the series limits for recombination into isolated terms, such as the $1s$ and $2p$ states of the atom appear as peaks in the continuum. On the high-frequency side of such peaks the continuum should again decrease as $e^{-h\nu/kT}$ according to the above theory. The slope of the theoretical frequency-dependent portion calculated for $T=16\,000$°K is indicated on Fig. 4. Slopes of corresponding sections of the experimental curve deviate strongly, except for the visible region of the spectrum, from the theoretical value. As a result, the frequency-dependent portions of the continuum do not yield a unique value for the plasma temperature.

Busz and Finkelnburg[15] have measured relative continuum intensities under the same arc conditions as here with results which they believed to be in agreement with the Kramers-Unsöld theory. Their results have been normalized to our value at 5500 A and are plotted for comparison in Fig. 4. The validity of the theory cannot be judged on the basis of their measurements over such a limited frequency range.

IV. DISCUSSION

A summary of the theoretical expressions relating the true lowering of the ionization potential, ΔV_S, associated with the Saha equation to electron density and temperature is given in Table I where ΔV_m denotes the microfield term and ΔV_p the polarization term. Unsöld[3] has considered only the microfield effect on the lowering of the ionization potential where Z is the charge of the perturbed particle, Z' that of the perturbing particle, and the mean distance between them is r_0. Rompe and Weizel,[6] on the other hand, have treated only the polarization effect by considering the energy required to remove an electron-ion pair from the plasma under the conditions of Debye screening. Ecker and Weizel[5] have derived the Saha equation adding the following interaction term:

$$U_w=-\left[\frac{2e^2\alpha}{\bar{r}}+\frac{(1+\sqrt{2})}{2\sqrt{2}}\frac{e^2}{D}\right], \qquad (2)$$

to the internal energy per electron-ion pair of the system and in the process obtained a theoretical expression for the total lowering of the ionization poten-

[15] G. Busz and W. Finkelnburg, Z. Physik 139, 212 (1954).

TABLE I. Comparative results of several theories on the lowering of the ionization potential.

Author	$\Delta V_S=\Delta V_m+\Delta V_p$ ΔV_m	ΔV_p	$T=16\,000°$K $n_+=n_e=2.2\times10^{17}$ cm^{-3} ΔV_m (volts)	ΔV_p (volts)
Unsöld	$[Z+2(ZZ')^{\frac{1}{2}}]\frac{e}{r_0}$	$\cdots$	0.42	$\cdots$
Rompe and Weizel	$\cdots$	$\frac{1}{3}\frac{(1+\sqrt{2})}{\sqrt{2}}\frac{e}{D}$	$\cdots$	0.07
Ecker and Weizel	$\frac{8}{3}\bar{\alpha}\frac{e}{\bar{r}}$	$\frac{1}{2}\frac{(1+\sqrt{2})}{\sqrt{2}}\frac{e}{D}$	0.41	0.11
Brunner	$\frac{8}{3}\bar{\alpha}\frac{e}{\bar{r}}+2.3\frac{e}{r_0}$	$\frac{1}{2}\frac{(1+\sqrt{2})}{\sqrt{2}}\frac{e}{D}$	0.73	0.11

$\bar{r}=(1/n_+)^{\frac{1}{3}}$; $r_0=(3/4\pi n_+)^{\frac{1}{3}}$; $D=[kT/(4\pi e^2\sum_i n_iZ_i^2)]^{\frac{1}{2}}$; $\bar{\alpha}=1.76$.

tial. The first term of Eq. (2) represents the lattice interaction energy which is treated independently of the Debye polarization. $\bar{\alpha}$ is a mean Madelung coefficient which has been assumed equal to that of a cubic lattice ($\bar{\alpha}=1.76$). Since there is no fixed lattice, α varies with time and there has been some question about the validity of the assumption of the above mean value.[16,16a]

Brunner[7] has considered as free those electrons which are able to transfer from atom to ion because of the perturbing effect on the atom by the microfield of the nearest ion. He makes the assumption that these electrons contribute to the conductivity of the plasma in a manner analogous to hole conduction in a semiconductor, and consequently they should be added to those freed from the atom by the "lattice interactions" considered by Ecker and Weizel.[5] He has made what he considers to be an improved calculation of the Unsöld relation taking into consideration the distance the ions can move during the transit time of the electron and claims that Ecker and Weizel's comparison of their microfield term with the Unsöld term is not correct. It is the author's impression that Brunner has erroneously counted the effect of microfields twice.

Comparative numerical values of ΔV_m and ΔV_p have been calculated for a singly ionized plasma and are given in Table I. As both the Brunner and Ecker and Weizel papers point out, the value of ΔV_R obtained from the frequency characteristics of the electron continuum must be equal to or larger than the ΔV_S used with the Saha equation and is probably larger. This is due to the fact that atomic energy levels near the ionization limit are Stark broadened by the microfields to the extent that they become part of the continuum insofar as radiative properties are concerned. This does not mean that electrons in these levels are free in the sense that they are to be included with those computed according to the Saha equation. It is, therefore, not correct to equate ΔV_S and ΔV_R.

Although a direct measurement of ΔV_S does not seem possible, an upper bound for its value can be obtained from spectral observations. The λ5606 Ar I spectral line which arises from an upper level well above the observed ionization limit, as shown on Fig. 5, has been observed to be emitted from this experimental plasma but is quite weak and extremely broadened relative to other lines. Even the complete disappearance of the line into the continuum due to Stark broadening would not be sufficient evidence to permit one to consider the level from which the line arises to have been cut off by the true lowering of the ionization potential. From this spectral observation we can conclude that $\Delta V_S<0.65$ v. Since it has been shown that $\Delta V_S<0.65<\Delta V_R$, it indeed appears that Brunner has counted doubly the microfield effect and this then can account for the agreement of the ΔV_S calculated according to his theory with the measured value of ΔV_R.

Using the definition of $\bar{r}$ and r_0 given in Table I, the three theoretical expressions for ΔV_m may be written in the form $\Delta V_m=\beta e/r_0$, where, for single ionization ($Z=Z'=1$), $\beta_{\mathrm{U}}=3.0$, $\beta_{\mathrm{EW}}=2.9$ and $\beta_{\mathrm{B}}=5.2$. Using these three values for β the composition of the argon plasma at 1-atm pressure has been calculated iteratively in the temperature range of 5000–20 000°K assuming only single ionization. In these calculations the sum over states for the atomic partition function was cut off at the highest level which satisfied the expression

$$E_n<e(V_1-\Delta V_1), \tag{3}$$

where V_1 represents the first ionization potential. The results are shown in Fig. 6, where they are compared with earlier calculations that did not consider ΔV_S and

[16] O. Theimer, Z. Naturforsch. **12a**, 518 (1957).

[16a] As the result of a private communication with G. Ecker on Oct. 11, 1961, it was learned that he has reviewed his theoretical work on plasma polarization and particle interactions and has concluded that there is indeed a critical electron density, $n_C\approx(kT/e^2)^3$, above which only the microfield term applies and below which only the polarization term applies in the Ecker and Weizel theory. For the plasma treated here $n_C\approx$ Po^{19} cm^{-3} thus α should be set equal to zero.

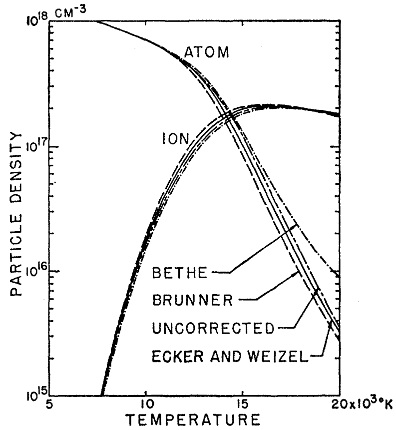

FIG. 6. Compositions of the atmospheric argon plasma calculated according to different theories for lowering of the ionization potential. Partition function cutoff was consistent with the calculated ΔV.

used the statistical weights tabulated by Unsöld[17] as approximate partition functions. Since there is a negligible difference between the Unsöld and the Ecker and Weizel microfield terms, only the Ecker and Weizel calculation was performed. Also shown are results of calculations including partition function corrections only, according to the method of Bethe,[2] which agree so closely with results of calculations considering only the polarization term ($\beta=0$) that only the one curve is included.

V. CONCLUSIONS

It has been concluded, as was first pointed out by Ecker and Weizel[5] and later by Brunner,[7] that the true ionization potential lowering, ΔV_S, cannot be accurately determined from the observed radiation characteristics of the plasma. A review of the many theories which relate ΔV_S to electron density and temperature has led to the conclusion that for plasmas at pressure below 10 atm the microfield term disappears leaving only the Debye polarization term. This means that the widely used Unsöld[3] relation is not correct for most plasmas. That only the polarization term should be retained in the theory is consistent with experimental observations of Boldt[18] and Wiese and Shumaker[19] in which ΔV_R determined from the radiation characteristics of oxygen plasmas is smaller than the ΔV_S computed from either the Unsöld or Ecker and Weizel theories but larger than that given by the polarization term alone. The exceptionally large value of ΔV_R determined here for the argon plasma might be expected because of the greater concentration of energy levels near the ionization limit of the argon atom which would permit Stark smearing to affect an overlap of levels farther below the true ΔV_S cutoff than would be expected in the case of oxygen.

On the basis of the results of the several composition calculations performed in the course of this work it can also be concluded that the cutoff of the argon atom partition function resulting from polarization only has a more pronounced effect on computed densities than the corresponding lowering of the ionization potential. Finally it is concluded that an experimental check of the theoretical value for ΔV_S is quite difficult and can probably be made only by comparing it with the value required to bring computed densities into agreement with experimental values measured by some method which is independent of the computed composition in a volume element where the temperature is accurately known.

ACKNOWLEDGMENTS

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[17] A. Unsöld, *Physik der Sternatmosphären* (Springer-Verlag, Berlin, 1955), 2nd ed., pp. 90–91.

[18] G. Boldt, Z. Physik **154**, 319 (1959).

[19] W. L. Wiese and J. B. Shumaker, Jr., J. Opt. Soc. Am. **51**, 937 (1961).